2D Materials Focus Topic
Room: 212C - Session 2D+EM+NS+PS+SP+SS+TF-MoM

2D Materials: Growth and Fabrication
Moderator: Cory Dean, Columbia University, Peide Ye, Purdue University

8:20am **2D+EM+NS+PS+SP+SS+TF-MoM1 Growth and FTIR Characterization of 2D Hexagonal Boron Nitride on Metal Substrates**, ***Boris Feigelson**, V.M. Bermudez, J.K. Hite, Z.R. Robinson, V.D. Wheeler, K. Sridhara, S.C. Hernández*, US Naval Research Laboratory

Atomically thin two dimensional hexagonal boron nitride (2D h-BN) is one of the key materials in the development of new van der Waals heterostructures due to its outstanding properties including an atomically smooth surface, high thermal conductivity, high mechanical strength, chemical inertness and high electrical resistance. The development of 2D h-BN growth is still in the early stages and largely depends on rapid and accurate characterization of the grown monolayer or few layers h-BN films.

In this work, the IR-active out-of-plane vibrational mode of 2D h-BN films grown in vertical reactor by atmospheric-pressure CVD on metal substrates (mainly Cu but also Ni) is exploited to identify 2D h-BN directly on substrates and studied both computationally and experimentally.

Fourier transform grazing-incidence infrared reflection absorption spectroscopy (FT-IRRAS) data have been used to characterize monolayer and few-layer h-BN films directly on metal substrates. Two sub-bands of the A_{2u}(LO) vibrational mode were, for the first time, found for thin 2D h-BN films in contact with Cu and Ni [1]. To unveil the nature of the discovered sub-bands, ab-initio calculations were performed and verified using 2D h-BN films grown on various Cu substrates with varying coverage and with individual crystallites of different shapes and size up to 4 mm. It was shown that the lower-energy A_{2u}(LO)1 sub-band around 819 cm^{-1} is related to 2D h-BN coupled with Cu substrate, while the higher energy A_{2u}(LO)2 sub-band around 824 cm^{-1} is related to decoupled (essentially free standing) 2D h-BN. These findings demonstrate not only a new and facile method for immediate 2D h-BN identification and characterization, but also a method that provides a simple means to characterize the degree of coupling between 2D h-BN and the substrate. This approach also provides an opportunity to determine which growth conditions lead to the absorption of foreign species on the substrate prior to the h-BN deposition and which conditions can prevent the formation of the interfacial layer between h-BN and the substrate. Such interfacial layers, like oxidized Cu, were shown to result in easily-recognizable shifts in the A_{2u}(LO) peak. The degree to which the interaction of the h BN layer with the substrate is uniform and homogenous can also be assessed easily by examining the width and fine structure of the A_{2u}(LO) band. The developed approach can also be used to study growth and formation of h-BN/graphene and other 2D heterostructures.

References

1. B. N. Feigelson, V. M. Bermudez, J. K. Hite, Z. R. Robinson, V. D. Wheeler, K. Sridhara, and S. C. Hernandez, Nanoscale **7,** 3694 (2015)

8:40am **2D+EM+NS+PS+SP+SS+TF-MoM2 Effect of Surface Termination on the Growth of Graphene on Cu Single Crystal Substrates**, ***Tyler Mowll**, E.W. Ong,* University at Albany-SUNY*, P. Tyagi,* GLOBALFOUNDRIES*, Z.R. Robinson,* College at Brockport-SUNY*, C.A. Ventrice, Jr.*, SUNY Polytechnic Institute

The most common technique for synthesizing single-layer graphene films with large lateral dimensions is chemical vapor deposition (CVD) on Cu foil substrates. The primary reasons for choosing Cu substrates are the extremely low solubility of carbon in Cu, which allows a self-limited growth of graphene, and the relatively low cost of the Cu foil substrates. However, the transport properties of the CVD grown graphene films are typically a couple of orders of magnitude lower than for graphene flakes mechanically exfoliated from graphite. One of the reasons for the reduction in transport properties is the presence of crystalline defects in the CVD grown films. These structural defects arise in part from the multidomain structure of the Cu films. In order to achieve a better understanding of the influence of the surface termination of the Cu substrate on the crystallization of graphene during the CVD growth process, a systematic study of graphene growth on Cu(100), Cu(110), and Cu(111) crystals has been performed. The growth process is performed in an ultra-high vacuum (UHV) chamber that has been modified to perform CVD growth at pressures as high as 100 mTorr. The precursor gas used is ethylene. This growth procedure allows for the preparation of the clean surfaces in UHV, growth under typical CVD conditions, and characterization of the surface structure in UHV, without exposing the sample to atmospheric contaminants. Our results indicate that the Cu(111) surface has the lowest catalytic activity of the three surfaces for the decomposition of ethylene. In fact, the decomposition rate is so low that graphene growth is suppressed because of the sublimation of Cu at the elevated temperatures used to grow the graphene. By using an Ar overpressure, it was found that graphene could be grown on that surface. The surface symmetry of the Cu substrate has a strong influence on the rotational alignment of the graphene grains as they nucleate on each surface. For Cu(111), single-domain graphene growth can be achieved for ethylene pressures of 5 mTorr or less. For both Cu(100) and Cu(110), a minimum of two graphene domains is always observed.

9:00am **2D+EM+NS+PS+SP+SS+TF-MoM3 Thermally Annealed and Electropolished Cu Substrates for CVD Growth of 2D Materials: Graphene, h-BN and MoS_2**, ***Karthik Sridhara,*** Texas A&M University*, B.N. Feigelson, J.K. Hite,* US Naval Research Laboratory*, A. Nath,* George Mason University*, M. Fuhrer,* Monash University, Australia*, D.K. Gaskill,* US Naval Research Laboratory*, H. Castaneda, L.O. Nyakiti*, Texas A&M University

The growth of two dimensional (2D) materials such as graphene, hexagonal boron nitride (h-BN) and molybdenum disulphide (MoS_2) have been demonstrated by chemical vapor deposition (CVD) on polycrystalline catalytic copper substrates. These Cu foil substrates (25 µm thick) are produced by metallurgical rolling leading to the formation of irregular ridges on the foil surface along with a film of native oxide on the surface. These processing artifacts are a limiting factor for controlled and reproducible large area (several cm^2) growth of 2D materials. Greater control of growth can be achieved by controlling the density of nucleation sites and improving the catalytic activity of Cu by removing the Cu native oxide on the surface. Previous attempts to pre-treat the Cu substrate by using wet chemistry or thermal annealing to control growth has been weakly addressed.

In this work, electropolishing combined with prior thermal annealing at 1030°C for 5 hrs under H_2 is used to control the degree of roughness of cold rolled polycrystalline Cu foils, and subsequently, to explore the influence of electropolishing on the growth of 2D materials: graphene, h-BN and MoS_2. Electropolishing dissolves a thin surface layer of Cu, which contains surface defects and contaminants. This helps in decreasing the density of spontaneous nucleation sites by producing a morphologically uniform and contaminant-free surface. Secondary effects, etch pits which are ascribed to O_2 bubbling at random nucleation sites on Cu surface, are mitigated by using additives, such as acetic acid and ethylene glycol, in the H_3PO_4 electrolyte. Thermal annealing and electropolishing results in this work reveal that a roughness of ~1.2 nm (R_q) can be achieved as measured by Atomic Force Microscope (AFM) along with a greatly planarized Cu foil. AFM will also be used to establish the Cu substrate morphology and its relationship to the growth of 2D materials. Fourier Transform Infrared, and Raman spectroscopy will be used to confirm the existence of the 2D material. Preliminary growth studies of h-BN on these high quality Cu substrates demonstrate improved growth, as assessed by the metrics of size and count of h-BN crystals from Scanning Electron Microscopy (SEM) micrographs [1]. This work will demonstrate that thermal annealing followed by electropolishing leads to optimization of Cu foil surface resulting in the larger crystal size and a reduction in nucleation sites that induce 2D material crystal growth [1].

[1] K. Sridhara. “Growth of hexagonal boron nitride on electrochemically prepared polycrystalline Cu substrates.” M.S. Thesis, University of Maryland, College Park, MD, 2014.

9:20am **2D+EM+NS+PS+SP+SS+TF-MoM4 *In Situ* Optical Diagnostics During Molybdenum Disulfide Chemical Vapor Deposition**, ***Berc Kalanyan**, J.E. Maslar, W.A. Kimes, B.A. Sperling,* National Institute of Standards and Technology (NIST)*, R. Tieckelmann, T. Orzali,* SEMATECH*, R. Beams, S.J. Stranick, A.V. Davydov*, National Institute of Standards and Technology (NIST)

Two dimensional (2D), layered transition-metal dichalcogenides (TMDs), e.g., MoS_2, are of increasing interest for next-generation nanoelectronic and optoelectronic devices. These materials have thickness dependent optical and electrical properties that make them suitable for a variety of applications including integrated circuits. For many applications, high volume manufacturing (HVM) of devices based on TMDs will require deposition techniques that are capable of reproducibly growing wafer-scale, 2D TMD films with monolayer control. To date, such a capability has not been widely demonstrated with typical TMD deposition processes.

This work aims to identify promising chemistries for HVM TMD chemical vapor deposition (CVD) processes. We focus on MoS_2 CVD using a variety of precursors (including organometallics, elemental sulfur, and organosulfur compounds) in a research grade single-wafer deposition system equipped with *in situ* optical diagnostics. The precursor flux is measured using optical mass flow meters installed on the delivery lines while deposition chemistry is characterized in the reactor volume above the deposition surface using *in situ* Fourier transform infrared (FR-IR) spectroscopy. As-deposited and annealed films are characterized with *ex situ* techniques, including Raman and photoluminescence spectroscopy, scanning and transmission electron microscopy, and X-ray photoelectron spectroscopy.

Stoichiometric MoS_2 films have been prepared from (η^5-ethylcyclopentadienyl)-dicarbonylnitrosyl molybdenum and elemental sulfur. As-grown films are smooth and continuous with major MoS_2 Raman modes present. Film thickness scales approximately with Mo precursor exposure time and few-layer films can be produced using pulsed injection mode. Furthermore, optical *in situ* diagnostics allow us to relate metal precursor flux to film crystallinity and facilitate the study of precursor decomposition in the thermal boundary layer.

9:40am **2D+EM+NS+PS+SP+SS+TF-MoM5 Controlled Interfaces in 2D Materials**, ***Arend van der Zande***, University of Illinois at Urbana Champaign **INVITED**

Interfaces are ubiquitous in material science and technologies. For example, grain boundaries often dominate the mechanical and electrical properties in crystalline materials, while interfaces between dissimilar materials form the fundamental building blocks to diverse technologies, such as building electrical contacts in transistors and PN diodes in solar cells. Interfaces become even more important in 2D materials such as graphene and transition metal dichalcogenides, where the lack of dangling bonds enables material stability down to a single monolayer. In this entirely surface-dominated limit, the usual rules governing 3D interface devices, such as depletion regions, break down.

In this talk, we will discuss our work on engineering in- and out-of-plane 2D materials interfaces. We will first examine the structure of atomically-thin membranes and the impact of defects such as grain boundaries on the mechanical, optical, and electronic properties. We fabricate out-of-plane interfaces by stacking 2D materials to form heterostructures, which we utilize to tailor the bandgap in 2D materials and build new optoelectronic devices such as tunable photodiodes. Looking to the future, the rapidly expanding family of 2D materials with a diverse set of electronic properties provide a promising palette for discovering emergent phenomena and a motivation for developing overarching design principles for understanding and controlling interfaces in 2D.

10:40am **2D+EM+NS+PS+SP+SS+TF-MoM8 Obtaining Clean Suspended CVD Graphene: Comparative Examination of Few Transfer and Cleaning Protocols**, ***Alexander Yulaev***, National Institute of Standards and Technology (NIST), University of Maryland (UMD), *G. Cheng, A. Hight Walker,* National Institute of Standards and Technology (NIST), *M. Leite,* University of Maryland (UMD), *A. Kolmakov*, NIST

Clean suspended graphene is used as supporting media in TEM, filtering membranes, and as electron transparent windows in ambient pressure electron spectroscopy and microscopy. CVD grown graphene is the most popular material for these applications due to its large-scale and high yield production. Multiple approaches such as sacrificial layer based methods [1] and direct transfer method on perforated carbon mesh by IPA droplet [2] have been implemented to transport graphene from copper or nickel foil onto a target substrate. However, the cleanness of the suspended graphene remains to be an issue, and controversial results on lateral size of atomically clean graphene domains have been reported [2-5]. We conduct the comparative analysis of the most widely-used CVD graphene transfer and cleaning protocols. In particular, using extreme surface sensitivity of low energy SEM, we compare the standard PMMA based approach with direct graphene transfer method. We also propose alternative graphene transfer protocol which is based on employment of polycyclic aromatic hydrocarbon (PAH) as a sacrificial layer. The advantage of PAH method over others consists in facile sublimation of sacrificial layer upon heating PAH material within moderate temperature range of 100-150 ^{o}C. All three methods of graphene transfer were compared under the same conditions followed by similar graphene cleaning procedures by platinum catalysis [4] and activated carbon adsorption [5]. Both SEM and TEM study revealed the superiority of PAH method to achieve cleaner suspended CVD graphene. We envision that novel approach of graphene transfer can be employed under conditions when exposure of the sample to moisture is prohibited such as in battery research.

[1] "Transfer of CVD-Grown Monolayer Graphene onto Arbitrary Substrates", Ji Won Suk *et al*., ACS Nano, 2011, 5 (9), pp. 6916.

[2] "A direct transfer of layer-area graphene", William Regan *et al*., Appl. Phys. Lett., 2010, 96, 113102.

[3] "Low-energy electron holographic imaging of gold nanorods supported by ultraclean graphene", Jean-Nicolas Longchamp *et al*., Ultramicroscopy 145 (2014) 80.

[4] "Ultraclean freestanding graphene by platinum-metal catalysis", Jean-Nicolas Longchamp *et al*., J. Vac. Sci. Technol. B 31, 020605 (2013).

[5] "Dry-cleaning of graphene", Gerardo Algara-Siller *et al*., Applied Physics Letters 104, 153115 (2014).

11:00am **2D+EM+NS+PS+SP+SS+TF-MoM9 Low-Energy Electron Microscopy of Transition Metal Dichalcogenides Prepared by Various Methods**, ***Sergio de la Barrera***, *S. Satpathy, R. Feenstra,* Carnegie Mellon University, *S. Wu, X.D. Xu,* University of Washington, *S. Vishwanath, X. Liu, J. Furdyna, D. Jena, H. Xing,* University of Notre Dame, *Y.-C. Lin, S.M. Eichfeld, J.A. Robinson,* Pennsylvania State University, *P. Mende*, Carnegie Mellon University

Recent work on two-dimensional materials has focused on transition metal dichalcogenides (TMDs), owing to their semiconducting behavior. Characterizing as-grown TMDs is crucial in improving the understanding of the effects of growth conditions, and ultimately improving material quality. Low-energy electron microscopy (LEEM) is a powerful tool for this purpose, providing real-space images with ~10 nm spatial resolution as well as selected-area low-energy electron diffraction (µLEED) of local crystal orientation at length scales down to ~ 1 µm. Additionally, by varying the incident electron beam energy, low-energy electron reflectivity (LEER) spectra are extracted.

In this work, comparative LEEM results are presented from three TMD materials: MoS_2 prepared by exfoliation (onto Si), $MoSe_2$ grown by molecular beam epitaxy (MBE) (on epitaxial graphene), and WSe_2 grown by chemical vapor deposition (CVD) (also on epitaxial graphene). It is found that for TMDs generally, the LEER spectra do not exhibit the oscillatory behavior (in the 0 – 6 eV range) that is seen for both graphene and hexagonal boron nitride (h-BN) for various numbers of monolayers (MLs). This lack of oscillatory behavior is interpreted as being due to the weak coupling of the interlayer states localized in between the MLs, which is itself a result of the relatively large out-of-plane lattice parameter. Nevertheless, additional "band structure" features in the LEER spectra permit clear identification of the TMD materials relative to the substrates. The exfoliated flakes are seen to extend over many 10's of mm, the MBE-grown $MoSe_2$ forms a nearly continuous film, and the CVD-grown WSe_2 forms triangular islands several mm in extent. µLEED studies of the MBE-grown $MoSe_2$ and CVD-grown WSe_2 reveal preferential orientation with the underlying graphene substrates.

The reduced work functions of the TMD materials relative to the underlying substrate are clearly evident in the onset voltages for the LEER spectra (i.e. the onset shifts in accordance with the local work function of the surface). Most significantly, for the WSe_2 islands, a predominant "tail" is observed in this onset, extending about 5V below the usual onset location. This tail is tentatively interpreted as arising from charging of the islands, perhaps due to polar termination at the edges of the TMD islands. Comparison of the data with simulated LEER spectra will be presented, as a test of this model for edge charge of the islands.

Work supported by the Center for Low Energy Systems Technology (LEAST), one of six SRC STARnet Centers sponsored by MARCO and DARPA, and by NSF-EFRI-1433496.

11:20am **2D+EM+NS+PS+SP+SS+TF-MoM10 Atomically-Thin 2D Layers of Group IV Semiconductors**, ***Joshua Goldberger***, The Ohio State University **INVITED**

Similar to how carbon networks can be sculpted into low-dimensional allotropes such as fullerenes, nanotubes, and graphene with fundamentally different properties, it is possible to create similar "allotropes" of Ge or Sn with unique optoelectronic properties as well. Here, we will describe our recent success in the creation of hydrogen and organic-terminated group 14 graphane analogues, from the topochemical deintercalation of precursor Zintl phases, such as $CaGe_2$. We will discuss how the optical, electronic, and thermal properties of these materials can be systematically controlled by substituting either the surface ligand or via alloying with other Group 14 elements. Additionally, we have also developed an epitopotaxial approach for integrating precise thicknesses of Germanane layers onto Ge wafers that combines the epitaxial deposition of $CaGe_2$ precursor phases with the topotactic interconversion into the 2D material. Finally, we will describe

our recent efforts on the synthesis and crystal structures of Sn-containing graphane alloys in order to access novel topological phenomena predicted to occur in these graphanes.

Electronic Materials and Processing
Room: 210E - Session EM+NS+PS-MoM

More Moore! Materials and Processes to Extend CMOS Another Decade
Moderator: Christopher Hinkle, University of Texas at Dallas

8:20am **EM+NS+PS-MoM1 Effects of Deposition Temperature and Pre-rapid Thermal Process on Electrical and Interfacial Characteristics of Alumina on GaSb**, ***Seongkyung Kim***, *H.J. kim*, Seoul National University, Korea, Republic of Korea

Recently Ⅲ-Ⅴ compound materials have attracted significant attention as promising channel materials for sub-10 nm logic MOSFET due to their high mobility. GaSb is a strong candidate for pMOSFETs because of its high hole mobility in addition to the insolubility of its native oxides. Even with the outstanding electrical properties of GaSb, there are some drawbacks related to the instability of its native oxides and metallic layer of elemental Sb. The native oxides and metallic layer of elemental Sb are considered to be sources of Fermi level pinning and flat C-V curves. Therefore, it is necessary to improve surface treatment methods. Since it is possible to eliminate its native oxides and elemental Sb by heating them, it is essential to research temperature related surface treatments.

In this study, various ALD temperatures from 190 ^oC to 310 ^oC and pre-RTP(Rapid Thermal Process), which is first introduced here as a pre-deposition treatment, have been adopted for eliminating the remaining native oxides after cleaning. N_2 gas atmosphere is used to suppress the oxygen to interact with GaSb surface for the pre-RTP. GaSb metal-oxide-semiconductor capacitors were fabricated on p-type GaSb, which has a carrier concentration of 1.0~2.0 x 10^{17} cm^{-3}. GaSb was degreased with acetone, ethanol, and isopropane for 5 minutes each and then etched by HCl. 10 nm of Al_2O_3 has been deposited as a gate dielectric with TMA and DI water by thermal ALD. For the metal gate, a Pt electrode has been deposited with an electron-beam evaporator.

When the deposition temperature increases, the Ga_2O_3 peak increases and the substrate peak decreases under XPS analysis. It is observed that the amount of Sb increases at the GaSb/Al_2O_3 interface as the deposition temperature increases in AES depth profiles. Both Ga2O3 and elemental Sb have increased generation as the deposition temperature increases, since the surface chemical reactions are accelerated by increased temperature. The CV curve becomes flat as the deposition temperature increases. It indicates that Ga_2O_3 has a flattening effect of the CV curve and the more amount of Ga_2O_3 that is generated, the flatter the CV curve will become.

Desorption of the native oxides and elemental Sb should occur by annealing the substrate. After the pre-RTP, the amount of elemental Sb increases, since the remaining native oxide, after cleaning, is reduced by increased temperatures. The remaining native oxide Sb_2O_3, after cleaning, supplies oxygen to the substrate and becomes elemental Sb. The leakage current increases with pre-RTP. It shows that the elemental Sb increases the leakage current. Further study on optimizing pre-RTP conditions is needed.

8:40am **EM+NS+PS-MoM2 Selective Wet Etching of III-V Semiconductors with HCl and H_2O_2**, ***Pablo Mancheno-Posso***, *. Jain, A.J. Muscat*, University of Arizona

The etching of III-V semiconductors is needed to insert these materials into current device flows to extend CMOS transistor technology. III-V oxides are detrimental to electrical performance and must be removed, because they adopt different oxidation states and can be soluble in water. Plasma etching to create profiles can damage and change the stoichiometry of the surface. Wet etching of these oxides can control the roughness and chemical termination of the surface by choice of oxidant and etchant, concentration, and pH. Wet etching of III-V semiconductors is accomplished by oxidizing acid and base chemistries that can preferentially remove group III or V atoms. In new 3 D transistor architectures, the formation of the channel fin requires a low etching rate to ensure a smooth surface and a highly selective etching bath with respect to other materials or crystal faces that are exposed. In this work, we varied the group III and V atoms across five binaries (GaAs, InAs, InP, GaSb, and InSb) and measured etching rates. These materials were etched using mixtures of HCl (0.01 M) and H_2O_2 (0.0001-5 M). The etching rate was measured using profilometry on wafers patterned with conventional photolithography. The chemical composition was monitored using X-ray photoelectron spectroscopy (XPS). The etching rate of GaAs and InAs (same group V atom) exhibited a volcano-shaped dependence on H_2O_2 concentration. At H_2O_2 concentrations of 5 to 100 mM, the etching rate increased linearly from 0.08±0.03 to 1.1±0.1 nm/s for GaAs and from 0.06±0.04 to 0.9±0.3 nm/s for InAs. The rate decreased to 0.04±0.01 nm/s for GaAs and 0.26±0.13 nm/s for InAs at 1 M H_2O_2. InP, which is often exposed during etching of another III-V, showed a linear dependence on H_2O_2 concentration (0.01 to 5 M), increasing from 0.003±0.001 to 0.012±0.009 nm/s. The selectivity of etching GaAs to InP at three points along the volcano was about 55, 140, and 4 at H_2O_2 concentrations of 0.01, 0.1, and 1 M. Like the arsenides, the antimonides etched at about the same rate, but the volcano dependence moved to lower peroxide concentrations. The etching rate of GaSb increased from 0.07±0.04 to 0.21±0.04 nm/s and InSb from 0.09±0.03 to 0.38±0.09 nm/s for H_2O_2 concentrations from 0.1 to 1 mM. The group V atom determined the etching rate and is involved in the rate determining step in the reaction. The presence of As-Cl bonds on the surface after etching GaAs in HCl was confirmed by temperature programmed desorption (TPD) experiments after immersion in 1.7 M HCl. The mechanism for etching III-V semiconductors will be discussed based on the etching rate data and chemical composition of the surface.

9:00am **EM+NS+PS-MoM3 Border Trap Analysis and Reduction for ALD High-k InGaAs Gate Stacks**, ***Kechao Tang***, Stanford Univ., *R. Winter,* Technion – Israel Inst. of Tech., *T. Kent,* UC, San Diego, *M. Negara,* Stanford Unive., *R. Droopad,* Texas State Univ., *A.C. Kummel,* UC, San Diego, *M. Eizenberg,* Technion – Israel Inst. of Tech., *P. McIntyre*, Stanford Univ.

For future high performance III-V n-channel MOS devices, $In_{0.53}Ga_{0.47}As$ is a promising material for the channel due to its high electron mobility. Atomic layer deposited (ALD) Al_2O_3 has a large conduction band offset to InGaAs and can form a low defect-density interface with InGaAs [1]. ALD-HfO_2 can achieve a very low EOT (effective oxide thickness) with low gate leakage [2]. Therefore, both of these oxides have received extensive attention as candidate dielectric layers for InGaAs nMOSFETs. Apart from the well-known oxide/InGaAs interface charge traps that may pin the Fermi level of the channel, traps in the oxide layer, called border traps, may also reduce the charge in the channel and thus degrade the on-state performance of InGaAs MOSFET devices. We report a study of the effects of various approaches to reduce the density of border traps (N_{bt}), such as variation of the ALD temperature, and of post-gate metal forming gas (5% H_2/95% N_2) anneal (FGA) conditions.

Experimental methods employed include quantitative interface trap and oxide trap modeling [3, 4] of MOS capacitor data obtained over a range of frequencies and temperatures. We find that MOS capacitors fabricated using trimethylaluminum (TMA)/H_2O at an ALD temperature of 120°C have a considerably lower border trap density while maintaining a low interface trap density (D_{it}) compared to samples prepared with a more standard 270°C Al_2O_3 ALD temperature. It is also found that large-dose (~6,000 L) exposure of the $In_{0.53}Ga_{0.47}As$ (100) surface to TMA immediately after thermal desorption of a protective As_2 capping layer in the ALD chamber is an important step to guarantee the repeatability of high quality Al_2O_3/InGaAs samples made at Al_2O_3 ALD temperatures much lower than 270°C. The reduction of N_{bt} is consistent with time-of-flight secondary ion mass spectrometry depth profiles that show more effective hydrogen incorporation in the low-temperature ALD-grown Al_2O_3 films during post-gate FGA.

The N_{bt} of Al_2O_3 under various conditions will be compared with that of low-temperature ALD-grown HfO_2 films on InGaAs substrates. For the HfO_2 case, we also confirm the independence of border trap response on the electrical measurement temperature and check the influence of the crystal orientation of the InGaAs surface on MOS interface characteristics.

This work was supported by the US-Israel Binational Science Foundation.

References

[1] J. Ahn et al., Appl. Phys. Lett. 103 (2013), 071602

[2] V. Chobpattana et al., J. Appl. Phys. 114 (2013), 154108

[3] H. Chen et al., IEEE TED 59 (2012), 2383-2389

[4] Y. Yuan et al., IEEE TED 59 (2012), 2100-2106

9:20am **EM+NS+PS-MoM4 Self-LIMITING CVD of an Air Stable Silicon Oxide Bilayer for Preparation of Subsequent Silicon or Gate Oxide ALD on InGaAs(001)-(2x4)**, ***Mary Edmonds***, *T. Kent, S. Wolf,* University of California at San Diego, *J. Kachian, N. Yoshida, M. Chang,* Applied Materials, *D. Alverez,* Rasirc, Inc, *R. Droopad,* Texas State University, *A.C. Kummel*, University of California at San Diego

A broader range of channel materials allowing better carrier confinement and mobility could be employed if a universal control monolayer (UCM) could be ALD or self-limiting CVD deposited on multiple materials and crystallographic faces. Si-OH is a leading candidate for use as the UCM, as

silicon uniquely bonds strongly to all crystallographic faces of $InGa_{1-x}As$, $In_xGa_{1-x}Sb$, $In_xGa_{1-x}N$, SiGe, and Ge enabling transfer of substrate dangling bonds to silicon, which may then subsequently be functionalized with an oxidant such as HOOH(g) in order to create the UCM terminating Si-OH layer. This study focuses on depositing a saturated Si-OH seed layer on InGaAs(001)-(2x4) at a substrate temperature of 350°C. XPS in combination with STS/STM were employed to characterize the electrical and surface properties of the saturated Si-OH seed layer on InGaAs(001)-(2x4).

The 350°C self-limiting CVD procedure includes a decapped $In_{0.53}Ga_{0.47}As$(001)-(2x4) surface dosed with total 87.6 MegaLangmuir Si_2Cl_6 followed by 210.55 MegaLangmuir total anhydrous HOOH(g). Complete saturation of silicon coverage is determined to occur once further dosing with Si_2Cl_6 leads to no further increase in the silicon 2p or further decrease in the substrate gallium 3p peak areas. Complete surface saturation of $Si-O_x$ on InGaAs(001)-(2x4) was determined to occur once no further increase in the O 1s peak was seen with additional anhydrous HOOH(g) doses. Following Si-OH surface saturation, 300,000 L TMA was dosed at 250°C, and XPS shows the emergence of Al 2p and C 1s peaks indicative of TMA surface nucleation. The surface was then dosed with 500 L atomic H at 250°C to remove the methyl groups on the surface aluminum and replace with -H termination as well as remove any residual chlorine left on the surface. The surface was then exposed to air for 30 minutes, dosed with an additional 500 L atomic H at 250°C, and then STS measurements were performed. STM measurements of the $Si-O_x$ surface show uniform surface coverage. STS measurements show the surface Fermi level position moves towards midgap due to a surface dipole formation from –OH groups and oxygen bonding to the surface. TMA dosed on the $Si-O_x$ surface shifts the Fermi level back towards the conduction band, consistent with unpinning and the -OH induced surface dipole being lessened through surface bonding with dimethylaluminum groups. Following hydrogen dosing and air exposure, the surface Fermi level remains near the conduction band edge consistent with the surface being stable and unreactive in air. Preliminary MOSFET studies on InGaAs(001) show equivalent performance with Si_2Cl_6 predosing compared to in-situ cleaning with atomic H.

9:40am **EM+NS+PS-MoM5 Going Big in Two-Dimensions**, ***Joshua Robinson***, The Pennsylvania State University **INVITED**

The last decade has seen nearly exponential growth in the science and technology of two-dimensional materials. Beyond graphene, there are a variety of layered materials that provide a broad range of electronic characteristics useful for transistors, flexible electronics, sensors, and photodetectors, to name a few. However, bridging the gap between science and teechnology often lies in one's ability to synthesize materials on the wafer scale (or bigger). In this talk, I will discuss recent breakthroughs for direct growth of two-dimensional atomic layers and heterostructures with scalable techniues such as metal-organic chemical vapor deposition. We have demonstrated the direct growth of MoS_2, WSe_2, MoS_2/WSe_2, and hBN on epitaxial graphene to form large area van der Waals heterostructures. We reveal that the properties of the underlying substrate dictate properties of the layers and heterostructures, and that the direct synthesis of TMDs on epitaxial graphene exhibits atomically sharp interfaces. Our work has lead to a better understanding of vertical transport in 2D heterostructures, and we have identified new phenomenon in multi-junction heterostructures that has lead to resonance tunneling between layers and ultimately negative differential resistance.

1. Eichfeld, S. M.; Hossain, L.; Lin, Y.-C.; Piasecki, A. F.; Kupp, B.; Birdwell, A. G. G.; Burke, R. A.; Lu, N.; Peng, X.; Li, J.; et al. Highly Scalable, Atomically Thin WSe2 Grown via Metal-Organic Chemical Vapor Deposition. ACS Nano 2015.

2. Y.C. Lin, C.-Y. Chang, R. Ghosh,J.Li, H.Zhu, R.Addou, B.Diaconescu, T.Ohta, X.Peng, N.Lu, M.J. Kim, J.T. Robinson, R.M.Wallace, T.Mayer, S.Datta, L.J. Li, J.A. Robinson; Atomically Thin Heterostructures based on Single-Layer Tungsten Diselenide and Graphene; *Nano Letters*

3. M. S. Bresnehan, G. Bhimanapati, K. Wang, D.Snyder, J.A.Robinson; Impact of Copper Overpressure on the Synthesis of Hexagonal Boron Nitride Atomic Layers; *ACS Appl. Mater. Interfaces*, 6, 16755–16762 (2014)

4. S.M. Eichfeld, C.M. Eichfeld, Y.C. Lin, L. Hossain, J.A. Robinson; Rapid, non-destructive evaluation of ultrathin WSe2 using spectroscopic ellipsometry; *APL Materials* 2 (9), 092508

5. Y.C. Lin, N. Lu, N. Perea-Lopez, J. Li, C.H. Lee, Z.Lin, P.N. Browning, M.S. Bresnehan, L. Calderin, M.J. Kim, T.S. Mayer, M. Terrones, J.A. Robinson; Direct Synthesis of van der Waals Solids on Epitaxial Graphene; *ACS Nano* 8 (4), 3715-3723 (2014)

10:40am **EM+NS+PS-MoM8 2D Bipolar Devices for Novel Logic Applications: Fabrication, Characterization and Applications**, ***Ji Ung Lee***, SUNY Polytechnic Institute **INVITED**

The three pillars in semiconductor device technologies are (1) the p-n diode, (2) the MOSFET and (3) the Bipolar Junction Transistor (BJT). They have enabled the unprecedented growth in information technology that see today. For any new material, therefore, the development of these three devices is critical for providing benchmark performance against highly scaled Si-based technologies. Here, we will describe our efforts to fabricate and characterize these three benchmark devices in 2D materials, including graphene and transition metal dichalcogenide semiconductors (TMDs).

Although graphene is gapless, we will describe device concepts based on graphene p-n junctions that can lead to steep subthreshold slope devices. Critical to realizing such devices is the demonstration of relativistic Klein tunneling, a property of chiral carriers that arise from the unique electronic structure of graphene. Here, we will describe the fabrication and characterization of graphene p-n junctions, and discuss the unique tunneling properties that arise in these junctions and our efforts to realize high efficiency switching devices.

Using TMD materials, we have fabricated a single device that can reconfigure into p-n, MOSFET, and BJT devices. The reconfigurable device allows us to provide fundamental linkages between material properties and device performance not possible by fabricating the three devices individually. We will provide our method of fabrication and describe electrical and optical properties of the reconfigurable device.

11:20am **EM+NS+PS-MoM10 Electron Transport and Tunneling in Graphene-based Heterostructures**, ***Emanuel Tutuc***, The University of Texas at Austin **INVITED**

Vertical heterostructures consisting of atomic layers separated by insulators can open a window to explore the role of electron interaction in these materials, otherwise not accessible in single layer samples, as well as to explore device applications.

We describe here the realization of vertical heterostructures consisting of graphene, hexagonal boron nitride (hBN), and transition metal dichalcogenides realized using a layer-by-layer transfer. In double bilayer graphene heterostructures separated by hBN dielectric [1] where the two layers are rotationally aligned the interlayer tunneling current measured as a function of interlayer bias reveals a gate-tunable resonance thanks to momentum conserving tunneling. [2, 3] We discuss potential device application based on these experimental observations, as well as metrics that allow a benchmarking of their performance.

We also discuss the realization and characterization of graphene-MoS_2 heterostructures, which reveal a strong negative compressibility in the MoS_2 layer as a result of electron-electron interaction. [4]

Work done in collaboration with Kayoung Lee, Babak Fallahazad, Sangwoo Kang, Stefano Larentis, Hema C. P. Movva, Sanjay K. Banerjee, Leonard F. Register, Takashi Taniguchi, and Kenji Watanabe, and with support from the NRI-SWAN Center, Office of Naval Research, and Intel Corp.

[1] "Chemical potential and quantum Hall ferromagnetism in bilayer graphene", K. Lee, B. Fallahazad, J. Xue, D. C. Dillen, K. Kim, T. Taniguchi, K. Watanabe, E. Tutuc, Science 345, 58 (2014).

[2] "Gate-Tunable Resonant Tunneling in Double Bilayer Graphene Heterostructures", B. Fallahazad, K. Lee, S. Kang, J. Xue, S. Larentis, C. Corbet, K. Kim, H. C. P. Movva, T. Taniguchi, K. Watanabe, L. F. Register, S. K. Banerjee, E. Tutuc, Nano Letters 15, 428 (2015).

[3] "Bilayer Graphene-Hexagonal Boron Nitride Heterostructure Negative Differential Resistance Interlayer Tunnel FET", S. Kang, B. Fallahazad, K. Lee, H. C. P. Movva, K. Kim, C. Corbet, T. Taniguchi, K. Watanabe, L. Colombo, L. F. Register, E. Tutuc, S. K. Banerjee, IEEE Electron Device Letters 36, 405 (2015)

[4] "Band Offset and Negative Compressibility in Graphene-MoS_2 Heterostructures", S. Larentis, J. R. Tolsma, B. Fallahazad, D. C. Dillen, K. Kim, A. H. MacDonald, E. Tutuc, Nano Letters 14, 2039 (2014).

Plasma Science and Technology
Room: 210A - Session PS+SE-MoM

Atmospheric Pressure Plasma Processing I
Moderator: François Reniers, Université Libre de Bruxelles

9:00am **PS+SE-MoM3 Modeling Non-Equilibrium Plasma Jets at Atmospheric Pressure**, ***Leanne Pitchford***, CNRS and University of Toulouse 3, France **INVITED**

The considerable recent interest in 'microdischarges' (discharges in small, spatially-confined geometries) is largely due to their remarkable stability. That is, stable, non-thermal, atmospheric-pressure plasmas can be generated and maintained in electric discharges in small geometries. Further interest in microdischarges is due to the fact that 'plasma jets', initiated from microdischarges operating with pulsed or RF excitation and with an axial helium flow, can propagate in the helium jet which extends some distance (cm's) into the open air past the exit of the microdischarge, while causing little or no increase in the gas temperature. Fast imaging shows that most of the light emitted by the plasma jet is produced in a small 'plasma bullet' that propagates in the helium jet at speeds of some tens of kilometers per second. The possibility to generate non-thermal plasmas in ambient air has incited considerable interest for applications in the biomedical field, among others.

Modeling is an important tool for developing an understanding of microdischarges. It has been shown that the plasma jet is very similar to a cathode streamer (ionization wave) guided by air surrounding the more easily-ionized helium jet. This talk will focus on results from two-dimensional fluid modeling. The properties of the streamer in helium and of the plasma channel behind the streamer head as a function of parameters such as the electrode geometry and voltage pulse waveform will be discussed. We will focus in particular on the the configuration developed by the team of Vincent Puech at the Laboratoire de Physique des Gaz et des Plasmas at the Université Paris Sud in Orsay. This configuration consists of a dielectric tube, some mm in diameter, with an inner, hollow electrode (high voltage) and an outer ring electrode (ground). A discharge is initiated inside the dielectric tube by applying high voltage pulse (some kV's with 100 ns risetime) to the inner electrode. Models reproduce the main features of plasma jets observed experimentally, and quantities such as energy deposition in the plasma jet itself can be obtained from modeling, whereas it is much more difficult to extract such information from experiments. More work is needed to quantify the plasma chemistry triggered by the plasma jet and in particular of the influence of the remnant excitation and ionization on the properties of the subsequent plasma jets.

9:40am **PS+SE-MoM5 Vacuum Ultraviolet Polymer Etching and Modification by a Remote Atmospheric Pressure Plasma Jet**, ***Andrew Knoll***, *P. Luan, E.A.J. Bartis, G.S. Oehrlein*, University of Maryland, College Park

In this study, we investigate the etching mechanism of atmospheric pressure plasma jet (APPJ) treated poly(methyl methacrylate)-based 193 nm photoresist polymer and polystyrene-based 248 nm photoresist polymer using *in situ* ellipsometry to monitor film thickness and refractive index in real time. The kHz-driven, two-ring electrode APPJ used in this work operated with low admixtures of O_2 and N_2 to Ar feed gas flowed at 2 slm. Additionally, we used attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) and x-ray photoelectron spectroscopy to characterize the surface modifications post treatment. With pure argon feed gas, we observed etching of the photoresist polymers even when the visible plume is not in direct contact with the polymer surface. This etching rate is sensitive to the Ar gas flow rate and local gas environment. APPJ treatments were compared to a surface microdischarge source with a O_2/ N_2 gas flow added but no etching was seen for that source. Furthermore, the etching was shown to be directional by placing a grounded mesh directly over the sample during treatment. No etching was seen without direct line of sight from source to sample. Optical filters were used to investigate the effect of high energy photons on polymer etching and modification. When a MgF_2 filter with a 114 nm cutoff wavelegth is placed directly over the sample, etching still occurs. When a sapphire filter with cutoff wavelength of 142 nm is used, no etching is seen. Ar_2* excimer species are known to be created in atmospheric pressure plasma and emit photons at 128 nm. Vacuum-ultraviolet (VUV)-induced etching is further supported by experiments that show that etching increases in nitrogen environments compared to oxygen environments as oxygen more effectively absorbs VUV radiation. ATR-FTIR of treated samples shows comparable bulk modifications with or without MgF_2 filter over the sample. These results are consistent with photoresists treated with VUV from low pressure plasma. APPJs are sources of a variety of reactive chemical species which can be used for numerous industrial and medical applications. While the VUV effect of APPJ sources on biodeactivation has been investgiated[1,2], polymer etching has not been seen prior to this work. The authors gratefully acknowledge financial support by US Department of Energy (DE-SC0001939) and National Science Foundation (PHY-1415353).

[1] Lackmann, J. W., et al. (2013). Journal of the Royal Society Interface 10(89).

[2] Schneider, S., et al. (2011). Journal of Physics D-Applied Physics 44(29).

10:00am **PS+SE-MoM6 Recent Development and Application of Low Cost and Portable Atmospheric Pressure Microplasma Generation Devices**, ***Cheng-Che Hsu***, *P.K. Kao, Y.J. Yang, Y.H. Huang*, National Taiwan University, Taiwan, Republic of China

Low cost and portable atmospheric pressure microplasma generation devices (MGD) offer great opportunities in several applications when plasmas in-situ, on-demand and/or in-field are desired. This study presents the development of simple and economical MGD made on copper clad laminate. This MGD can be sustained using a portable power supply (less than two pounds) that can be powered by 12V-batteries. Matching of the device capacitance with power arrangement is extremely important for this power to properly function. The use of such devices for gas conversion, selective area treatment, and fabrication microfluidic paper-based analytical device (μPAD) on demand will be presented. Such a MGD can be used to perform surface patterning of hydrophobic/hydrophilic contrasts with sub-mm spatial resolution and to effectively decompose CO2 into CO. In addition, using this MGD to fabricate μPADs is demonstrated. With a proper design of the MGD electrode geometry, μPADs with 500 μm-wide flow channels can be fabricated within 1 min and with a cost of less than $USD 0.1/device. We then test the μPADs by performing quantitative colorimetric assays and establish calibration charts for detection of glucose and nitrite. The results show a linear response to glucose assay for 1 -50 mM and nitrite assay for 0.1 -5 mM . This low cost and portable MGD can be used for in-field diagnostic tests, and is believed to bring impact to the field of biomedical analysis, environmental monitoring, and food safety survey.

10:40am **PS+SE-MoM8 Experimental Study of Micron-Scale, Field Emission-Driven Microplasmas**, ***Mihai Bilici***, *C.R. Boyle,* Case Western Reserve University, *D.B. Go,* University of Notre Dame, *R.M. Sankaran*, Case Western Reserve University

Microplasmas are miniaturized versions of low-pressure, direct-current glow discharges that can be stabilized at high pressures, up to and exceeding atmospheric pressure. In particular, atmospheric-operation has resulted in interest in their applications in materials processing, environmental remediation, and ionization sources for mass spectrometry. At these small electrode dimensions, new properties emerge that may also be important for fundamental study. For example, as the electrode gap is reduced to less than ~10 μm, gas breakdown has been found to deviate from Paschen's law due to an additional contribution to electron emission from field emission. In addition, field emission leads to a "pre-breakdown" regime where gas-phase electrons can interact with the background gas and even ionize the gas before complete breakdown occurs. However, to date there is little experimental evidence of these field-emission driven microplasmas to support theoretical predictions.

Here, we present a study of field-emission driven microplasmas using a custom-built tip-to-plane microplasma setup with environmental control and nanometer-resolution stepper motor control. The tip electrode is mounted on a micro-positioning system (Model Newport SMC100CC) and approaches a planar substrate in precise increments of ~20 nm. The entire setup is housed in an acrylic glove box that can be pumped to ~100 Torr and backfilled with a desired gas such as argon. The gap between the electrodes and subsequent breakdown of the gas is imaged by a camera system (Model Dino-Lite AM4115ZTL). Current-voltage (I-V) measurements are obtained at each gap by a programmable voltage supply and a current monitoring system.

Our results show that at small gaps of less than ~10 μm, the I-V curves exhibit a turn-on voltage, defined as the voltage where a current above the noise of ~100 nA is measured, followed by a non-linear, approximately exponential increase in current with applied voltage. The turn-on voltage is found to increase with gap from ~1-10 μm. Above ~10 μm, the non-linear regime is not observed and the I-V curve abruptly increases as a result of complete gas breakdown. To analyze the results, we have fitted the I-V curves at small gaps to Fowler-Nordheim theory, confirming that the current is produced from field emission. However, a major challenge is reproducibility of the data because of tip and substrate damage which continually affect field-emission behavior. We will discuss these issues and show our efforts to connect the experimental data to existing theory.

Keywords: microplasmas, field emission

11:00am **PS+SE-MoM9 Precise Energy and Temperature Measurements in Dielectric Barrier Discharges (DBD) at Atmospheric Pressure.**, *B. Nisol,* Groupe des Couches Minces (GCM) and Department of Engineering Physics, Polytechnique Montréal, Canada*, M. Archambault-Caron, H. Gagnon,* Groupe des Couches Minces (GCM) and Department of Engineering Physics, Polytechnique Montréal*, S. Lerouge,* Department of Mechanical Engineering, École de Technologie Supérieure (ETS), and Centre de Recherche du CHUM (CRCHUM)*,* ***Michael Wertheimer***, Groupe des Couches Minces (GCM) and Department of Engineering Physics, Polytechnique Montréal, Canada

A specially designed dielectric barrier discharge (DBD) cell and associated equipment has been used to carry out precise measurements of electrical energy, E_g, dissipated per discharge cycle of the applied a.c. voltage, V_a, over the frequency range $5 \leq f \leq 50$ kHz. Twin pairs of several different dielectric materials (2.54 cm diameter discs, thicknesses = 2.0 or ca. 0.1 mm) with relative permittivities between $2.1 \leq K' \leq 9.5$ were used as dielectric barriers in DBDs of four different gases: He, Ne, Ar and N_2. Much of the work relates to the study of atmospheric pressure glow discharge (APGD) plasma in flowing He gas; five separate thermometers (including fiber-optic probes immune to high voltage and high-frequency electromagnetic fields) have enabled us to perform a detailed calorimetric (heat balance) investigation in He APGD, believed to be the first of its kind. Fair agreement in the overall energy balance, which includes vacuum ultraviolet (VUV) light emission, lends strong support to the validity of both measurements and methodology. The latter includes refined algorithms that permit rapid data acquisition and processing. The present results are compared with literature, allowing several important conclusions / recommendations to emerge.

Next, we turn to the particular case of DBD in Ar in a pilot-scale reactor dedicated to deposition of thin organic films (PECVD) for biomedical applications. We have found that transfer of data from the small to the large (near 50-fold greater surface area) apparatus has been very successful, and that we can now precisely measure the amount of energy (ΔE_g) consumed in a particular PECVD process. We finish by presenting specific example reactions and link energy measurements with physico-chemical characteristics of deposits.

11:20am **PS+SE-MoM10 Plasma-Induced Conductivity in Dielectrics: A Study of Dielectric Barrier Discharges**, ***Floran Peeters****, FOM Institute DIFFER, Netherlands, *R.F. Rumphorst,* Eindhoven University of Technology, Netherlands, *M.C.M. van de Sanden*, FOM Institute DIFFER, Netherlands

In plasma devices, the surfaces bounding the plasma form an integral part of the system. Despite this, surfaces are generally described as perfect absorbers for electrons and ions, without any further consideration of potentially relevant processes taking place within the material. Dielectric surfaces, for instance, are treated as single capacitive elements, providing a wall potential. For most discharges this model is sufficiently accurate, but if the characteristic dimensions of dielectric and plasma are very dissimilar, such as in etched micro- and nanostructures or if the discharge itself is non-uniform, understanding the build-up of surface charges and their subsequent behavior becomes of paramount importance.

In our work, we use a typical non-uniform discharge to investigate the plasma-dielectric interaction: the dielectric barrier discharge (DBD) in filamentary mode. Filamentary DBDs can be described by an equivalent circuit which assumes discharging occurs uniformly across the surface, i.e. by treating the dielectric as a single continuous capacitive element. This is counter-intuitive, since DBD actually consists of many spatially and temporally separated, transient microdischarges. Studying the electrical characteristics of DBDs more closely, using both conventional *Q-V* diagrams combined with a circuit designed to record the transferred charge per filament, we developed an improved electrical model of the DBD. An extension to the electrical model for DBDs introduced by Manley in 1943, our model explicitly takes into account the localized nature of the discharge. Using this model, we find that individual filaments are always roughly equivalent; irrespective of the phase or amplitude of the applied voltage. We show that this leads to limited control over the chemical processing efficiency of DBD. The fundamental cause of the insensitivity of the discharge to the applied voltage is identified as the constant redistribution of surface charge on the dielectric.

Further investigation reveals that this redistribution of charge does not occur via the gas-phase of the residual plasma, as is often assumed, but is likely the result of excess charge carriers being introduced into the dielectric by the discharge. We provide corroborative evidence that these excess charge carriers, involving free electron and hole densities not normally seen in high-band gap materials, provide a boost to the conductivity of the material in locations affected by the plasma. As shown here for a DBD, this plasma-induced conductivity can have a significant effect on the behavior of the discharge and should be considered in any models of plasma involving dielectric surfaces.

11:40am **PS+SE-MoM11 Fabrication of Flexible, Electrically-Conductive Features by Microplasma Reduction of Cation-Cross-Linked Polyacrylic Acid (CCL-PAA) Films**, ***Souvik Ghosh****, *R. Yang, P.X.-L. Feng, C.A. Zorman, R.M. Sankaran*, Case Western Reserve University

Patterned metal formation on substrates is typically achieved by subtractive methods. Recently, additive manufacturing techniques have emerged that can selectively deposit materials to produce patterned structures. Examples of additive methods include ink-jet, aerosol, and screen printing. A common feature of all of these approaches is the ink, a solution of stabilized colloidal metal nanoparticles that is deposited onto an arbitrary substrate. Removal of the organic stabilizers is often carried out by annealing at high temperatures (>200 ºC) to produce electrically conductive features, limiting what substrates can be used. There are also challenges with deposition of the inks associated with the viscosity and adhesion of the inks to the substrate.

An alternative approach to fabricating patterned metals in polymers is *in situ* reduction of metal containing polymers. Here, we present an atmospheric-pressure microplasma process for the selective reduction of metal ions in polymer films to produce flexible, electrically-conductive metal patterns [1]. The films are made from polyacrylic acid (PAA) which reversibly cross links with metal cations such as silver (Ag^+). The films are subsequently exposed to a microplasma formed in a flowing argon gas on a two-dimensional scanning stage to "write" a desired pattern. Characterization of the films by X-ray diffraction (XRD) confirms that the Ag^+ is reduced to crystalline Ag after exposure to the microplasma. Further materials analysis by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDX) show that reduction leads to the formation of Ag nanoparticles whose size and morphology depend on the exposure conditions (i.e. plasma current, scanning rate, etc.). Cross-sectional characterization of the films shows that the reduction does not penetrate through the film bulk. We suggest that the Ag^+ diffuses to the film surface during reduction, leading to a near-surface layer of reduced crystalline Ag with bulk resistivity ~1 mΩ-cm. Stretchable films have been produced by casting PAA-Ag^+ films on top of a polydimethylsiloxane (PDMS) substrate, followed by exposure to the microplasma. Dynamic mechanical analysis (DMA) of the multilayer films yield a breaking force value of >3 MPa and the films can be stretched to >100%. Electrical measurements are performed on the films as a function of strain to analyze the change in resistivity with stretching. We will also present our recent efforts to reduce the size of the patterns, which is currently ~100 µm, to approximately 10 µm by incorporating stencil masks.

[1] S. Ghosh *et al.*, ACS Appl. Mater. Interfaces **6**, 3099 (2014).

Plasma Science and Technology
Room: 210B - Session PS-MoM

Advanced FEOL/Gate Etching
Moderator: Chanro Park, GLOBALFOUNDRIES

8:20am **PS-MoM1 FEOL Patterning Challenges for Sub 14nm FDSOI Technology**, ***Sébastien Barnola****, N. Posseme, P. Pimenta-Barros, C. Vizioz,* CEA, LETI, MINATEC Campus, France*, C. Arvet,* ST Microelectronics, France*, O. Pollet, A. Sarrazin,* CEA, LETI, MINATEC Campus, France*, M. Garcia-Barros,* ST Microelectronics, France*, L. Desvoivres*, CEA, LETI, MINATEC Campus, France **INVITED**

Fully-depleted SOI devices (FDSOI) are proven to provide excellent control of gate electrostatics. This makes them a real solution to meet performance requirements down to 10nm technology node, however new architectures such as stacked silicon nanowires will be required to maintain low leakage current when further downscaling gate length. Additionally new materials are required to build transistor channel complying with ON-state current expectations, such as new channel materials such as germanium or compound semiconductors or low k materials at the spacer level.

These changes in transistor integration raise quite a number of new challenges for etching and stripping in that they introduce new materials with uncommon properties compared to usual silicon-based devices.

Another challenging aspect of device downscaling is the enhanced demand for high-selectivity etch. In spacer definition for instance, maximum allowable silicon recess in source / drain regions is less than 0.5nm for the 14nm node. To this end new techniques are being developed that involve a prior modification of the etched layer down to a controlled depth, followed

* **Coburn & Winters Student Award Finalist**

by the removal of the modified layer selectively to the non-modified material.

On the technology side, immersion 193nm lithography has reached its limits in resolution and the most critical levels require costly dual or quad-patterning technique to achieve stringent CD specifications in current 14nm and beyond. Solutions to further expand 193nm lithography capabilities at lower costs are showing promising results, such as sidewall image transfer (SIT) or directed self-assembly (DSA). Nevertheless these newly developed techniques involve process adaptations on the plasma etching side since they induce changes in the masking materials.

9:00am **PS-MoM3 Material and Etch Interaction Comparisons for SIT Patterning**, ***John Sporre***, IBM Corporation, *A. Raley*, TEL Technology Center, America, LLC, *D. Moreau*, STMicroelectronics, *M. Sankarapandian, P.K.C. Sripadarao, J. Fullam, M. Breton, R. Chao, S. Kanakasabapathy*, IBM Corporation, *A. Ko*, TEL Technology Center, America, LLC

Sub-Lithographic pitch patterning requires advanced patterning techniques capable of achieving reduced dimensions with current lithography technology. Novel techniques are employed to pattern gates with critical dimensions below the current resolution limits of optical lithography. One such technique is Sidewall Image Transfer (SIT), where the critical dimension of the gate is established by the controlled deposition of a spacer on top of a Lithographically defined mandrel. The material selection of the mandrel and spacer materials can influence the functionality of the SIT process, and this paper specifically compares the use of an ashable organic mandrel to an inorganic mandrel. Organic mandrels for mandrel removal selective surrounding spacer material. However inorganic mandrels, are resistant to profile modifications. In this paper, we compare both approaches with specific focus on the influence of plasma etch chemistries on mandrel profile characteristics.

9:20am **PS-MoM4 Trim Etch for sub-20 nm Technology**, ***Guangjun Yang***, *D. Keller, Y. Rui, R. Benson, A. Schrinsky*, Micron Technology

Photo resist trim with isotropic etch is a common practice in industry for CD control and line width roughness (LWR) improvement for sub 35 nm features imaged with 193nm lithography. As CD shrinks further, it becomes more challenging to control CD, to reduce line buckling or wiggling and to manipulate etch profile. For CDs below 20 nm, hardmask trim and live structure trim play an important role. In this talk, we will present a few examples of isotropic trim for sub-20 nm technology using mainly ICP chambers. In one case, DUV photo resist was trimmed from 40 nm to 15 nm with good LWR and good remaining height. In another case, a Si3N4/metal stack was trimmed down to 8 nm from 15 nm with good SWR (space width roughness) and etch profile. In the third case, we selectively trim DLC (diamond-like-carbon) in the bottom portion of the profile to make the etch profile straighter. Also we will discuss some challenges in developing a good isotropic trim process such as trim etch selectivity to materials and to location, etch uniformity. Finally we will discuss some opportunities for etch tool development.

9:40am **PS-MoM5 Laser-Assisted Dry Etch of poly-Si and SiO_2 for Semiconductor Processing**, ***Jason Peck***, *G.A. Panici, I.A. Shchelkanov, D.N. Ruzic*, University of Illinois at Urbana-Champaign

Dry etch assisted by laser (DEAL) of silicon and silicon dioxide via $Ar/SF_6/C_4F_8/O_2$ capacitively-coupled plasma was studied, with goals including form control for sub-22 nm features and uniformity for 450 mm wafer processes. The first phase of the work confirmed the feasibility of the proposed concept. The second phase of the work was focused on pulse frequency, length and wavelength influence on etching rate. Two lasers with different repetition rates, wave lengths and pulse widths were used. The first one is a (2.5 – 7 ns FWHM) Nd:YAG laser with repetition rate of 100 Hz. The Nd:YAG laser was capable to produce emission at 1064, 532 and 266 nm wavelengths. The second laser was a 1043 nm IMRA laser with 300 fs pulses and 1 MHz pulse rate. Continuous wave (CW) laser systems were also tested.

The etch rate enhancements were determined. The predominant laser-assisted etch mechanism was interpreted to be electrochemical, with electron-hole pairs catalyzing chemical etching at the surface. The influence of laser repetition rate was studied in both SF_6 and C_4F_8 etch. The beam intensity profile influence onto etch pattern was studied. In all cases, an emphasis on low power density kept the experiments well under the ablation threshold, minimizing pyrolytic damage by the incident beam. Impact on current industry processes will be discussed.

10:00am **PS-MoM6 Spatial Resolution Considerations for Uniformity Improvement by Gas Cluster Ion Beam Etch**, ***Joshua LaRose***, TEL Technology Center, America, LLC, *B. Pfeifer, V. Gizzo*, Tokyo Electron, *N. Joy, N.M. Russell*, TEL Technology Center, America, LLC

Abstract

Sub-14nm CMOS requires a demanding level of integrated thickness control at several critical layers in the fabrication process in order to meet functional and parametric yield/Cpk goals. Gas cluster ion beam (GCIB) etching is becoming increasingly adopted to meet this need by using precise corrective etching with location specific processing (LSP) to meet within-wafer and wafer-to-wafer control requirements. LSP etch correction may be driven by any input map delivered to the tool via factory automation, or may be driven by on-board integrated metrology. In either case the extent to which a uniformity pattern can be corrected may be limited by the length scale of non-uniform features as compared to the size of the beam, and the ability of the metrology sampling plan to resolve the features. Here we characterize in some detail, the influence of sampling density and non-uniformity length scale on LSP resolution capability.

LSP was able to substantially reduce the standard deviation of a model incoming non-uniformity map for features with > 8 mm length scale, and to adequately resolve such features, requires a metrology sampling plan corresponding to > 89 points on a 300 mm wafer. For wafer-edge non-uniformity, we show similar capability to resolve features > 10 mm by LSP, with sufficient metrology sampling density, and introduce a hybrid edge model scheme that can enable improved resolution of edge features with as few as 37 metrology points. Here we describe in detail the techniques used to determine the resolution performance, summarize results from several relevant cases, and present clear guidelines on sampling strategies for LSP etching.

10:40am **PS-MoM8 Analysis of Surface Reaction Layers formed by Highly Selective Etching with Pulsed Microwave Plasma**, ***Miyako Matsui***, Hitachi Ltd., Japan, *M. Morimoto, N. Ikeda, T. Ono*, Hitachi High-Technologies Corp. **INVITED**

Three dimensional (3D) transistors, such as a Fin-FET, have increasingly necessitated etching processes with higher selectivity and greater anisotropy. For example, a Si_3N_4 spacer layer needs to be anisotropically etched with a vertical profile without leaving residue on the sidewalls of the fins while keeping high selectivity in regard to Si fins. To provide more highly selective and more anisotropic etching for fabricating next-generation 3D devices, an etching system combining a pulsed-microwave ECR plasma and time-modulated wafer bias was developed.

In this study, the mechanism of highly selective etching with a pulsed-microwave ECR plasma was investigated by analyzing surface-reaction layers formed on etched materials. To clarify the etching mechanisms of poly-Si, Si_3N_4, and SiO_2, surface-reaction layers formed not only on unpatterned surfaces but also at the bottoms of line-and-space patterns were analyzed by XPS. Specimens were etched using an $HBr/O_2/Ar/CH_4$ gas chemistry for poly-Si etching and using a $CH_3F/O_2/Ar$ gas chemistry for Si_3N_4 etching. The XPS results revealed that a modified layer formed on all etched materials and that a polymer layer formed on the modified layer. To determine the effects of the etching parameters on etching selectivity, the thickness and composition of the reaction layers, which were the polymer layer and the modified layer, were quantitatively analyzed. To examine the thermal reactivity between the reaction layers and the etched materials, etched surfaces were analyzed by TDS.

Highly selective etching mainly originated from the difference in the thickness of the polymer layers that formed on the etched materials under the pulsed plasma. The thickness of the polymer layer was controlled so that etching did not stop even at a low wafer bias voltage. Reactivity between the reaction layers and the etched material was controlled by adjusting the composition of the reaction layers. Especially in the case of Si_3N_4 etching, the N in the Si_3N_4 layer thermally reacted with the reaction layers, forming NH_3 or HCN, and the Si in the Si_3N_4 layer had high reactivity with the F in the reaction layers. Due to the high reactivity between the F-rich reaction layers and the Si_3N_4 layer caused by the pulsed plasma, the polymer layer became thin even at a low wafer bias and thus promoted ion-assisted etching. As a result, wide process windows were provided by formation of the reaction layers under the pulsed plasma.

11:20am **PS-MoM10 Improvement of Gate Shoulder Retention and SiN Selectivity over Si in Spacer Process**, ***Yohei Ishii***, *K. Okuma, N. Negishi, J. Manos*, Hitachi High Technologies America Inc.

To achieve improvements in semiconductor device performance, 3D transistors (FinFET) were introduced due to limitations in planar structures. Because of the complexity of the structure and high aspect ratio features, new challenges have appeared. Among many processes, spacer etch is one process that could have an impact on device performance. During spacer

etch, there are several issues that arise such as SiN selectivity over Si and gate shoulder retention.

In this presentation, we will demonstrate a spacer etching process, using a novel gas, and utilizing a Hitachi microwave Electron Cyclotron Resonance (M-ECR) etcher. SiN selectivity over Si is improved compared to a conventional gas chemistry such as CH3F base process. In addition, while the spacer is etched, the gate shoulder has to be protected. Finally, we will also introduce an etching method that overcomes the trade-off relationship between gate shoulder retention and spacer etch.

11:40am **PS-MoM11 Advanced Patterning Applications Using High Selectivity Etch Chemistry**, ***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, A. Itou,* ZEON Chemicals L.P.*, H. Matsumoto*, Zeon Corporation, Kawasaki, Japan

Image reversal has been utilized in semiconductor manufacturing to invert line/space [US6221562 B1] and hole/pillar [US6358856 B1] patterns. Since this process requires the ability to remove one material with high selectivity to another, traditionally either contrasting dielectrics (such as SiN/SiOx) or complementary types of photoresist (e.g. positive/negative tone) have been used. While carbon-based soft materials are easier to deposit than dielectric films, lack of selectivity and physical integrity can potentially hinder successful image reversal processes when they are combined with hard materials, e.g. metals, dielectrics.

We present an image reversal process by depositing an organic planarizing layer (OPL) material into a hole array patterned in SiN to create pillars, which are a commonly required shape for a variety of emerging technologies. By using a gas chemistry with an extremely high selectivity to OPL, plasma etch removal of the SiN is possible, allowing pattern fidelity to be maintained at pitches below 100nm. We demonstrate control of the pillar CD by controlling the time of the OPL etchback step.

For applications requiring minimal mask budget, we utilize the same chemistry's selectivity to SiOx to demonstrate patterning of SiN hard mask features with reduced LER/LWR and iso/dense loading ratio. We demonstrate hard mask patterning of 80nm thick SiN with 35nm SiOx hard mask for 50nm pitch lines, with potential applications for advanced technology nodes. The results were achieved in both RLSA and ICP plasma sources.

Electronic Materials and Processing
Room: 210E - Session EM+NS+PS-MoA

More Moore! II
Moderator: Christopher Hinkle, University of Texas at Dallas, Andrew C. Kummel, University of California at San Diego

2:20pm **EM+NS+PS-MoA1 Effect of *Ex Situ* and *In Situ* Surface Cleaning on the Quality of Al_2O_3-SiGe(001) Interfaces**, *K. Sardashti, **Kai-Ting Hu***, UC San Diego, *S. Madisetti,* College of Nanoscale Science and Engineering, Albany-SUNY, *K. Tang,* Stanford University, *S. Oktyabrsky,* College of Nanoscale Science and Engineering, Albany-SUNY, *P.C. McIntyre,* Stanford University, *S. Siddiqui, B. Sahu,* Globalfoundries, *N. Yoshida, J. Kachian,* Applied Materials Inc., *A.C. Kummel*, UC San Diego

Silicon-Germanium has shown a great promise for future CMOS technology by combining the high hole and electron mobility of Ge with the ability to have both tensile and compressive strain by fabrication of alloys of higher and lower Ge content. In contrast to Si, SiGe native oxide is a combination of SiO_2 and GeO_2, SiGeOx, which has low interface quality and stability in comparison with SiO_2 due to the presence of the GeOx. Therefore, instead of thermal oxide growth, it is necessary to employ atomic layer deposition (ALD) for gate oxide deposition in SiGe MOS devices. The effects of the ex-situ wet chemical clean (such as HF and $(NH_4)_2S$ dip) and in-situ NH_3 plasma clean prior to ALD, were determined on Al_2O_3/SiGe; interface quality quantified by oxide leakage, interfacial trap density, and near-interface trap density. MOS capacitors fabricated by Al_2O_3 ALD at 120°C. Compared to HF clean, both ex-situ $(NH_4)_2S$ clean and in-situ NH_3 plasma resulted in smaller density of interface and smaller leakage current in accumulation. Furthermore, both methods resulted in high surface stability in air; queue times up to an hour could be tolerated. Angle-resolved X-ray photoelectron spectroscopy (AR-XPS) measurements on SiGe(001) with 0.8nm thick Al_2O_3 showed that $(NH_4)_2S$ clean significantly reduces the amount of GeOx at the in Al_2O_3/SiGe(001) interface, compared to HF clean.

2:40pm **EM+NS+PS-MoA2 Surface Passivation for ALD-Al_2O_3/SiGe MOS Devices**, ***Liangliang Zhang***, Stanford University, *V. Hassan, C. Lo, C. Olsen, M.A. Foad,* Applied Materials Inc., *P.C. McIntyre*, Stanford University

We report a study of passivation of the SiGe surface, a critical challenge for future SiGe MOSFET technology. Epitaxially grown p-type SiGe films on lightly doped Si substrates are investigated. The layered surface structures of native oxide coated, as-received SiGe samples are characterized using soft x-ray synchrotron photoemission electron spectroscopy (PES). It is observed that the surface of as- received SiGe wafers have a mixed SiO_x/GeO_x oxide layer. Angle-resolved PES shows that this layer is SiO_x-rich at the top surface and GeO_x-rich below. Lab source x-ray photoelectron spectroscopy (XPS), hard x-ray PES and x-ray reflectivity (XRR) are used to characterize the interface region between atomic layer deposited (ALD) Al_2O_3 gate dielectrics and SiGe. Prior to ALD, 2% HF(aq) solution is used to remove the surface oxides, and a high quality Al_2O_3 layer on the SiGe substrate is deposited with the help of efficient sites for $Al(CH_3)_3$ (TMA) precursor adsorption produced by H_2O oxidant pre-dosing of the SiGe surface immediately prior to the TMA/H_2O ALD process. It is observed from XPS and PES that there is an increase of the SiO_x peak intensity after Al_2O_3 deposition, while there is little or no detectable Ge core level feature associated with GeO_x. The thermodynamic preference of Si (compared to Ge) atoms bonding to oxygen agrees well with the identity of the layered oxide structures extracted by fitting measured XRR data from the processed samples.

Both Pt, a metal that is a known catalyst for H_2 dissociation, and Al are investigated as gate metals for ALD-Al_2O_3/SiGe MOS capacitors (MOSCAPs) subjected to post metal forming gas (5% H_2/95% N_2) anneal (FGA). The effects of the identity of the gate metal on post-FGA interfacial oxide composition and interface trap response is studied. Capacitance-voltage analysis of Al/Al_2O_3/p-SiGe MOSCAPs detects minimal frequency dispersion in depletion and accumulation. The extracted density of interface traps is peaked near the valence band, with a maximum value of ~ $3x10^{11}$ ($eV^{-1}cm^{-2}$).

3:00pm **EM+NS+PS-MoA3 Harnessing Chemistry to deliver Materials and Process for theNext 10 Years of CMOS Evolution**, ***Robert Clark***, TEL Technology Center, America, LLC **INVITED**

Harnessing Chemistry to Deliver Materials and Processes for the Next 10 Years of CMOS Evolution

Robert Clark

TEL Technology Center, America, LLC

Albany, NY 12203

Robert.clark@us.tel.com

The continued scaling of the Integrated Circuits (ICs) according to Moore's law has led to a doubling of the number of devices per unit area in semiconductor microchips approximately every 2 years since 1962. Over the past decade traditional scaling by simple linear shrinking has effectively ceased as IC makers have adopted new 3-dimensional device structures, complex integration schemes and new processes and materials for an expanding number of applications in order to overcome fundamental physical limits. In order to continue Moore's law in the coming decade this trend will not only continue, but intensify as devices are scaled to a level approaching atomic dimensions. Broadly speaking, two major trends are influencing the development of future IC manufacturing processes: the need to harness the third dimension to extend Moore's law; and the need for "self-something" processes. "Self-something" processes refers to processes or schemes that are directed chemically to attain a desired result and includes processes that are self-limited (e.g. ALD or ALE), self-directed (e.g. directed self-assembly or selective deposition), or self-aligned (e.g. self-aligned contacts) in some way that enables device density scaling. "Self-something" processes are required in order to harness the third dimension and make use of new non-planar device architectures (e.g. FinFETs and DRAM capacitors), device arrays/stacking (e.g. 3D NAND and cross-point memory), and 3D integration (e.g. monolithic 3D, and chip stacking). Highly tailored ALD processes are being investigated to fabricate functional material layers. Interspersed treatments and doping may be used to modify the physical and electrical properties of ALD films further in order to optimize the resulting physical or electrical properties. To improve device contacts, ultra-thin dielectric and metal layers may be deposited inside of high aspect ratio contact structures in order to provide lower contact resistivity. Selective deposition processes can be used to deposit functional materials only where they are needed, thus reducing the patterning burden during IC manufacturing. Depositing dopant layers by ALD for thermal solid source doping can be used to conformally dope 3-D device structures without the damage caused by implantation. Examples of these and similar processes will be described and discussed along with the chemical processes and transformations governing film deposition, composition, structure, and interface control.

3:40pm **EM+NS+PS-MoA5 Materials Selection for Oxide-based Resistive Random Access Memory (RRAM)**, ***John Robertson***, *Y. Guo*, Cambridge University, United Kingdom of Great Britain and Northern Ireland **INVITED**

Resistive random access memory (RRAM) is a main challenger non-volatile memory technology to Flash memory. The favored materials are based on the formation of a conductive filament of oxygen vacancies across a film of a wide gap oxide. However, a wide range of material systems are presently being studied, which use various different switching mechanisms. Materials selection requires us to understand which material properties control each aspect of device performance, such as switching speed, resistance window, retention time and endurance. Here, the energies of various atomic processes in resistive random access memories (RRAM) are calculated for four typical oxides, HfO_2, TiO_2, Ta_2O_5 and Al_2O_3, to define a materials selection process. Oxygen vacancies have the lowest defect formation energy in the O-poor limit, and to dominate the processes. A band diagram defines the operating ranges of Fermi energy and O chemical potential. It is shown how scavenger metals can be used to vary the O chemical potential and thus vary the O vacancy formation energy. The high stability of amorphous phase of Ta_2O_5 is relevant to the high endurance of its RRAM.

4:20pm **EM+NS+PS-MoA7 Lower Temperature Silicon Nitride ALD on $Si_{0.5}Ge_{0.5}$(110) with No Solid By-product Formation**, ***Steven Wolf***, *M. Edmonds*, *T. Kent*, University of California at San Diego, *D. Alvarez*, RASIRC, *R. Droopad*, Texas State University, *A.C. Kummel*, University of California at San Diego

A silicon nitride passivation layer on semiconductor surfaces can serve several practical uses, such as acting as a diffusion barrier or channel passivation layer prior to dielectric deposition in FinFets or MOSFETs. When employed as a channel passivation layer, further reaction with an oxidant, such as anhydrous peroxide, can leave Si-N-OH termination, which is reactive with all metal ALD precursors thereby providing high nucleation density. Previous studies show stoichiometric ALD Si_3N_4 growth on Si(100) by hydrazine and Si_2Cl_6 at temperatures in excess of 350°C with solid ammonium chloride by-product formation[1]. The first half reaction of N_2H_4 leaves N-H_x surface termination, and the second reaction with Si_2Cl_6 adds silicon to the surface and creates a gaseous HCl by-product. An ammonium chloride by-product is usually caused by wall reactions of unreacted precursors. This study focuses on developing a low temperature silicon nitride ALD process with no unwanted solid by-product formation. STM/STS and XPS are employed to characterize SiN_x film growth on $Si_{0.5}Ge_{0.5}$(110).

A test chamber consisting of a reactor chamber, dosing lines, and a dry pump was created and heated to 125°C for 12 hours to allow for sufficient heating of all stainless steel components. In excess of 100 ALD cycles were ran in the test chamber with no visible evidence of powder formation on any walls, and it was concluded that this lengthy heating process prior to SiN_x ALD is necessary to eliminate the unwanted powder by-product formation. Next, at a substrate temperature of 275°C and wall temperature of 20°C, the silicon nitride ALD procedure was performed on a p-type $Si_{0.5}Ge_{0.5}$(110) surface that underwent an ex-situ wet organic clean followed by a dip into a 2% HF/water solution with a toluene layer on top. The sample was pulled through toluene and loaded into UHV as quickly as possible to minimize native oxide formation. After a 315 MegaLangmuir anhydrous hydrazine dose, XPS shows N-H_x surface termination, and removal of half of the initial carbon contamination. A subsequent 21 MegaLangmuir Si_2Cl_6 dose followed by 17 cycles of 3 MegaLangmuir hydrazine and 3 MegaLangmuir Si_2Cl_6 leads to increased silicon nitride growth as shown by a large increase in XPS Si 2p and N 1s peaks, as well as a decrease in the Ge 3d substrate peak. After the ALD cycling with room temperature walls, a white powder, presumed to be ammonium chloride, was seen in the reactor, but will now be avoided using the 125°C wall temperature.

1. S. Morishita *et. al*., Appl. Surf. Sci., **112**, p:198-204 (1997).

4:40pm **EM+NS+PS-MoA8 Novel Delivery of Unstable Precursors for Atomic Layer Deposition**, ***Daniel Alvarez***, *J. Spiegelman*, *E. Heinlein*, *R. Holmes*, *C. Ramos*, *S. Webb*, *K. Johnson*, RASIRC

A considerable amount of effort has gone into the development of novel metal precursors for Atomic Layer Deposition (ALD). This is primarily driven by the need for new high *K* materials and metals films. Largely ignored has been the need for novel oxidants and sources of nitrogen. This paper focuses on the delivery of anhydrous hydrogen peroxide and anhydrous hydrazine for ALD applications.

Hydrogen Peroxide (H_2O_2) in aqueous form is commonly used in semiconductor manufacturing for cleaning and surface preparation operations. Thirty percent and fifty percent two-component mixtures have been investigated in a few ALD studies with moderate success. Especially noteworthy are Kummel's findings that the use of hydrogen peroxide leads to a 3x increase in nucleation density on Ge versus water. However, H_2O_2 has limited general utility in aqueous form due to the volatility of water. At 30C, Raoult's law predicts a headspace concentration of 294ppm H_2O_2 and 32373ppm for water, where the H_2O/H_2O_2 ratio is over 100. Clearly these are not optimal conditions for hydrogen peroxide ALD. However, in its pure state, hydrogen peroxide is highly unstable and has a propensity to decompose, forming water and oxygen. Our approach entails the use of a membrane delivery system where 99.6% hydrogen peroxide is dissolved in an organic solvent. Hydrogen peroxide permeates the membrane and is delivered to the ALD chamber, while the solvent does not permeate and remains in the liquid state. In this way, concentrations much higher than predicted by Raoult's law for aqueous mixtures are delivered to the process chamber in the absence of water.

Next generation devices have low thermal budgets and high aspect ratio structures that create new challenges for ALD grown nitride films. The use of ammonia is limited due to temperature constraints. Known Plasma methods cannot uniformly coat the side walls of the device structures and create surface damage. Hydrazine (H_2NNH_2) has been proposed as a thermal ALD low temperature nitride source.Hydrazine is highly flammable and its flash point decreases with reduced water content. In an analogous approach, we have developed a new method and formulation for the delivery of anhydrous Hydrazine by the use of an inert organic solvent and membrane delivery system. Precursor vapor pressure is maintained at levels viable for ALD. Moreover, the addition of a high boiling solvent lowers the risk of explosion by raising the solution flash point.

Preliminary ALD data will be presented showing unique properties of these new precursors along with theoretical data on precursor delivery under variable ALD conditions.

5:00pm **EM+NS+PS-MoA9 Passivation and Functionalization of SiGe(001) and (110) for ALD Nucleation in FinFET Structure**, ***SangWook Park***, *H. Kim*, University of California at San Diego, *B. Sahu*, *S. Siddiqui*, GLOBALFOUNDRIES U.S. Inc., *N. Yoshida*, *A. Brandt*, Applied Materials, Inc., *E. Chagarov*, *A.C. Kummel*, University of California at San Diego

Silicon Germanium (SiGe) is a promising candidate for FinFET channels, sources, and drains due to its high mobility and utility in strain engineering. Since FinFETs are composed of three-dimensional structures utilizing multiple crystalline planes, the cleaning and passivation must provide uniform and clean surfaces in each plane to combine high mobility with low interface trap density (Dit). In this study, passivation and functionalization of SiGe(001) and (110) surfaces are discussed, using scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), and x-ray photoelectron spectroscopy (XPS).

The SiGe(001) is dimer terminated while the SiGe(110) is dimer-free leading to differences in surface stoichiometry and order. STM and XPS measurements indicate that clean (001) is mostly terminated with Ge atoms with a uniform and well-ordered structure while (110) is terminated with adatoms of both Si and Ge atoms and lower surface order. STS measurements indicate the clean (001) surface is unpinned while the clean (110) surface is pinned mid gap between the valence and conduction band edge due to adatom dangling bonds. The sputter cleaned SiGe(110) surface was dosed at 300°C with 3,600L dose of atomic H to passivate the dangling bonds of the adatoms. STS measurements demonstrate the atomic H dosed (110) surface is unpinned with a Fermi level near the valence band due to Si-H and Ge-H bonds on adatoms. The unpinned SiGe (001) and (110) surfaces were dosed at room temperature with a saturation dose of H_2O_2(g) leaving the SiGe surface terminated with an ordered monolayer of only Ge-OH sites on (001) and both of Ge-OH and Si-OH sites on (110). STS shows that on the HOOH dosed SiGe(001) and (110), the Fermi level is shifted to near the valence band edge due to the large surface dipole from the hydroxyl bonds. TMA was subsequently dosed on the HOOH/SiGe(001) and HOOH/atomic H/SiGe(110) surfaces forming an ordered monolayer of Al-O-Si bonds. In order to understand the thermal stability of the TMA dosed SiGe surfaces, the surface was annealed to 300°C and XPS measurements verify that Al-O bonds are totally transferred from Ge atoms to Si atoms forming Al-O-Si bonds on both (001) and (110) indicating that the strong affinity between Si and oxygen is pulling Si atoms toward the surface to bond with oxygen or hydroxyls while pushing Ge atoms into the subsurface during the annealing. STS indicates this unpins the Fermi level on both surfaces, leaving an electrically passive ordered layer which serves as an ideal template for further high-k ALD.

5:20pm **EM+NS+PS-MoA10 Band Structure and Critical Points of Pseudomorphic $Ge_{1-y}Sn_y$ Alloys on Ge**, ***Nalin Fernando***, *T.N. Nunley*, *S. Zollner*, New Mexico State University, *D. Zhang*, *R. Hickey*, *J. Kolodzey*, University of Delaware

We calculate the dependence on composition and strain of the band structure of $Ge_{1-y}Sn_y$ alloys grown pseudomorphically on Ge and compare with spectroscopic ellipsometry measurements. Germanium is an indirect band gap material with limited optoelectronic applications. Because the band structure of Ge is a strong function of strain, a transition from an indirect to a direct band gap has been found for Ge under a tensile strain, which constrains the layer thickness and the composition of the substrate for heterostructure growth. Indirect to direct band gap crossover of unstrained $Ge_{1-y}Sn_y$ has been reported for y~6-10% indicating the possibility of widespread applications of Ge-based photonic devices and paving the way for the design of $Ge_{1-y}Sn_y$ lasers. Hence it is important to study the compositional dependence of the $Ge_{1-y}Sn_y$ band structure through measurements of the optical properties of $Ge_{1-y}Sn_y$ alloys. The complex pseudodielectric functions of pseudomorphic $Ge_{1-y}Sn_y$ alloys grown on Ge by MBE were measured using spectroscopic ellipsometry at 300 K in the 0.76-6.6 eV energy range for Sn contents up to 11%. Dielectric functions of $Ge_{1-y}Sn_y$ alloys were obtained to investigate the compositional dependence of the E_1 and $E_1+\Delta_1$ critical point (CP) energies. CP energies and related parameters were obtained by analyzing the second-derivative of the dielectric function. Our experimental results are in good agreement with the theoretically predicted E_1 and $E_1+\Delta_1$ CP energies of compressively strained $Ge_{1-y}Sn_y$ on Ge based on deformation potential theory. We will discuss the compositional and strain dependence of the direct and indirect band gaps as well as E_1 and $E_1+\Delta_1$ CP energies and related parameters of $Ge_{1-y}Sn_y$ alloys. We will present the nature of the band gap of pseudomorphic $Ge_{1-y}Sn_y$ on

Ge and will discuss the effects of strain which critically depend on the bowing parameter of the lattice constant.

Plasma Science and Technology
Room: 210B - Session PS+EM-MoA

Directed Self Assembly and Plasma Synthesis of Novel Materials
Moderator: Eric Joseph, IBM T.J. Watson Research Center

2:20pm **PS+EM-MoA1 Forward and Inverse Computational Tools for Directed Self-Assembly**, *G.H. Fredrickson, **Sean Paradiso***, University of California at Santa Barbara **INVITED**

This presentation will provide a tutorial on the physics of bulk block copolymer self-assembly, explaining how molecular parameters such as polymer architecture, composition, and molecular weight influence the size and symmetry of nanoscale domains. In thin films, additional variables such as surface and substrate interactions and substrate topology are important in "directing" the self-assembly and thereby achieving morphologies and features useful for pattern transfer in lithography. A powerful computational framework based on polymer field theory will be described that enables simulations to be conducted for a wide range of block copolymer formulations subject to arbitrary topological confinement ("grapho-epitaxy") or substrate chemical modulation ("chemo-epitaxy"). Our recent work at UCSB has involved computational studies of block copolymer directed self-assembly (DSA) in a variety of confining templates that can be produced using conventional lithography tools and targeting both line/space patterns and vertical interconnects (VIAs). The research aims to identify polymer architectures and compositions along with template geometries and surface treatments that lead to robust DSA structures. Beyond process windows for perfect structures, we have studied defect states and the free energy landscape connecting them to perfect states, thereby providing estimates of equilibrium defect populations and kinetic barriers for defect annealing. I will finish the presentation with an example of an "inverse design" calculation, namely the identification of a template and polymer composition that optimally produces a desired self-assembled pattern. Further developments in this area will be necessary for DSA to become a practical tool in next generation lithography.

3:00pm **PS+EM-MoA3 Improvement of Block Copolymer Masked Silicon Etch Profile using Neutral Beam**, ***Deokhyun Yun**, J.W. Park, H.S. Kim, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

These days, bottom-up block copolymer (BCP) lithography is widely investigated as alternative patterning method for deep nanoscale device replacing conventional top-down photolithography. The most widely used BCP material is polystyrene (PS)/polymethyl methacrylate (PMMA) and, nanoscale PS mask features formed on the substrates after the direct self-assembly are easily damaged by the plasma processing. Previously, neutral beam etching has been used to etch semiconducting materials without surface charging and damaging by using a highly directional radical beam instead of conventional plasma assisted ion beam. In this study, the nano-structured silicon was fabricated for nano-devices such as optical devices and transistor devices using BCP as the mask and the effect of Cl_2/Ar neutral beam instead of Cl_2/Ar ion beam on the etch characteristics of BCP and silicon was investigated. The use of neutral beam instead of ion beam decreased the degradation of BCP during the etching, therefore, more anisotropic silicon etch profile in addition to the improved etch selectivity of silicon over BCP could be observed. Also, by using the neutral beam instead of ion beam, the improvement of line edge roughness could be obtained.

3:20pm **PS+EM-MoA4 Plasma Etching of Directed Self Assembly based Patterns for Aggressively Scaled CMOS Applications**, ***Hiroyuki Miyazoe**, H. Tsai, R.L. Bruce, S.U. Engelmann, M. Brink, A. Pyzyna,* IBM T.J. Watson Research Center, *C. Liu,* IBM Albany Nanotech Center, *A. Vora, D. Sanders,* IBM Almaden Research Center, *M. Maher, W. Durand, C. Ellison, G. Willson,* The University of Texas at Austin, *M. Guillorn, E.A. Joseph*, IBM T.J. Watson Research Center

As the feature size in CMOS technology continues to shrink, patterning below 30 nm pitch faces many challenges. Directed self-assembly (DSA) [1] and sidewall image transfer (SIT) [2] patterning techniques can augment conventional lithographic patterning by providing sublithographic multiplication of feature pitch. Recently, our group successfully demonstrated the electrical characterization of FinFET devices comprising fins formed by DSA of poly (styrene-block-methyl methacrylate) (PS-b-PMMA) block copolymers (BCPs) at 28nm fin pitch [3]. In addition, we demonstrated copper lines with dielectric patterns formed by DSA at 28nm pitch followed by metallization [4]. Patterning of Si, SiNx and SiOx at a ~24 nm feature pitch using PS-b-PMMA BCP was also shown [3]. In this work, we discuss a parametric study of factors impacting fine feature patterning to further optimize DSA line-space patterning using PS-PMMA BCPs at 28 and 24nm pitch, and high chi BCP at 20nm and 18.7nm pitch. The use of templated DSA to generate line-space structures in the aforementioned materials was used to investigate the control of critical dimension (CD), line edge roughness (LER) and line width roughness throughout the patterning process. The line roughness of the hardmask becomes smaller at the lower substrate temperature during etch. The CD of lines was controlled well between 11nm and 15nm at 28nm pitch by controlling the etching time while keeping the LER constant (at ~3nm). We also confirmed that O_2-free plasma gas chemistry is more advantageous for BCP patterning in case of organic-organic polymer. These initial patterning studies may play an important role in understanding feature formation and density limiting ground rules.

[1] J. Cheng et al., SPIE 2010, [2] H. Yaegashi. SPIE 2012, [3] Tsai, IEDM 2014, [4] Pyzyna VLSI 2015

4:00pm **PS+EM-MoA6 Microplasma Based Synthesis of Nanomaterials**, ***Michael Gordon***, University of California at Santa Barbara **INVITED**

We present a hybrid plasma spray deposition technique, based on geometrically-confined, supersonic microplasma jets, which can create a wide range of metal, metal oxide/sulfide, and semiconductor nanoparticles and nanostructured thin film materials (e.g., CuO/CuS, ZnO, SnO_2, NiO/$NiFe_2O_4$) on virtually any surface. Organometallic or aerosolized precursors are broken down in a hollow cathode microplasma jet under different reducing/oxidizing atmospheres at high pressure (10-100 torr), creating a directed flux of active metal and oxide species for the subsequent growth of nanostructured films. Interaction of the jet afterglow with the background gas can create additional species (e.g., excited neutrals, radicals, etc.) which participate in film growth. By adjusting supersonic flow characteristics and plasma operating conditions, deposits ranging from isolated nanoparticles to films of fibers, aggregates, nanowires, and dense columns can be realized. The talk will highlight our recent efforts in nanomaterial synthesis via microplasmas with emphasis on the physics of the jet source, dynamics of the growth process, and applications such as solar cell electrodes, photo(electro)catalysis, and nanogranular films for magnetic exchange bias applications.

4:40pm **PS+EM-MoA8 Nucleation of Silicon Nanocrystals in a Remote Plasma without Subsequent Coaguation**, ***Ilker Dogan***, Eindhoven University of Technology, Netherlands, *S.L. Weeks, S. Agarwal,* Colorado School of Mines, *M.C.M. van de Sanden*, Dutch Institute for Fundamental Energy Research (DIFFER), Netherlands

We report on the growth mechanism of spherical silicon nanocrystals (Si-NCs) in a remote expanding Ar plasma using a time-modulated SiH_4 gas injection in the microsecond time range. Under identical time-modulation parameters, we varied the local density of the SiH_4 gas by changing its stagnation pressure on the injection line over the range 0.1-2.0 bar. We observed that nanocrystals were synthesized in a size range from 2 nm to 50 nm with monocrystalline morphology. Smaller nanocrystals (2-6 nm) with narrower size distributions and with higher number densities were synthesized with an increase of the SiH_4 gas-phase density. We related this observation to the rapid depletion of the number density of the molecules, ions and radicals in the plasma during nanocrystal growth, which can primarily occur via nucleation with no significant subsequent coagulation. In addition, in our remote plasma environment, rapid cooling of the gas in the particle growth zone from 1500 K to 400 K significantly reduces the coalescence rate of the nanoparticles, which makes the coagulation process highly unlikely. Our observations on nanocrystal formation via nucleation indicated that subsequent coagulation for further growth is not always an essential step on nanoparticle formation.

5:00pm **PS+EM-MoA9 Atmospheric Plasma Synthesis of Metallic Platinum Nanoparticles for PEMFC Technology using an Organometallic-Carbon Solution Nebulized in the Post-Discharge of an RF Torch**, ***Joffrey Baneton**, D. Merche,* ULB, Belgium, *M. Raes,* VUB, Belgium, *V. Debaille,* ULB, Belgium, *G. Caldarella, V. Stergiopoulos,* ULg, Belgium, *H. Terryn,* VUB, Belgium, *N. Job,* ULg, Belgium, *F.A.B. Reniers*, ULB, Belgium

Catalytic layers are one of the most important components of proton exchange membrane fuel cells (PEMFC) because they directly influence the transport of matter and the reactivity of the electrodes [1]. In many cases, platinum associated with carbon black forms the most interesting material because of its very high catalytic activity [2]. Unfortunately, some limitations remain due to the cost of platinum and the difficulty to control the structure of the carbon support.

In this study, we propose a new promising technique using platinum (II) acetylacetonate [Pt(acac)$_2$] powder mixed with porous carbon and nebulized in a RF atmospheric plasma torch directly on commercial gas diffusion layer (GDL). This fast and "one-pot" methodology leads to the formation of homogeneous and reproducible samples with a variable and controlled content of metallic platinum on the surface, as analyzed by X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM). The catalytic activity per mass unit can be studied by a combination of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and electrochemical measurements.

We demonstrate that the plasma treatment and mostly the reactive oxygen species play a critical role in the activation of the support surface and the binding of the platinum nanoparticles on it, reinforcing previous observations [3,4]. In the case of an argon-oxygen plasma pretreatment of the GDL, a significant increase of the platinum content on the surface can be observed.

The influence of different process parameters on the synthesis of the platinum nanoparticles was studied. We show that the carrier gas flow rate, the power injected in the discharge and the treatment time do not have a significant impact on the surface composition. On the other hand, some nebulizer parameters such as the number of pulses or the loading of Pt-C allow the tuning of the amount of Pt grafted on the surface without altering its metallic nature.

Finally, the influence of the type of carbon powder (e.g. CB, CX or CNTs) was investigated. It appears that it can modify the surface organization and consequently also the intrinsic characteristics of the material. It reveals that the distribution of platinum nanoparticles and the access to the catalytic sites can be optimized depending of the porosity and the active surface of the carbon support.

[1] Gasteiger et al. Handbook of Fuel Cells – Fundamentals, Technology and Applications. **2003**, 3, 593

[2] Chatenet et al. New and Future Developments in Catalysis. **2013**, 401-423

[3] Pireaux et al. Method for Depositing Nanoparticles on Substrates, **2002** (Patent)

[4] Claessens et al. *Nanotechnology*, **2010**, 21, 38, 385603

5:20pm **PS+EM-MoA10 Low Energy Helium Ion Irradiation Induced Surface Modification of Metals**, ***Irem Tanyeli**** , FOM Institute DIFFER, Netherlands, *L. Marot, D. Mathys,* University of Basel, Switzerland, *M.C.M. van de Sanden,* FOM Institute DIFFER, Netherlands, *G. De Temmerman*, ITER Organization

Many applications, such as energy harvesting, energy storage, optoelectronics, demand nanomaterials and/or nanostructured surfaces for an enhanced activity. Various techniques, which can be grouped under top-down and bottom-up approaches, exist and are worked on by many researchers in order to fulfill the demands of these applications. There are some critical requirements that needs to be satisfied by nanostructures before being implemented in any application, such as high porosity, good contact between different crystallites and good electrical conductivity. Standard nanostructuring approaches, such as wet-chemical processing, can give very homogeneous particle sizes, but the contact between the particles is often poor and a necking treatment is needed to alleviate this limitation. In this study, Helium ion induced nanostructuring is proposed as an efficient technique. This top-down approach provides a good control over morphology, high porosity, good conductivity and it enables post processing, such as oxidation and nitridation.

Metal surfaces are exposed to pure Helium plasma under extreme ion flux (in the range of 10^{23} $m^{-2}s^{-1}$) and low ion energy (< 100 eV) conditions at Pilot-PSI, linear plasma generator. Different surface modifications on various metals, such as iron, titanium, copper and aluminum, are observed.[1] Pillar like structures are formed on copper and aluminum surfaces, whereas fiber like nanostructures are observed on iron surface. Controlled nanostructure formation on tungsten and molybdenum surfaces has been reported.[2] Consistently, nanostructure formation on iron surface has been controlled with surface temperature and ion fluence in this study.[3] It has been known that metal oxides are good candidates to be used as photoelectrodes in photoelectrochemical cells. WO_3 and α-Fe_2O_3 are two of the most widely studied photoanodes. Hence, Helium ion induced tungsten and iron nanostructured surfaces are oxidized to the desired phases to be tested in photoelectrochemical cells. 1mA/cm^2 of photocurrent density for WO_3 has been achieved.[4]

[1] **I. Tanyeli**, L. Marot, D. Mathys, M. C. M. van de Sanden, G. De Temmerman, Sci. Rep. 5:9779-8, 2015.

[2] G. De Temmerman et al., J. Vac. Sci. Technol. A, 30, 041306-6, 2012.

[3] **I. Tanyeli**, L. Marot, M. C. M. van de Sanden, G. De Temmerman, ACS Applied Materials & Interfaces 6 (5), pp 3462-3468, 2014.

[4] M. de Respinis, G. De Temmerman, **I. Tanyeli**, M. C. M. van de Sanden, R. P. Doerner, M. J. Baldwin, R. van de Krol , ACS Applied Materials & Interfaces 5 (15), pp 7621-7625, 2013.

Plasma Science and Technology
Room: 210A - Session PS-MoA

Plasma Diagnostics, Sensors and Control I
Moderator: Erik Johnson, LPICM-CNRS, Ecole Polytechnique, France, Jeffrey Shearer, IBM Research Division, Albany, NY

2:20pm **PS-MoA1 Submillimeter Studies of Molecular Plasmas: Applications to Semiconductor Plasma Processing**, ***Frank De Lucia***, Ohio State University **INVITED**

The use of submillimeter (smm) absorption spectroscopy to study molecular plasmas is well established. This has been driven by a number of applications including the molecular astrophysics of free radicals and ions, diagnostics of excitation and energy transfer in laser plasmas, and fundamental physical chemistry.

Attributes of smm spectroscopy of plasmas include: (1) They are transparent and essentially noise free in the smm, (2) Very high resolution leads to essentially 'absolute' specificity and low clutter backgrounds, (3) It is a non-invasive probe with straightforward sampling, (4) Calibration free measurement of absolute concentrations can be obtained from first principles, (5) The spectra provide measurements of the rotational/translational temperatures, (6) The technique can probe 'dark' chambers, and (7) Measurements can be 'real time.

Limitations include: (1) The molecules require a dipole moment, (2) The technique is more challenging as pressure is raised above 1 Torr, and (3) Because of diffraction, it requires a larger probe beam.

In this talk we will first discuss the basic physics and chemistry that underlies the smm spectroscopy of low-pressure plasmas. We will then describe results initially obtained on a test reactor at OSU provided by Applied Materials, followed by results obtained on production and research reactors at Applied Materials. This will include measurements of concentrations and temperatures of plasma constituents as a function input flows, discharge power, and time.

3:00pm **PS-MoA3 Using Broadband Absorption Spectroscopy to Elucidate Energy Partitioning and its Impact on Surface Reactivity**, ***Joshua Blechle**, A.R. Hanna, E.R. Fisher*, Colorado State University

The partitioning of energy within plasma systems is of vital importance to plasma chemistry as it provides insight into reactivity via possible species formation and decomposition mechanisms as well as its significant contribution to surface reactivity of individual plasma species. Here, such investigations are used to determine the internal and kinetic energies of species within a variety of inductively coupled plasma systems. To obtain this information, broadband absorption spectroscopy (BAS) and the imaging of radicals interacting with surfaces (IRIS) technique were utilized to determine species energetics (vibrational, rotational, and translational temperatures). In particular, the vibrational and rotational temperatures of NO, N_2, OH, and O_2 in various gas mixtures are measured, indicating significantly higher vibrational temperatures (i.e. >3000K) than rotational temperatures (i.e. <1000K) are obtained. One focus of this work is the development of a BAS system and the impact of various methods of data collection on determined temperatures evaluated using different computational models. These data are also used to demonstrate the relationship between internal energetic and observed surface scatter coefficients (*S*) for NO, OH, and other plasma species, which is directly related to surface reactivity (*R*). Such observations allow for unique insight into these plasma systems and the integral role energy partitioning plays in the assessment and understanding of complex plasma chemistry.

3:20pm **PS-MoA4 CF_3^+ Fragmentation by Electron Impact Ionization of Perfluoro-Vinyl-Ethers**, ***Yusuke Kondo**, K. Ishikawa, T. Hayashi, Y. Miyawaki, K. Takeda, H. Kondo, M. Sekine, M. Hori*, Nagoya University, Japan

In plasma etching processes, the densities of chemically reactive species have attracted attention. A higher etch yield for SiO_2 at lower ion impact energies was reported when using CF_3^+ ions.[1] Perfluoro-vinyl-ether

* **Coburn & Winters Student Award Finalist**

forming selectively CF_3^+ ions were reported.[2] Here we extensively studied in details the gas phase fragmentations of perfluoro-vinyl-ether.

A quadrupole mass spectrometer (QMS; Hiden Analytical, EQP) was installed in the chamber wall of the commercial plasma etching reactor. PPVE (CF_3-CF_2-CF_2-O-CF=CF_2, $C_5F_{10}O$) or PMVE (CF_3-O-CF=CF_2, C_3F_6O) was introduced into the chamber and maintained at a pressure of 1.0 Pa.

Dissociative ionization caused by impact with 20 eV electrons provided positive ion fragmentation pattern to three peaks for PMVE: CF_3^+, $C_2F_2O^+$ and $C_3F_6O^+$, and five peaks for PPVE: CF_3^+, $C_2F_2O^+$, $C_2F_5^+$, $C_3F_7^+$ and $C_5F_{10}O^+$. Figure 1 shows comparison of the ion efficiency for CF_3^+ between (a) PPVE and (b) an isomer of PMVE. The large ionization efficiency of CF_3^+ was experimentally observed significantly as the leading cause of large cross-sections for dissociative ionization of CF_3^+ ions. For comparison, the CF_3^+ ion density fragmented from perfluoro-alkanes is only 30 to 40%. By the energetic electron impact on the perfluoro-vinyl-ethers, excess energy is distributed among internal energies at the vinyl-ether bond, due to polarization of the charge on the bridging oxygen atom. The fragmentation via direct bond rupture into smaller product ions occurs more favorably than the rearrangement or cleavage into molecules with large mass.

[1] K. Karahashi *et al.* J. Vac. Sci. Technol. A **22** 1166 (2004). [2] M. Nagai *et al.*, Jpn. J. Appl. Phys. **45** 7100 (2006); Y. Morikawa *et al*., Jpn. J. Appl. Phys., **42**, 1429 (2003).

3:40pm **PS-MoA5 A Comprehensive Quantitative Study of Low Pressure Inductively-Coupled Plasmas in Cl_2, O_2 and Mixtures**, *M. Foucher, D. Marinov, P. Chabert,* LPP-CNRS, Ecole Polytechnique, France, *A. Agarwal, S. Rauf,* Applied Materials Inc., ***Jean-Paul Booth***, LPP-CNRS, Ecole Polytechnique, France

Inductively-coupled plasmas in diatomic electronegative gases such as Cl_2 and O_2 are widely used in semi-conductor fabrication for gate etching and photo-resist stripping. Moreover they are an archetype for plasmas in simple electronegative gases with the advantage that techniques exist to measure the densities of nearly all their stable and reactive species. They provide an opportunity to benchmark models such as the Hybrid Plasma Equipment Model. We are then undertaking a comprehensive set of measurements in the pure gases and their mixtures.

The plasma is sustained in a cylindrical chamber (55 cm diameter,10 cm height) by a 4-turn planar coil excited at 13.56 MHz above a dielectric window. Pure gases (Cl_2 and O_2) were studied over a range of pressure [5-80 mTorr] and RF power [50-550 W]. The effect of O_2 addition (0-100%) to Cl_2 plasmas was studied at 10 mTorr 500W. The electron density was determined by hairpin resonator probe. The Cl and O atom absolute densities and surface reaction coefficients were obtained by Two-Photon Absorption Laser-Induced Fluorescence. A novel ultra-broadband high sensitivity absorption bench was used to measure ground state and vibrationally excited Cl_2 and vibrationally excited O_2, as well as OCl, OClO and Cl^- ions.

In all gas mixtures, the electron density was observed to increase initially with gas pressure, pass through a maximum and then decrease at higher pressure. In O_2 a broad maximum is observed around 40 mTorr, whereas for Cl_2 the electron density peaks at 10 mTorr before dropping sharply. This difference can be attributed to rapid dissociative attachment of electrons in the case of Cl_2. In all cases the electron density increases with RF power. In O_2, highly vibrationally excited molecules $O_2(v)$ were observed (with v up to 18), and analysis of the rotational structure of the O_2 Schumann-Runge bands showed rotational temperatures (=translational temperatures) ranging from 400 K (10mTorr 100W) to 900 K (80 mTorr 500W). The non-equilibrium vibrational distribution may be attributed to electron impact excitation combined with low rates of V-T energy transfer processes in O_2. In contrast, in pure Cl_2 the vibrational temperature is equal to the gas translational temperature, (~1000K) due to efficient V-T transfers between Cl_2 and Cl atoms. In Cl_2/O_2 mixtures the densities of electrons and Cl and O atoms all decreased when O_2 or Cl_2 is added to the pure gas (Cl_2 or O_2). This coincides with the formation of ClO and OClO, which consumes the atoms which are easier to ionize than molecules.

We are currently working on modeling of these results to obtain a deeper understanding of the kinetics of Cl_2/O_2 plasmas.

4:00pm **PS-MoA6 Optical Emission Diagnostics for Detection of High Energy Electrons in Argon Plasmas**, ***Shicong Wang**, J. Boffard, C.C. Lin, A.E. Wendt*, University of Wisconsin - Madison

The electron energy distribution function (EEDF) is one of the most important and fundamental parameters in low temperature plasmas. The high-energy range of the EEDF in particular is responsible for ionization, excitation and gas phase chemistry, which are critical for many industrial applications. Non-invasive OES diagnostics provide an attractive means to measure EEDFs, using emissions from argon states excited by electron collisions [1,2]. Emission lines dominated by excitation of ground state argon atoms are particularly sensitive to the population of high energy (>13 eV) electrons. We report on optical emission diagnostics for detection of energetic electrons in argon plasmas. The OES diagnostic makes use of an emission model based on measured argon excitation cross sections that computes the relative emission intensities at a selected set of wavelengths, with a trial EEDF as input. The trial EEDF that produces the best fit to the spectrum measured in the experiment is determined after a search in which the shape and average energy of the trial EEDF is varied. In both pulsed argon inductively coupled plasmas (ICPs) and capacitively coupled plasmas (CCPs), a high electron temperature has been previously observed at the beginning of the pulse period in time-resolved OES measurements. Meanwhile, the relative argon emission intensities between emissions originating from upper levels populated primarily by high energy and low energy electrons , respectively, (i.e., 420.07/419.83 nm line ratio) imply the existence of a `hot tail' of energetic electrons, as compared to a Maxwellian distribution. In addition, the OES method of detecting high energy electrons is explored in the presence of a supplemental source of energetic electrons. A biased auxiliary set of heated filaments will be used to inject high energy electrons into an argon inductively coupled plasma. The filament bias voltage will be varied to control the energy of emitted electrons, and the filament heater current will be controlled separately to vary the emitted electron flux. The OES diagnostic is used to observe the changes in emission spectra and extracted EEDF caused by the supplemental energetic electrons. The OES method will be examined and compared to Langmuir probe measurements of EEDF as the energy and current of the supplemental electron population are systematically varied.

The authors acknowledge support from NSF grant PHY-1068670.

[1] Wang et al., JVSTA 31, (2013) 021303.

[2] Boffard et al., Plasma Sources Sci. Tech. 19 (2010) 065001.

4:20pm **PS-MoA7 Plasma Characteristics in a Dual-Frequency Inductively Coupled Plasma Source for the Etch Tool**, ***Vladimir Nagorny***, Mattson Technology, *V. Godyak*, RF Plasma Consulting

It is always desirable to have more than one antenna in ICP plasma source for etch for better both radial uniformity control and process window. So, configurations with two antennas are being used in ICP for quite a while. However, there is always a question about their interference.

Recently Mattson Technology introduced an etch tool with a dual frequency ICP plasma source [1]. The logic behind complementing a standard 13.56MHz antenna with a 2MHz antenna with ferrite core was quite simple - no interference between antennas, high efficiency 2MHz design [1–3] of the second antenna and respectively low additional cost. This source demonstrated large operating window, high plasma stability in both electro-positive and electro-negative gases, good process control. With this source design it is possible to tune process uniformity (Max-Min) down to 1% and better on a blanket wafer.

Energizing plasma with different frequencies put a reasonable question, if the two essentially different frequencies create similar processing plasmas comparing to a 13.56MHz drive or not. To answer this question, a comprehensive study of the electron energy probability functions, EEPF have been measured in Ar and in real processing plasmas, including gas mixtures that generate depositing plasma. The measurements performed in a wide range of processing condition with different power ratio at 13.56 and 2 MHz have demonstrated independence of the measured EEDFs on frequency, but only on the total absorbed power, gas composition and its pressure. These results are in agreement with earlier observation in different reactors [4] and with analysis of ionization and electron energy balances in gas discharge plasma [5].

[1] V. Nagorny, D. Lee and A. Kadavanich, *US PTO Publication* US20140197136, *patent pending*

[2] V.A. Godyak, *US Patent* 8920600.

[3] V.A. Godyak, C. Crapuchette, V. Nagorny, *US PTO Publication patent pending*.

[4] N. Hershkowitz, J. Ding, R.A. Breun, R.T.S. Chen, J. Mayer, and A.K. Quick 1996 *Phys.Plasmas* **3** 2197

[5] V.A. Godyak 2006 *IEEE Trans. Plasma Sci.* **34** 755

4:40pm **PS-MoA8 Spatial Oscillations and Frequency Shifts in Pulsed Capacitively Coupled Plasmas**, ***John Poulose**, L.J. Overzet,* The University of Texas at Dallas, *S. Shannon,* North Carolina State University, *D. Coumou,* MKS Instruments, *M.J. Goeckner*, The 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 spectral lines from pulsed plasmas through Ar, O_2, N_2, CF_4 gases and $CF_4/O_2/Ar$ gas mixtures have been collected. The OEIs measured from $CF_4/O_2/Ar$ gas mixtures show an axial oscillation of intensity with an approximate speed of 10^6 cm per second. This oscillation starts at the plasma strike and dampens to the background during the first 10 µs in 1 kHz pulse frequencies or lower. Radio frequency voltage and current measurements show changes over similar time periods. The transient reactance has been observed to correspond to the sheath formation in the OEI studies. Measured current and voltage frequencies have been observed to shift/pull by as much as 400 kHz during the initial turn on phase. The amount of the frequency pull is dependent on gas composition, electrode gap, pressure, and pulse properties. This shift occurs as a reaction to the plasma formation, specifically, the sheath development. We will present these results and the effects of other parameters on the transitory behavior of pulsed discharges.

5:00pm **PS-MoA9 Curling Probe Measurement of Electron Density in Pulse-Modulated Plasma at High Frequency**, ***Anil Pandey***, Chubu University, Japan, *W. Sakakibara,* DOWA Thermotech, Japan, *H. Matsuoka,* DOWA Thermotech, *K. Nakamura, H. Sugai*, Chubu University, Japan

Curling probe (CP), a modified form of microwave resonator probe has recently been proposed [1] which enables the local electron density measurement even in reactive plasma for non-conducting film deposition. The electron density is obtained from a shift of ¼ wavelength-resonance frequency of the spiral slot antenna in discharge ON and OFF monitored by a network analyzer (NWA). CP is a compact monitoring tool (minimum diameter 6 mm) coated with alumina or yttria for applications to semiconductor plasma processing. A variant of CP installed with an optical fiber, called *opto-curling probe* (OCP) has also been developed which enables simultaneous monitoring of electron density and optical emissions from plasma [2]. In this paper we demonstrate that CP can be applied not only to a constant density plasma but also to a plasma pulse-modulated at high frequency such as several tens of kHz. In case of pulse-modulated discharge, synchronization of discharge pulse with frequency sweep of NWA must be established [3]. Such CP measurement was performed in a pulsed glow discharge plasma primarily used for metal-nitridation. A CP of 16-mm diameter was inserted in a cylindrical chamber of 60 cm in diameter and 50 cm in length. A negative high-voltage pulse of -1.0 to -2.0 kV was applied to a cathode, which generates a pulsed glow plasma in different discharge gas at varying pressures. The pulse frequency was changed from 0.4 to 25 kHz with various duty cycle ratios. The NWA (Agilent E5071C) was externally triggered using *on point* mode and the electron density in glow phase and afterglow phase was measured in time-resolved manner in argon, nitrogen and hydrogen discharges. At higher pulse frequencies (>5 kHz), the electron density was found to be time-modulated and didn't decay completely to zero. Also, a minimum time resolution of 2 µs was attained. Thus, CP is concluded to be a powerful tool for the time-resolved electron density monitoring in pulse-modulated plasma often used in industrial materials processing.

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

[2] A. Pandey, K. Nakamura, and H. Sugai, Appl. Phys. Express 6, 056202 (2013).

[3] A. Pandey, W. Sakakibara, H. Matsuoka, K. Nakamura, and H. Sugai, Appl. Phys. Lett. 104 (2014) 024111.

5:20pm **PS-MoA10 Detection of Biomedically Relevant Reactive Oxygen Species in Atmospheric Pressure Plasmas**, ***Sandra Schröter****, *J. Bredin, K. Niemi, J.P. Dedrick,* University of York, UK, *M. Foucher,* Ecole Polytechnique, France, *N. de Oliveira, D. Joyeux, L. Nahon,* Synchrotron Soleil, France, *J.-P. Booth,* Ecole Polytechnique, France, *E. Wagenaars, T. Gans, D. O'Connell*, University of York, UK

Cold atmospheric pressure plasmas (APP) are known to be sources for reactive oxygen species (ROS) [1,2], which makes them potentially well suited for biomedical applications. Examples of ROS of interest are atomic oxygen (O) and hydroxyl radicals (OH) because of their high reactivity and as potential precursors for longer lived reactive species. In order for APPs to achieve widespread usage in therapeutic applications, controlled production of the species of interest and hence their quantification is essential. However, at atmospheric pressure this is particularly challenging due to the short lifetimes of excited states as a result of their rapid de-excitation by collision induced quenching. Additionally, determination of the exact gas composition in APPs is difficult, especially in the jet region, where a gradual transition from the feed gas to the ambient air occurs.

In order to overcome these challenges, we will present three advanced diagnostic techniques used to quantify absolute densities of reactive species in helium RF APPJs with molecular admixtures, namely picosecond Two-photon Absorption Laser Induced Fluorescence (ps-TALIF) [3], high-resolution Fourier-transform synchrotron VUV absorption [4,5] and UV-Broad-Band Absorption Spectroscopy (UV-BBAS). Under a variation of the water content in the gas phase, absolute densities of OH and O were determined in the plasma core to be in the order of 10^{20} m^{-3} and 10^{19} m^{-3} respectively. The densities were found to increase with increasing water admixture. Additional insight was gained about the air diffusion into the plasma effluent by mapping the lifetimes of the excited atomic oxygen in the axial and radial directions. Typical lifetimes in the order of a few nanoseconds were decreasing away from the nozzle and radial centre of the plasma jet due to diffusion of air from the ambient environment into the jet region.

Acknowledgements: The authors acknowledge support by the UK EPSRC (EP/K018388/1 & EP/H003797/1) and the York-Paris Low Temperature Plasma Collaborative Research Centre. This work was performed within the LABEX Plas@par project and received financial state aid, managed by the Agence National de la Recherche as part of the programme "Investissements d'avenir" (ANR-11-IDEX-0004-02).

References:

[1] M. G. Kong et al., New J. Phys. **11** (2009) 115012

[2] D. B. Graves, J. Phys. D: Appl. Phys. **45** (2012) 263001

[3] J. Bredin et al., "Picosecond-TALIF measurements of atomic oxygen in RF driven atmospheric pressure plasma jets", 67th Gaseous Electronics Conference, Raleigh, NC (Nov 2014)

[4] K. Niemi et al., Appl. Phys. Lett. **103** (2013) 034102

[5] L. Nahon et al., *J. Synchrotron Rad.*, **19**, 508 (2012)

*** Coburn & Winters Student Award Finalist**

Plasma Science and Technology
Room: 210A - Session PS+BI+SM-TuM

Plasmas for Medicine and Biological Applications
Moderator: Satoshi Hamaguchi, Osaka University, Japan

8:00am **PS+BI+SM-TuM1 Glow-Discharge Plasma Applications in the Biomedical Sciences: Frontiers and Horizons**, ***Buddy D. Ratner***, University of Washington **INVITED**

Plasma treatments for biomedical applications have been explored since the early 1960's, possibly earlier than that. Plasma treatments for medical devices and for materials used in biotechnology are now widely used and have improved he performance and safety of many devices. A few advanced technologies for biomedicine exploiting plasma deposition of organic thin films will be described. These include non-fouling surfaces, thermally responsive surfaces, biodegradable surfaces, rate-limiting barriers for controlled release and surfaces that permit the growth of precision polymeric brushes by atom transfer radical polymerization (ATRP). Frontiers for plasma deposition include better control of deposition chemistry, strategies to deposit unusual chemistries and depositions that integrate biological molecules and plasma-deposited chemistries.

8:40am **PS+BI+SM-TuM3 Non-Equilibrium Plasmas in Contact with Solutions: Biological Interactions and Material Synthesis**, ***Peter Bruggeman***, University of Minnesota **INVITED**

Non-equilibrium atmospheric pressure plasmas interacting with liquids offer a unique source of highly reactive chemistry beneficial for many applications in biology, medicine and advanced materials manufacturing. It has been shown that these plasma-liquid interactions can lead to inactivation of bacteria and virus and the synthesis of nanoparticles. Nonetheless the underpinning mechanisms are at least poorly understood. My group has been strongly involved in the study of the reactive chemistry of a well-characterized RF driven atmospheric pressure plasma jet and its interaction with liquids.

The presentation will highlight some examples of reaction pathways responsible for the inactivation of bacteria and virus in solution and the synthesis of silver nanoparticles from $AgNO_3$ solutions. I will illustrate the importance of reactive plasma chemistry induced by neutral gas phase reactive species such as OH, H_2O_2 NO, O, H, O_3 and singlet oxygen. In addition, we will show that UV emission, which is often neglected as a possible mechanism, can be important in some cases.

9:20am **PS+BI+SM-TuM5 Plasma Biomedicine and Reactive Species**, ***David Graves***, University of California at Berkeley **INVITED**

Low temperature plasma research directed towards biomedical applications such as sterilization, surgery, wound healing and anti-cancer therapy has seen remarkable growth in the last 3-5 years, but the mechanisms responsible for the biomedical effects have remained mysterious. It is known that CAP readily create reactive oxygen species (ROS) and reactive nitrogen species (RNS). Other potentially important plasma-generated species effects include charges, fields and photons. ROS and RNS (or RONS), in addition to a suite of other radical and non-radical reactive species, are essential actors in an important sub-field of aerobic biology termed 'redox' (or oxidation-reduction) biology. I will review the evidence suggesting that RONS generated by plasmas are responsible for their observed therapeutic effects. In addition, I will present several ideas about the most likely biological response mechanisms that are likely involved in therapeutic plasma biomedicine.

11:00am **PS+BI+SM-TuM10 Cold Atmospheric Plasma for the Treatment of Chronic Infected Wounds**, ***Jennifer Granick***, *V.S.S.K. Kondeti, A. Truong, R.C. Hunter, P.J. Bruggeman*, University of Minnesota

Two percent of the US population suffers from chronic non-healing wounds, often complicated by antibiotic-resistant bacterial infections, and the staggering cost of wound care exceeds $50 billion per year. Of increasing concern are multi-drug resistant bacteria, including methicillin-resistant *Staphylococcus aureus* and multi-drug resistant *Pseudomonas aeruginosa* infections. Within wounds, these bacteria adopt a biofilm-like state, and become notoriously recalcitrant to conventional antibiotic therapies. Currently approved products for the treatment of chronic wounds have not proven to be a panacea due to the complex nature of wound healing.

The ideal therapy for chronic, infected wounds would be non-painful, bactericidal without risk of resistance, able to break-up biofilms and enhance wound healing. Recently, there has been interest in the use of cold atmospheric plasma (CAP) technology for the treatment of infections and non-healing wounds. The technology could potentially fulfill the requirements of an ideal wound healing therapy. CAP devices producing ionized gas have been developed that can operate in ambient air and that are safe to touch without any pain sensation. CAP generates a complex mixture of reactive oxygen and nitrogen species (RONS) that are able to kill bacteria, while stimulating host cell growth. CAP has the potential to combine antiseptic and wound healing capabilities in a single treatment procedure and could eliminate the risk of cytotoxicity present in many current treatment methodologies for infected wounds.

The effects of CAP on bacteria and mammalian keratinocytes and fibroblast cells have been evaluated *in vitro*. Our prototype argon CAP device produces antibacterial effects on planktonic bacterial cultures of *S. aureus* and *P. aeruginosa* at a maximal treatment duration of 20 ml/min at conditions that do not impact cell viability of fibroblasts and keratinocytes *in vitro*. We have also recently demonstrated that CAP is effective in reducing the viability of *P. aeruginosa* biofilms grown *in vitro*. When grown on the surfaces of PVC microtitre plates for 48 h, argon-air derived CAP treatment of established biofilms showed a 95% reduction in cell viability, as determined by resazurin fluorescence, relative to untreated controls, when treated at a dose of 30min/ml, which is similar to the treatment time equivalent of mammalian cell treatment.

As part of the early investigations of the use of CAP treatment as a viable therapy for chronic-infected wounds, the presentation will focus on bacterial biofilm reduction by CAP treatment *in vitro* as well as in a mouse skin wound model. The effects on mouse host cells will be examined.

11:20am **PS+BI+SM-TuM11 Humidity Effect on the Surface Modification and Bio-Deactivation of Lipopolysaccharide (LPS) by Surface Micro-Discharge (SMD)**, ***Pingshan Luan***, *E.A.J. Bartis, A.J. Knoll,* University of Maryland, College Park, *C. Anderson, D.B. Graves,* University of California at Berkeley, *J. Seog, G.S. Oehrlein*, University of Maryland, College Park

The surface micro-discharge (SMD), due to its scalable large area and flexibility of working gases, has great potential for many applications such as material processing and plasma medicine. The SMD normally works under ambient air conditions that contain not only N_2 and O_2 but also water vapor which can have a large impact on both the discharge behavior and plasma gas chemistry. In this study, we evaluate the effect of ambient humidity on SMD in various N_2/O_2 mixtures and the subsequent effect on the surface modification and bio-deactivation of lipopolysaccharide (LPS). Electrical behavior and optical emission spectrum (OES) of the SMD source were studied. We found that while the additional moisture did not help create strong OH (A-X) emission from SMD, it resulted in lower plasma density and extra power dissipation. We used X-ray photoelectron spectroscopy (XPS) to characterize the surface modification of LPS after treatment. We found that all SMD-treated LPS surfaces show oxygen uptake and formation of surface-bound NO_3, while the amount of these modifications was strongly dependent on the ambient gas composition. By comparing the XPS of wet-treated (50% relative humidity at 20 °C) surfaces with their dry counterparts, we find that the water vapor reduces both the oxygen uptake and surface NO_3 formation, and that the difference between wet- and dry-treated surfaces decreases with the increasing fraction of ambient N_2. When the N_2 fraction is up to 80% (synthetic air), the LPS surface shows comparable amount of modification with or without humidity. Among all the dry- and wet-N_2/O_2 mixtures, the dry 5% of N_2 ambient shows the greatest modification rate. We also evaluated the bio-deactivation efficiency of the SMD on LPS using enzyme-linked immunosorbent assay. Similar to surface modification, we found that the bio-deactivation rate of SMD in dry ambient is much higher than that of SMD in their wet counterparts, except the synthetic air condition which shows similar amount. The authors gratefully acknowledge financial support by the US Department of Energy (DE-SC0001939) and National Science Foundation (PHY-1004256 and PHY-1415353).

11:40am **PS+BI+SM-TuM12 Plasma Diagnostics of Dielectric Barrier Discharge within a Sealed Meat Package**, ***Vladimir Milosavljevic***, Dublin Institute of Technology, Ireland, *J. Lalor, P. Bourke, P.J. Cullen*, Dublin Institute of Technology

Atmospheric pressure, non-thermal plasma DBD is increasingly used in many processing applications. Despite their widespread usage, it remains largely unknown whether cold atmospheric plasma DBD maintains similar characteristics, such as gas temperatures and particle flux, when they breakdown while arcing or whether they possess different operating modes. It is essential for laboratory/industrial adoption of such plasmas that plasma diagnostics of the process are provided. Optical emission and absorption

spectroscopy have been used as diagnostics techniques with an added avantage of their non-intrusive nature.

The type of operating gas influences the stability of atmospheric plasma discharges. In this study is used a sealed meat package filled with one of two gas mixtures: O_2-CO_2 and N_2-CO_2 . Different concentrations of nitrogen or oxygen and carbon-dioxide could cause the transition from a stable homogeneous discharge into a filamentary discharge. Atmospheric plasma discharges are affected by the surrounding ambient air, and for sealed packages from transfer between the package gas and the surrounding ambient atmosphere. In the vast majority of atmospheric plasma discharges, reactive nitrogen species dominates the ionic composition of atmospheric discharge and has an impact on the breakdown voltage. When N_2 is added/mixed with CO_2 plasma discharges, the CO_2 emission lines are significantly quenched. In the case of O_2-CO_2 chemistry, nitrogen is not a carrier gas but it still present in the package due to contaminant transfer with the surrounding ambient air, modifying the plasma chemistry in the package. The plasma's optical spectrum in O_2-CO_2 chemistry shows molecular oxygen, nitrogen and OH peaks. Oxygen could come from the ambient air, the O_2-CO_2 gas mixture or from humidity in the package. Electron impact excitation of molecular oxygen, at low collision energies, is of particular importance because of its role in atmospheric physics and has been objective of this study. In our study we have also recorded the O_3 band-head that belongs to the Hartley Band. Ozone plays very important role for the biological aspect of this study and shows the highest change in a concentration with the processing time. Combining the results from spectral radiation in the package provides an electron energy distribution function. The study includes a detailed experimental investigation of the spatial and temporal spectroscopic data and links them with plasma kinetics.

The research leading to these results has received funding from the European Union´s Seventh Framework Programme managed by REA Research Executive Agency (FP7/2007-2013) under Grant Agreement number 605125.

12:00pm **PS+BI+SM-TuM13 Low-Temperature Plasma Surface Modification of Porous Polymeric Materials for Environmental and Medical Applications**, *Michelle Mann*, *A. Pegalajar-Jurado, E.R. Fisher*, Colorado State University

Three-dimensional (3D) porous polymeric materials are widely used in biomedical and environmental applications, such as wound healing and water filtration. Polymers used for these applications are chosen for their mechanical properties and porosity, yet the surface properties, such as hydrophobicity, limit their use in aqueous environments. For example, polymeric ultrafiltration membranes typically require pretreatment before use and tend to foul due to adsorption of biomolecules in the watercourse. Bioresorbable polymeric scaffolds used for wound healing are prone to attachment of bacteria, leading to prolonged infection at the wound site. These issues can be addressed with two simultaneous approaches. To prevent bacterial attachment and proliferation, antibacterial properties can be introduced into the materials via incorporation of biocidal agents or antibacterial coatings. Moreover, surface modification can be used to create more compatible polymeric materials by increasing wettability. Through plasma processing, tailored surface modification can be achieved while retaining the morphology and bulk properties of the material. Here, we will describe the modification of ultrafiltration polysulfone (UPS) membranes and poly(ε-caprolactone) (PCL) scaffolds to create low-fouling materials with enhanced wettability. $H_2O_{(g)}$ plasma treatment of UPS membranes and PCL scaffolds results in materials with significantly enhanced wettability while scanning electron microscopy (SEM) images demonstrate porous morphology is maintained. X-ray photoelectron spectroscopy (XPS) data show an increase in surface oxygen content throughout the membrane cross-section after plasma treatment, and modified UPS membranes demonstrate a significant increase in initial water flux. In addition, the performance of modified UPS membranes in the filtration of biological solutions will also be discussed. Furthermore, the biological performance of PCL scaffolds incorporated with various biocidal agents will be presented along with biocidal agent leaching studies.

Plasma Science and Technology
Room: 210B - Session PS-TuM

Advanced BEOL/Interconnect Etching
Moderator: Tetsuya Tatsumi, Sony Corporation, Japan

8:00am **PS-TuM1 Interconnect Patterning in the EUV Era**, ***John Arnold***, IBM Research Division, Albany, NY **INVITED**

The semiconductor industry is currently passing through a pivotal moment as EUV lithography transitions from patterning research to industrial-scale integrated technology development. This change will have ramifications far beyond the lithography itself, including impacts on adjacent unit processes, process complexity, development and manufacturing cycle times, product cost, and product yield, quality, and reliability. The most direct and immediate changes will be in plasma etch, where the combination of new materials and new dimensions will drive significant new challenges – and opportunities. The timing of EUV's readiness for practical utilization is such that most of the initial applications will be at the wiring levels, both BEOL and MOL, and this presentation will focus on those. We will begin with an examination of EUV's placement in the overall technology roadmap and a review of the important differences between EUV and conventional lithography. The bulk of the presentation will be dedicated to applications for contact, local interconnect, and BEOL, with particular emphasis on lithography and especially etch process behavior and performance. A discussion of the operational ramifications of incorporating EUV into a mainstream technology development program will be followed by a brief consideration of the anticipated benefits for the final manufactured products. We will conclude with a critical comparison of EUV to 193nm-based multiple patterning approaches for the 7nm node.

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

8:40am **PS-TuM3 Challenges for the sub-32nm Pitch Self-aligned Quadruple Patterning (SAQP) at Back End of Line (BEOL)**, ***Nihar Mohanty***, *R. Farrell, A. Raley, E. Franke, J. Smith, S. Song, A. Ko, A. Ranjan, A. deVilliers, P. Biolsi,* TEL Technology Center, America, LLC, *W. Wang, G. Beique, C. Labelle, L. Sun, R. Kim*, Globalfoundries, Ny, Usa

Critical back end of line (BEOL) M_x patterning at 7nm technology node requires sub-36nm pitches necessitating the use of either extreme ultraviolet (EUV) lithography or 193nm-immersion-lithography based self-aligned quadruple patterning (SAQP). With enormous challenges being faced in getting EUV lithography ready for production, SAQP is expected to be the front up approach for M_x grid patterning for most of industry. In contrast to the front end of line (FEOL) fin patterning, which has successfully deployed SAQP approach since 10nm node technology, BEOL M_x SAQP is challenging owing to the required usage of significantly lower temperature budgets for film stack deposition. This has an adverse impact on the material properties of the as-deposited films leading to emergence of several challenges for etch including selectivity, uniformity and roughness.

In this presentation we will highlight those unique etch challenges associated with our BEOL Mx SAQP patterning strategy and summarize our efforts in optimizing the etch chemistries, process steps and plasma etch parameters for meeting the 7nm technology node targets. With the mandrel definition parameters being the most significant input function for final pattern performance, we will detail our efforts in improving the CD uniformity (CDU), profile and line edge roughness (LER) / line width roughness (LWR) for both the mandrel definition etches. All of the etch development for this work has been conducted in our dual frequency capacitively coupled plasma (CCP) chamber with optimized gap for good baseline uniformity and independent ion flux & energy control.

9:00am **PS-TuM4 Novel Patterning Process for the 7xnm and Beyond**, ***Toru Hisamatsu***, Tokyo Electron Miyagi Limited, Japan, *T. Oishi, S. Ogawa,* Tokyo Electron Miyagi Limited, *Y. Kihara, M. Honda*, Tokyo Electron Miyagi Limited, Japan

Multiple exposures with double (quadruple) patterning has been adopted due to recent advancements in miniaturization with mask patterning techniques, and as the technology continues to develop, EUV exposure will be used in the near future. Extending the current techniques into the next generation is approaching the limit to satisfy required fabrication specifications, as it is required to have fabrication control of less-than- a-nm-order.

In the patterning process, multilayer patterning with high accuracy to form a fine patterning is becoming critical, especially in regards to line-roughness (LER/LWR) reduction, pattern-size dependency reduction of ARDE origin, and selectivity enhancement of thin EUV-resist. Furthermore, patterning with universal CD shrinkage independent of the pattern types (hole, oval, L/S) is also being required.

To this date, challenges of precise CD controllability have been solved by combining DC-superimposed plasma which reduces line-roughness by its accelerated electron-beam to cure resist surface, followed by the Si coating effect and optimization of etch condition to form a protection layer on the surface[1,2]. However, it is evident that those current techniques will soon face the limit as the resist thickness is reduced with the employment of EUV exposure; therefore the breakthrough with the new approach is essential.

As a result of various feasibility studies put into effect for a problem solution of fine pattern formation, "fusion of ALD technology and etching" was confirmed to be very beneficial for its capability of atomic-level

formation of surface protection film during the etch process. This technology enabled line-roughness reduction with pattern-size dependent CD shrink control, since the ALD step is used according to the optimum timing during the etch process, which forms proportional deposition on any type of patterns. This paper discusses the optimization of ALD step timing, its layer thickness and composition of corresponding etch flow, and introduces a possible solution to various patterning process issues without trade-offs. This technique enables atomic-level control during the etch process and thus, is promising for further miniaturization of the patterning process.

Reference

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

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

9:20am **PS-TuM5 Advanced Interconnect Process Techniques with EUV Photolithographic Masks and Sub-50nm Pitch Structures**, ***Jessica Dechene***, *J.C. Shearer*, IBM Research Division, *A.P. Labonte*, GLOBALFOUNDRIES, *J. Lucas, H. Matsumoto, B. Messer, A. Metz,* TEL Technology Center, America, LLC, *C. Labelle,* GLOBALFOUNDRIES, *J.C. Arnold*, IBM Research Division

As the semiconductor industry moves into the sub-10nm technology nodes, feature pitches below 50nm become ubiquitous. To avoid the complications of SADP processing, EUV photolithography is being explored as a means to continue direct patterning. This brings forth etch processing challenges in three ways: First, EUV resists are thinner, softer and suffer from greater LER than 193nm optical resists. Second, the small dimensions and tight pitches are causing old problems, once thought of as solved, to reappear. Pattern collapse, aspect ratio dependent etching, ion deflection induced profile bowing, and feature induced CD variation are a few examples. Third, new integrations seeking the use of self-alignment, including self-aligned etch are becoming more prevalent. These self-aligned methods at such small dimensions require innovated etch techniques in order to be enabled.

In this paper, we will discuss the theory behind the various process solutions used to solve these etch challenges. Bias pulsing was used to address aspect ratio dependent etching concerns, and gas pulsing was used to improve material and corner selectivity in a self align etch process. Dielectric etch process solution on a dual-frequency capacitively coupled plasma (CCP) system were applied to the EUV lithographic masks. Superimposing a negative DC voltage to control the emission of ballistic electrons along with chemistry balance was used to minimize feature-dependent etch CD bias. These innovative process options allowed for the development of dielectric RIE processes that hit target specifications in the demanding pitch and CD sizes generated by the EUV lithography.

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

9:40am **PS-TuM6 Advanced Plasma Etch Techniques for Sub-50nm Pitch Contact & Interconnect Etches**, ***Andre Labonte***, Globalfoundries, NY, USA, *R. Chao, J.M. Dechene,* IBM Albany Nanotech Center, *B. Nagabhirava, P. Wang, P. Friddle,* Lam Research, *N. Rassoul,* ST Microelectronics, *C. Labelle,* Globalfoundries, NY, USA, *J.C. Arnold,* IBM Albany Nanotech Center, *M. Goss*, Lam Research

As the semiconductor industry drives into sub-50nm pitches, EUV patterning as well as SADP and SAQP techniques are being explored as means to achieve the desired CDs and pitches needed. EUV patterning is attractive for enabling direct patterning and in principle, is significantly less complicated than SADP, let alone SAQP. However, EUV patterning comes with its own set of challenges, such as softer and thinner resists relative to optical 193nm resists. Also, to date, EUV resists have exhibited more LER/LWR than optical 193nm resists. Finally, the smaller features and pitches are resulting in the reoccurrence of old scaling issues such as RIE lag and pattern collapse. Many of these challenges are being met with innovative plasma etch techniques.

In this paper we discuss the theory behind many of the techniques used to solve the afore mentioned challenges associated with EUV and sub-50nm pitch patterning. In particular, RF pulsing and Bias pulsing are used to increase EUV resist selectivity, reduce LER/LWR, avoid pattern collapse and improve RIE lag in the dielectric etch. In addition we will also discuss the theory and application of AMMP (Advanced mixed mode pulsing) to improve the corner selectivity of low-k spacer in MOL to allow for the generation of self-aligned contacts. Finally, AMMP techniques were used to mitigate feature to feature CD variation incoming from litho.

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

11:20am **PS-TuM11 Characterization of Patterned Porous Low-*k* Dielectrics after Plasma Patterning and Subsequent Wet Processing/Cleaning**, ***QuocToan Le***, *E. Kesters, S. Decoster, B.T. Chan, F. Holsteyns*, IMEC, Belgium, *S. De Gendt*, IMEC, KU Leuven Belgium

Porous dielectrics have been commonly used in micro- and nanotechnologies since the past decade. Their chemical composition and porous properties make them more susceptible to physical and chemical damage. In particular, pattern etching and subsequent processes for removal of resist layers and/or post-etch residues are critical steps that potentially modify the dielectric properties [1].

This study first focuses on the modification of the porous dielectric material (pore structure, surface sealing, wettability) using a patterned line/trench test structure of 45 nm ½ pitch (Fig. 1). Several methods were applied for characterization of the patterned structure used in this study, including ellipsometric porosimetry (EP), X-ray photoelectron spectroscopy (XPS), and Fourier transform Infrared spectroscopy (FTIR). Fig. 2 shows the variation of the polarization state, expressed here by Delta angle, as a function of the relative pressure of toluene (used as a probe for porosity change). For the 45 nm patterned structure, the rapid change in Delta angle reflects the adsorption of toluene into the porous network. This clearly indicates that the patterned low-k surface remained unsealed after the C_4F_8/CF_4-based etch plasma process. In contrast, the surface of the blanket low-k film was almost sealed, evidenced by a very slow and irreversible toluene adsorption. Note that the sealing layer is only concerned the surface. The approach and characterization methods utilized for determination of the sealing thickness and the internal hydrophobic/hydrophilic properties [2] of the patterned porous low-k structures will be discussed.

Another aspect of this study concerns the surface composition of the patterned feature, type of the residues generated during the plasma etch, and the effect of a subsequent wet clean step. The latter is usually required before the deposition of the barrier layer. Substantial amount of fluorinated etch residues were detected on both the TiN surface and the dielectric sidewall and bottom. As shown in Fig. 3, the XPS F 1s core-level spectrum for the surface after the OSG etch consisted of two main components: the peak centered at ~684.6 eV corresponds to F-Ti bonds and the peak at 688.4 eV can be assigned to C-F bonds. The efficiency of the removal/dissolution of CFx and TiFx by the wet chemistries can be clearly demonstrated using this 45 nm test structure. For instance, dilute HF and TMAH:H_2O_2 mixture are efficient for TiFx removal but only show very limited dissolution of CFx polymer. In the presentation, the change in the low-k dielectric and TiN properties due to the plasma etch and subsequent wet cleans will also be presented and discussed.

11:40am **PS-TuM12 Cryogenic Etching of Porous Organosilicate Low-k Materials: Reduction of Plasma Induced Damage**, ***Floriane Leroy***, *T. Tillocher*, GREMI CNRS/Université d'Orléans, France, *L. Zhang*, IMEC, KU Leuven, Belgium, *P. Lefaucheux,* GREMI CNRS/Université d'Orléans, France, *K. Yatsuda,* TEL, Japan, *K. Maekawa,* TEL Technology Center, America, LLC, *J.-F. de Marneffe, M. Baklanov,* IMEC, Belgium, *R. Dussart*, GREMI CNRS/Université d'Orléans, France

Porous Organosilicate (OSG) low-k materials were introduced as inter-metal dielectrics, in order to reduce RC signal delay and energy dissipation. Low-k value is achieved by enlarged open porosity and pore size, but integration of porous low-k is impeded by plasma induced plasma (PID). Several low-damage processes have been reported in the literature. Recently, cryogenic etch, using SF_6-based plasma, was studied as an alternative approach [1]. It was observed that the PID is reduced by decreasing the wafer temperature to cryogenic region (-120°C). At such a low temperature, a passivation layer forms on the pore sidewalls in the low-k bulk, and minimize reaction with damaging radicals.

In this work, we investigate the mechanisms behind this cryogenic low damage process on blanket sample glued on a SiO_2 carrier wafer. The etch rate and the refractive index were measured by in-situ ellipsometry and ex-situ FTIR was used to evaluate methyl group depletion. Species desorbed during the warm-up of the cooled OSG films were detected by a mass spectrometer mounted on the diffusion chamber. In the case of a pure SF_6 plasma, the main desorbed species are C_xF_y, SF_x, SO_xF_y and SiF_x. SOF_2^+ increases first from -120°C to -80°C and decreases from -80°C to 20°C, which shows that a strong desorption of SOF_4 occurs in this range of temperature and play a major role in SF_6 silicon etching [2]. SiF_3^+ and $C_2F_4^+$ mainly desorb at -60°C. It is known that SiF_4 is involved in passivation mechanisms for cryogenic etching, but this result suggests that fluorocarbon species also play a significant role. This is why it was proposed to add C_4F_8 to further protect the low-k material. This new SF_6/C_4F_8 chemistry was studied for various temperatures (from -120°C to +20°C). PID were minimized at -120°C and lower than with pure SF_6. In addition, the increase of the refractive index during the etching process reveals that C_4F_8 condenses into the pores, which is believed to enhance the protection of the material. The desorption of the C_xF_y, SF_x, and SiF_x species is still observed by mass spectrometry. It appears that SiF_3^+ and $C_2F_4^+$ peaks intensity exhibit

two local maxima: -120°C, due to desorption of condensed C_4F_8, and -60°C, due to the desorption of the passivation layer. In addition, in-situ XPS experiments was carried out to determine the fluorine based stoichiometry of the passivation layer [3]. Finally, profiles etched with SF_6/C_4F_8 chemistry at -120°C will be presented.

[1] L. Zhang *et al.,* ECS J. Solid State Sci. Technol. 2(6), N131-N139 (2013)

[2] X. Melhaoui *et al.*, J. Appl. Phys 98, 104901 (2005)

[3] J. Pereira *et al.,* Appl. Phys. Lett. 94, 071501 (2009)

12:00pm **PS-TuM13 Remote Shielded Microwave Mini Plasma Source for Sample Cleaning**, ***Herman Bekman****, R.J. Bolt, F.A. Nennie, P.M. Muilwijk, F.T. Molkenboer, N.B. Koster, O. Kievit*, TNO Technical Sciences, Netherlands

In EUV contamination control, but also more generally, there is a desire for a cleaning technique that can remove hydrocarbon contaminants without inflicting damage to the underlying substrate, e.g. in electron microscopy. Plasma cleaning based on shielded microwave using hydrogen is such a cleaning technique. Generally microwave plasma cleaners are quite big, but at TNO we are pursuing miniaturized plasma cleaners to enable local in-situ cleaning.

In an earlier attempt a mini plasma cleaner has been developed based on a resonant cavity partially filled with a high dielectric material. The source could be operated inside a vacuum system. Due to unexpected thermal issues the source operated only a limited number of times. Furthermore we experienced that it was difficult to judge from the outside why the plasma source was not igniting anymore. A desire for detailed diagnostics during plasma ignition attempts was evident.

A second generation mini microwave plasma cleaner was subsequently designed, built, and tested. The aim was to realize a mini plasma cleaner that should fit on small load locks. Thus substrate could be cleaned prior or after an inspection/processing step. A microwave test setup was designed that allowed simultaneous supply of high power microwave signal at a fixed microwave frequency, for ignition of the plasma, and supply of a low power swept microwave frequency signal for resonator characterization.

This presentation will focus on realization and characterization of the mini plasma source. Cleaning rate as well as detailed microwave characterization measurements have been performed. The microwave measurements demonstrated in real time the effect of plasma ignition on resonance behavior of the cavity.

Advanced Surface Engineering
Room: 212A - Session SE+PS+SM-TuM

Atmospheric Pressure Plasmas, CVD and Other Deposition Methods
Moderator: Hana Barankova, Uppsala University, Sweden, Michael Stueber, Karlsruhe Institute of Technology

8:00am **SE+PS+SM-TuM1 Synthesis of Hybrid Nanoparticles - Fluorinated (Super)Hydrophobic Coatings by Atmospheric Plasma : Possibilities and Challenges**, *J. Mertens, J. Hubert, N. Vandencasteele,* ***François Reniers***, Université Libre de Bruxelles, Belgium

In order to obtain superhydrophobic coatings, one has to combine a low surface energy surface with a specific roughness. We propose a simple method to obtain such coatings by depositing by atmospheric plasma fluorinated coatings starting from C_6F_{12} or C_6F_{14} in argon or helium onto surfaces previously decorated with SiO_2 or TiO_2 nanoparticles. The loading (concentration) and size of nanoparticles were varied, as well as the plasma parameters (nature of the process gas and precursor, plasma power, deposition time). Depending on the experimental parameters, coatings exhibiting water contact angles from 110° to more than 160° could be obtained. The mechanisms for the polymer synthesis have been studied by a combination of atmospheric mass spectrometry and X-ray photoelectron spectroscopy, and the influence of the process gas on the final chemical structure of the coating is evidenced and explained. A higher fragmentation pattern is shown for Argon, due to the higher electron density and the higher energy available in the filamentary discharge. This is responsible for a change in the CF_2 and CF_3 moieties in the final coating. Similarly, the nature of the oxide nanoparticles has a strong influence on the chemistry of the coating: whereas SiO_2 particles do not modify the CFx films, the TiO_2 nanoparticles contribute to a significant degradation of the chemistry of the coating. This method can easily be implemented on any industrial process line, provided a good adhesion of the final coating on the subtrate is obtained.

8:20am **SE+PS+SM-TuM2 Deposition of Antifouling PMOXA-like Coatings using Atmospheric Pressure Helium Plasma Jet**, ***Sameer Al-Bataineh****, A. Cavallaro, M. Ramiasa, K. Vasilev*, University of South Australia

Antifouling interfaces are important in a wide range of applications such as food packaging, water purification, marine biofouling and biomedical devices.[1,2] In recent years, poly(2-oxazoline)s have attracted much attention due to their numerous biological applications as antifouling polymers.[3,4] Poly(2-methyl-2-oxazoline)(PMOXA) has antifouling properties comparable to the gold standard PEG, and has better stability in a range of aqueous solution and biological media.[5] Atmospheric pressure plasma (APP) is an emerging technology with a wide range of applications including material processing.[6] The advantage of using APP for surface modification is that it eliminates the use of expensive vacuum equipment and enables continuous surface modification processes. This study aims to develop PMOXA-like coatings using atmospheric pressure helium plasma jet.

The plasma jet system used in this study consisted of a glass capillary tube with an internal diameter of 1mm that was surrounded by two external hollow electrodes separated by 4mm. The carrier helium gas was sent through a glass container at a flow rate of $1L.min^{-1}$ and carried the oxazoline monomer (2-methyl-2-oxazoline, MOXA) vapour into the glass tube. The plasma jet was operated at an applied voltage of 5.5 kV_{pk-pk} and a frequency of 10 kHz. Deposition of the plasma coatings was carried out under static deposition conditions with 3mm separation distance between the end of the capillary tube and the substrate. To enhance stability of the coatings, substrates were heated during plasma deposition process.

Surface elemental composition and molecular structure of oxazoline plasma polymer coatings were thoroughly characterised using XPS and ToF-SIMS. Stability of the plasma coatings were examined by incubation in PBS buffer solution at room temperature overnight. The antifouling properties of the plasma coatings are now under investigation towards resisting protein adsorption and bacterial cell adhesion. In addition, the surface chemistry and functionality of the coatings produced in this study will be briefly compared to those prepared with an RF low pressure plasma.[7]

This study offers a convenient alternative single step strategy for preparation of oxazoline-based antifouling coatings.

1. Lowe S, et al., *Polym. Chem.*, 2015, 6, 198.

2. Zou L, et al., *J. Membr. Sci.*, 2011, 369, 420.

3. Luxenhofer R, et al., *Macromol. Rapid Commun.,* 2012, 33, 1613.

4. Sedlacek O, et al., *Macromol. Rapid Commun.,* 2012, 33, 1648.

5. Konradi R, et al., Langmuir, 2008, 24, 613.

6. Merche D, et al., *Thin Solid Films*, 2012, 520, 4219.

7. Ramiasa MN, et al., *Chem. Commun.,* 2015, 51, 4279.

8:40am **SE+PS+SM-TuM3 Antibacterial Silicon Oxide Thin Films Doped with Zinc and Copper Grown by Atmospheric Pressure Plasma Chemical Vapor Deposition**, *E. Jäger,* Montanuniversität Leoben*, J. Schmidt, A. Pfuch, S. Spange, O. Beier,* INNOVENT e.V.*, O. Jantschner, R. Daniel,* Montanuniversität Leoben*,* ***Christian Mitterer***, Montanuniversität Leoben, Austria

Zn- and Cu-doped SiO_x films were applied by atmospheric pressure plasma chemical vapor deposition to study their antibacterial efficiency against Gram-negative *Escherichia coli* and their cytotoxic effect on the growth of mouse cells. ZnO_x and CuO_x particles were found to be homogeneously embedded within the SiO_x films. For both doping elements, bacteria are killed already within the first three hours after exposure to the film surface. In contrast, mouse cells grow well on the surfaces of both film types, with a slight inhibition effect present only after the first day of exposure, due to the more pronounced release of zinc and copper. The obtained results indicate that the films show a high potential for use as effective antibacterial surfaces for medical applications

9:00am **SE+PS+SM-TuM4 Carbon Bridge Incorporation in Organic-Inorganic Hybrid Coatings using Atmospheric Plasma Deposition in Ambient Air**, ***Linying Cui****,* Stanford University*, G. Dubois,* IBM Almaden Research Center*, R.H. Dauskardt*, Stanford University

Atmospheric plasma deposition in ambient air has a huge potential for large-scale coating synthesis at reduced cost for energy, display, and aerospace applications. However, the abundant oxygen in air poses significant oxidation challenge for incorporating specific oxygen sensitive components in the coating. In this work, the oxygen sensitive carbon bridge structure was successfully incorporated into the inorganic silicate network in the oxygen-helium atmospheric plasma in ambient air. The mechanism of incorporating the specific carbon structure in an oxidative species rich environment was elucidated by a kinetics model which takes into account the probability of oxidation, adsorption, and desorption of different

precursor species during gas transport and on the substrate surface. The key tuning knobs were identified as the precursor chemistry and the precursor delivery rate. The resulting carbon bridged organo-silicate coatings exhibited significantly improved plasticity, more than doubled adhesion, and up to four times increase of moisture resistance in terms of the driving energy threshold for debonding in humid air, compared to plasma silica coatings and commercial sol-gel polysiloxane coatings. In order to further improve the interfacial bonding of the coating to oxygen sensitive substrate in an oxidative atmospheric plasma environment, other deposition parameters were also investigated in order to fully activate but not over-oxidize the substrate. The resulting carbon bridged, highly adhesive coating showed remarkably enhanced hydrothermal stability, a key requirement for application in exterior coatings and functional membranes. As an example for application, the carbon-bridged coating was deposited between hard scratch-resistant coatings and oxygen-sensitive polymer substrate to enhance the adhesion of hard coatings for airplane window protection.

9:20am **SE+PS+SM-TuM5 Atmospheric Plasma in Liquids***, **Ladislav Bardos**, H. Barankova*, Uppsala University, Sweden **INVITED**

Experiments using spark discharge above the water level were reported already in 1784 by Henry Cavendish after his study of air. His results inspired in 1894 Lord Rayleigh and William Ramsay and led to an important discovery of argon present in air. Studies of water electrolysis and interactions of a glow discharge with water solutions were described in 1887 by J. Gubkin and followed in 1952 by R.A. Davies and A. Hickling. The first type of plasma discharge submerged directly into water was an arc. The arc discharges are used for the underwater welding already since 1930. A number of applications of submerged arcs have already been tested and reported. Rapid developments of non-thermal (cold) atmospheric plasma sources during last century led to new studies of plasma in liquids. Studies of the plasma-assisted electrolysis and different phenomena observed on surfaces of electrodes during electrolysis in water electrolytes enhanced an interest in different types of submerged discharges. New processes were developed like the plasma electrolytic oxidation (PEO), formation of nanoparticles and nanotubes, novel plasma-chemical reactions, plasma cleaning, disinfection and "activation" of water or water solutions. This presentation summarizes several interesting systems and results on the submerged plasma in liquids. Examples of the experimental systems and the results of tests of cold plasma discharges in water using different power generators and an efficient low power production of hydrogen from the mixtures of water with ethanol will be presented and discussed in more details.

11:00am **SE+PS+SM-TuM10 Study of Polymer Confinement Effects in Nanocomposite Thin Films Synthesized by Initiated Chemical Deposition***, **Chia-Yun(Sharon) Hsieh**, K.K.S. Lau*, Drexel University

Initiated chemical vapor deposition (iCVD) is a liquid-free polymer synthesis technique that simultaneously deposits the polymers as thin films on supporting substrates. It produces well-defined polymers that are spectroscopically identical to corresponding polymers synthesized in the liquid phase. A wide range of polymers have been produced by iCVD, including hydrophilic polyglycidol (PGL), hydrophobic polytetrafluoroethylene (PTFE), semicrystalline polyethylene oxide (PEO), and amorphous poly (methyl methacrylate) (PMMA). In addition, iCVD is an effective approach for integrating polymers within porous 3D inorganic nanostructures to produce polymer nanocomposite thin films. By utilizing inorganic nanostructural templates such as mesoporous TiO_2 nanoparticle networks, good dispersion of the nanoparticles can be ensured by adopting well-established dispersion procedures. Conformal and uniform polymer growth within the pore space can be achieved by operating under reaction-limited iCVD conditions that allow efficient delivery of reactive precursors by gas and surface diffusion. Quantitative measurements using thermogravimetric analysis has shown that 90–100% of the available pore space can be filled in porous layers of up to 12 μm in thickness with 10–20 nm diameter interconnected pores. As a result, we are able to achieve polymer nanocomposite thin films with high inorganic content (>80 wt%) that are well-dispersed. This ability provides an ideal platform for studying polymer confinement effects that lead to significantly altered polymer properties compared to its bulk 2D planar film counterpart with no inorganic filler. For example, iCVD PGL-TiO_2 nanocomposite thin films has shown a significant increase of 50–60°C in the polymer glass transition temperature (a transition between the glassy, brittle state to the rubbery, pliable state) compared with bulk PGL. This has been attributed to the strong hydrogen bonding interactions between the polar oxygen groups on PGL with the hydroxyl groups on the TiO_2 surface. Here, we will detail the iCVD approach in making different polymer nanocomposite thin films and discuss the resulting nanoscale confinement effects on polymer properties as a result of different polymer-substrate interactions. This knowledge has critical implications in applying polymers in the design of nanostructured devices as bulk polymer properties might not be followed in these systems.

11:20am **SE+PS+SM-TuM11 Persistent Superhydrophilicity of Polycarbonate Surfaces *via* Nanoimprint Lithography *and* Atomic Layer Deposition***, **Xue Li**,* Institute of Materials Research and Engineering (IMRE), Singapore*, K.S.L. Chong, M.S.M. Saifullah, R.B. Yang, C.S. Lee, Y.C. Loke,* Institute of Materials Research and Engineering (IMRE)*, A.Y. He*, Loke

Superhydrophilic surfaces are often exploited for their anti-fog ability and typically rely on coatings which modify the surface energies of the materials to create such effects. Such traditional coatings are often applied wet and are not long lasting. A persistent superhydrophilic coating with both anti-fog and anti-UV properties have been fabricated on polycarbonate (PC) surfaces *via* a combination of nanoimprint lithography and atomic layer deposition (ALD) process. Nanoimprint lithography was used to pattern anti-reflection (AR) structures on to a PC surface. These samples were then coated with a thin layer titanium dioxide (TiO_2) layer *via* a low temperature ALD process (<80 °C). The PC sample with AR patterns demonstrated enhanced visible light transmittance upto 94% and reduced transmittance in the UV wavelengths (<400 nm). The TiO_2 layer is superhydrophilic and the resultant samples showed a persistent superior anti-fog effect. More importantly, the superhydrophilicity can be recycled via rinsing in an oxidant solution, and had demonstrated stability upto 4 months.

11:40am **SE+PS+SM-TuM12 Enhanced CO_2 Permeation Characteristics Performance On A Crack-Free Nanostructured Ceramic Membrane***, **Ngozi Nwogu**, E. Gobina*, Robert Gordon University, UK

Carbon capture from point source emissions have been acknowledged as one of numerous strategies required for alleviating unrestricted release of greenhouse gases (GHGs) into the atmosphere. To keep greenhouse gases at controllable levels, large drops in CO_2 emissions through capturing and separation will be necessary. Reduction and manipulation of materials at nanometre scale are key experiments in nano-science and nanotechnology. In this work, an experimental study is made on the preparation, the morphological characterization and the gas permeation of ordered ceramic multilayer membranes with silica top layer. We developed and manufactured a crack-free thin film membrane on a fresh tubular alumina ceramic membrane with pore diameter of 6000nm. By using a hybrid material of appropriate proportion, the nano-fabrication conditions are then controlled with extremely high carbon dioxide permeance due to the membrane immersion in a silica solution. Results obtained from the experiments show that the nanostructured silica membranes have potential applications in the treatment of large gas streams under low pressure conditions like carbon dioxide separation from flue gases.

Keywords: Carbon capture, CO_2 Permeation, nanostructured ceramic membrane & flue gases

Electronic Materials and Processing
Room: 210E - Session EM+MN+PS-TuA

More than Moore: Novel Approaches for Increasing Integrated Functionality
Moderator: Andy Antonelli, Nanometrics, Sean King, Intel Corporation

2:20pm **EM+MN+PS-TuA1 Maintaining the Pace of Progress as we Approach the end of Moore's Law: *Heterogeneous Integration, New Materials, New Processes, New Architectures*, *Bill Bottoms***, 3MTS **INVITED**

The environment is rapidly changing as we approach the end of Moore's Law scaling. Scaling continues but benefits in performance, power and cost are reduced. At the same time drivers for the electronics industry are impacted by the emerging Internet of Things and Migration to the Cloud. Satisfying the requirements of these emerging drivers cannot be accomplished with the current technology. It will require innovative heterogeneous integration approaches to satisfy demands for power, latency, bandwidth, reliability and cost in an environment where transistors will wear out.

Overcoming the limitations of the current technology will require heterogeneous integration using different materials, different device types (logic, memory, sensors, RF, analog, etc.) and different components incorporating multiple technologies including electronics, photonics, and MEMS in new, 3D, system-in-package (SiP) architectures. New materials, manufacturing equipment and processes will be required to accomplish this and meet the market demand for continuous reduction in cost per function.

The requirements, difficult challenges and potential solutions will be discussed.

3:00pm **EM+MN+PS-TuA3 More than Moore - Wafer Scale Integration of Dissimilar Materials on a Si Platform**, ***Thomas Kazior***, *J. LaRoche*, Raytheon Company **INVITED**

Advances in silicon technology continue to revolutionize microelectronics. However, Si cannot do everything, particularly for high performance, high frequency RF and mixed signal applications. As a result circuits based on other materials systems, such as III-V semiconductors, are required. However, these other device technologies do not enjoy the integration density, cost benefit and manufacturing infrastructure of Si. So how can we get the 'best of both worlds'? What is the best way to integrate these dissimilar materials with Si? In this paper, we review different heterogeneous integration approaches and summarize our results on the successful wafer-scale, 3D heterogeneous integration (3DHI) of GaN HEMTs and Si CMOS.

Our Au-free GaN HEMTs have been successfully fabricated entirely in a Si foundry on semi-standard, 200 mm diameter Si wafers using Cu damascene interconnects. RF performance compares favorably with GaN on SiC devices fabricated in a III-V foundry with Au-based contact and interconnect metallurgy. Oxide bonding is being used to integrate these GaN on Si wafers with Si CMOS wafers. Through-dielectric-vias (TDVs) are used to interconnect the high performance GaN RF devices/circuits with high density CMOS control and logic circuits, resulting in ultra-short, wide-bandwidth interconnects enabling circuit optimization through intimate and arbitrary placement of CMOS logic and control circuitry relative to III-V devices. Through-substrate-vias (TSVs) are used for thermal management. This 'flexible' wafer-scale, integration platform is compatible with other III-V devices, other (non-Si) device/component technologies and any node of Si CMOS or SiGe BiCMOS. The 3DHI process is being used to fabricate cost effective, high performance, digitally enhanced, RF and mixed signal ICs such as 'intelligent' and adaptive/reconfigurable transceivers.

Plasma Science and Technology
Room: 210A - Session PS1-TuA

Novel Materials and Etch Chemistry
Moderator: David Lishan, Plasma-Therm LLC

2:20pm **PS1-TuA1 Low-Damage Etching Technology for Nitride Semiconductor Devices**, ***Makoto Sekine***, *Z. Liu, J. Pan, K. Ishikawa, K. Takeda, H. Kondo, M. Hori*, Nagoya University, Japan **INVITED**

Plasma etching of GaN is necessary for fabricating high performance Nitride semiconductor devices. However plasma exposure causes defects and residues, which could reduce the performances. It is required that the plasma induced damages (PID) should be removed especially in the power electronics device fabrication. Post annealing could recover PID, but preferential N loss causes Ga-rich surface. The stoichiometric surface was reported to be deteriorated with annealing up to 1000°C after N_2^+ sputtering at room temperature (RT)[1], We have revisited the surface reactions at high temperature (HT). We made a HT etcher. A VHF-ICP was generated and 13.56-MHz rf power was applied to the substrate. Sample stage can be heated up to 800°C by an IR lamp as fast as 100°C/s.

GaN surface was roughened with 9.88 nm RMS as exposed to Ar plasma at 600°C. XPS showed Ga metallic state or Ga cluster with the shoulder peak at 18.9 eV in Ga 3d. In contrast, no significant roughness increase (1.46 nm) was observed after N_2 plasma at 600°C. Nevertheless, the HT N2 plasma failed to provide a preferable PL property[2].

For Cl_2 plasma, PL spectra of GaN etched at HT showed no obvious variation of yellow luminescence at 2.2-2.3 eV, suggested no Ga vacancies were formed. We focused on the near band edge emission (NBE) at 3.4 eV. The PID in bulk GaN behave as nonradiative centers of deep level states, which trap and recombine carriers. The NBE intensities for all GaN films etched at HT were degraded and as a consequence, the etching process at 400°C was optimum, because of its preferable stoichiometry, PL and smooth surface.

By covering the sample surface with a transparent window with or without the gap, we separated the effects of ion, photon and radical exposures. It was found the ion-induced damages dominated at 300°C, then decreased at 400°C, and removed at 500°C. Furthermore, photon-induced damages were not observed up to 400°C. Above 500°C, PL properties were degraded by photon. Since photons could not mainly induce damages at RT[4], the synergy with thermal annealing enhanced the PL deterioration.

Therefore, by the results of depressed ion-induced damages and undeveloped photon-induced damages with a smooth surface at 400°C, the Cl_2 plasma etching at 400°C is most appropriate to the low-damage process for GaN-based devices.

This work was supported by the Knowledge Cluster Initiative (Second Stage), MEXT, Japan.

1. Z.-Q. Fang, et al., Appl. Phys. Lett. **82,** 1562 (2003).

2. R. Kometani, et al., Appl. Phys. Express **6,** 056201 (2013).

3. Z. Liu, et al., To be published in Jpn. J. Appl. Phys. **54**, (2014).

4. M. Minami, et al., Jpn. J. Appl. Phys. **50,** 08JE03 (2011).

3:00pm **PS1-TuA3 Limitation of Surface Defects in GaN Deep Etching**, *N. Gosset*, ***Thomas Tillocher***, GREMI CNRS/Université d'Orléans, France, *J. Ladroue*, ST Microelectronics, France, *P. Lefaucheux*, GREMI CNRS/Université d'Orléans, France, *M. Boufnichel*, ST Microelectronics, France, *R. Dussart*, GREMI CNRS/Université d'Orléans, France

Gallium nitride (GaN) is a III-V semiconductor with attractive physical properties for power microelectronics. It actually combines a wide and direct bandgap, a high electron mobility and strong chemical bonds. Therefore, GaN power components can operate under higher temperature, higher power and higher frequency than silicon devices.

For Schottky diodes with pseudo-vertical structure, GaN MESA features with a height between 6 and 10 µm are required. This is considered as deep etching, compared to the thickness typically etched for light emitter devices (a few hundred nm). Ion-enhanced plasma etching with chlorine-based chemistry is commonly used for GaN deep etching.

Previous studies have already shown that GaN can be etched in Cl_2/Ar inductively coupled plasmas (ICP) with etch rates as high as 1 $\mu m.min^{-1}$. However, after etching, the etched surface exhibits three types of defects

such as columns, pits and a high roughness ("White GaN"). Columns and pits are related to nanopipes and dislocations created during epitaxial growth of GaN. In addition, oxygen based species, coming from either the SiO_2 coverplate and mask, or the alumina/quartz tube, play an important role in the columnar regime. They preferentially oxidize dislocations, leading to the observed columns. "White GaN" origin is a surface over-oxidation. Such defects must be suppressed in order to provide good electrical contact.

A comparative study of GaN etching has been performed on different reactors: an ICP reactor with a diffusion chamber, another ICP reactor with no diffusion chamber, a dual-frequency capacitive reactor and an Ion Beam Etching system. The etched surface state was subsequently analyzed by means of SEM, EDX, AFM and XPS. This study revealed a correlation between the etch rate, the surface defects density and the surface composition. Actually, with the IBE chamber, the etch rate was the lowest and no defects were observed on the surface. The dual-frequency capacitive reactor allows the highest etch rate and no defects were found on the surface. But, the Ga:N relative density was altered in both cases, resulting in poor electrical properties. Consequently, a trade-off should be made between process performances and electrical properties. ICP chambers met this compromise.

Moreover, it has been demonstrated that surface fluorination, by addition of a fluorine-containing gas, leads to a limitation of surface defects. Fluorine species are able to protect GaN surface with the formation of a Ga_xF_y -like "passivation layer", detected by XPS. This result led to the development of a defect-free time-multiplexed etching process consisting in alternating etching and passivation steps.

3:20pm **PS1-TuA4** ***In Situ* Monitoring of GaN in Process Plasma**, ***Daisuke Ogawa***, *Y. Nakano, K. Nakamura*, Chubu University, Japan

Next to a great success of blue LEDs, gallium nitride (GaN) is now looking for another success, the application with high-power devices. The wide bandgap of GaN is attractive when considering the integration and fabrication of devices on a substrate. The integration process requires the use of plasma, but the plasma sometimes creates undesirable change on devices, noticed as plasma-induced damages (PID). Therefore, it is important to understand how process plasma creates changes on GaN and what mainly causes the change.

In-situ monitoring is one of ways to understand the damage development of GaN. Towards to the goal, we have used steady-state photoluminescence (PL) emitted from the surface of GaN. The PL represents the optically-transferrable intermediate states that are mainly created with the defects and impurity in GaN. The depth of the PL measurement depends on the wavelength of excitation. Our experiment setup uses 313 nm wavelength for the excitation so that we basically monitored the change of the intermediate states down to ~75 nm below the top surface.

Our in-situ measurements showed that the exposure of argon plasma changed PL spectrum from the GaN; the total PL intensity turned down to 33 % of the original spectrum. We also increased the chuck bias, showing that the total PL intensity decreased even worse. This means that the argon ion affected the change of PL in our system assuming that plasma density stayed the same. We also made ex-situ measurements with X-ray photoelectron spectroscopy (XPS). The measurement showed that the change of atomic distribution was observed down to 4 nm at deepest. In this depth range, gallium and nitrogen atoms dissociated from the surface, and oxygen atoms defused into deeper levels. However, this depth was only ~5 percent of the depth where PL spectrum informs us. This means that the change of PL was caused by the structural change in GaN, such as crystal dislocation.

We also changed the gas that formed the plasma. In general, chlorine gas is utilized to etch GaN. In this measurement, we used the mixture gas of argon and chlorine with the ratio of 2:1. Interestingly, the PL from GaN stayed almost constant even when GaN was exposed into the plasma. We double-checked the etch rate, finding the rate at 100s nm/min. This result indicates that chlorine likely etched GaN without making a major change in the optical intermediate states even though argon could have made some damages during the plasma exposure.

In this presentation, we will show our latest analysis of damage development of GaN that is exposed in plasma, in particular, the plasma that is possibly used in the material process.

4:20pm **PS1-TuA7 Thermodynamic-aided Selection of Non-PFC Plasma Chemistries**, ***Nicholas Altieri***, *J.K.C. Chen, L. Minardi, J.P. Chang*, University of California Los Angeles

Continued reduction in the size of microelectronics and nanoscale features has necessitated the use of low-k dielectric interlayer materials in an effort to curtail parasitic capacitance and RC delay. Patterning these low-k films requires consideration of both etching efficacy and environmental impact. To address these issues, a generalized methodology is developed based on a thermodynamic approach to analyze etchants and additive gases to assist in selection of plasma chemistries whose environmental effects can be more easily mitigated.

Thermodynamics is an enabling tool for assessing a reacting system, such as plasma etching of carbon doped porous silica, specifically through analysis of Gibbs free energy. A system at equilibrium has reached a minimal Gibbs free energy which can be expressed as the sum of its constituents and their corresponding chemical potentials. With known reactants, potential products, and free energies of formation as inputs, the total Gibbs energy is minimized to calculate an output quantity of each species. This calculation was then repeated across a range of temperatures at fixed pressure. Using CF_4 etching of silica as the reference and monitoring the formation of volatile etch product $SiF_4(g)$ via volatility diagrams, a range of carbon doped porous silica, a list of viable etchants including perfluorocarbon gases, $NF_3(g)$, $CF_3I(g)$, as well as additive gases such as $H_2(g)$ and $NH_3(g)$ are examined. Based on thermodynamic calculations, $NF_3(g)$, a non-PFC gas with high abatement efficiency was predicted to generate the highest pressure of $SiF_4(g)$ overall. $CF_3I(g)$, though calculated to be not as effective as $NF_3(g)$, is another alternative due to its short atmospheric lifetime and low global warming potential. On the other hand, $H_2(g)$ was found to be the most effective additive with fluorocarbon etchants.

$CF_4(g)$ and $CHF_3(g)$ were studied separately with varying hydrogen addition to validate the thermodynamic calculations. Optical emission spectroscopy was used in parallel to monitor atomic fluorine intensities at 685.6 and 703.7 nm as a function of $H_2(g)$ feed percentage. Discharges of $CF_4(g)$ mixed with 20% $H_2(g)$ and CHF_3 with 10% $H_2(g)$ resulted in maximal etch rates of 215 nm/min and 166 nm/min respectively. A trend similar to etch rate dependence on feed composition was seen in the spectra of atomic fluorine, with maximal intensities recorded for CF_4 and CHF_3 at 20% and 10% H_2, respectively.

4:40pm **PS1-TuA8 Enhancing Selectivity for Self-Aligned Contact Etching by Employing Dual Fluorocarbon Etch Gas Processes**, ***Jeffrey Shearer***, IBM Research Division, *S.U. Engelmann, R.L. Bruce, E.M. Sikorski*, IBM Research Division, T.J. Watson Research Center, *T. Suzuki, M. Nakamura, A. Ito*, ZEON Chemicals L.P., *G. Matsuura, H. Matsumoto*, Zeon Corporation, Japan, *B. Messer, K. Horvath, A. Metz*, TEL Technology Center, America, LLC, *J.C. Arnold*, IBM Research Division, *E.A. Joseph*, IBM Research Division, T.J. Watson Research Center

As the industry moves from 10nm node to 7nm node and beyond, self-aligned contact (SAC) etch is becoming one of the most critical and challenging process elements in logic chip manufacturing. Extremely high selectivites are required to adequately stop on spacer and hard mask materials in addition to the ever continuing trend of scaling critical dimensions (CDs). For the self-aligned contact etch this translates into a classic trade-off relationship between increased selectivity by fluorocarbon deposition and random etch stop due to ion/neutral flux imbalances at reduced dimensions.

Our team has recently introduced a new etch gas (C_5HF_7) which is able to etch by selective deposition of a fluorocarbon (FC) layer, where the elemental fluorine content was reduced due to feedgas optimization. Even though the C_5HF_7 gas yielded better protection of the spacer material than the comparable C_4F_6 process, adequate etch depth was not achieved in aggressive 10nm test structures (etch stop was observed).

We enhanced this process further by decomposing the etchant supply of the fluorocarbon gas by the use of dual FC etch chemistries. While one FC gas is targeted to deliver radicals for FC deposition and selectivity enhancement, another FC gas is added to supply FC radicals that promote the oxide etch. We are reporting our results from this approach by two trusts: On a more fundamental level, we evaluated the dual FC etch gas approach in detail, with gas optimization and a survey of multiple spacer materials. We found that for SiN spacer materials our C4F6 process showed selectivities of approx. 9, the C_5HF_7 process showed selectivities of up to 23 and the dual FC process showed selectivities of up to 38.

Furthermore, C_5HF_7 has been deployed for SAC applications in 10nm and 7nm product demonstrations. This paper will show that this new gas is able to match the performance of the C_4F_6 while at the same time significantly improving raw process time.

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

[1]M. Schaepkens, T.E.F.M. Standaert et al., J. Vac. Sci. Technol. A 17, 26 (1999)

[2]M. Schaepkens, G.S. Oehrlein and J.M. Cook, J. Vac. Sci. Technol. B18, 848 (2000)

[3]R.L. Bruce, T. Suzuki et al., AVS 61st Int. Symp. & Exhibit. (2014)

5:00pm **PS1-TuA9 Pushing the Limits of Dielectric Etch with Novel Fluorocarbon Etch Gases**, ***Robert Bruce***, IBM Research Division, T.J. Watson Research Center, *T. Suzuki*, ZEON Chemicals L.P., *J. Lee*, IBM Albany Nanotech Center, *E.A. Joseph, S.U. Engelmann*, IBM Research Division, T.J. Watson Research Center, *A. Itou, M. Nakamura*, ZEON Chemicals L.P., *G. Matsuura*, Zeon Corporation, Kawasaki, Japan, *J.C. Arnold*, IBM Albany Nanotech Center, *E.M. Sikorski*, IBM Research Division, T.J. Watson Research Center

As the semiconductor industry continues to drive critical dimensions smaller moving to 7nm technology node and beyond, the challenges to dielectric etch for BEOL fabrication become ever greater. Plasma etch using fluorocarbon passivation gas to establish selectivity and maintain straight profiles during pattern transfer has been the mainstay of patterning into dielectrics. We have previously reported the superior performance of etching SiO2 and low-k using the hydrofluorocarbon gas C5HF7, which had greater selectivities and reduced sidewall damage compared to other passivation gases such as C4F8 and C4F6. This was due to the greater deposition behavior of C5HF7 because of fluorine scavenging by intramolecular hydrogen. Using C5HF7, we have fabricated dual damascene structures in various low-k dielectrics ranging from k2.7 to 2.4. In addition, we have recently demonstrated low-k etch at 7nm node with superior profile control compared to C4F8-based etch. In this talk, we investigate the reasons behind the improved etch performance using C5HF7 compared to other passivation gases and potential future applications.

5:20pm **PS1-TuA10 First-Principles Theoretical Investigation on Mechanism of New Transition Metal Etching Process using Oxygen and argon Neutral Beams and Ethanol Gas**, ***Tomohiro Kubota***, *Y. Kikuchi, S. Samukawa*, Tohoku University, Japan

Anisotropic and damage-free etching of transition metals (especially magnetic materials) is important for realization of MRAM. However, it is generally difficult to etch such materials with conventional plasma etching and Ar ion milling has been widely used which causes problems such as damage, re-deposition, and etc. Recently Gu et al. reported [1] that anisotropic and damage-free etching of transition metal (Ta, Ru, and Pt) is possible based on complex reaction of transition metal by introduction of ethanol gas and irradiation of argon/oxygen neutral beam [2]. It is expected the process proceeds as following: (1) metal surface is oxidized by bombardment of oxygen neutral beam, (2) ethanol molecules adsorb at the surface, and (3) metal complex like $Ta(OC_2H_5)_5$ is formed by argon neutral beam bombardment. However, detail of the mechanism (especially, why oxidation is needed) was not clear. To understand the etching mechanism, computational investigation was performed using first principle calculation.

Calculations based on density functional theory and cluster model were performed using a SGI UV1000/2000 system in Institute of Fluid Science, Tohoku University.

First, adsorption of ethanol on tantalum oxide and metallic tantalum was investigated. As a result, it was found that ethanol adsorbs spontaneously on both surfaces. It means that adsorption step is not a reason why oxidation is needed for the etching.

Then, we investigated possible reaction which may occur after the adsorption of ethanol. It was found that O–H bond in the adsorbed ethanol can be dissociated, the H can be moved, and a new O–H bond can be formed between an oxygen atom in the metal oxide and the dissociated hydrogen (hydrogen movement). This should cause dissociation of Ta-O bonds in the oxide to proceed etching. Note that this process should not occur at metallic tantalum surface because it does not have oxygen atom to accept the moving hydrogen, and this should be the reason why oxidation is needed for etching.

Furthermore, it was found that collision of argon caused the hydrogen movement reaction mentioned above. It means that the hydrogen movement reaction and possibly tantalum etching can occur in the experimental condition under argon neutral beam irradiation.

Acknowledgement: We thank Dr. Nozawa from Tokyo Electron Ltd. for valuable discussions.

[1] X. Gu, Y. Kikuchi, T. Nozawa and S. Samukawa: J. Phys. D: Appl. Phys. **47** (2004), p. 322002.

[2] S. Samukawa, K. Sakamoto and K. Ichiki: Jpn. J. Appl. Phys. **40** (2001), p. L779.

[3] M. Yonemoto, K. Sano, K. Endo, T. Matsukawa, M. Masahara and S. Samukawa: Jpn. J. Appl. Phys. **48** (2009), p. 04C007.

5:40pm **PS1-TuA11 Generalized Approach for Selecting Viable Plasma Chemistries in Patterning Magnetic Metals**, ***Jack Kun-Chieh Chen****, *T. Kim, N.D. Altieri, J.P. Chang*, University of California Los Angeles

As advanced memory devices begin to dictate the adoption of complex magnetic and multiferroic materials, overcoming the challenge of achieving high-fidelity patterning for these multifunctional films becomes imperative. Physics- and chemistry-based modeling affords tremendous understanding of elementary reaction mechanisms in plasma patterning; however, the parameters necessary for kinetic modeling are sometimes difficult to obtain experimentally for novel multifunctional compounds. Developing a comprehensive framework for selecting viable chemistries in plasma patterning of magnetic metals has the potential to reduce the time and cost associated with design of experiments.

In this work, a generalized methodology, combining thermodynamic assessment of various etching chemistries and kinetic verification of etching efficacy, is proposed. To screen various chemistries, reactions between the dominant vapor phase/condensed species at various partial pressures of reactants are first considered. The volatility of etch product is determined to aid the selection of viable etch chemistry. Magnetic tunnel junction (MTJ) based MRAM (Magnetic Random Access Memory) was used as a case study to address the challenge of patterning constituent materials of multilayers. Ar ion beam milling was a traditional method in patterning MRAM devices; however, sidewall re-deposition results in electrical shorts as the features become smaller with higher aspect ratios. Selected metals (Fe, Co, Pt) and their alloys within the MRAM were studied by the generalized approach. To validate the thermodynamic calculation, films were patterned using a modified reactive ion etch process of halogen discharge with subsequent H_2 plasma exposure. To further improve selectivity to mask materials, a separate novel method of surface modification using Ar ion beam assisted chemical etch (IBACE) was then investigated.

The etch rate of Fe, Co, and Pt were enhanced 40%, 25%, and 20% respectively with secondary H_2 chemistry. X-ray photoelectron spectroscopy (XPS) suggested chemical removal of non-volatile metal chlorides by H_2 plasma. Moreover, characterization through superconducting quantum interference device (SQUID) proved that coercive field strength of magnetic alloy after Cl_2 plasma can be recovered by additional H_2 plasma exposure from 63.6 to 20.9 Oe. Etching of metals and alloys was further examined in organic solution by mass spectroscopy to verify formation of organometallic complexes predicted by thermodynamics. IBACE, a vacuum-compatible process was developed and proven to be effective in patterning magnetic metal stacks.

6:00pm **PS1-TuA12 Short- and Damage-Free Process for Patterning Magnetic Tunnel Junctions for High-Density Application**, ***Dunja Radisic***, *L. Souriau*, IMEC, Belgium, *V. Paraschiv*, SC Etch Technology Solutions, *D. Goossens*, IMEC, Belgium, *F. Yamashita, N. Koizumi, S. Tahara, E. Nishimura*, Tokyo Electron Miyagi Limited, Japan, *W. Kim, G. Donadio, D. Crotti, J. Swerts, S. Mertens, T. Lin, S. Couet, D. Piumi, GS. Kar, A. Furnemont*, IMEC, Belgium

The short- and damage-free patterning still remains the major challenge for the STT-MRAM high-volume commercialization. High-volume reactive ion etching (RIE) based short- and damage- free magnetic tunnel junction (MTJ) patterning was developed and electrically tested for isolated devices of sizes starting from 200nm down to 75nm and below. There was a tight TMR distribution measured after patterning (standard deviation of 7-14% was achieved) indicating that the process was short-free and it had no detrimental effect on the stack magnetic performance. In addition, measured TMR showed no significant size dependence, i.e., the TMR value was in the same, constricted range, for devices of different sizes. The process yield was 100%, meaning that all of the measured devices were functional and fitting the narrow TMR distribution.

The basic patterning sequence consisted of noble gas-based dry etch in RIE reactor followed by an in-situ SiN encapsulation in the RLSA reactor (both from Tokyo Electron Limited). MTJ stack was CoPt-based bottom pin with perpendicular anisotropy. Either TiN or Ta was used as a hard mask for etching. The stack was partially etched using medium bias process which resulted in some metallic re-deposition on the sidewalls. The remaining stack was etched and the sidewall residues efficiently removed using the high bias process step. For both steps, only noble gasses were used, so that the damage by reactive plasma species was prevented. The device performance dependency on the temperature in RIE reactor was studied by using either -20ºC or 60ºC ESC. The effect of the post-etch oxidation, aimed to convert possible metallic remains on the sidewalls into non-conductive metal oxides, was also tested. The in-situ SiN encapsulation was applied after etching to prevent possible stack properties modifications due

*** Coburn & Winters Student Award Finalist**

to interaction with the atmosphere. The in-situ etch and deposition capability allowed for patterning sequences where multiple etching and deposition steps were combined. The approach with whole stack etch followed by encapsulation, as well as the approach with partial stack etch (down to MgO), followed by SiN spacer formation, remaining stack etch and final SiN encapsulation were used. In the second case, the SiN spacer formed after etching stopping in MgO was intended to act as a dielectric medium preventing the shorts caused by re-deposition.

The best device performance was achieved by using Ta HM, approach with partial etching stopping in MgO, spacer formation, followed by the remaining stack etching and final encapsulation. The oxidation steps were applied after etch stopping in MgO, and after etching of remaining MTJ stack.

Plasma Science and Technology
Room: 210B - Session PS2-TuA

Plasma Modeling
Moderator: Saravanapriyan Sriraman, Lam Research Corporation

2:20pm **PS2-TuA1 Realistic Plasma Etch Simulation for High Aspect Ratio Contact Hole using Graphics Processing Units**, ***Yeon Ho Im***, Chonbuk National University, Republic of Korea **INVITED**

With the continuous decrease in nanoscale design dimensions, semiconductor plasma processing is confronting the limits of physicochemical fabrication routes at the atomic scale. Especially, one of the emerging challenges is to achieve the ideal high-aspect ratio nanostructures without abnormal profiles, such as cylinder capacitors, shallow trench isolation, through-silicon vias. In spite of significant contributions of research frontiers, these processes are still unveiled due to their inherent complexity of physicochemical behaviors, and gaps in academic research prevent their predictable simulation. To overcome these issues, a Korean plasma consortium began in 2009 with the principal aim to develop a realistic and ultrafast 3D topography simulator of semiconductor plasma processing coupled with zero–D bulk plasma models. In this work, aspects of this computational tool are introduced. The simulator was composed of a multiple 3D level-set based moving algorithm, zero-D bulk plasma module including pulsed plasma processing, a 3D ballistic transport module, and a surface reaction module. The main rate coefficients in bulk and surface reaction models were extracted by molecular simulations or fitting experimental data from several diagnostic tools in an inductively coupled fluorocarbon plasma system. Furthermore, it is well known that realistic ballistic transport is a simulation bottleneck due to the brute-force computation required. In this work, effective parallel computing using graphics processing units was applied to improve the computational performance drastically. Finally, it is demonstrated that 3D feature profile simulations coupled with bulk plasma models can lead to better understanding of abnormal behaviors, such as necking, bowing, etch stops and twisting during high aspect ratio contact hole etch.

3:00pm **PS2-TuA3 Validation of Inductively Coupled Plasmas Sustained in Halogen Chemistries**, ***Ankur Agarwal***, Applied Materials Inc., *M. Foucher,* LPP-CNRS, Ecole Polytechnique, France, *S. Rauf,* Applied Materials Inc., *J.-P. Booth, P. Chabert,* LPP-CNRS, Ecole Polytechnique, France, *K.S. Collins*, Applied Materials Inc.

The growing complexity of industrial plasma processing systems and increasingly stringent technological requirements for plasma processes have necessitated the use of modeling and simulation for design of these systems in recent years. Impressive advances have been made in the development of computer models for plasma equipment design[1,2] and feature profile evolution.[3,4] Validation of these models with experimental data over a wide range of operating conditions is a critical step in making these models a mature development tool. While plasma equipment models have been benchmarked with ion/electron density measurements[5], RF and DC self-bias voltages[6], characterization of neutral species in industrially relevant chemistries is complicated and hence few benchmarking opportunities exist. Characterization of neutral species is critical as they serve as the precursors to any plasma etching (and deposition) process and are an important parameter for plasma equipment models to quantify for use in feature profile models.

In this work, we report on validation of Applied Materials' fluid plasma model, CRTRS, in an inductively coupled plasma (ICP) reactor sustained in halogen chemistries. Halogen-based ICPs are typically used to etch shallow trench isolation (STI) features and defining gate structures in both logic and memory devices. The density of Cl atoms in Cl_2 chemistries (or Br in HBr chemistries) is an important parameter to characterize the etching process. Recently, researchers have reported on electron and absolute Cl densities and gas temperature in a Cl_2 ICP reactor over a wide range of operating conditions.[7] The fluid plasma model was validated against these experiments for an ICP sustained in Cl_2 and Cl_2/O_2 mixtures over a pressure range of 10 mTorr to 90 mTorr and varying ICP power of 200 W to 500 W. We found gas temperature to be an important parameter to accurately predict the electron and atomic Cl densities as it governs the kinetics of gas phase chemistry and also affects diffusion coefficient.

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

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

[3] P.J. Stout, S. Rauf, A. Nagy, and P.L.G. Ventzek, J. Vac. Sci. Technol. B **24**, 1344 (2006).

[4] S. Rauf, W.J. Dauksher, S.B. Clemens, K.H. Smith, J. Vac. Sci. Technol. A **20**, 1177 (2002).

[5] P. Subramonium and M.J. Kushner, Appl. Phys. Lett. **79**, 2145 (2001).

[6] A. Agarwal, L. Dorf, S. Rauf, and K. Collins, J. Vac. Sci. Technol. **30**, 021303 (2012).

[7] J.P. Booth, Y. Azamoum, N. Sirse, and P. Chabert, J. Phys. D **45**, 195201 (2012).

3:20pm **PS2-TuA4 Enhanced SiN Etching by Hydrogen Radicals during Fluorocarbon/Hydrogen Plasma Etching; Molecular Dynamics Simulation Analyses**, ***Yuichi Murakami****, M. Isobe, K. Miyake,* Osaka University, Japan, *M. Fukasawa, K. Nagahata,* Sony Corporation, *T. Tatsumi,* Sony Corporation, Japan, *S. Hamaguchi*, Osaka University, Japan

Selective etching of silicon nitride (SiN) over silicon dioxide (SiO_2) or vice versa has been widely used in microelectronics fabrication processes. Plasmas derived from fluorocarbon (FC) gas with hydrogen (H_2) and/or hydrofluorocarbon (HFC) gas are typically used for etching processes of SiN. Our recent study using molecular dynamics (MD) simulations on surface reactions of SiN and SiO_2 with incident CHF_2^+ and CF_2^+ ions supplied by a HFC or FC/H_2 plasma has found that hydrogen supplied from incident ions inhibits the formation of FC polymer on the SiN surface during the process, which facilitates the formation of volatile SiF_x species on the SiN surface and therefore enhances its sputtering yield [1]. In the present study, we have also examined whether hydrogen reacts with a SiN or SiO_2 surface directly, by supplying more hydrogen to SiN and SiO_2 surfaces in MD simulations. An earlier experimental study [2] has showed that the SiN sputtering yield increases as the supply of hydrogen to the CF plasma increases. Following such an experiment, in this study, we have varied the amount of hydrogen radicals supplied to the SiN and SiO_2 surfaces and examined how their sputtering yields by CF_x^+ ions change, depending on the amount of hydrogen adsorbed on the surfaces. Detailed examinations of desorbed species and surface chemical compositions obtained from MD simulations of such processes have indicated that hydrogen in FC/H_2 plasmas react with nitrogen of the SiN surface to form volatile NH_x, most dominantly NH_3, to promote the surface etching whereas it hardly affects the sputtering yield of SiO_2 under the same conditions.

References

[1] K. Miyake, *et al*., Jpn. J. Appl. Phys. **53** 03DD02 (2014).

[2] M. Fukasawa, *et al*., Jpn. J. Appl. Phys. **48** 08HC01(2009).

4:20pm **PS2-TuA7 Plasma-induced Surface Roughening and Ripple Formation during Plasma Etching of Silicon**, ***Kouichi Ono***, Kyoto University, Japan **INVITED**

Atomic- or nanometer-scale surface roughness has become an important issue in the fabrication of nanoscale devices, because the roughness at feature sidewalls and bottom surfaces affects the variability in transistor performance. A better understanding of the mechanisms for the plasma-induced surface roughening is indispensable for suppressing the evolution of the roughness during plasma etching; moreover, the surface roughening through plasma exposure is positively employed in some cases, to obtain surface nanostructures such as nanopillars and nanocolumns. This paper presents a numerical and experimental study of surface roughening and ripple formation during Si etching in Cl-based plasmas, with emphasis on modeling, analysis, and control of the plasma-surface interactions concerned. A three-dimensional atomic-scale cellular model (ASCeM-3D) based on the Monte Carlo algorithm, which was developed to simulate plasma-surface interactions and the feature profile evolution during plasma etching, exhibited the nanoscale surface roughening and rippling in response to ion incidence angle onto substrate surfaces [1]: randomly roughened surfaces at normal incidence, and ripple structures or slit-like grooves perpendicular and parallel to the direction of ion incidence at oblique and grazing incidences, respectively. Such roughening and rippling of etched surfaces were found to be crucially affected by the ion scattering or reflection on microscopically roughened feature surfaces. Experiments of

the surface roughening during Si etching in inductively coupled Cl_2 plasmas showed roughening and smoothing (or non-roughening) modes which occur depending on ion incident energy [2]. The analysis with the help of plasma diagnostics and the ASCeM-3D and classical molecular dynamics (MD) simulations [3] indicated that these two different modes of surface roughening correlate essentially to changes in the predominant ion flux from ions with high reflection probabilities to those with lower ones on surfaces on incidence at increased ion energy. The experiments further demonstrated that the pulse-biasing is effective for reducing the surface roughness during plasma etching, and the surface rippling with oblique and grazing ion incidences onto substrate surfaces was demonstrated using a sheath-control plate placed thereon.

[1] H. Tsuda *et al*., J. Vac. Sci. Technol. B **32**, 031212 (2014).

[2] N. Nakazaki *et al*., J. Appl. Phys. **116**, 223302 (2014).

[3] N. Nakazaki *et al*., Jpn. J. Appl. Phys. **53**, 056201 (2014).

5:00pm **PS2-TuA9 Feature Scale Modeling of Semiconductor Processes**, ***Phillip Stout***, Applied Materials **INVITED**

An overview of monte carlo feature scale modeling work will be presented. The two major areas of discussion will be etching and metallization processes.

In high aspect ratio (HAR) oxide etch processes the mask gates the amount of etchants and passivants entering the feature and has a large influence on the resulting etched profile. Mask sidewall slopes alter the path of ions entering the feature thereby modifying the ion strike map inside the feature. Mask geometry also influences polymer deposition within mask and bow formation in oxide. Mechanisms for off-axis profiles and profile distortion include: off-axis ion incidence to wafer, non-uniform polymer deposition at opening, re-deposition of etch byproducts, feature geometry (mask), mask reflow, charging in feature, and off-angle yield curve peaks. Two cases illustrate the interplay of these profile distortion mechanisms: pattern distortion dependence on etch stop layer charging properties, and the influence of a tilted hard mask on HAR trench oxide etch profile. Feature scale models can be used to study integration issues in multi-step processes. A thirteen step spacer double patterning integration has been studied showing the importance of the spacer etch step. An STT-MRAM (Spin Transfer Torque - Magnetoresistive Random Access Memory) etch process will be discussed. Removal of metal sidewall deposits resulting from re-deposition of sputtered MTJ metal layers is a major issue. The study looks at ion beam etching.

The metallization topics reviewed will inlcude copper physical vapor deposition (PVD) in dual-damascene (DD) features, predicting across wafer coverage in feature, and copper reflow studies. In DD features a sloped inner via sidewall can have faster yields than the trench bottom. With reactor models supplying across wafer flux and aedfs it is possible to predict feature coverage properties as a function of wafer position. With smaller feature sizes copper reflow is being explored as a means to fill via and trench structures for back end of line interconnects. Using a simple hopping surface diffusion model, reflow behavior is shown. The model predicts the initial reflow causes rounding of the Cu surfaces and a shrinking of the opening as the surfaces round to a more minimal surface configuration.

5:40pm **PS2-TuA11 Pattern Loading in Etch through Profile Simulation**, ***Yiting Zhang***, *S. Sriraman, J. Belen, A. Paterson,* Lam Research Corporation, *M.J. Kushner*, University of Michigan, Ann Arbor

Pattern transfer in microelectronics fabrication extensively uses plasma-assisted etching processes. Optimization of etch processes for 3D structures, such as FinFETs and Tri-Gate transistors, utilized in current technology nodes is considerably more difficult. For example, etching of 3D structures and mask layouts typically require longer over-etch process time to clear material, especially in corners, introducing additional selectivity challenges to maintain feature scale critical dimensions (CDs). In addition, feature open area, feature orientation, and proximity to other nearby structures can influence process etch outcomes. While for past technology nodes, 2D etch profile models were sufficient to optimize features and connect reactor scale properties to feature evolution, 3D structures are not well represented by 2D profile simulations.

In this paper, we report on the recent development and progress of a 3D profile simulator: the Monte Carlo Feature Profile Model (MCFPM-3D). The modeling platform in MCFPM-3D includes many advanced features such as charging, mixing, implantation, and photon-stimulated processes. The model addresses reaction mechanisms resulting in etching, sputtering, mixing, and deposition on the surface to predict profile evolution based on fluxes of radicals, 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). Results from profile simulations of feature pattern loading in etching of 2D and 3D structures will be presented. Phenomena such as reactive ion etch lag and aspect ratio dependent etching will be discussed.

6:00pm **PS2-TuA12 Plasma Modeling of a Magnetized Inductively-Coupled Plasma Reactor**, ***Jason Kenney***, *S. Rauf, K.S. Collins*, Applied Materials, Inc.

Modification of plasma properties with applied magnetic fields is fundamental to the study of plasma physics. In plasma reactor design, magnetic fields are regularly employed to modify plasma density profiles, e.g. as a tuning knob for plasma processing applications or as a means to prevent wall losses through confinement. Recently [1,2], their impact on electron energy distributions has also been measured and modeled in inductively-coupled plasma (ICP) systems.

In this work, we consider the application of static magnetic fields in an ICP reactor using a 2D fluid plasma model [3]. The model has been updated to include solution of the 3D inductively-coupled electric field components in the presence of a static 2D magnetic field [4] and has appropriate modification of electron mobility and diffusion coefficients to their tensor forms. We investigate the impact of magnetic field structure and strength on plasma density profile, electron temperature, ion energy distribution, and plasma chemistry for a variety of processing conditions (pressures, powers, feedstock gases), focusing on both the region near the ICP source and in close proximity to the processing stage. We also consider the form and intensity of electric field components and impact on power deposition region when a magnetic field is applied and discuss model validation with peer-reviewed experimental data.

[1] V.A. Godyak, Physics of Plasmas 20, 101611 (2013).

[2] S.H. Song, et al., Physics of Plasmas 21, 093512 (2014).

[3] S. Rauf, et al., Journal of Applied Physics 105, 103301 (2009).

[4] R.L. Kinder and M.J. Kushner, JVSTA 19, 76 (2001).

Advanced Surface Engineering
Room: 212A - Session SE+PS-TuA

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

2:20pm **SE+PS-TuA1 Strategy for Tuning the Average Charge State of Metal Ions Incident at the Growing Film during HIPIMS Deposition**, ***Grzegorz Greczynski,*** Linköping University, Sweden, *I. Petrov,* University of Illinois at Urbana Champaign, *J.E. Greene,* University of Illinois at Urbana-Champaign, *L. Hultman*, Linköping University, Sweden

Energy- and time-dependent mass spectroscopy is used to determine the relative number density of singly- and multiply-charged metal ions incident at the substrate during high-power pulsed magnetron sputtering (HIPIMS) as a function of the average noble-gas ionization potential. We selected Ti as the sputtering target since the microstructure, phase composition, properties, and stress-state of Ti-based ceramic thin films grown by HIPIMS are known to be strongly dependent on the charge state of Ti^{n+} (n = 1, 2, …) ions incident at the film growth surface. [1,2] Mass spectroscopy results show that the flux of Ti_{n+} with $n > 2$ is insignificant; thus, the Ti_{2+}/Ti_{+} integrated flux ratio J_{Ti}^{2+}/J_{Ti}^{+} is measured at the substrate position as a function of the choice of noble gas -- Ne, Ar, Kr, Xe, as well as Ne/Ar, Kr/Ar, and Xe/Ar mixtures -- supporting the plasma. We demonstrate that by changing noble-gas mixtures, J_{Ti2+} varies by more than two orders of magnitude with only a small change in J_{Ti+}. This allows the ratio J_{Ti}^{2+}/J_{Ti}^{+} to be continuously tuned from less than 0.01 with Xe, which has a low first-ionization potential IP^1, to 0.62 with Ne which has a high IP^1. The value for Xe, IP^1_{Xe} = 12.16 Ev, is larger than the first ionization potential of Ti, IP^1_{Ti} = 6.85 Ev, but less than the second Ti ionization potential, IP^2_{Ti} = 13.62 Ev. For Ne, however, IP^1_{Ne} = 21.63 Ev is greater than *both* IP^1_{Ti} and IP^2_{Ti}. Therefore, the high-energy tail of the plasma-electron energy distribution can be systematically adjusted, allowing J_{Ti}^{2+}/J_{Ti}^{+} to be controllably varied over a very wide range, from 0.01 with Xe to 0.62 with Ne. [3]

[1] G. Greczynski, J. Lu, M. Johansson, J. Jensen, I. Petrov, J.E. Greene, and L. Hultman, *Surf. Coat. Technol.* 206 (2012) 4202

[2] G. Greczynski, J. Lu, M. Johansson, J. Jensen, I. Petrov, J.E. Greene, and L. Hultman, *Vacuum* 86 (2012) 1036

[3] G. Greczynski, I. Petrov, J.E. Greene, and L. Hultman, *Vacuum* 116 (2015) 36

2:40pm **SE+PS-TuA2 Study of High Power Pulsed Magnetron Sputtering Under Differing Magnetic Field Configurations**, ***Priya Raman***, *I.A. Shchelkanov, J.T. McLain,* University of Illinois at Urbana Champaign, *S. Armstrong,* Kurt J. Lesker Company, *D.N. Ruzic*, University of Illinois at Urbana Champaign

There is an increasing demand for high quality, wear-resistant, low-friction and corrosion resistant coatings in the microelectronics, automotive, tooling and other industries. High power magnetron sputtering is a type of magnetron sputtering technique where short high power pulses are applied to the magnetron target at very low duty cycles leading to higher degree of ionization of the target material. These ionized sputtered material assist in film growth leading to more adhesive, dense, and smoother films compared to conventional DC Magnetron Sputtering (dcMS) techniques. Unfortunately HPPMS suffers from lower deposition rates due to "return effect" of the ionized sputter materials [1]. Further reach of the HPPMS technology largely depends on whether it can produce deposition rates comparable or higher than dcMS. Recent studies of HPPMS discharges have shown that the magnetic field in the region above the sputter target defines the plasma properties and potential distribution in that region. The "ε" magnet pack [2] had already demonstrated increased deposition rates by carefully changing the magnetic field pattern above the target surface. Cylindrically symmetric "TriPIMS" magnet was developed based on magnetic field design solutions from "ε" magnet pack to keep the high deposition rates but improve deposition uniformity. In order to fully understand the behaviour of high current pulsed discharge in this new magnetic field configuration, TriPIMS magnet pack, was tested with Huettinger HiPIMS, Z-pulser MPP, Starfire Impulse and DC power supplies. Plasma parameters (ne, Te, ionization fraction), deposition rate, deposited film density, uniformity, and stress were measured. Reason for higher deposition rate is discussed.

[1] Papa F et al 2011 Thin Solid Films 520.5 1559-1563.

[2] Raman, Priya, et al. "High power pulsed magnetron sputtering: A method to increase deposition rate." *Journal of Vacuum Science & Technology A* 33.3 (2015): 031304.

3:00pm **SE+PS-TuA3 Reactive High-power Impulse Magnetron Sputtering and Pulsed Magnetron Co-sputtering of Multifunctional Films**, ***Jaroslav Vlcek***, *J.R. Rezek, P.M. Mares*, University of West Bohemia, Czech Republic **INVITED**

In the presentation, we report on discharge and deposition characteristics (including the ion flux characteristics at the substrate), and on film structure and properties for two different pulsed reactive magnetron sputtering techniques.

High-power impulse magnetron sputtering (HiPIMS) with a pulsed reactive gas flow control was used for high-rate reactive depositions of densified, highly optically transparent, stoichiometric ZrO_2 and HfO_2 films, and of Ta-O-N films with tunable composition and properties. The depositions were performed using a strongly unbalanced magnetron with a planar directly water-cooled Zr, Hf or Ta target in Ar-O_2 or 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 50 – 200 µs voltage pulse lengths and the total pressure close to 2 Pa. An effective reactive gas flow control made it possible to produce high-quality ZrO_2, HfO_2 and Ta-O-N films with high deposition rates (up to 120 nm/min, 345 nm/min and 190 nm/min, respectively, for the target-to-substrate distance of 100 mm) and to adjust the composition of the Ta-O-N films from Ta_2O_5 to a mixture of Ta_3N_5 and TaN. We prepared almost stoichiometric TaON 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. Selected results obtained using a parametric model for the controlled reactive HiPIMS of the ZrO_2 films are presented.

Pulsed dc magnetron co-sputtering of a single segmented target (B_4C-M, where M = Ti, Zr and Hf, or B_4C-Hf-Si) in Ar gas or 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 – 1.7 Pa. Energy-resolved mass spectroscopy was used to correlate the energy of Ar^+ ions bombarding the growing films with high positive voltage overshoots after the negative voltage pulses and with the energy of Ar atoms backscattered from the sputtered targets. We present the results obtained for nanocolumnar ZrB_2-type Zr-B-C films and nanocomposite Zr-B-C-N films exhibiting a high hardness (37 GPa) and high electrical conductivity, and for nanostructured HfB_2-type 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.

4:20pm **SE+PS-TuA7 Target Poisoning in Mixed Ar, N_2 and CH_4 Atmosphere, in Processes Using Different Target Materials for HIPIMS/DC and DC Cathode Modes.**, ***Anna Oniszczuk***, *A.P. Ehiasarian,* Sheffield Hallam University, United Kingdom of Great Britain and Northern Ireland, *C.F. Carlström, M. Ahlgren*, Sandvik Coromant, Sweden

Reactive sputtering in mixed Ar+N_2+CH_4 atmosphere is a widely used industrial process however the poisoning of different target materials under different sputtering discharges in this complex environment is insufficiently described.

In mixed Ar+CH_4+N_2 atmosphere, at low flow processes were influenced by methane whereas at high flow they were dominated by nitrogen indicating the formation of carbide and then carbonitride compounds. This was observed for both TiAl and V targets in DC as well as in HIPIMS mode.

Vanadium targets operating in DC mode were poisoned at 55% of reactive gas flow. Poisoning resulted in a 2-fold increase in total pressure, a 50 % increase in discharge voltage/current ratio, a 5 fold drop in V(I) optical emission intensity and a 10 fold drop in V^+ and Ar^+ fluxes obtained from energy-resolved mass spectroscopy.

TiAl targets in DC mode poisoned at lower reactive gas flows and exhibited narrower hysteresis than V due to the higher reactivity of the target material. The voltage/current ratio of TiAl targets went through a minimum with a flow, while for V target it increased with flow.

For HIPIMS both targets poisoned earlier and the hysteresis was narrower than in DC mode. As confirmed by trends in the partial pressure, the voltage/current ratio and ion fluxes of metals and reactive gasses. These effects are due to higher reactivity of the plasma as evidanced by higher fluxes of N^+ and N_2^+ and radicals containing H, C and N. The voltage/current ratio reduced by 50% as the target is poisoned in contrast to operation in DC mode where it increased. This could be attribiuted to efficient ionization and drop in plasma impedance.

Pathways for poisoning and resulting ion fluxes are discussed.

4:40pm **SE+PS-TuA8 Structure and Properties of Cr_2O_3 Coatings Deposited using DCMS, PDCMS, and DOMS**, ***Jianliang Lin***, Southwest Research Institute, *W.D. Sproul*, Reactive Sputtering, Inc.

The properties of oxide coatings are strongly tied to the crystallinity of oxide phases. In general, a well-crystallized oxide phase is desired because it is usually related to improved mechanical and chemical properties. This paper presents a comparative study of the chromium oxide (Cr_2O_3) coatings deposited by deep oscillation magnetron sputtering (DOMS), mid-frequency pulsed dc magnetron sputtering (PDCMS) and continuous dc magnetron sputtering (DCMS). Without applying external substrate heating, the processing techniques strongly affected the crystallinity of the Cr_2O_3 coatings. The DCMS-Cr_2O_3 coating exhibited an amorphous like structure. The coating deposited by PDCMS contained a mixture of amorphous and crystalline phases. In contrast, the DOMS-Cr_2O_3 coating showed a strong crystallinity with a (110) preferential orientation. The improved crystallinity of the DOMS-Cr_2O_3 coating is due to the higher ion bombardment and higher substrate saturation temperature, which is related to the high energy electron bombardment associated with deep oscillation pulses. Improved mechanical properties and wear resistance were achieved in the DOMS-Cr_2O_3 coatings as compared to the coatings deposited using DCMS and PDCMS. This study also showed that the bias voltage strongly affected the structure of the DOMS-Cr_2O_3 coatings by changing the substrate current characteristics.

5:00pm **SE+PS-TuA9 Strategy to Tailor the Composition of Silicon Oxynitride Thin Films Deposited by Reactive High Power Impulse Magnetron Sputtering using Nitrous Oxide as a Single-source Precursor**, ***Tuomas Hänninen***, *S. Schmidt, J. Jensen, L. Hultman, H. Högberg*, Linköping University, Sweden

Silicon oxynitride (SiON) is a material with tunable optical and electrical properties. It is used as thin films in antireflection coatings, surface passivation layers, and optical waveguides. Commonly two reactive gases, O_2 and N_2, have been employed for the reactive magnetron sputter deposition of SiON. The two-gas approach is, however, limited by the non-linear target effects as a function of reactive gas flow rates, which makes an accurate control of the deposition process challenging.

In this study we present SiON thin films deposited by reactive high power impulse magnetron sputtering from a pure Si target in Ar/N_2O plasmas. The influence of the average target power while maintaining a fixed pulse frequency (1000–4000 W at 1000 Hz and 1200–3000 W at 600 Hz) and the frequency at a fixed energy per pulse (300–1000 Hz at 4 J) on the resulting film properties were investigated.

The ~ 300 nm thick films show a dense and featureless morphology when viewed in cross-sectional scanning electron microscopy. X-ray diffraction reveals that the films are X-ray amorphous and exhibit compressive residual

stresses in the range of 500–1500 Mpa. The chemical bonding structure and the elemental composition of the films were studied with X-ray photoelectron spectroscopy. The spectra acquired from the as-deposited samples show mixed Si—O, Si—N, and Si—Si bonding. The ratio between these type of bonds correlates with the atomic concentrations of Si, O, and N in the films. A decreased average power at a fixed pulse frequency induces an increase in O content (from 13 at.% to 51 at.% at 1000 Hz and from 17 at.% to 43 at.% at 600 Hz) while the N concentration remains virtually unaffected. An exception are films with the highest O content, showing a decrease in N content from ~ 26 at.% to 9 at.% at 1000 Hz and to 16 at.% at 600 Hz. A similar behavior is observed when the pulse frequency is lowered at a constant pulse energy, the film O content increases from 13 at.% to 43 at.%, followed by a decrease in N concentration from ~ 26 at.% to 17 at.%. Film densities as measured by X-ray reflectivity are found to range between 2.6–2.9 g/cm^3. The refractive indices and extinction coefficients at 633 nm, measured by variable-angle spectroscopic ellipsometry, show that the films with highest total O plus N content have the lowest refractive index (1.6–1.8) and extinction coefficient (~ 0) values. The refractive index values are comparable to those of SiO_2 (~ 1.45) and Si_3N_4 (~ 2.0), confirming that the optical properties of the studied films can be tailored to range between SiO_2 and Si_3N_4.

5:20pm **SE+PS-TuA10 Phase Changes Observed on AlCr Composite Cathodes due to the Exposure to Cathodic Arc Plasmas in N_2 and O_2 Atmospheres**, ***Robert Franz****, F. Mendez Martin, G. Hawranek,* Montanuniversität Leoben, Austria, *P. Polcik*, PLANSEE Composite Materials GmbH, Germany

Hard and wear-resistant coatings based on the system aluminium and chromium represent the state of the art in the protection of tools used in metal cutting operations. Using cathodic arc deposition techniques in nitrogen and/or oxygen atmospheres, nitrides, oxides or oxynitrides can be synthesised. The growth conditions encountered in processes employing cathodic arc plasmas are typically characterised by a high degree of ionisation and high deposition rates. For the supply of the non-gaseous elements during the deposition, it is common to use multi-element cathodes containing the desired Al/Cr ratio. These cathodes are usually composite cathodes and are widely used in industrial-scale deposition systems since they facilitate an easier process control and reproducibility. However, the plasma conditions in the cathodic arc plasma using such multi-element cathodes and their erosion behaviour in reactive atmospheres are only scarcely studied.

In the present investigation, AlCr composite cathodes with compositions of 75/25, 50/50 and 25/75 at.-% were exposed to cathodic arc plasmas in N_2 and O_2 atmospheres. Due to periodic melting and solidification of the cathodes' near-surface region in the cathode spots, an intermixing of the elements Al and Cr and the formation of intermetallic phases occurred which was analysed by recording elemental distribution maps in the cross-sections using scanning electron microscopy. By comparing regions of strong erosion with areas less affected by the cathodic arc plasma, poisoning effects due to reactions of the metals in the cathodes and the background gas could be identified and were analysed in detail. The conductivity of the formed nitrides and oxides on the surface of the AlCr composite cathodes was decisive for the characteristics of the cathodes' erosion behaviour. All results regarding the cathode erosion and the phase changes are compared to similar studies on TiAl [1] and $Al_{0.7}Cr_{0.3}$ [2, 3] cathodes and are put in context with recently reported arc plasma properties obtained with the same AlCr cathodes and gas atmospheres [4, 5].

References:

[1] D. Rafaja, C. Polzer, G. Schreiber, P. Polcik, M. Kathrein, Surf. Coat. Technol. 205 (2011) 5116–5123.

[2] J. Ramm, A. Neels, B. Widrig, M. Döbeli, L.D.A. Vieira, A. Dommann, H. Rudigier, Surf. Coat. Technol. 205 (2010) 1356–1361.

[3] M. Pohler, R. Franz, J. Ramm, P. Polcik, C. Mitterer, Surf. Coat. Technol. 206 (2011) 1454–1460.

[4] R. Franz, P. Polcik, A. Anders; *IEEE Trans. Plasma Sci.* 41 (2013) 1929–1937

[5] R. Franz, P. Polcik, A. Anders; *Surf. Coat. Technol.* 272 (2015) 309–321

5:40pm **SE+PS-TuA11 Optimization of Linear Scanning Magnetron Array Performance**, ***Vladimir Kudriavtsev****, A. Riposan, D.W. Brown, C. Smith, T. Bluck*, Intevac, Inc.

In this presentation we discuss Linear Scanning Magnetic Array (LSMA) technology for magnetron sputtering in conjunction with in-line substrate processing. In this approach, the magnet array (pole) scans over planar target spreading the erosion pattern in a controlled fashion. Thus, high quality, dense films with good uniformity can be produced at significant advantages over static magnetrons, such as significantly higher target utilization, longer uptime, and prevention/removal of target defects related to re-deposition.

We review the influence of magnet motion acceleration/deceleration, the influence of endpoint motion offset (stagger), and the influence of magnet - to - substrate velocity ratio, on target utilization and lead-to-trail edge film uniformity. Trade-offs between uniformity and target utilization were established and characterized.

The optimization method we use employs a combination of theoretical simulations and experimental measurements. Theoretical analysis utilizes ANSYS static magnetic field simulations, erosion profile calculations including motion integration effects, and ray tracing method for sputtering film thickness calculations (MATLAB). The structure and uniformity of LSMA-deposited thin films was characterized experimentally by XRF and SEM, and the target erosion measured by weight and erosion profiles of spent targets.

We have demonstrated that, with a judicious design approach, an optimal range of operating parameters can be defined and target utilizations above 70%can be reached, while maintaining deposition uniformity below 2% with excellent film properties. This makes the LSMA plasma source (using planar targets) more economically competitive than static and rotatable magnetrons.

6:00pm **SE+PS-TuA12 Correlation of Microstructure of Deposited Thin Films with Discharge Characteristics by Modulated Pulsed Power Magnetron Sputtering (MPPMS)**, ***M.K. Lei***, Dalian University of Technology, China

Pure Cu thin films and TiAlSiN nanocomposite thin films are deposited in a closed field unbalanced magnetron sputtering system using the modulated pulsed power magnetron sputtering (MPPMS), in order to understand the correlation of the microstructure and texture of deposited thin films with the discharge characteristics by MPPMS. The discharge processes at different pressures on the metallic targets are numerically modeled with considering the loss of electrons by cross-B diffusion. With increasing the pressure from 0.1 to 0.7 Pa, both the ion bombardment energy and substrate temperature which are estimated by the modeled plasma parameters decrease, corresponding to the observed transition of the deposited Cu thin films from a void free structure with a wide distribution of grain size into an underdense structure with a fine fiber texture in the extended structure zone diagram. The TiAlSiN thin films are deposited at the ratio of the nitrogen flow rate to the total gas flow rate (f_{N2}) ranging from 0 to 40%. An optimized nanocomposite structure of *nc*-TiAlN/*a*-Si_3N_4 is formed with the 5–10 nm TiAlN nanocrystallites embedded in the 2–3 nm amorphous Si_3N_4 matrix. Further increasing f_{N2}up to 40%, the grain size of nanocrystallites increase to 10–20 nm with the gradually precipitation of AlN phase, albeit the composition keeps constant. With increasing the partial pressure, the increased ion bombardment energy and substrate temperature are believed to be responsible for the complete phase separation of the *nc*-TiAlN/*a*-Si_3N_4 nanocomposite thin films.

Plasma Science and Technology
Room: 210B - Session PS+2D+SE-WeM

Plasma Diagnostics, Sensors and Control II
Moderator: Colin Wolden, Colorado School of Mines

8:20am **PS+2D+SE-WeM2 Diagnostics for Ionized Physical Vapor Deposition Chambers**, ***YuiLun Wu***, *P. Piotrowicz,* University of Illinois at Urbana-Champaign, *I.A. Shehelkanov,* National Nuclear Research University (MEPhI), *D.N. Ruzic*, University of Illinois at Urbana-Champaign

As the critical dimension of the semiconductor device continues to shrink and aspect ratio continues to rise, more diagnostics are needed to accurately predict the deposition profile of features on the wafer. Traditionally, the incident ion fluxes are considered to be perfectly normal to the wafer plane due to the electric field of the plasma sheath. However from simulation results [1] the ion flux from a magnetron discharge has a narrow angular distribution and this distribution is becoming more significant as the aspect ratio increases. In order to confirm and adjust this predicted distribution a sensor to measure angular distribution of ions in an industrial scale chamber is designed and developed. The sensor is a combined gridded energy analyzer (GEA) and a quartz crystal microbalance (QCM) [2], with a high aspect ratio collimator in place of the normal electron repeller grid for angular measurement distribution measurements. The collimator is made of 3D-printed plastic elements with 600µm nominal openings which provides 1 degree angular resolution. This combined QCM and GEA setup is capable to determine fluxes of metal ions, metal atoms and argon ions at 30kW DC magnetron nominal target power. The setup is 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 discharge. A time resolved triple Langmuir probe was also employed to measure the plasma parameters such as electron temperature and density and scanning in a three dimensional map.

References:

1. Stout, P. J., et al. "Comparing ionized physical vapor deposition and high power magnetron copper seed deposition." *Journal of Vacuum Science & Technology B* 20.6 (2002): 2421-2432.

2. Meng, Liang, et al. "Downstream plasma transport and metal ionization in a high-powered pulsed-plasma magnetron." *Journal of Applied Physics* 115.22 (2014): 223301.

8:40am **PS+2D+SE-WeM3 Probing the Plasma Chemistry that Underpins Diamond Chemical Vapour Deposition**, ***Michael Ashfold***, University of Bristol, United Kingdom of Great Britain and Northern Ireland, *M.W. Kelly, B.S. Truscott,* University of Bristol, UK, United Kingdom of Great Britain and Northern Ireland, *Y.A. Mankelevich*, Moscow State University, Russia, Russian Federation **INVITED**

Most diamond chemical vapour deposition (CVD) employs microwave (MW) activated C/H (typically CH_4/H_2) gas mixtures. Many previous studies have sought to explore (and optimise) radical formation in such activated gas mixture, and the ways in which these radicals add to, and are accommodated on and in, the growing diamond surface.

Our activities in this area employ an interrelated three-pronged approach, *i.e*.

i) electronic spectroscopy methods (cavity ring down absorption and optical emission spectroscopies) to determine the spatial distributions of selected species (*e.g*. H atoms, CH and C_2 radicals) as functions of process variables like the process gas mixing ratio, flow rate and total pressure, and MW power,

ii) complementary 2-dimensional (2-D) modelling of the plasma chemistry and composition with the aim not just of rationalising the spatial resolved column density data obtained in (i), but also enabling prediction of the concentrations of other key gas phase species (*e.g*. CH_3 radicals, which are generally regarded as the dominant growth species) that are not amenable to spectroscopic detection, as functions of process condition, and

iii) quantum mechanical (QM) and QM-molecular mechanics (MM) calculations of the energetics of the elementary steps involved in radical addition to, migration on, and eventual accommodation on, a growing diamond surface.

This invited presentation will summarise the current understanding of diamond CVD from traditional C/H gas mixtures and results of recent studies designed to explore and explain the significant growth rate enhancements that can be achieved by adding trace amounts of nitrogen to such gas mixtures.

9:20am **PS+2D+SE-WeM5 Ionization Zones and the Deposition of Thin Films in the Transition Region from Non-Reactive to Reactive Magnetron Sputtering including dc, HiPIMS, and Burst-HiPIMS Modes**, ***Yuchen Yang***, *X. Zhou, A. Anders*, Lawrence Berkeley Lab, University of California, Berkeley

Research has been done for copper and chromium targets in conventional non-reactive HiPIMS, revealing the disappearance of localized ionization zones when operating at high power due to high metal neutral supply from the target. However, relatively little research has been done for reactive HiPIMS. In this work we investigate the existence of ionization zones in various forms of reactive magnetron sputtering: direct current (dc) and HiPIMS for conventional pulse patterns and in burst mode. Copper and chromium targets are selected with nitrogen as reactive gas because (i) in the non-reactive regime Cu and Cr can be operated with or without ionization zones, and (ii) these target materials form application-relevant compound films, e.g. of interest in wear and corrosion-resistant applications, medical implants, metallization layers, etc.

Work at LBNL is supported by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

11:00am **PS+2D+SE-WeM10 Modelling of the Reactive High Power Impulse Magnetron Sputtering (HiPIMS) process**, ***JonTomas Gudmundsson***, University of Iceland, *D. Lundin,* Université Paris-Sud, France, *N. Brenning,* KTH Royal Institute of Technology, Sweden, *T. Minea*, Université Paris-Sud, France

Reactive high power impulse magnetron sputtering (HiPIMS) [1] provides both a high ionization fraction of the sputtered material and a high dissociation fraction of the molecular gas. We demonstrate this through an ionization

region model (IRM) [2] of the reactive Ar/O_2 HiPIMS discharge with a titanium target that was developed to study the temporal behavior of the discharge plasma parameters. We explore the influence of oxygen dilution on the discharge properties such as electron density, the ionization fraction of the sputtered vapour, the oxygen dissociation fraction and the onset and role of self sputtering. We discuss the important processes and challenges for more detailed modeling of the reactive HiPIMS discharge. Furthermore, we discuss experimental observations during reactive high power impulse magnetron sputtering sputtering (HiPIMS) of Ti target in Ar/N_2 and Ar/O_2 atmosphere. The discharge current waveform is highly dependent on the reactive gas flow rate, pulse repetition frequency and discharge voltage. The discharge current increases with decreasing repetition frequency. This we attribute to an increase in the effective secondary electron emission yield during the self-sputtering phase of the pulse, as nitride [3] or oxide [4] forms on the target.

[1] J. T. Gudmundsson, N. Brenning, D. Lundin and U. Helmersson, J. Vac. Sci. Technol. A, 30 030801 (2012)

[2] M. A. Raadu, I. Axnäs, J. T. Gudmundsson, C. Huo and N Brenning, Plasma Sources Science and Technology, 20 065007 (2011) 065007

[3] F. Magnus, O. B. Sveinsson, S. Olafsson and J. T. Gudmundsson, J. Appl. Phys., 110 083306 (2011)

[4] F. Magnus, T. K. Tryggvason, S. Olafsson and J. T. Gudmundsson, J. Vac. Sci. Technol., 30 (2012) 050601

11:20am **PS+2D+SE-WeM11** ***Pulsed Magnetron Sputtering Plasma Optimization for Large Area Growth of Two-dimensional MoS_2***, ***Andrey Voevodin***, Air Force Research Laboratory, *C. Muratore,* University of Dayton, *A.R. Waite, J. Bultman, A. Safriet, J. Hu*, Air Force Research Laboratory

Pulsed magnetron sputtering process provides and alternative scalable and reduced temperature growth pathway for the direct synthesis of two-dimensional (2D) materials for electronic device applications [1]. To avoid defect generation by excessive ion bombardment, while maintaining sufficient adatom mobility on the condensation surface at low substrate temperatures, the ion flux and kinetic energy must be modulated. In this study a variable intensity magnetic field was used to control chemistry, energy, and spatial density distribution characteristics of plasma produced by pulsed magnetron sputtering of MoS_2 in 15 mTorr argon. An electromagnetic coil positioned above the substrate generated a 5-15 G magnetic field near substrate surface, causing redirection of magnetron particle flux for tuning of electron and ion densities at the substrate surface. Both plasma emission and mass-spectroscopy analysis showed an abundance of excited and ionized Ar as well as Mo and S species with no

evidence for MoS radicals. Wavelength specific plasma imaging and mass/energy spectroscopy studies demonstrated that the applied magnetic field mostly affects excited and ionized Ar generated in background gas collisions with electrons trapped by the magnetic field lines, while the trajectories of Mo and S species generated from the target surfaces are influenced to a much lesser degree. The imposed magnetic field intensity was adjusted to selectively filter Ar species from reaching the substrate and to find a balance between reducing unnecessary Ar bombardment and preventing shifting energy distributions of all arriving ions above 8 Ev, where point defect generation is expected for hexagonal MoS_2. Plasma studies were used to select optimum growth conditions for 2D MoS_2 synthesis on SiO_2 surfaces at 700 ^{0}C. Film thickness uniformity was verified by producing 2-3 monolayer layer thick hexagonal polycrystalline MoS_2 films over 25-50 mm scale area sizes as confirmed by in-situ Raman spectroscopy and TEM microscopy.

[1]. C. Muratore, J.J. Hu, B. Wang, M.A. Haque, J.E. Bultman, M. L. Jesperson, P.J. Shamberger, M. E. McConney, R.D. Naguy, A.A. Voevodin, "Continuous ultra-thin MoS_2 films grown by low-temperature physical vapor deposition", Applied Physics Letters 104 (2014) 261604 1-5

11:40am **PS+2D+SE-WeM12 Molybdenum Nitride Formation by N_2 Plasma Exposure on Molybdenum Disulfide: In-situ Surface Study**, ***Angelica Azcatl**, X. Qin, Q. Wang, N. Lu, M.J. Kim, C.L. Hinkle, R.M. Wallace*, The University of Texas at Dallas

Two-dimensional molybdenum disulfide (MoS_2) is currently considered as a potential channel material for CMOS applications. Electron mobilities on the order of 470 cm^2/Vs [1] have been reported for few-layer MoS_2 based FETs. Such promising results have fueled the efforts on synthesis of large area and high quality mono and few-layer MoS_2. Yet, the development of MoS_2 processing techniques of interest for device fabrication (i.e. doping, etching, functionalization) is still in an early stage.

Recently, it has been reported that when MoS_2 is exposed to SF_6, CF_4 or CHF_3 plasma treatments, fluorine can be introduced in the MoS_2 structure as an acceptor dopant, resulting in p-type doping. In parallel, due to the weak van der Waals interlayer forces, layer etching occurred as a side effect after these fluorine-based plasma exposures. [2]

Following the exploration of the effect of plasma exposures on MoS_2, in this study nitrogen plasma exposures on MoS_2 were performed, while the surface chemistry was monitored by in-situ by X-ray Photoelectron Spectroscopy. Theoretical studies have shown that substitution of sulfur with nitrogen in MoS_2 leads to p-type doping. [3,4] Here, the chemical analysis obtained by XPS indicates that nitrogen will covalently interact with molybdenum to generate molybdenum nitride. It was found that the nitrogen content in MoS_2 can be controlled with exposure time. The thermal stability of MoN_x formed due to sulfur replacement with nitrogen will be discussed. Finally, Raman Spectroscopy studies and Scanning Transmission Electrons Microscopy imaging on the MoN_x/MoS_2 structure will be presented to discuss the impact of the Mo-N bonding environment on the MoS_2 structure. This study will give an important insight for the understanding of the interaction of MoS_2 with a non-metal dopant atom, nitrogen, which has implications on the electrical properties of MoS_2.

This work is supported in part the Center for Low Energy Systems Technology (LEAST), one of six centers supported by the STARnet phase of the Focus Center Research Program (FCRP), a Semiconductor Research Corporation program sponsored by MARCO and DARPA, and by the SWAN Center, a SRC center sponsored by the Nanoelectronics Research Initiative and NIST.

References

[1] W. Bao, et al. Applied Physics Letters 102, 042104 (2013).

[2] M. Chen, et al., Appl. Phys. Lett. 103, 142110 (2013).

[3] H.-P. Komsa, et al., Phys. Rev. B 88, 035301 (2013).

[4] Q. Yue, et al., Phys. Lett. A 377, 1362 (2013).

12:00pm **PS+2D+SE-WeM13 Low Temperature Synthesis of $AlYB_{14}$ by High Power Pulsed Magnetron Sputtering**, ***Oliver Hunold**, Y.T. Chen, D. Music,* RWTH Aachen University, Germany, *P.O.A. Persson,* Linköping University, Sweden, *J.M. Schneider*, RWTH Aachen University, Germany

The influence of ion bombardment on the structure evolution of $AlYB_{14}$ was studied by using high power pulsed magnetron sputtering (HPPMS). The structure was analyzed by X-ray and electron diffraction. The diffraction data are consistent with the formation of crystalline $AlYB_{14}$ domains in an amorphous matrix. As the growth temperature was 675 °C synthesis was conducted at 725 °C below the bulk synthesis temperature. It is reasonable to assume that this decrease in the growth temperature is facilitated by bombardment of ions formed in the HPPMS discharge resulting in enhanced surface diffusion and hence higher adatom mobility. This work may be relevant for synthesizing other boron rich solids with low symmetry crystal structures at temperatures well below their bulk synthesis temperature.

Plasma Science and Technology
Room: 210A - Session PS+SS+TF-WeM

Atomic Layer Etching (ALE) and Low-Damage Processes I
Moderator: Geunyoung Yeom, Sungkyunkwan University, Republic of Korea

8:00am **PS+SS+TF-WeM1 Atomic Layer Etching to Escape Process Tradeoffs for 7nm Technology and Beyond**, ***Alok Ranjan**, M. Wang, S. Sherpa*, TEL Technology Center, America, LLC, *P. Ventzek*, Tokyo Electron America, Inc. **INVITED**

With shrinking critical dimensions, dry etch faces more and more challenges. Minimizing each of aspect ratio dependent etching (ARDE), bowing, undercut, selectivity, and within die uniformly across a wafer are met by trading off one requirement against another. The problem of trade-offs is especially critical for 10nm and beyond technology. At the root of the problem is that roles radical flux, ion flux and ion energy play may be both good and bad. Increasing one parameter helps meeting one requirement but hinders meeting the other. Self-limiting processes like atomic layer etching (ALE) promise a way to escape the problem of balancing trade-offs. ALE [1] was realized in the mid-1990s but the industrial implementation did not occur due to inherent slowness and precision loss from improper balance of self-limiting passivation and its removal processes. In recent years interest in ALE has revived and strides have been made by etch equipment manufacturers primarily through temporal, spatial or combination of these two pulsing approaches. Moderate success has been reported with some of the trade-offs purported to be managed. Difficulty meeting requirements is due to the inability of plasma technologies to control ion energy at low and precise values.

We overcome many of the practical implementation issues associated with ALE by precise passivation process control using plasmas with low electron temperature. Very low plasma potential, high radical flux and high bombardment flux are indispensable for achieving ALE. We demonstrate that ALE can achieve zero ARDE and infinite selectivity. Experimental results will highlight that careful consideration of surface process physics is required to achieve ALE and not simply "slow etching". Without profile control, ALE is not useful. Profile control will be shown to rely on careful management of the ion energies and angles. For ALE to be realized in production environment, tight control of IAD is a necessary. Experimental results are compared with simulation results generated using MCFPM [2] and theoretical scaling models to provide context to the work.

[1] S. Athavale and D. J. Economou, *J. Vac. Sci. Technol. B,* 14, 3702 (1996).

[2] M. Wang and M. J. Kushner, *J. Appl. Phys.,* 107, 023308 (2010)

8:40am **PS+SS+TF-WeM3 Understanding of new processes for Atomic Layer Etching**, ***Florentin Chambettaz,** L. Vallier, J. Dubois,* Univ. Grenoble Alpes-CNRS-CEA/Minatec-LTM,38000 Grenoble-France, *O. Joubert*, Univ. Grenoble Alpes-CNRS-CEA, France

In the pace of downscaling in microelectronic, current plasma etching processes show their limits. Actually for critical dimension smaller than 10 nm, atomic precision has to be reached during etching. In this study we are developing an Atomic Layer Etching (ALE) process by focusing on the induced damages related to the chemical and physical interaction(s) with hydrogen (This subject has already been broached in other studies on graphene [1] or carbon nanotubes [2]) and helium plasmas. Hydrogen plasmas have been used for years in the microelectronic industry and studied in the fields of deposition (PECVD, Plasma Enhanced Chemical Vapor Deposition), surface processing (surface passivation, hydrogenation) and plasma etching [3]. However the mechanisms related to these processes are not fully understood yet mainly because hydrogen is an element with peculiar characteristics such its low mass and its electronegativity. Helium plasmas have been also used for many years in the microelectronics industry. Helium is often employed in plasma processes as an additives gas due to its low chemical reactivity and low mass. Consequently ionic species present in the plasma and their effect are well known. To modify the surface of ultrathin layers without damaging the materials, a very low ion bombardment is required (conditions similar to those obtained in a pulsed ICP reactor [4]). At the same time, high energy plasmas are required to obtain satisfying etch rates when several nanometers have to be etched away. In this study we focus on plasma etching of silicon nitride by hydrogen plasma exposure in a commercially available 300 mm reactor, in

order to develop an ALE process for spacer etching of future 10nm transistors. Several process conditions are achieved with different ion energies and ion densities, on thin silicon nitride blanket samples. The generated damages in the structure were quantified with an Electron Spin Resonance (ESR) spectroscopy and electrical characterization. The effect of these etching processes on silicon nitride will be discussed.

1. E.Despiau-Pujo, A.Davydova, G.Cunge, L.Delfour, L.Magaud, and D. B.Graves, Journal of Applied Physics, **113** (2013)

2. A.Hassanien, M.Tokumoto, P.Umek, D.Vrbanic, M.Mozetic, D.Mihailovic, P.Venturini, and S.Pejovnik, Nanotechnology, **16**, 278 (2005)

3. M.Sode, T.Schwarz-Selinger, and W.Jacob, Journal of Applied Physics, **113** (2013)

4. C. Petit-Etienne, M. Darnon, P. Bodart, M. Fouchier, G. Cunge, E. Pargon, L. Vallier, O. Joubert, and S.Banna, Journal of Vacuum Science & Technology B, **31** (2013)

9:00am **PS+SS+TF-WeM4 Self-Limited Ion Implantation for Precise Low-k Spacer Etching**, ***Nicolas Posseme***, Cea-Leti, Minatec, France, *M. Garcia-Barros, C. Arvet,* ST Microelectronics, *O. Pollet,* Cea-Leti, Minatec, *S. Lagrasta, P. Maury,* ST Microelectronics, *F. Leverd,* ST Microlectronics, *C. Richard,* ST Microelectronics, *S. Barnola*, Cea-Leti, Minatec, France

With aggressive device shrinking, parasitic capacitances through the spacer become a greater contributor to the total device capacitance. This issue is exacerbated by the common use of SiN spacers. Since SiN has a relatively large dielectric constant (k~7.5), a simple approach to reduce capacitive coupling through the spacer is to supplant it with a low-k material [1]. Therefore, the reduction of spacer k value is a key for the high performance devices. In this context, Low-k films like SiCO, SiOCN or SiBCN have been proposed for the C014 technology node to replace the traditional silicon nitride investigated.

Today, the Low-k spacer etching is considered as one of the most challenging step in the high performance FDSOI devices realization. A trade-off has to be found between silicon germanium (or silicon) recess, foot formation and CD control impacting the device performances. The etch process must also be compatible with epitaxial step.

In a recent study, we proposed a new etch approach [2] for silicon nitride spacer etching. This new etching process is based on a Self-Limited Ion Implantation by plasma. In a first step, the film is modified in volume by a Hydrogen plasma performed in a conventional etch tool (CCP or ICP) followed in a second step by a 1%HF wet cleaning to remove the modified layer selectively to the non-modified material. We demonstrated that the silicon germanium recess was estimated to less than 6A with no foot formation, while a silicon germanium has grown by epitaxy without defects [2].

In this study, we propose to evaluate the compatibility of this new etch approach with low-k films like SiCO or SiCBN. By playing on plasma operating conditions performed in ICP etch tool, we will demonstrate that the Low-k films can accurately be etched with atomic layer control, stopping on SiGe or Si. The key parameters for such etch precision are identified as H ion energy and H ion dose implanted in the low-k film. The etch mechanisms to remove the modified layer by wet cleaning process will be understood on blanket wafers thanks to XPS and infrared spectroscopy analyses.

Finally the compatibility of this new Low-k spacer etching process with the epitaxial step will also be presented for C014 FDSOI integration.

References

[1] H. Niebojewski, C. Le Royer, Y. Morand, M-A. Jaud, O. Rozeau, E. Dubois, T. Poiroux, *" Extra-low Parasitic Gate-to-Contacts Capacitance Architecture for sub-14nm Transistor Nodes"*, IEEE Euro SOI conference, 2013

[2] N.Posseme, O. Pollet, S.Barnola, *"Alternative process for thin layer etching: Application to nitride spacer etching stopping on silicon germanium"*, Appl. Phys. Lett. 105, 051605 (2014)

9:20am **PS+SS+TF-WeM5 Self-limiting Cyclic Etching of Silicon Nitride using Infrared Irradiation**, ***Nobuya Miyoshi***, Hitachi, Japan, *H. Kobayashi, K. Shinoda,* Hitachi, *M. Matsui,* Hitachi, Japan, *M. Miyake, K. Maeda,* Hitachi, *Y. Kouzuma,* Hitachi High-Technologies, Japan, *Y. Kudo, T. Kanekiyo, M. Izawa*, Hitachi High-Technologies

Advanced semiconductor device fabrication requires precise control of device dimensions down to the atomic level. Current efforts to achieve atomic level control are focused on cyclic etching that repeatedly forms and removes a reactive layer on a surface. The cyclic etching of SiO_2, for example, has been achieved by repeatedly forming and removing of ammonium hexafluorosilicate ($(NH_4)_2SiF_6$) [1]. The essential point in realizing atomic level control is achieving a self-limiting process. Fluorocarbon-based plasma produces a $(NH_4)_2SiF_6$ layer on silicon nitride surfaces [2]. We have reported the preliminary results of the cyclic etching of silicon nitride using the formation and removal of the $(NH_4)_2SiF_6$ layer [3]. An analysis using x-ray photoelectron spectroscopy (XPS) revealed that the $(NH_4)_2SiF_6$ layer formed on silicon nitride after exposure to fluorocarbon-based plasma and was desorbed by annealing the sample.

In this study, the removal of the $(NH_4)_2SiF_6$ layer using IR irradiation was investigated to achieve high-throughput cyclic etching. The reactive layer of $(NH_4)_2SiF_6$ was formed on a silicon nitride sample after exposure to radicals in fluorocarbon-based plasma. After formation of the reactive layer, IR light was irradiated to the sample for removal. The sample surface was analyzed by XPS, and the dependence of the etching depth on the radical exposure time was investigated. The temperature of the sample increased over 160°C under IR irradiation for 10 s. A nitrogen 1s peak at 402 Ev, which is attributed to $(NH_4)_2SiF_6$, disappeared after IR irradiation for 10 s. This result shows that IR irradiation is expected to result in fast removal of the reactive layer within 10 s. The etching depth after IR irradiation saturated at 1 nm as the radical exposure time was increased to over 300 s. Therefore, a self-limiting process for silicon nitride was obtained by forming and removing the $(NH_4)_2SiF_6$ layer. Finally, the cyclic etching was investigated by repeatedly forming and removing the reactive layer. The number of cycles was changed between 1 and 10. The total etching depth increased linearly with the number of cycles, demonstrating the cyclic etching of silicon nitride with high precision.

[1] H. Nishio, et al., J. Appl. Phys. **74**, 1345 (1993).

[2] W. R. Knolle et al., J. Electrochem. Soc. **135**, 2574 (1988).

[3] K. Shinoda et al., AVS Atomic Layer Etching workshop 2015 (2015).

9:40am **PS+SS+TF-WeM6 Prospects for Thermal Atomic Layer Etching: Materials and Selectivity**, ***Steven George***, *Y. Lee, J.W. DuMont*, University of Colorado at Boulder

Thermal atomic layer etching (ALE) of Al_2O_3 and HfO_2 has recently been demonstrated using sequential, self-limiting reactions [1-3]. Al_2O_3 and HfO_2 ALE were performed using $Sn(acac)_2$ and HF as the reactants [1-3]. Recent work has also shown that Al_2O_3 ALE can be accomplished using $Al(CH_3)_3$ and HF as the reactants. The ALE reaction mechanism is believed to involve fluorination and ligand-exchange. For Al_2O_3 ALE using $Sn(acac)_2$ and HF, HF exposures convert Al_2O_3 to AlF_3. $Sn(acac)_2$ then accepts F from AlF_3 and donates acac to AlF_3 to produce volatile $Al(acac)_3$ or $AlF(acac)_2$.

The prospects for thermal ALE are very promising. Thermochemical calculations suggest that many materials should be etched with similar reactions. Metal oxides, metal nitrides, metal phosphides, metal arsenides and elemental metals can all be fluorinated with fluorine reactants such as HF or XeF_2 to form the corresponding metal fluoride. Ligand-exchange reactions can then be conducted with a variety of metal precursors that accept fluorine from the metal fluoride and donate one of their ligands to the metal in the metal fluoride. The metal reaction products then can leave the surface if they are stable and volatile. Preliminary results for GaN etching suggest that metal nitrides are good candidates for thermal ALE.

The metal fluoride reaction products produced by the ligand-exchange process provide pathways for selectivity during thermal ALE. Selectivity can arise depending on the stability of the metal reaction product. For example, $Sn(acac)_2$ is a metal beta-diketonate that donates acac ligands to the metal in the metal fluoride. Because most metals bind with acac ligands, $Sn(acac)_2$ may not lead to significant selectivity. In contrast, $Al(CH_3)_3$ is a metal alkyl that donates CH_3 ligands to the metal in the metal fluoride. Because some metals do not easily form sigma-bonds to bond to CH_3 ligands, more complete selectivity between different materials may be expected for $Al(CH_3)_3$. The selectivity observed between Al_2O_3 and ZrO_2 etching will illustrate this concept.

1. Younghee Lee and Steven M. George, "Atomic Layer Etching of Al_2O_3 Using Sequential, Self-Limiting Thermal Reactions with $Sn(acac)_2$ and HF", *ACS Nano* **9,** 2061 (2015).

2. Younghee Lee, Jaime W. DuMont and Steven M. George, "Mechanism of Thermal Al_2O_3 Atomic Layer Etching Using Sequential Reactions with $Sn(acac)_2$ and HF" *Chem. Mater*. (In Press).

3. Younghee Lee, Jaime W. DuMont and Steven M. George, "Atomic Layer Etching of HfO_2 Using Sequential, Self-Limiting Thermal Reactions with $Sn(acac)_2$ and HF", *J. Solid State Sci. Technol*. **4**, N5013 (2015).

11:00am **PS+SS+TF-WeM10 Atomic Layer Etching of Al_2O_3 Using Sequential, Self-Limiting Thermal Reactions with Trimethylaluminum and Hydrogen Fluoride**, ***Younghee Lee***, *J.W. DuMont, S.M. George*, University of Colorado, Boulder

A new approach for the atomic layer etching (ALE) of Al_2O_3 was demonstrated using sequential, self-limiting thermal reactions with trimethylaluminum (TMA) and hydrogen fluoride (HF) as the reactants.

Previously, Al_2O_3 thermal ALE was reported using $Sn(acac)_2$ and HF as the reactants [1,2]. HfO_2 ALE was also demonstrated using $Sn(acac)_2$ and HF as the reactants [3]. This new approach using TMA expands the variety of ALE reactants and excludes the possibility that Sn could be left on the etched Al_2O_3 film.

Quartz crystal microbalance (QCM) experiments monitored Al_2O_3 ALE at temperatures from 275-325°C. The Al_2O_3 ALE was linear versus number of TMA and HF reaction cycles. The QCM studies showed that the sequential TMA and HF reactions were self-limiting versus reactant exposure. The QCM analysis measured a mass change per cycle (MCPC) of -16 ng/(cm^2 cycle) at 300°C. This MCPC corresponds to an Al_2O_3 etch rate of 0.53 Å/cycle. X-ray reflectivity analysis confirmed the linear removal of Al_2O_3 and etching rates. Fourier transform infrared spectroscopy measurements also monitored Al_2O_3 ALE by observing the loss of infrared absorbance from Al-O stretching vibrations.

Al_2O_3 ALE is believed to follow the reaction: $Al_2O_3 + 4Al(CH_3)_3 + 6HF \rightarrow 6AlF(CH_3)_2 + 3H_2O$. The proposed reaction mechanism involves fluorination and ligand-exchange. The HF exposure fluorinates Al_2O_3 and forms AlF_3 with H_2O as a reaction product. During ligand-exchange, $Al(CH_3)_3$ accepts F from AlF_3 and donates CH_3 to AlF_3 to produce volatile $AlF(CH_3)_2$ reaction products. Similar reaction mechanisms based on fluorination and ligand-exchange reactions may extend the range of thermal ALE to a wide variety of additional materials.

1. Younghee Lee and Steven M. George, "Atomic Layer Etching of Al_2O_3 Using Sequential, Self-Limiting Thermal Reactions with $Sn(acac)_2$ and HF", *ACS Nano* **9,** 2061 (2015).

2. Younghee Lee, Jaime W. DuMont and Steven M. George, "Mechanism of Thermal Al_2O_3 Atomic Layer Etching Using Sequential Reactions with $Sn(acac)_2$ and HF" *Chem. Mater*. (In Press).

3. Younghee Lee, Jaime W. DuMont and Steven M. George, "Atomic Layer Etching of HfO_2 Using Sequential, Self-Limiting Thermal Reactions with $Sn(acac)_2$ and HF", *J. Solid State Sci. Technol*. **4**, N5013 (2015).

11:20am **PS+SS+TF-WeM11 Low Damage Etch Chamber for Atomic Layer Etching**, ***Leonid Dorf**, S.R. Dorf, T.G. Monroy, K. Ramaswamy, K.S. Collins, Y. Zhang*, Applied Materials

The use of novel, ultra-sensitive materials requires low-damage plasma etching with atomic layer precision, which imposes progressively stringent demands on accurate control over ion energy and radical composition during plasma processing. Using electron sheet beam (e-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. Furthermore, since dissociation is performed only by high-energy beam and not plasma electrons, and the dissociation cross-section drops off considerably at beam energies of about 1–2 keV, the beam created plasma is typically poor in radicals, which allows an independent control over plasma radical composition. In this presentation, we describe the Low Damage Etch Chamber (LoDEC) for atomic layer etching (ALE). The apparatus consists of (1) an e-beam source for creating radical-poor, low-T_e plasma in the processing chamber, (2) a remote plasma source (RPS) for producing and supplying radicals to the substrate, and (3) a bias generator for creating the voltage drop (with fine control in 0 – 50 V range) between the substrate and the plasma to accelerate ions over etch-threshold energies. Using patterned wafers, we have developed low-bias power (0 – 10 W) processes resulting in very high selectivity (as per high-resolution TEM images) of Si_3N_4 to SiO_2 and poly-Si in fluorocarbon based chemistries. In application to ALE, we note that one existing approach to ALE of Si prescribes injecting Cl atoms to passivate the surface, and then replacing the processing gas with Ar and applying bias to the substrate to initiate the etching. Once the passivation layer is removed, the etch stops, provided Ar^+ ions have energies below sputtering threshold. By repeating passivation and etching steps, this scheme can be used to remove silicon in equally thick portions composed of one to a few atomic layers (few Amgstroms), without tight control over the duration of the bias part of the cycle. In LoDEC, this recent pulsed-ALE technique can be performed at ion energies much lower than that in conventional tools, thus minimizing damage to the processed materials. LoDEC also allows implementation of a unique, truly low damage, continuous-ALE technique by using electron beam to create plasma with very low ion energies (with or without an application of low-power bias to accelerate ions) and RPS to create radicals. The results of ALE experiments in LoDEC will be presented.

11:40am **PS+SS+TF-WeM12 Modeling of Electron-Beam Generated Plasmas: Validation and System Design**, ***Shahid Rauf**, A. Agarwal, L. Dorf, K.S. Collins*, Applied Materials, Inc., *D.R. Boris, S.G. Walton*, US Naval Research Laboratory

Plasmas generated using energetic electron beams have unique properties that make them attractive for emerging plasma processing applications. In the work done at the Naval Research Laboratory, [1] it has been demonstrated that electron temperature (T_e) in the electron-beam plasmas generated in molecular gases is typically < 0.6 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 than RF plasmas with a much higher ion to neutral radical density ratio in electron beam plasmas. 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 becoming attractive for plasma processing in the semiconductor industry.

This paper focuses on a multi-dimensional computational model for electron-beam generated plasmas. A fluid model for the bulk plasma is coupled with a Monte Carlo kinetic model for beam electrons. The fluid plasma model uses the drift-diffusion approximation for electrons and negative ions. The momentum equation is solved for positive ions. The model includes the effect of magnetic field on charged species transport. The Monte Carlo model for beam electrons considers electron motion in the ambipolar electric field and externally imposed static magnetic field. Additionally, important collision processes including elastic collisions, ionization, excitation, dissociation and dissociative attachment are considered during the Monte Carlo simulation.

The computational model is validated in Ar, Ar/N_2 and O_2 plasmas using probe measurements over a range of gas pressures and electron beam properties. One factor that has important implications on quantitative accuracy of the model is the influence of magnetic field on electron transport properties. The paper will discuss the classical transport model as well as variations based on semi-empirical approximations. The validated model is applied to the design of electron beam based plasma processing systems.

This work was partially supported by the Naval Research Laboratory Base Program.

[1] S.G. Walton *et al.*, ECS Journal of Solid State Science and Technology, 4 (6) N5033-N5040 (2015)

12:00pm **PS+SS+TF-WeM13 Enhanced Reaction Rate and Precursor Transport in Focused Electron Beam Induced Etching Via Pulsed Laser Assistance**, ***JooHyon Noh***, University of Tennessee, *J.D. Fowlkes*, Oak Ridge National Laboratory, *R. Timilsina, M.G. Stanford, B.B. Lewis, P.D. Rack*, University of Tennessee

Focused electron-beam-induced etching (FEBIE) is a versatile, selective or direct write nanomaterials etching technique, and is an alternative to focused ion beam (FIB) etching. FIB etching can cause collateral sub-surface damage due to knock-on collisions and ion implantation. FEBIE in contrast is minimally invasive because of the low electron mass and offers high etch selectivity between different materials. Additionally, the FEBIE process has better spatial resolution due to the smaller beam spot size. However, the low FEBIE etch rate has been a limiting factor for high-throughput applications.

The FEBIE process is governed by an electron-induced reaction with a precursor at the substrate surface, resulting in the volatile etch by-products. This complex process can be rate limited by different mechanisms depending on the electron and precursor parameters, the electron stimulated reaction rates, and the by-product volatility (or residence time). While substrate heating can reduce the by-product residence time, the higher temperature concomitantly decreases the reactant residence time, which can reduce the reactant equilibrium coverage and result in the electron stimulated etching rate. In order to enhance the etch rate, we introduce a laser-assisted focused electron-beam-induced etching (LA-FEBIE) process which emulates an atomic layer etching process. The focused electron beam catalyzes the first half reaction which forms a pseudo-volatile byproduct. The periodic and appropriately synchronized pulsed laser can locally and briefly raise the surface temperature, which can affect the reactant and byproducts and facilitate the reaction kinetics. In this presentation we will overview the laser-assisted electron beam induced etching of Ti with a XeF_2 gas chemistry and will correlate the mechanisms to a selected area atomic layer etching process. We will show results that the Ti electron stimulated etch rate via the XeF_2 precursor can be enhanced up to 6 times with an intermittent pulsed laser assist. The etching evolution is correlated to in situ stage current measurements and scanning electron micrographs as a

function of time. Other relevant work on conventional fluorine-based titanium plasma etching suggests the mechanism of Ti-F etching is attributed to the reaction of F radicals with Ti to form TiF_x products; where progressive fluorine incorporation drives x towards the volatile product of TiF_4. Notably TiF_3 is a stable solid at room temperature. The increased etch rate with laser assistance is attributed to photothermally enhanced Ti−F reaction and TiF_4 desorption and in some regimes enhanced XeF_2 surface diffusion to the reaction zone.

Plasma Science and Technology
Room: 210B - Session PS+AS+SS-WeA

Plasma Surface Interactions
Moderator: Steven Vitale, MIT Lincoln Laboratory

2:20pm **PS+AS+SS-WeA1 *In Situ* FTIR Diagnostics and Characterization of Etch By-Product Deposition on Chamber Walls and Wafer Surface during Halogen Etching of Silicon**, ***Neema Rastgar***, *S. Sriraman, R. Marsh, A. Paterson*, Lam Research Corporation

Plasma etching is a critical technology for nanoelectronics fabrication, but the use of a vacuum chamber limits the number of in situ, real-time diagnostics measurements that can be performed during an etch process. Byproduct deposition on chamber walls during etching can affect the run-to-run performance of an etch process if there is build-up or change of wall characteristics with time. Knowledge of chamber wall evolution and the composition of wall-deposited films are critical to understanding the performance of plasma etch processes, and an in situ diagnostics measurement is useful for monitoring the chamber walls in real time.

In this talk, we report the use of attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) to perform in situ diagnostics of a vacuum chamber's walls during plasma etching. Using ATR-FTIR, the relative thickness and makeup of chamber wall deposits in real time is monitored. This information is then used to develop a chamber wall cleaning process in order to maintain reproducible etching conditions from wafer to wafer. In particular, we report mid-IR (4000-650 cm^{-1}) absorption spectra of chamber wall-deposited silicon byproducts formed during halogen etching of silicon wafers. Preliminary results demonstrating measurements of on-wafer etch byproduct evolution as well as its correlation to chamber wall deposits will be discussed.

2:40pm **PS+AS+SS-WeA2 Particle as a Temperature Probe: Thermal Effects in Non-Thermal Plasmas**, ***Thomas Lopez***, *L. Mangolini*, University of California Riverside

Silicon nanocrystals are currently under investigation for several applications including nanoelectronics, light emitting devices, photovoltaics, thermal electric devices, and energy recovery and storage. Continuous flow nonthermal plasmas reactors are ideal for silicon nanaparticle production for many reasons; continuous flow non thermal plasma reactors are a scalable system, they readily produce completely amorphous to completely crystalline samples, and they have the ability to control size and size distributions of produced particles [1]. Extensive *in-situ* and *ex-situ* characterization on continuous flow non-thermal plasma reactors has been carried out characterizing nucleation, growth, and structural evolution [2]. Particle size, structure, and surface termination are all particle properties that are directly correlated to the particles' interactions with ions and other plasma produced radicals during their creation [2]. It has been shown that the interactions between particles, ions and other radicals in non-thermal plasmas leads to a thermal annealing process [3], meaning particles in non-thermal plasmas are heated well above the temperatures of their respective carrier gases. We probe the temperature of silicon nanoparticles produced via continuous flow non-thermal plasma reactors by monitoring their surface termination. *In-situ* FTIR has been utilized to track changes in the surface chemistry of particles, which have then been correlated to the particle temperature as a function of plasma power. FTIR data shows that hydrogen termination of silicon nanoparticles as they flow through a plasma is power dependent, with higher power leading to a decrease in hydrogen surface termination. We attribute this behaviour to thermally induced desorption from the particle surface. A discussion on the characterization of nanoparticle interactions with the plasma based on *in-situ* FTIR, optical emission spectroscopy and ion density measurements will be presented.

1. Lopez, T. and L. Mangolini, *Low activation energy for the crystallization of amorphous silicon nanoparticles*, Nanoscale, 2014. **6**(3): p. 1286-1294

2. Lopez, Thomas, and Lorenzo Mangolini. Journal of Vacuum Science & Technology B 32.6 (2014): 061802.

3. Kramer, N.J., R.J. Anthony, M. Mamunuru, E.S. Aydil, and U.R. Kortshagen, *Plasma-induced crystallization of silicon nanoparticles*, Journal of Physics D: Applied Physics, 2014. **47**(7): p. 075202.

3:00pm **PS+AS+SS-WeA3 Plasma-Surface Interactions at Low and High Pressure**, ***Vincent Donnelly***, University of Houston **INVITED**

This talk will review studied of the interactions of low pressure Cl_2, HBr, and O_2 inductively-coupled plasmas with reactor chamber walls, with and without Si etching, using the "spinning wall" technique. The spinning wall is part of the reactor chamber walls, allowing near-real-time analysis of the composition of surface layers via Auger electron spectrometry, and determination of species desorbing off the walls by mass spectrometry. Langmuir-Hinshelwood (L-H) reactions, with surface residence times > 0.5 ms can be studied by this technique. Many commonalities were found for the different source gas plasmas. For example, when the walls were coated with SiO_x or AlO_x layers, A + B recombination reactions including O + O, O + Cl, Cl + Cl and H + Br are detected, provided that the surface contains a level of oxygen above some critical value. During Si etching, surfaces coated with Si-halide products tend to be less catalytic toward L-H recombination reactions, while Si-oxyhalides films formed on chamber walls when oxygen is present in the plasma are much more active in promoting L-H recombination, as well as adsorption and delayed desorption of Cl_2. At most sites, O is believed to be in the inactive form of Si-O-Si. In relatively few cases, O cannot coordinate to a second Si and the active Si-O- forms. This quickly forms Si-O-A and then mobile B on the surface forms Si-O-AB, followed by desorption of AB, which could also be delayed. For all of the products observed, formation and desorption of AB is exothermic. Si etching with small oxygen addition leads to "sticky" products with a range of masses up to at least the limit of our mass spectrometer (m/e = 500) that desorb from chamber wall surfaces in ms to min after plasma exposure. Gaseous products contain -O-Si-O- linkages are prominent, in addition to Si-mono and tri-halides. In HBr-containing plasmas, products contain little or no H. Experiments have also begun to study plasma-surface interactions at atmospheric pressure. Species present within one mean free path of a quartz substrate exposed to a He jet plasma in ambient air and in a sealed chamber with gas additives are spatially resolved using a new near-field optical emission spectroscopy method.

4:20pm **PS+AS+SS-WeA7 Measurements of IIEE Emitted Electrons from Chemically-Cleaned and Sputtered-Cleaned Semiconductor Surfaces**, *D. Urrabazo*, ***Lawrence Overzet***, University of Texas at Dallas

Plasma-surface interactions with semiconductors comprise a variety of interesting phenomena in addition to etching and deposition. One such phenomenon is ion induced electron emission (IIEE). IIEE has historically been viewed as extremely surface sensitive; but recent measurements have suggested that the IIEE yield from semiconductors, unlike metals, may in fact depend on the sub-surface properties as well. We investigated the effects of the surface and sub-surface properties (doping type, Fermi level, cleanliness level) on the relative IIEE yields from Si and Ge. Our measurements indicate that the relative IIEE yields did not depend on the doping type to a significant degree independent of the level of cleanliness. This result is consistent with IIEE theory. We further explored the sensitivity of the IIEE yield to surface cleanliness by making XPS and UPS measurements on the surface chemistry and approximate surface density of states (sDOS) of the semiconductors. By combining the theoretical IIEE model with the sDOS, we were able to replicate the changes in the IIEE emitted electron distribution functions due to surface cleanliness changes. Thus, we confirmed that the IIEE yield is affected by the cleanliness of the surface primarily through the change in the surface density of states.

Acknowledgement: This material is based upon work supported by the Department of Energy under Award Number DE-SC-0009308.

4:40pm **PS+AS+SS-WeA8 Effects of Hydrogen on Etching Processes for Transparent Conducting Films**, ***Hu Li****, *K. Karahashi,* Osaka University, Japan, *M. Fukasawa, K. Nagahata, T. Tatsumi,* Sony Corporation, Japan, *S. Hamaguchi*, Osaka University, Japan

The market demand for high-resolution optoelectronic devices such as head-mounted displays has accelerated the development of micro pattern formation technologies for transparent conducting oxides (TCOs) with a pattern resolution of sub-microns or even nanometers. Reactive ion etching (RIE), which has been widely used in the fabrication of semiconductors, is also a promising technology for patterning of TCOs. Tin-doped indium oxide (ITO) and Zinc oxide (ZnO) are widely used TCOs in the industry. The goal of this study is therefore to establish RIE technologies for ITO and ZnO for high-resolution patterning.

Typical RIE processes for ITO and ZnO use plasmas based on organic gases such as CH_4 and CH_3OH. CH_4 and CH_3OH are non-corrosive gases and RIE processes with such gases are expected to achieve high etching rates with less process damages. In this study, we have mostly focused on ZnO etching processes and evaluated sputtering yields and analyzed surface reaction characteristics of ZnO by various chemically reactive species such as CH_x^+, H^+, and H^*, using a mass-selected ion beam system. The mass-

*** Coburn & Winters Student Award Finalist**

selected ion beam system allows one to examine surface reactions caused by specific ion species with a given incident energy incident upon the sample substrate set in an ultra-high vacuum (UHV) reaction chamber. Simultaneous injection of hydrogen radicals have been also performed with a hydrogen radical source. Surface chemical composition after such beam injections have been analyzed by *in-situ* X-ray Photoelectron Spectroscopy (XPS) installed in the reaction chamber.

Our previous study [1] found that the sputtering yield of ZnO strongly depends on the number of hydrogen atoms contained in each incident molecular ions. In this study, we have clarified the effects of incident hydrogen ions and radicals. When ZnO is etched by simultaneous injection of energetic CH^+ ions and abundant hydrogen radicals, it has been found that etching proceeds with no carbon deposition and the sputtering yield of ZnO is closed to that of the corresponding physical sputtering. This result suggests that hydrogen radicals prevent carbon accumulation on ZnO and energetic hydrogen ion incidence leads to the formation of a surface damage layer, which is more easily sputtered by incident energetic ions. Therefore the presence of CH_3^+ ions is not indispensable in such a RIE process and the embrittlement of ZnO by hydrogen is more crucial to the achievement of efficient etching processes for ZnO.

[1] H. Li, K. Karahashi, M. Fukasawa, K. Nagahata, T. Tatsumi, and S. Hamaguchi, AVS61st Int. Symp. Exh. Abst. 4892, PS-TuM11.

5:00pm **PS+AS+SS-WeA9 Mechanisms of Hydrocarbon Based Polymer Etch using Pulsed Plasmas**, ***Barton Lane**, P. Ventzek, M. Matsukuma, A. Suzuki, A. Koshiishi*, Tokyo Electron Limited

Dry etch of hydrocarbon based polymers is important for semiconductor device manufacturing. The etch mechanisms for oxygen rich plasma etch of hydrocarbon based polymers has been studied but the mechanism for lean chemistries has received little attention. We report on an experimental and analytic study of the mechanism for etching of a hydrocarbon based polymer using an Ar/O2 chemistry in a single frequency 13.56 MHz test bed. The experimental study employs an analysis of transients from sequential oxidation and Ar sputtering steps using OES and surface analytics to constrain conceptual models for the etch mechanism. The conceptual model is consistent with observations from MD studies and surface analysis performed by Vegh, et al. and Oehrlein, et al. [1,2] and other similar studies. Parameters of the model are fit using published data and the experimentally observed time scales. [1] J.J. Vegh, D. Nest, D. B. Graves, R. Bruce, S. Englemann, T. Kwon, R. J. Phaneuf, G. S. Oehrlein, B. K. Long, and C. G. Willson, Jour. of Applied Physics **104**, 034308 (2008), [2] G.S. Oehrlein, R. J. Phaneuf, D. G. Graves, J. Vac. Sci. Tech. B 29, 010801-1 (2011).

5:20pm **PS+AS+SS-WeA10 Role of Plasma Density in Damage Characterization and its Impact on Low-Damage Plasma Process Design**, ***Koji Eriguchi**, M. Kamei, Y. Nakakubo, K. Ono*, Kyoto University, Japan

Plasma process-induced damage (PID) is one of critical issues in designing metal−oxide−semiconductor field-effect transistors (MOSFETs) with higher performance and reliability. The damage creation mechanisms—plasma-induced physical damage (PPD) and charging damage (PCD) [1]—have been characterized by various techniques so far [2] to design low plasma processes. In this study, conflicting results leading to erroneous conclusions in designing future plasma processes are presented, where ion flux and charge injection from plasma (~ plasma density) play a key role in these conventional characterizations. Firstly, regarding PPD, n-type (100) Si wafers were exposed to Ar-based ICP and CCP discharges [3] and the localized defects were created in the Si substrates by ion bombardment. It is found that, although the average energy of incident ions (E_{ion}) is larger for the case of CCP, the latent defect density (n_{dam}) of CCP-damaged samples is smaller than that of ICP, even after the damaged-layer removal. This observation is in sharp contrast to previous pictures, i.e., the larger E_{ion} leads to the larger PPD. Secondary, MOSFETs with "high-k" ($HfSiO_x$) gate dielectric were damaged by the Ar-based ICP plasma and the high-k damage (~ carrier trap site generation) by PCD is evaluated by time-dependent dielectric breakdown (TDDB) measurement [4]. We identify that the TDDB lifetime becomes longer under a certain amount of charge injection by plasma-induced current. This finding implies that one might be misled to an erroneous design rule of future LSIs. We propose a model explaining these conflicting results, where both ion flux and charge injection from plasma and the nature of the analysis techniques are taken into account. Since modern FinFETs with high-k dielectrics [5] are susceptible to PPD and PCD, the present model should be intensively implemented in designing future "low-damage" plasma processes.

This work was supported in part by a Grant-in-Aid for Scientific Research (B) 25630293 from the Japan Society for the Promotion of Science.

[1] For example, K. Eriguchi and K. Ono, J. Phys. D 41, 024002 (2008).

[2] M. Fukasawa et al., Dry Process Symposium, 183, (2013).

[3] Y. Nakakubo et al., ECS J. Solid State Sci. Technol., 4 N5077 (2015).

[4] M. Kamei et al., IEEE Int. Integrated Reliability Workshop Final Report, 43 (2014).

[5] For example, I. Ferain et al., Nature 479, 310 (2011).

5:40pm **PS+AS+SS-WeA11 Dry Deep Etching Of Bulk Titanium By Plasma Processes**, ***Edouard Laudrel**, T. Tillocher, P. Lefaucheux,* GREMI CNRS/Université d'Orléans, France*, B. Boutaud,* Sorin Crm, France*, R. Dussart*, GREMI CNRS/Université d'Orléans, France

Bio-MEMS have emerged these last years with applications for biosensors, drug delivery, etc. The biocompatibility, the mechanical strength and the hydrophilicity properties have made titanium a widely used material with a great interest in the biomedical field. This element was chosen to fabricate body implantable devices with the help of microfabrication methods from microelectronics technologies in order to pattern structures with vertical sidewalls and smooth surfaces. Most of the literature with an interest in titanium deep etching relies on chlorine plasma processes. They are performed at room temperature of the substrate with typical etch rates close to 1 $\mu m.min^{-1}$ and provide rather smooth surfaces. TiO_2 or Ni are typically used as hard mask. However, a thick (several 10s of microns) SU8 layer, which is a negative photoresist, has also been reported as an alternative mask because it can be easily patterned and stripped.

Samples used in our experiments consist of coupons of a patterned titanium wafer glued on a silicon carrier wafer. The titanium wafer is 300 µm thick with a 15 µm thick backside thermal TiO_2 layer and the mask is a 15 µm electrochemically deposited thick nickel layer. The samples were processed in two different ICP reactors. Two different chemistries can be used to etch titanium. A chlorine-based chemistry at low pressure can be used to obtain anisotropic profiles but with reduced etch rates at room temperature. With the first reactor, equipped with a diffusion chamber, titanium etch rate was 1 $\mu m.min^{-1}$. A fluorine-based chemistry admits higher etch rate (as 4 $\mu m.min^{-1}$) at higher pressure (few Pa) with isotropic profiles if the sample temperature is sufficient to form volatile etch by-products. Both chemistries, as well as $Cl_2/Ar/SF_6$ mixture, produced non-reproducible results and a high roughness. These observations were attributed to the redeposition of etch by-products (like $SiOCl_x$) on the sample surface. It induces a micro-masking effect which generates a high roughness and leads to reproducibility issues. The so-called APETi (Alternated Process for the deep Etching of Titanium) process has been developed to prevent this roughness and increase the reproducibility. An average etch rate of 1.4 $\mu m.min^{-1}$ has been achieved with reproducible features.

Comparative experiments have started on a second ICP reactor which enables higher etch rates due to a higher self-bias voltage and higher density species. The substrate holder temperature can also be higher, which should help to enhance chemical etching processes with a fluorine chemistry.

6:00pm **PS+AS+SS-WeA12 Particle Transport with Wafer Potential Controlled by Dipole Electrostatic Chuck Electrodes**, ***Masaki Ishiguro**, M. Sumiya*, Hitachi High-Technologies Corp., Japan

In plasma etching for semiconductor manufacturing, it is important to prevent particle attachment on the wafer during processing to maintain high yield rate. As the device size continue to be scaled down, smaller particles should be taken care not to attach onto the wafer. It is said that 10 nm particles will be critical for semiconductor manufacturing in 2019 [1]. One important approach to prevent particle attachment on the wafer is controlling particle transport. Electrostatic force is one of the suitable forces to control particle transport. In the case that particle charge and wafer potential polarity is opposite, large number of small particles can be attracted onto the wafer. In plasma etching process, plasma on and off periods are periodically repeated. Kobayashi *et. al.* revealed that in plasma on period, the particles are trapped at the plasma sheath boundary and there is a less-risk of particle attachment to the wafer [2]. It suggested that, in plasma off period, there is a large-risk of particle attachment to the wafer if the wafer and the particles have opposite charge respectively.

In this study, the relationship between particle attachment to the wafer and wafer potential in plasma off period was investigated. Particle count on the wafer was measured at different wafer potential during plasma-off period by changing voltage settings of dipole electrostatic chuck electrodes (ESC) in Ar, O_2 and N_2 plasma. In the case of negative wafer potential, particle counts increased as the plasma off time was prolonged. On the other hand, in the case of positive or 0 wafer potential, particle count was relatively low

level and it did not increase even if plasma off time was prolonged. This result suggests that, in our experimental condition, the particles charge positive during plasma off period and they are continuously generated from inner chamber wall. If the wafer has negative potential, the particles are attracted by electrostatic force. The numerical simulation result will also be shown to understand the effect of electrostatic force on small particle attachment.

In plasma on period, wafer has plasma floating potential and the potential remains on the wafer even after plasma discharge is finished. It leads to increase of particle attachment risk as mentioned above. In this time, newly developed wafer potential control sequence with ESC electrodes to reduce wafer potential during plasma off period will be reported. This sequence enables to reduce particle attachment during plasma off period.

[1] International Technology Roadmap for Semiconductors 2013.

[2] H. Kobayashi, *et al*., IEEE trans. Semicond. Manuf., **22**, 462 (2009).

Plasma Science and Technology
Room: 210A - Session PS+TF-WeA

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

2:20pm **PS+TF-WeA1 Plasma Prize Talk: Plasma Processing of Materials: What makes Plasma Special and Future Outlook?**, ***Richard van de Sanden****, DIFFER **INVITED**

Plasma processing of materials is at the heart of present day technologies such as found in the manufacturing of IC's, liquid crystal displays and large scale production of solar cells, to name only a few. For a basic understanding of the key processes determining the processing quality advanced in situ diagnostics for both the plasma phase as well as diagnostics to characterize the plasma-surface/material interaction are required. This basic understanding will enable control over these processes, such as the controle of the ion energy distribution function by tailoring the bias voltage on the materials processed.

The aspects which differentiates plasma processing from other processing technologies such as the presence of charge, short living reactive radicals and nonequilibrium species distribution to name a few, will be discussed. In a future outlook I will argue that the nonequilibrium aspects, especially connected to the vibrational populations in molecular plasmas, are not yet exploited to its full extent. If we succeed in controlling the population of the vibrational states many novel applications in catalysis, gas and surface processing of materials come within reach.

3:00pm **PS+TF-WeA3 Feature Scale Simulation of Atomic Layer Deposition via FPS3D**, ***Paul Moroz,*** Tokyo Electron US Holdings, *D.J. Moroz*, University of Pennsylvania

Atomic layer deposition (ALD) allows accurate atomic-scale deposition of materials layer-by-layer with almost conformal feature profiles. Together with atomic-layer etching (ALE), it provides the tools necessary for satisfying the ever increasing demands for improved accuracy and miniaturization, and is becoming one of the leading methods among advanced semiconductor technologies. ALD requires cycling processing, with each cycle consisting of at least two timesteps, each timestep having its own parameters corresponding to different fluxes of species and different surface chemistry. Numerical simulation of ALD could be accomplished at the levels of quantum chemistry (QC), molecular dynamics (MD), or feature-scale (FS) calculations. While QC provides an ab-initio approach, MD depends on approximations of interactions with inter-atomic potentials, and FS methods rely on reactions between species. The reactions used in FS simulations could be estimated from experiments or they could be taken from MD or QC calculations. We present here numerical simulations of ALD for the case of deposition of silicon nitride film onto silicon utilizing dichlorosilane gas and ammonia plasma. Our calculations were carried out via the feature-scale simulator FPS3D [1-3], which can efficiently simulate multi-timestep operations and which allowed us to replicate the results of considered ALD experiments. In correspondence with the experiments, the reactions were selected such that the deposition of a single monolayer was produced not in a single cycle, but in two cycles, even when the duration of each timestep was long enough for the processes to saturate. FS simulations run much faster and can operate on a much larger scale than can MD and, especially, QC methods. FS methods can efficiently simulate processing of entire features with complex profiles both in 2D and 3D. We simulate the feature profiles obtained during processing at different conditions and initial settings, and we discuss various effects which could change the roughness of profiles. We also analyze the effects of partial conformity of obtained profiles and the effects of incomplete ALD, during which some reactions may not self-limit due to insufficient processing time.

[1] P. Moroz, IEEE Trans. on Plasma Science, **39**, 2804 (2011).

[2] P. Moroz, D. J. Moroz, ECS Transactions, **50**, 61 (2013).

[3] P. Moroz, D. J. Moroz, Journal of Physics: CS **550**,012030 (2014).

3:20pm **PS+TF-WeA4 Plasma Enhanced Atomic Layer Deposition Applications using an Ion Source**, *F. Papa,* Gencoa USA, *V. Bellido-Gonzalez, H. Li,* Gencoa Ltd, UK, *HD. Ngo,* University of Applied Sciences Berlin, Germany, *K. Kröhnert,* Fraunhofer Institut IZM Berlin, Germany, *O. Ehrmann, K.D. Lang, P. Mackowiak, Piotr,* TU Berlin, Germany, ***William Sproul***, Reactive Sputtering, Inc

Atomic Layer Deposition (ALD) has been slowly gaining acceptance in the field of thin film deposition. Although firstly described in the 1960's as molecular layering by researchers in the former USSR, the introduction of the technology to the world came via Tuomo Suntola's group in 1974 (**1**). The application to ZnS highly ordered films was a real success, and made the electroluminescent displays a reality. Since then the concept has been applied into other technology areas. There are many benefits of ALD, however, in terms of deposition rates, film stress and management of reactive gas species in complex 3D structures there is still a long road ahead.

In order to lower the film stress plasma technology has been applied. Plasma Enhanced ALD (PEALD) has been introduced in order to lower the temperature requirements for the ALD process and also in order to control the properties of the ALD deposited film. The industrialization of such process presents a number of challenges. In PEALD, it is of interest to control the nature and degree of interaction of such plasmas with the surface chemistry. Plasma sources which can control the energy of the ion beam are of special interest. Also, from the industrialisation point of view the sources would need to be able to upscale the process. For those reasons, the authors believe that a Linear Ion Sources (LIS) could help move ALD processes into mass production. LIS's have been slowly pushing their way through into vacuum coating technology market for over 15 years. Only last year a small circular ion source, which can replicate the functional properties of large LIS's was introduced (**2**). This development has enabled rapid transitions from prototyping to manufacturing. The use of such a source is interesting for PEALD as the processes developed in the lab could be easily implemented at an industrial level. As part of the investigation the authors have used the ion source PEALD process on etched silicon wafers in order to produce low temperature conformal depositions. The wafers were etched with different features, like deep aspect ratio trenches, which are of great interest in today's semiconductor devices. Results will be presented.

1.- Riikka L. Puurunen, "A Short History of Atomic Layer Deposition: Tuomo Suntola's Atomic Layer Epitaxy" http://onlinelibrary.wiley.com/doi/10.1002/cvde.201402012/pdf

2.- F. Papa, D. Monaghan, V. Bellido-Gonzalez, R. Brown, A. Azzopardi, I. Sorzabal-Bellido, "New Circular Ion Sources for Fast Process Development", Proceedings to the 2014 Society of Vacuum Coaters Conference, Chicago, USA, 505/856-7188, pages 187-191.

4:20pm **PS+TF-WeA7 Plasma-Assisted ALD of SiN_x: The Surface Chemistry Studied by Infrared Spectroscopy**, ***Roger Bosch***, *L.E. Cornelissen, C.K. Ande, W.M.M. Kessels*, Eindhoven University of Technology, The Netherlands

Silicon nitride (SiN_x) deposited by ALD is gaining a lot of interest lately, as it allows for conformal films prepared at low temperatures while maintaining a high film quality and uniform thickness. This is challenging for conventional deposition techniques, such as CVD and PECVD. Within the work presented in this contribution, the growth of SiN_x by ALD and the associated surface chemistry have been studied. The chosen plasma-assisted ALD process employs bis(tertiary-butylamino)silane ($SiH_2[NHC(CH_3)_3]_2$,BTBAS) as precursor and N_2 plasma as co-reactant. Various *in situ* studies have been performed and the experimental work has been complemented with DFT calculations.

More particularly, to study the surface chemistry we developed a versatile setup, which combines ALD with Fourier transform infrared spectroscopy. A sample manipulator was designed that enabled us to study the species present at the surface, with a submonolayer sensitivity, as a function of substrate temperature (100-300°C) and incident angle of the IR beam. The setup also allowed for gas phase measurements.

Gas phase infrared measurements have been performed to identify which species were present in the reactor after the precursor dose and N_2 plasma exposure. The measurements revealed that *tert*-butylamine ($(CH_3)_3CNH_2$) is the main reaction product after precursor exposure. This indicates that the

*** PSTD Plasma Prize**

Si-N bond in the precursor molecule breaks when it interacts with active sites at the surface.

Surface infrared measurements have been conducted at different temperatures to determine which species were present at the surface after one of the ALD half cycles, i.e. after the BTBAS half cycle and after the N_2 plasma half cycle. Amongst others, a pronounced density of Si-H at the surface has been established, and at lower temperatures (~100°C) also a signal from C-H groups was clearly observed after BTBAS dosing. From these infrared measurements, complemented with DFT calculations and additional thin film studies, we propose a mechanism for the growth of SiN_x by ALD using BTBAS and N_2 plasma, which will be discussed during the presentation.

4:40pm **PS+TF-WeA8 Structural Characterization of Surface Dielectric Barrier Discharges (SDBD) for Atmospheric Pressure Plasma Enhanced Spatial ALD (PE-S-ALD)**, ***Yves Creyghton**, J. Emmelkamp, F. Roozeboom*, TNO Technical Sciences, Netherlands

Spatial ALD (S-ALD) is an emerging technology with substrates passing a series of spatially separated gas injector zones. This concept enables up to 100x faster deposition rates with respect to conventional ALD. TNO constructed an S-ALD process toolbox for high throughput ALD on wafers, sheets and foils. Recently, SDBDs were selected to extend the toolbox to plasma enhanced ALD. Implementing an SDBD source in an existing rotary wafer reactor, homogeneous PE-S-ALD was shown for the first time. The operating temperature was reduced down to 80°C allowing deposition on polymer foils. Using plasma in N_2, N_2-O_2 and N_2-H_2, new materials were made like TiN, SiO_2, TiO_2 , InZnO and Ag, so far inaccessible for atmospheric pressure S-ALD.

Contrary to low-pressure plasma, atmospheric plasma tends to filamentary structures (micro-discharges). The past 2 decades, world-wide efforts have been undertaken to improve plasma homogeneity in DBD systems with the electrodes located at both substrate sides and using He gas, short pulses, high frequencies and gas flows. Single-sided SDBD electrode configurations provide remarkably homogeneous and reproducible plasmas in practical gases. Usually the electrical discharge is a mixture of surface glow and micro-discharges, the latter being generated with a sufficient density to reach homogeneous deposition. There is a striking analogy between the saturating charge principle of the planar SDBD and the surface limited surface reaction, as characteristic for ALD processes. Merging both technologies yields the best of two worlds.

As a standard condition, SDBD plasma has been generated parallel and close to the rotating substrate. Obviously, when conductive, semiconductor or highly capacitive substrates are used the SDBD plasma may generate filaments towards the substrate and/or electrostatically interact with electric field sensitive structures. Thus we built various alternative remote SDBD sources minimizing electrical-substrate interaction. For the study of the influence of geometry and flow parameters, thin films were deposited by PE-S-ALD using the different sources.

Also static substrate tests were done with both parallel plasma and remote jet treatments using amorphous C-layer etching to visualize the plasma reactivity and homogeneity. The plasma structures visualized by C-layer transmission show the importance of control of flow and plasma homogeneity. The spatial discharge study is complemented by visual light photography and IR thermography. The experimental data have been validated with a CFD model of plasma species transport yielding a deep understanding of the effects of flow, diffusion and temperature of the SDBD source.

5:00pm **PS+TF-WeA9 Plasma Deposited Barrier Coatings on Plastics: Plasma Characterization and Thin Film Analysis**, ***Peter Awakowicz**, F. Mitschker,* Ruhr-University Bochum, Germany, *A. Nave,* INP-Greifswald, Germany, *J. Röpcke,* INP-Greifswald, *G. Grundmeier*, Univ. of Paderborn **INVITED**

Thin SiO_2 barrier layers are deposited by microwave plasma enhanced CVD (PECVD). The pulsed mw power is fed in with a plasma line system. In addition, the flat or hollow PET substrates are rf-biased in order to increase film quality and minimize defect density.

Plasma diagnostics is performed with quantitative optical emission spectroscopy (Q-OES) based on a collisional radiative model for nitrogen and confirmed with multipole resonance probe measurements. In addition, nine carbon hydride and carbon oxide species are measured by laser absortion IR measurement while plasma diagnostics is performed.

Analysis of the 30 nm thin films are performed by XPS measurements and defect density measurements. Film porosity is measured with proton exchange measurements and cross linking by looking at the fine structure of the Si 2p peak with highly resolved XPS.

Finally it can be shown that good barrier improvement is realized with the applied deposition method on PET foils and a correlation between plasma parameters and film qualtiy is presented.

5:40pm **PS+TF-WeA11 Flexible, Durable, Self-Cleaning Optical Coatings for Optoelectronics**, ***Thomas Fuerst**, C.A. Wolden*, Colorado School of Mines

A wide variety of applications such as solar cells, displays, and electrochromics require coatings that manipulate light and provide protective barriers. Silica-titania multilayers have long served as optical components on rigid substrates. Expanding this platform to flexible substrates would allow compatibility with roll-to-roll manufacturing, which would increase manufacturing efficiencies while decreasing costs. Incorporating self-cleaning properties into these coatings would enable longer lifetime, improved efficiency, and reduced maintenance costs for the devices. In this work we describe the design, fabrication, and evaluation of flexible multilayer coating deposited by plasma-enhanced chemical vapor deposition (PECVD) at low temperature. The high and low refractive index materials were TiO_2 and silicone, respectively. PECVD enables the deposition of high quality material at temperatures compatible with polymeric substrates. Silicone is a mechanically robust polymer that imparts flexibility to the coatings and TiO_2 provides UV protection and self-cleaning functionality. The optical stacks were designed using commercial software and validated using UV-Vis-NIR spectrophotometry. The nanoscale control achievable in this process was demonstrated through the fabrication of several Bragg mirrors that were designed to produce blue, green, and red coatings. A five layer broadband anti-reflective (AR) coating was designed and deposited onto a variety of substrates including 1 mm glass, 3 mm FTO-coated glass (TEC-15), flexible polyethylene terephthalate (PET) thin films, and CdTe solar cells built on TEC-15. The absolute transmission of AR-coated glass and PET samples increased by ~5% across the visible spectrum, and solar cells experienced a commensurate boost in efficiency due to improved short circuit density. The multilayer coatings on PET proved to be mechanically robust, as their optical properties remain unchanged after 50,000 cycles of automated bend testing, including both tensile and compressive stress. Lastly, a five layer IR reflector was designed and applied to 1 mm glass and PET. The visible transmittance remained unchanged while the near IR (800-1200 nm) transmission was reduced from 88% to 27% on PET. Studies are underway to assess the long term durability of these coatings to UV exposure and examine the self-cleaning capability through measurements of contact angle and contaminant removal. These results indicate that these nanolaminates show great promise for use in a variety of flexible optoelectronic applications.

6:00pm **PS+TF-WeA12 Microwave Plasma Assisted Chemical Vapor Deposition of High Quality, Single Crystal Diamond Substrates**, ***Shreya Nad**, Y. Gu, J. Asmussen*, Michigan State University

Single crystal diamond (SCD) substrates have very useful properties like their high thermal conductivity, extreme hardness and chemical inertness and are thus deemed to be novel materials for applications in a varied range of fields like high power electronics and X-ray optics. Microwave Plasma Assisted CVD (MPACVD) is one of the most suitable and efficient methods for the synthesis of diamond substrates. MPACVD is carried out in a microwave cavity plasma reactor (MCPR) which consists of a brass cavity to contain the microwave power, a quartz dome and a water cooled substrate holder.

The reactor is first tuned using the 4 length variables to achieve maximum power coupling efficiency. A mixture of methane and hydrogen gasses flows within the quartz dome. The cavity probe excites the plasma at ~ 5 Torr. The plasma discharge is positioned directly above and adjacent to the seed substrate for the growth process to proceed efficiently. Pressure is then gradually increased and depending upon the growth conditions maintained at a high synthesis pressure of 180 – 240 Torr. The substrate temperature is maintained within 1050 – 1150°C for a smooth, high rate growth of SCD. The stable plasma creates a chemically and thermally suitable environment for SCD deposition. The high pressure and high gas temperatures at the core of the plasma discharge break down the methane and hydrogen gas molecules into the important growth radicals. These growth radicals (like CH_3, C_2H_2 etc.) then diffuse through the boundary layer between the plasma and the seed substrate and then deposit on the substrate surface.

The MPACVD method has been used for the growth of both SCDs and polycrystalline diamond (PCD) substrates at high pressures of 160 – 240 Torr, with high growth rates of 20 – 32 µm/hr and for long growth times of 24 – 72 hours. The diamond substrates are then separated from the underlying seed substrate by laser cutting and then the surfaces are mechanically polished for analyses. These substrates have been characterized using FTIR and UV/Vis spectroscopy, SIMS, optical microscopy and X-ray topography. The SCDs grown are of type IIa quality i.e. they have very low nitrogen concentrations of < 100 ppb. They have

high transmission even in the low wavelength range. Etch pit density measurements indicate that the substrates grown have low defect density of $\sim 10^4$ /cm^2.

This presentation describes in detail this efficient deposition process for SCDs and the high quality of the diamond substrates hence achieved.

Plasma Science and Technology
Room: 210A - Session PS+2D-ThM

Plasma Processing for 2D Materials
Moderator: Eric Hudson, Lam Research Corporation

8:00am **PS+2D-ThM1 Low Pressure Plasma Cleaning and Doping of CVD Graphene**, ***Daniil Marinov***, LPP-CNRS, Ecole Polytechnique, France, *G. Cunge,* LTM - CEA/LETI, France, *D. Ferrah,* CEA, LETI, MINATEC Campus, France, *E.V. Johnson,* LPICM-CNRS, Ecole Polytechnique, France, *J.-P. Booth*, LPP-CNRS, Ecole Polytechnique, France **INVITED**

The rising importance of graphene and other 2D materials presents interesting new challenges for plasma technology. Processing of atomically thin layers requires unprecedented control of plasma parameters such as the fluxes and energy distributions of both ions and neutrals at the substrate. With sophisticated control, plasma technology can offer solutions to the major technological bottlenecks associated with graphene applications. Polymer residues (originating from the transfer of CVD graphene or from photo-resist masks) uncontrollably alter the electronic and chemical properties of graphene, a major problem for graphene integration in sophisticated devices. Removal of these surface contaminants by selective hydrogen plasma etching can perform better than classical techniques (wet chemistry with annealing) in terms of efficiency, throughput and compatibility with device fabrication processes [1]. In order to avoid plasma induced damage during graphene cleaning, the ion energy must be kept low (e.g. below 12 Ev for H+ ions [2]). Band gap opening in graphene is another major challenge that can be tackled by plasma doping, provided that the ion energies can be controlled to favor substitutional doping rather than sputtering [3].

We are evaluating two types of plasma reactors for controllable cleaning and doping of graphene – a low density capacitive discharge excited by non-sinusoidal tailored voltage waveforms (TVW) and a high density pulse-modulated inductive plasma source. Both systems are capable of generating hydrogen plasmas with sufficiently low ion energies for low damage residue cleaning. The polymer (PMMA) etch rate obtained in the high density ICP is two orders of magnitude higher, making this system more suitable for graphene cleaning. The TVW discharge is particularly interesting for graphene doping. By changing the excitation voltage waveform in nitrogen CCP one can control the ion bombardment energy and hence the binding configuration of N dopants in single layer graphene. Using an ion bombardment energy of about 40 Ev nitrogen atoms can be incorporated with a total concentration of 5 at. %, with more than half of them in graphitic sites. When the ion energy is below 20 Ev only pyridinic and pyrrolic N is observed.

The role of the substrate carrying the graphene was found to be very important. In the case of hydrogen plasma treatment, ions passing through the graphene layer may participate in catalytic reactions at the substrate or lead to blister formation.

[1] Cunge *et al.* submitted to *ACS Nano*

[2] Despiau-Pujo *et al.J.Appl.Phys. 2013, 113,114302*

[3] Zhao *et al.Phys. Rev. B* 2012, 86, 165428

8:40am **PS+2D-ThM3 Sensing Cleanliness of PMMA Transferred CVD Grown Graphene**, ***Christian Teichert,*** *M.C. Kratzer,* Montanuniversität Leoben, Austria, *B.C. Bayer*, University of Cambridge, UK

Crystalline films of small organic semiconductors offer attractive potential for optoelectronic applications on flexible substrates. However, these applications require a transparent and flexible electrode material; and here the novel material graphene (Gr) comes into play. Since small conjugated molecules like the rod-like oligophenylene molecule para-hexaphenyl (6P) fits well to the hexagonal structure of graphene, growth of 6P on Gr can be expected in a lying configuration.

As demonstrated by in situ by low-energy electron microscopy, 6P grows at 240 K indeed in a layer-by-layer mode with lying molecular orientation on Ir(111) supported graphene [1]. Islands nucleate at Gr wrinkles [2]. At higher temperatures, needle-like 6P crystallites - also composed of lying molecules are observed [3]. Also on exfoliated, wrinkle-free graphene, such needles develop with discrete orientations defined by the Gr lattice as was detected by atomic-force microscopy (AFM) [4,5]. Needles are never observed on contaminations or on the silicon oxide substrate. There, exclusively islands composed of upright standing molecules are observed. Since these islands are easily detected by AFM, growth of 6P can be used to sense the cleanliness of a variety of graphene substrates as we have demonstrated for PMMA transferred CVD grown graphene. On the as grown samples, PMMA remainders hinder the growth of extended needles. For increasing anneling temperature, the 6P needles grow in length because the PMMA residues decrease substantially [6].

[1] G. Hlawacek, et al., Nano Lett. **11** (2011) 333. [2] G. Hlawacek, et al., IBM J. Res. Devel. **55** (2011) 15. [3] F. Khokar, et al., Surf. Sci. **606** (2012) 475. [4] M. Kratzer, et al., JVSTB **31** (2013) 04D114. [5] M. Kratzer, et al., e-J. Surf. Sci. Nanotechn. **12** (2014) 015303. [6] M. Kratzer, et al., Appl. Phys. Lett. **106** (2015) 103101.

9:00am **PS+2D-ThM4 Plasma Processes of Graphene and Related 2d Materials for Energy Applications**, *L.C. Chen,* ***Indrajit Shown***, National Taiwan University, Taiwan, Republic of China **INVITED**

Plasma-assisted direct-growth of arrayed graphene and related hybrids will be presented. The main advantages of this type of nanostructures include high conductivity, high surface area and corrosion resistance, making them excellent candidates as electrocatalytic supports or electrodes for electrochemical (EC) energy applications, including fuel cells, supercapacitors and solar fuels. We will demonstrate the fabrication of integrated energy devices in an on-chip manner. Since the carrier transfer rate of electrode plays a crucial role in determining the energy-conversion performance, special emphases will be placed on the control of interfaces. Vertically aligned and edge-oriented graphene arrays were first synthesized by microwave plasma-enhanced chemical vapor deposition. Subsequent chemical doping can also be done in the same plasma reactor via either in-situ or ex-situ manners. Interestingly, for nitrogen doping in graphene, plasma process resulted in selective bond configuration. When applied as an EC electrode, the arrayed graphene exhibits nearly reversible redox characteristics. By varying the process parameters, samples can be produced with controllable compressive or tensile strains, which in term show strong effects on the resultant catalytic properties.

The hierarchical graphene nanowalls can be directly grown on a variety of substrates, including Si wafers, carbon cloth as well as flexible and ultralight carbon nanofibers. The latter substrate makes such electrode an ideal portable platform having high gravimetric, areal, and volumetric electrochemical characterizations. For instance, the carbon nanofibers supported graphene-based supercapacitors exhibit excellent specific capacitance of 352.53 F/g (220.33 mF/cm^2) at a specific current of 13.33 A/g, which is among the highest reported to date. Meanwhile, 99 % of Coulomb efficiency and 98 % of the initial capacitance after 10,000 charge-discharge cycles were maintained. Finally, efficient and simple routes to further attach other heterogeneous nanostructures onto graphene nanowalls have also been developed. Cyclic voltammeter studies for electro-oxidation of methanol show a high ratio of forward anodic peak current to reverse peak current, suggesting an efficient oxidation of methanol to CO_2 on the graphene-based electrode. Our approach offers a promising route toward wafer-scale fabrication of graphene not only for fundamental research but also opens up various potential applications in sensing, catalysis, as well as energy storage and production.

11:00am **PS+2D-ThM10 Engineering Chemical Functionality in Graphene**, ***Sandra Hernandez***, *P.E. Sheehan, S. Tsoi, P. Dev, J.T. Robinson, C. Junkermeier, K.E. Whitener, W.K. Lee, T.L. Reinecke, S.G. Walton*, Naval Research Laboratory

Graphene has attracted enormous attention due to its unique properties. Equally important is the ability to further tailor these properties through modification of select attributes such as surface chemistry, number of layers, sheet width, and edge structures. Manipulating the surface chemistry of graphene is important since the chemical composition strongly impacts the electronic properties as well as chemical reactivity both globally and locally. Precise control of the surface chemistry of graphene can also allow for subsequent surface procedures focused on band gap engineering, device fabrication and sensor applications. Given the strong impact of adsorbates, global chemical modification provides opportunities towards greater control over the properties of graphene films. Control over the spatial distribution of these groups provides an even greater functionality in that the local graphene reactivity can be manipulated, opening up a wealth of opportunities in biosensing, plasmonics, catalysis, smart surfaces, and heterojunction devices.

Using the unique attributes of electron beam generated plasmas to manipulate the chemistry of graphene and employing patterning techniques to regulate the spatial distribution of various functional groups on the surface, we demonstrate further abilities to govern surface properties. Spatial control over structural and chemical changes is characterized through micro (m-Raman and high-resolution x-ray photoelectron

spectroscopy (XPS) mapping and electrical measurements are used to determine how local changes in chemistry influence the electronic properties. Lastly, we show that the resulting chemical moieties can be used to manipulate the local surface reactivity of graphene, enabling programmable, site-specific electrochemical deposition. These findings demonstrate the ability to tailor the locality of the surface chemistry on graphene surfaces opening up a wide range of reactivity studies and synthesis capabilities, such as programmable material deposition.

11:20am **PS+2D-ThM11 Formation of Aromatic Nitrogen Groups in Graphene Films by Post-Growth Treatment in Late-Afterglows of Nitrogen Microwave Plasmas**, ***Luc Stafford***, Universite de Montreal, Canada

Graphene films were exposed to the late afterglow of a reduced-pressure N_2 plasma sustained by microwave electromagnetic fields. X-ray photoelectron spectroscopy (XPS) shows that plasma-generated N atoms are incorporated into both pyridinic and pyrrolic groups, without excessive reduction of sp^2 bonding. Nitrogen incorporation was found to be preceded by N adsorption, where N adatom density increased linearly with treatment time while aromatic nitrogen saturated. This finding was confirmed by Raman spectra showing a linear increase of the D:G ratio attributed to constant surface flux of plasma generated species.

Combined Density Functional Theory calculations with a Nudged Elastic Band (DFT-NEB) approach indicate that incorporation reactions taking place at point vacancies in the graphene lattice requires an activation energy in the 2-6 eV range, but the energy required for the reverse reaction exceeds 8 eV. Stable nitrogen incorporation is therefore judged to be defect-localized and dependent on the energy transfer (6 eV) provided by $N_2(A)$-to-$N_2(X)$ metastable-to-ground de-excitation reactions occurring at the late-afterglow-graphene interface.

Surface Modification of Materials by Plasmas for Medical Purposes Focus Topic
Room: 211D - Session SM+AS+BI+PS-ThM

Plasma Processing of Biomaterials
Moderator: Deborah O'Connell, University of York, UK, Satoshi Hamaguchi, Osaka University, Japan

8:00am **SM+AS+BI+PS-ThM1 Potential of Low Temperature Plasma Sources in Cancer Treatment**, ***Jean-Michel Pouvesle***, GREMI CNRS/Université d'Orléans, France, *G. Collet*, CNRS, *E. Robert*, GREMI CNRS/Université d'Orléans, France, *L. Ridou*, CNRS-CBM, France, *S. Dozias, T. Darny*, GREMI CNRS/Université d'Orléans, France, *B. El Hafni-Rahbi, C. Kieda*, CNRS-CBM, France **INVITED**

The last decade has seen an impressive increase of the research dedicated to the biomedical applications of low temperature Non Thermal Plasmas (ltNTP), especially with plasma sources working at atmospheric pressure. Medical applications of ltNTP now concern a very wide range of domains including cancer treatment. The antitumor effect of ltNTP has been clearly shown *in vivo* on murine modelswith various cancer types (bladder, colon, glioblastoma, melanoma, ovary, pancreas). Although the involved mechanisms are far from being fully understood, the therapeutic effect is now totally admitted and the first clinical study (head and neck) has been reported [1]. In case of plasma jet experiments, the observed effect are most of the time attributed to the very rich chemistry generated by the interaction of the rare gas plasma plume with the surrounding environment constituted either from the ambient air, or this latter in complex interaction with liquids at the interface with the targeted organ. Our recent experiments performed on tissue oxygenation[2] or breast cancer treatments on immunocompetent mice [3] lead to the conclusion that probably the involved chemistry couldn't, alone, completely allow describing the observed phenomena. This, especially under very soft treatment conditions, is suggesting possible triggering of some immune system chain processes and also possible modifications in the microenvironment of tissue and tumors. In this context, there is still an unknown role of the electric field associated with the ionization front or generated in the environment of the plasma plume tip. Taking into consideration the recent vessel normalization based-cancer treatment, the ltNTP effect should be further investigated in view of blood vessels structure and function (blood flow) as well as tumor hypoxia compensation to confirm a possible ltNTP-based adjuvant approach for cancer treatments. These results suggest new ways, especially combined therapy, to consider the plasma and its therapeutic delivery in ltNTP-based tumor therapy. In this talk, after a presentation of the context and the plasma devices, we will go through the specific case of cancer treatment with what have been already demonstrated *in vitro* and *in vivo*, what can be directly linked with the produced discharges, including recent results on electric field measurements in plasma biological application conditions.

This work is supported by the APR Region Centre PLASMEDNORM.

References:

[1] H.R. Metelmann *et al* Clin. Plas Med. Doi.org/10.1016/j.cpme.2015.02.001

[2] G. Collet *et al* PSST **23** (2014) 012005

[3] G. Collet *et al* ICPM5, May 18-23, 2014, Nara (Japan)

8:40am **SM+AS+BI+PS-ThM3 Plasma Polymerized Polypyrrole Thin Films and Their Use in Drug Release Control**, *C. Li*, National Yang Ming University, Taiwan, Republic of China, ***Yung Te Lee***, National Central University, Taiwan, Republic of China, *J.H. Hsieh*, Ming Chi University of Technology, Taiwan, Republic of China

Polypyrrole thin films were deposited using a plasma polymerization process. During deposition, power input (between 30W to 70W), monomer (pyrrole) flow rate (30 sccm to 50 sccm), and Ar flow rate were varied. Optical emission spectroscopy (OES) was used to study the plasma characteristics under each deposition condition. After deposition, these films were characterized using FTIR, AFM, ellipsometry, ultraviolet–visible (UV–vis) spectroscopy, and surface profilometer. Eventually, these films were applied to control drug release rate under different thickness and structure. The results were correlated with the process parameters and plasma conditions.

9:00am **SM+AS+BI+PS-ThM4 Thin Film Metallic Glass: A Novel Coating for Various Biomedical Applications**, ***Chia-Chi Yu***, *Y. Tanatsugu, S. Chyntara, C.M. Lee, W. Diyatmika, J.P. Chu*, National Taiwan University of Science and Technology, Taiwan, Republic of China, *M.J. Chen, S.H. Chang, W.C. Huang*, Mackay Memorial Hospital Tamsui Campus, Taiwan, Republic of China

Thin film metallic glasses (TFMGs) exhibit unique properties such as high strength, smooth surface as well as good wear- and corrosion-resistances due to their amorphous atomic structure. The biocompatibility and antibacterial property of TFMGs can also be obtained, which show great potential for biomedical applications. In addition, the low surface free energy of TFMGs in certain compositions can be achieved and leads to the relatively high hydrophobicity and the low friction coefficient.

In this presentation, various applications of TFMG are discussed, including the property enhancements of dermatome blade and syringe needle, thrombosis reduction for intravenous catheter, and the suppression of cancer cell attachments. A Zr-based TFMG is coated on substrates by using magnetron sputtering. The TFMG-coated dermatome blade show a great enhancement of durability and sharpness, compared with those of the bare one. For the syringe needle, significant reductions in insertion and retraction forces for TFMG-coated needle are achieved due to the non-sticky property and relatively low coefficient of friction. For thrombosis reduction, less platelet aggregations are observed on the TFMG than that on the bare glass in platelets adhesion test, suggesting TFMG-coated catheters is potentially useful to be placed into vessels for long periods of time with reduced numbers of the aggregation of blood platelets. For cancer cell attachment suppressions, TFMG exhibits the least cancer cell attachment among other control groups. Thus, anti-proliferation and anti-metastasis of medical tools can be achieved with TFMG coating.

9:20am **SM+AS+BI+PS-ThM5 Plasma Surface Functionalization of Nano-structured Materials for Biomedical Applications**, ***Masaaki Nagatsu***, *H. Chou, A. Viswan, T. Abuzairi, M. Okada, M.A. Ciolan*, Shizuoka University, Japan, *N.R. Poespawati, R.W. Purnamaningsih*, University of Indonesia, *A. Sakudo*, University of the Ryukyus, Japan, *S. Bhattacharjee*, Indian Institute of Technology, Kanpur, India **INVITED**

In this study, we will present the recent experimental results on plasma surface functionalization of nano-structured materials for bio-medical applications.

First, with the graphite-encapsulated magnetic nanoparticles(MNPs), we studied the surface functionalization by using the Ar plasma pre-treatment followed by NH_3 plasma post-treatment, to introduce the amino groups onto the surface of the nanoparticles.[1)] The amino group population of each nanoparticle with a typical diameter of 20 nm was evaluated by using the conventional chemical technique using SPDP and DTT solutions and we obtained about 8×10^4 amino groups per nanoparticle.[2)] Immobilization of the antibody of influenza virus onto the surface of amino-modulated magnetic nanoparticles was then performed for aiming at studying the feasibility of collection and condensation of virus. After magnetic separation, we succeeded in a significant concentration of the influenza virus number compared with that of the initial sample.[3)] Using the same method, we also demonstrated a higher concentration of Salmonella about

70 times higher than that of initial sample by the magnetic separation.[4)] The present results suggest the feasibility of the proposed plasma surface functionalized MNPs for rapid concentration of influenza virus or various bacteria.

As the second topic, the selective ultrafine surface modification of functional groups onto the polymeric substrate or vertically aligned CNT dot-array with a dot size of several μm was investigated using the atmospheric pressure plasma jet with a nano/micro-sized capillary. The micro-sized surface modification of amino or carboxyl groups introduced onto the CNT dot-array were confirmed by the fluorescence labelling technique.[5)] With fluorescence-labeled avidin molecules, we also confirmed efficient capturing of avidin molecules by the biotin-immobilized CNT dot array through strong biotin-avidin binding process. The present result supports the feasibility of future biochip sensor to detect specific protein, virus or bacteria. In addition to these results, the other experimental results will be presented and discussed at the conference.

References

1) T. E. Saraswati, A. Ogino, M. Nagatsu, Carbon, 50 (2012) pp.1253-1261.

2) T. E. Saraswati, S. Tsumura, and M. Nagatsu, Jpn. J. Appl. Phys. 53 (2014) 010205(5 pages).

3) A. Sakudo, H. Chou, K. Ikuta, and M. Nagatsu, Bioorg. Med. Chem. Lett. 25 (2015) pp.1876–1879.

4) A. Sakudo, H. Chou, and M. Nagatsu, Bioorg. Med. Chem. Lett., 25 (2015) pp. 1012-1016

5) T. Abuzairi, M. Okada, Y. Mochizuki, N. R. Poespawati, R. Wigajatri and M. Nagatsu, Carbon, 89 (2015) pp. 208-216.

11:00am **SM+AS+BI+PS-ThM10 Tailoring Biomaterials-cell Interaction through Reactive Surface Modification**, ***Salvador Borros***, Institut Químic de Sarrià, Ramon Llull University, Barcelona, Spain **INVITED**

The immobilization of biologically active species is crucial for the fabrication of smart bioactive surfaces. For this purpose, plasma polymerization is frequently used to modify the surface nature without affecting the bulk properties of the material. Thus, it is possible to create materials with surface functional groups that can promote the anchoring of all kinds of biomolecules. Different methodologies in protein immobilization have been developed in recent years, although some drawbacks are still not solved, such as the difficulties that some procedures involve and/or the denaturalization of the protein due to the immobilization process. However, along with the chemical signals, the mechanical forces are critical for many tissues, since they are constantly suffering tension, shear, loading, etc. Essentially, the cell signaling exerted by forces is transduced through receptors that are in intimate contact with the matrix. Therefore, the main consequence of this receptor-matrix interaction is that cells and matrix are mechanically coupled, so that matrix deformation is considered the main cause of the mechanical signaling. By mimicking these mechanical forces in the surface of a material, it would be possible to obtain more physiological environments and thus a more physiological cell response. Again, the use of plasma polymerization techniques can help to design surfaces that can be tailored in terms of mechanical properties and chemical compositions and thus have a high potential for cells signaling.

This paper reports the work that we have developed in the last 10 years in the design, synthesis and characterization of thin films that can be a platform for studying the interaction between cells and separate influences of physical and chemical cues of a matrix on the adhesion, growth and final phenotype of cells.

11:40am **SM+AS+BI+PS-ThM12 Analysis of Amino Group Formation on Polystyrene Surfaces by Nitrogen-Hydrogen-Based Plasma Irradiation**, ***Kensaku Goto***, *D. Itsuki, M. Isobe, S. Sugimoto, S. Miyamoto, A. Myoui, H. Yoshikwa, S. Hamaguchi*, Osaka University, Japan

Polystyrene is a widely used cell-culture plate material. Currently cell culture plates on the market include those whose inner surfaces are covered with amino and/or carbonyl groups for a better control of cell adhesion to the plate surfaces. Such functional groups on a cell culture plate surface may immobilize glycoproteins or other biopolymers that function as extracellular matrices (ECM) and thus affect the environments where the cells are cultured. The goal of this research is to understand how such functional groups, especially amino groups, are formed on a polystyrene surface, depending on the deposition methods. Of particular interest are plasma-based methods of surface functionalization. In this study, we have observed experimentally how exposure of N_2/H_2 or N_2/CH_3OH plasmas to polystyrene surfaces form amino-group-like structures and also examined using molecular dynamics (MD) simulation how a polystyrene surface interacts with incident energetic ions such as NH_3^+ as well as abundant low-energy radicals such as NH_2 under conditions similar to our experiments. In the experiments, we used parallel-plate discharges with an inverter power supply whose peak-to-peak voltage was about 3kV and frequency was 20kHz at a relatively high gas pressure of 250 - 2,500 Pa. In MD simulation, we used a simulation code with interatomic potential functions that had been developed in-house based on quantum mechanical calculations of atomic interactions involved in this system. Results of MD simulations under the conditions similar to plasma enhanced chemical vapor deposition (PE-CVD) by ammonia plasmas or cyclopropylamine (CPA) [1] suggest that, with energetic ion bombardment, amino groups tend to be broken to form new covalent bonds by ion bombardment. Preliminary results of cell culture experiments with plasma-treated polystyrene cell plates will be also reported.

[1] A. Manakhov, L. Zajickova, *et al*. Plasma Process. Polym.11, (2014) 532.

12:00pm **SM+AS+BI+PS-ThM13 Tailoring the Surface Properties of Three-Dimensional, Porous Polymeric Constructs for Biomedical Applications Using Plasma Processing**, ***Morgan Hawker***, *A. Pegalajar-Jurado, E.R. Fisher*, Colorado State University

Utilizing bioresorbable polymers to fabricate constructs with three-dimensional (3D), porous architectures is desirable as these constructs mimic the extracellular matrix– a critical characteristic for many biomedical applications including tissue engineering, controlled-release drug delivery, and wound healing. Although the bioresorbability and architecture of these materials are suitable for such applications, the surface properties (i.e., chemical functionality and wettability) must often be customized depending on the desired function. Plasma processing is an attractive tool for surface modification of these delicate polymeric materials as it provides a low-temperature, sterile environment with a variety of precursor choices. The presented work will highlight the plasma modification of a variety of 3D, porous polymeric constructs. Specifically, we fabricated scaffolds via electrospinning and porogen leaching techniques using both poly(ε-caprolactone) (PCL) and polylactic acid (PLA) to develop a repertoire of native polymer constructs with differing bulk properties. We evaluated the efficacy of plasma-modifying 3D constructs using contact angle goniometry, X-ray photoelectron spectroscopy, and scanning electron microscopy to assess changes in wettability, chemical functionality, and scaffold architecture. The interactions of plasma-modified scaffolds with different biological species, including human dermal fibroblasts and *Escherichia coli* were explored, specifically to assess scaffold bioreactivity. Notably, we demonstrate that scaffold properties, and thus bioreactivity, can be customized depending on the choice of plasma precursor. We show that plasma treatment using fluorocarbon and hydrocarbon precursors (i.e., octofluoropropane, hexafluoropropylene oxide, and 1,7-octadiene) results in hydrophobic and bio-non reactive scaffolds. Additionally, precursors with nitrogen and oxygen functionality (i.e., allylamine, allyl alcohol, water, and ammonia) can be used to fabricate scaffolds that are hydrophilic and bio-reactive. Altogether, this work illustrates the comprehensive tunability of biologically-relevant polymeric constructs in terms of their bulk properties, surface properties, and cell-surface interactions.

Thin Film
Room: 114 - Session TF+EM+NS+PS+SM-ThM

Plasma ALD and Nano-applications
Moderator: Christophe Vallee, LTM, Univ. Grenoble Alpes, CEA-LETI, Richard Vanfleet, Brigham Young University

8:00am **TF+EM+NS+PS+SM-ThM1 Atomic Layer Deposition of Silicon Dielectrics: Precursors, Processes, and Plasmas**, ***Dennis Hausmann***, Lam Research Corporation **INVITED**

As the dimensions of modern semiconductor devices continue to shrink below the current 14 nm technology node, novel processes for the deposition of highly conformal, low temperature, silicon based dielectrics will be needed for applications that include sidewall spacers, barriers, and patterning layers. Atomic layer deposition (ALD) is an ideal method for achieving the high conformality and has been used in high volume manufacturing (HVM) to deposit high-k dielectric materials (HfO_2, ZrO_2, etc.) for several technology generations. Plasma assisted ALD is the best known method to meet low temperature (<500^0C) requirements and is now being used for depositing conformal silicon dielectrics such as silicon oxide (SiO_2) and silicon nitride (Si_3N_4).

In this presentation, we discuss the current state of the art of precursors, plasmas, and process conditions required to deposit conformal silicon dielectrics by plasma ALD. Theoretical and experimental data will be presented in order to explain the observed reaction characteristics for the

plasma ALD of silicon oxide (SiO_2), silicon nitride (Si_3N_4), and the lack (so far) of silicon carbide (SiC). Generic to all ALD processes is the high cost of the precursors relative to traditional chemical vapor deposition (CVD); in the case of silicon dielectric ALD, this is exacerbated by the relative low "reactivity to cost ratio" of available silicon precursors. Although plasmas enable low temperature deposition, they pose challenges for achieving isotropic film properties over the complex topography on today's semiconductor devices.

8:40am **TF+EM+NS+PS+SM-ThM3 ALD Dielectrics for Power Electronics**, ***Veena Misra***, NCSU **INVITED**

Owing to a high critical electric field and high electron mobility, wide band gap materials such as GaN and SiC are being sought for high voltage power electronics applications. In the case of GaN devices, the reliability continues to be a challenge to must be addressed before successful commercialization. In our work, different dielectrics deposited by Atomic Layer Deposition (ALD) have been investigated for improving the threshold voltage stability and dynamic reliability of AlGaN/GaN based MOSHFETs. A novel pulsed-IV-based methodology was developed and demonstrated to be applicable for detecting both shallow and deep traps and implemented on evaluating different high-k and low-k ALD dielectrics. Using physics-based simulation models and experimental data, it was demonstrated that the leakage at the surface of the AlGaN, whether through the passivation dielectric bulk or the dielectric/AlGaN interface, must be minimized to restrict the formation of a "virtual gate" and minimize current collapse. It was also found that an optimal passivation dielectric must create a high density of shallow interface donor traps to quicken the de-trapping of electrons from the "virtual gate" and the recovery of the channel underneath. Combining simulation and experimental results, an optimal set of ALD dielectrics for a reliable gate stack and access-region passivation regions, respectively, was determined and will be discussed. In the area of SiC devices, low inversion channel mobility, caused high density of interface states (Dit) at SiO2/SiC interface, limits the wide adoption of SiC MOS devices. Atomic Layer Deposition offers key advantages in the area of gate dielectrics such as good film quality, low substrate damage, superior uniformity, precise thickness control, and low process temperature. Additionally, deposited SiO2 enables interface engineering to independently control the interface properties. To enhance the channel mobility and maintain good overall gate dielectric properties, a thin layer of a different dielectric material can be inserted to improve interface properties and high quality deposited SiO2 can be used as the bulk gate dielectric. We have demonstrated a novel interface engineering technique utilizing ultra thin lanthanum silicate (LaSiOx) at the SiC/dielectric interface and ALD SiO2 as the bulk gate dielectric. The lanthanum silicate interface engineering dramatically improves the mobility of 4H-SiC metal oxide semiconductor field effect transistors (MOSFETs) and is attributed to the large driving force of La_2O_3 to react with SiO_2.

9:20am **TF+EM+NS+PS+SM-ThM5 $Pb(Zr_xTi_{1-x})O_3$ Magnetoelectric Tunnel Junctions for Magnetoelectric RAM (MeRAM) Memory Applications**, *D. Chien, X. Li, K. Wong, P. Khalili, K. Wang*, ***Jane P. Chang***, University of California at Los Angeles

As existing memory systems approach fundamental limitations, ultra-thin uniform conformal PZT films are needed for next-generation ultralow-power voltage-controlled non-volatile magnetoelectric RAM (MeRAM) memory devices. By utilizing the magnetoelectric effect, where an electric field or voltage can be used to control the magnetization switching (instead of current), the writing energy can be reduced, resulting in increased memory density (Amiri, P.K. et al., Journal of Applied Physics, 2013). Previous research has shown that the voltage-controlled magnetic anisotropy (VCMA) effect increases with the capacitance of the stack (Kita, K. et al., Journal of Applied Physics, 2012). Therefore, integrating an ultra-thin PZT film (having a dielectric constant 1-2 orders of magnitudes higher than currently used MgO) into the tunneling oxide layer will enhance the VCMA coefficient, allowing for a lower voltage to switch the magnetization of the free magnetic layer and thus decreasing the write energy.

Using atomic layer deposition (ALD), a surface-reaction controlled process based on alternating self-limiting surface reactions, an ultra-thin film of PZT can be synthesized with precise control of the film thickness and elemental composition (Zr/Ti = 52/48). 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 $Ti(O^{\cdot}i\text{-}Pr)_2(TMHD)_2$ 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. The bottom layers of Ta/CoFeB (free magnetic layer)/MgO were sputtered, the PZT film with thickness of 1.7 nm was deposited by ALD, the top layers of MgO/CoFeB (fixed magnetic layer)/Ta/Pt were sputtered, and the entire stack was annealed at 200^oC for 30 minutes in order to fabricate PZT magnetoelectric tunnel junctions (MEJs).

The perpendicular magnetic anisotropy (PMA) of the bottom free magnetic CoFeB layer was verified via superconducting quantum interference device (SQUID) magnetometer, confirming that the ALD PZT deposition process is a viable method for synthesizing PZT MEJs. The tunnel magnetoresistance (TMR) was measured to be 50%, demonstrating a promising read-out process. Due to the integrated ALD PZT layer in the tunneling barrier, the VCMA coefficient of PZT MEJ devices is expected to be double that measured for CoFeB/MgO/CoFeB devices (ξ = 37 fJ/V·m) (Zhu, J. et al., Physical Review Letters, 2012).

9:40am **TF+EM+NS+PS+SM-ThM6 Plasma-Assisted ALD of High-Quality Molybdenum Oxide Films**, ***Martijn Vos***, *B. Macco, N.F.W. Thissen, A.A. Bol, W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

In this contribution we present a novel plasma-assisted atomic layer deposition (ALD) process to deposit high-quality molybdenum oxide films, with a high growth per cycle (GPC) over a wide temperature range of 50 °C to 350 °C. This process complements existing (thermal) ALD MoO_x processes, which are less suited for deposition at low temperature, due to low GPC and contamination. A decent deposition process is of importance as MoO_x films have received great interest due to their remarkable optoelectronic and catalytic properties and find their use in many applications, including solid state lithium batteries, gas sensors, and more recently solar cells.

A variety of deposition techniques exists for the deposition of MoO_x, such as evaporation, sputtering, chemical vapor deposition and ALD. While many of the applications of MoO_x films can benefit from the merits of ALD, i.e. conformality and digital thickness control, only few ALD processes are known from literature [1, 2]. Recently bis(tert-butylimido) bis(dimethyamido) molybdenum ($(NtBu)_2(NMe_2)_2Mo$) appeared as a promising precursor for ALD of MoO_x films, using O_3 as oxidant [2].

The plasma-assisted ALD process we report on uses $(NtBu)_2(NMe_2)_2Mo$ and O_2 plasma and shows a relatively high GPC between 0.70 Å and 0.93 Å for amorphous films deposited at temperatures up to 250 °C. In comparison, the analogous O_3 process is featured by a low GPC of 0.17 Å at 150 °C. For deposition temperatures above 250 °C polycrystalline growth was observed, accompanied by an increase in GPC to 1.88 Å for 350 °C. From Rutherford backscattering measurements it was determined that the C and N content in the films is below the detection limit (3 at.% and 2 at.% respectively) for all deposition temperatures, which demonstrates the high-quality of the films (while the aforementioned O_3 process resulted in 9.2 at.% N). Furthermore the O/Mo ratio was found to be just below 3, indicative of oxygen vacancies, which are common for MoO_x films and can lead to an increased conductivity, which is beneficial for many applications. Additional material properties such as band gap, work function and surface morphology will also be discussed and finally an outlook to the application of this ALD process in silicon solar cells will be given.

[1] M. Diskus *et al.*, J. Mater. Chem. **21** (2011) 705

[2] A. Bertuch *et al.*, J. Vac. Sci. Technol. **32** (2014) 01A119

11:00am **TF+EM+NS+PS+SM-ThM10 Status and Prospects of Plasma-Assisted Atomic Layer Deposition**, ***Harm Knoops***, Oxford Instruments Plasma Technology, UK, *W.M.M. Kessels*, Eindhoven University of Technology, Netherlands **INVITED**

Plasma-assisted atomic layer deposition (ALD) or plasma ALD has established itself as a prominent branch in ALD processing and a wide range of plasma ALD processes are currently available. Due to the complexity of plasmas, plasma ALD is different from thermal ALD in various aspects. Even though the main relevant species in plasmas have been identified,[1] the effects of plasma chemistry and plasma-surface interaction need further study. In this contribution an overview on the status of plasma ALD is given and the key prospects for plasma ALD are highlighted.

Regarding the current understanding of plasma ALD, three subjects will be treated. First the basic plasma species (i.e., radicals, electrons, ions, and photons) and their role in plasma ALD will be discussed. For instance, potential damage to the surface from photons, but also cases where plasma species can repair defects (e.g., N_2 plasmas on GaN surfaces).[2] Second plasma chemistry and potential poisoning or inhibition processes will be treated, which can play a big role in the ALD of nitrides and conductive films. Third, dissociation in the plasma of reaction products can lead to redeposition effects which can have a large influence on for instance SiN_x and TaN_x ALD.

Several topics will be discussed regarding the prospects for plasma ALD. Even though plasma ALD provides additional possibilities, many cases exist where material properties or cycle times are still unsatisfactory and advances in reactor design such as the capability to provide additional energy in the form of a controlled ion bombardment are needed. In addition,

advanced processing schemes such as 3-step ABC ALD cycles can be beneficial as shown by ALD of noble metals at low deposition temperatures (e.g., Pt ALD).[3] Whether metal films initially grow as continuous films or as nanoparticles (as well as the particle size), will depend on the chemistry, the surface energy, and the growth temperature. Recently, plasma ALD has shown to allow ALD of Ag by spatial ALD at high pressure.[4] This case shows that more understanding of the plasma is needed because of an unexpected decreased growth at long plasma exposures (presumably caused by NH_3 poisoning). In general, increasing control of the plasma and understanding of the relevant processes at the surface and in the plasma will be key to further develop plasma ALD.

[1] Profijt et al., *JVST A* **29**, 050801 (2011)

[2] Chen et al., *Phys. Status Solidi A* (2014) / DOI 10.1002/pssa.201431712

[3] Mackus et al., *Chem. Mater.* **25**, 1769 (2013)

[4] Van den Bruele et al., *JVSTA* **33**, 01A131 (2015)

11:40am **TF+EM+NS+PS+SM-ThM12 A Novel Plasma-Enhanced ALD Process for HfO_2 using $HfCp(NMe_2)_3$ and O_2 Plasma**, ***Akhil Sharma**, V. Longo, A.A. Bol, W.M.M. Kessels*, Eindhoven University of Technology, The Netherlands

In atomic layer deposition (ALD) the associated precursor chemistry has a large effect on the quality and properties of the deposited thin films. The most commonly used hafnium precursor for ALD of HfO_2 is $HfCl_4$. This precursor is not ideal for all applications due to possible chlorine contamination and the generation of corrosive by-products during the ALD process. Organometallic precursors such as $Hf(NtMe)_4$ promise to be a better choice but they typically suffer from a limited thermal stability. In this context, $HfCp(NMe_2)_3$ might offer a better alternative because of its higher thermal stability. However, while using H_2O as oxygen source in a thermal ALD process it yields a low growth rate[1]. This creates an opportunity for studying this precursor in combination with other oxygen sources. In this work, we report on the development of a novel plasma-enhanced ALD (PE-ALD) process using $HfCp(NMe_2)_3$ in combination with an O_2 plasma to deposit HfO_2 thin films. To our knowledge, to date, the PE-ALD for this precursor has not been reported in the literature.

Our results show that the PE-ALD process offers significant advantages over the reported thermal ALD process such as a high growth rate, reduced deposition temperature, shorter cycle time and good control over composition of the deposited films. In contrast to the thermal ALD process using $HfCp(NMe_2)_3$ and water[1], the PE-ALD process has resulted into a wide ALD temperature range (150-400°C) with significantly higher growth per cycle values (1.1Å/cycle) and shorter cycle times which ultimately improves the wafer throughput. The level of impurities were found to decrease with increasing the deposition temperature as concluded from XPS and ERD analyses. The concentrations of residual carbon and hydrogen reduced from 1.0 at% to 0.2 at% and 3.4 at% to 0.8 at%, respectively, by increasing the deposition temperature from 200°C to 400°C. Moreover, RBS studies showed an improvement in stoichiometry of HfO_2 thin films with increase in deposition temperature resulting in a Hf/O ratio of ~0.5 at 400°C. Furthermore, GI-XRD measurements detected a strong transition from amorphous (300°C) to fully crystallized films (400°C), consisting of a mixture of monoclinic, tetragonal and cubic phases. These results therefore have demonstrated that PE-ALD using $HfCp(NMe_2)_3$ and O_2 plasma is a promising and viable alternative to the thermal ALD process producing high quality HfO_2 thin films over a wider temperature range and with faster cycle times.

1. Consiglio et al, J. Vac. Sci. Technol. A 30(1), 2012

12:00pm **TF+EM+NS+PS+SM-ThM13 Conductive Hafnium Nitride Layers By Plasma-Assisted Atomic Layer Deposition**, ***Saurabh Karwal**, B.L. Williams, W.M.M. Kessels, M. Creatore*, Eindhoven University of Technology, The Netherlands

Transition metal nitrides (TMNs) have gained much attention in the semiconductor industry due to their characteristics such as copper and lithium diffusion barriers, metal-like behaviour (i.e. low resistivity) and high hardness, mechanical strength and chemical inertness. Among TMNs, hafnium nitride exhibits a low bulk resistivity of 33 μΩcm and highest negative Gibbs free energy of formation (HfN: -88.2, TiN: -80.4, TaN: -60.3 kcal/mol) and hence could serve as novel material for several applications, such as diffusion barrier and gate electrode in microelectronics, and reflective back contact for CIGS solar cells.

Conductive hafnium nitride thin films were deposited by inductively coupled plasma (ICP)- assisted atomic layer deposition using a heteroleptic metalorganic hafnium precursor, tris(dimethylamino)cyclopentadienylhafnium $CpHf(NMe_2)_3$ [TDMACpH] and H_2-or N_2- fed plasmas serving as co-reactants. The effects of the substrate temperature, plasma chemistry and plasma exposure time have been investigated in terms of growth-per-cycle (GPC), chemical, electrical and morphological properties of the deposited layer. It has been observed that highly resistive (0.75 Ωcm) Hf_3N_4 thin films are obtained via an A-B type ALD cycle (TDMACpH/N_2 –fed plasma) with a GPC of 0.035 nm/cycle. Furthermore, a limited abstraction of the ligands leads to a residual carbon content in the layer of 7%.

Instead, conductive films (1.8 x 10^{-3} Ωcm) are achieved upon the application of an A-B-C ALD cycle where an intermediate H_2- fed plasma exposure step is included between the TDMACpH exposure and the N_2-fed plasma step, with a GPC of 0.045 nm/cycle. This intermediate step is found to be responsible for a more efficient removal of the precursor ligands and for the reduction of Hf^{4+} state to Hf^{3+} state, essential for guaranteeing electron conductivity. This transition of chemical and electrical properties of the deposited thin films is also accompanied by a change in crystallographic properties from amorphous (A-B ALD cycle) to conductive cubic HfN (A-B-C ALD cycle), as revealed by grazing incidence X-ray diffraction.

Contact: s.karwal@tue.nl

Plasma Science and Technology
Room: 210B - Session PS+AP+SE-ThA

Advanced Ion Implantation and Plasma Doping
Moderator: Aseem K. Srivastava, Applied Materials, Inc.

2:20pm **PS+AP+SE-ThA1 Evolutionary Trends in Ion Implantation**, ***Anthony Renau***, Applied Materials, Varian Semiconductor Equipment **INVITED**

Since the 1960s and 1970s ion implantation has been used for the p- and n-type doping of semiconductors. The ability of ion implantation to abruptly alter the stoichiometry of the substrate has made it a very attractive technology for making transistors with the required drive characteristics, by accuratley manipulating dopant concentrations in the contact and channel regions. It is used to control carrier density, channel length, contact resistance, isolation and other key device attributes.

There have been significant enhancements to enable ion implant to continue to meet semiconductor doping needs. These include the development of ribbon ion beams, substrate temperature control, accurate beam angle control and novel methods for precisely varying the dose over the substrate. These improvements have also enabled the technology to be used for a rapidly growing number of non-doping applications.

Today, the majority of implants are done not for doping, but are instead used for some form of materials modification or engineering. These include, for example, strain control, pre- or post-treatments to improve some other process step, and lattice enginering for isolation or diffusion control.

In this paper we will discuss some of the improvements to the technology and the applications that have benifited from these. We will also describe how directed ribbon beam technology, similar to that used for implanters, can also be used to improve materials engineering applications as diverse as etch and CMP.

3:00pm **PS+AP+SE-ThA3 Conformal Arsenic Doping using a Radial Line Slot Antenna Microwave Plasma Source**, ***Hirokazu Ueda***, Tokyo Electron Limited, Japan, *P. Ventzek,* Tokyo Electron America, Inc., *M. Oka, Y. Kobayashi, Y. Sugimoto,* Tokyo Electron Ltd., *T. Nozawa,* Tokyo Electron Ltd., Japan, *S. Kawakami*, Tokyo Electron Ltd. **INVITED**

Doping and activation of non-planar topographic structures is important for the fabrication of functional FinFET and nanowire based devices to name a few. Conformal plasma arsenic doping of topographic (fin) structures was achieved using RLSA™ microwave plasmas with low temperature annealing. To show that the arsenic concentrations were identical at the fin top and sides, dopant concentrations were measured precisely by TEM and SEM EDX for both plasma doping and subsequent annealing steps. We found that doping using plasmas generated by lower RF bias operation coincident with high microwave power was key to obtaining perfectly conformal arsenic dose/profiles after annealing. The RLSA™ microwave plasma facilitates high enough electron density at the plasma generation region to supply enough reactive dopants for sufficient dose. The high plasma density plasma allows for operation in a low RF power and high process pressure regime. This regime yields ions with sufficient flux and energy for dopant integration into and redistribution around the topographic structure. At the same time low enough energy ions can be controllably accessed to ensure fin damage is eliminated. We also demonstrate optimized rf bias power of the microwave RLSA™ plasma enables additional control of dopant conformality post SPM wet cleaning step. The wet clean poses a significant challenge for dose retention as cleans tend to remove oxidized or otherwise disordered silicon material. The source of dose retention is shown to be related to dopant transport through a ternary (As-Si-O) oxide layer, segregation effects and the stable nature of the oxide. The presentation will include experimental and computational results related to dose conformality and retention. Comments related to the future of plasma doping technology including advanced materials, metrology and control will round out the presentation.

4:00pm **PS+AP+SE-ThA6 Practical Application of Atom Probe to Analysis of Ion Implantation**, ***Ty Prosa***, CAMECA Instruments Inc. **INVITED**

Characterization of implanted dopants and impurity atoms within individual silicon nano-devices is critical to the semiconductor industry. While secondary ion mass spectrometry (SIMS) depth profiles achieve a high level of quantification with ion implanted standards in various matrices, atom probe tomography (APT) offers a unique combination of high analytical sensitivity coupled with high spatial resolution [1]. SIMS achieves its sensitivity by analyzing relatively unconstrained sample volumes, analyzed areas often greater than several hundred square microns. Square microns of material cannot be analyzed by APT and so it can never compete with SIMS for sensitivity at the micron scale; however, the situation is very different at the nanoscale—the regime of individual device volumes. Within this regime APT has high, uniform, quantitative chemical sensitivity with sub-nanometer spatial sensitivity.

Understanding the precision and accuracy of APT when applied to ion implanted dopant profiles is essential for general adoption by the semiconductor industry. Three-dimensional atom positions are determined using a simple point-projection methodology [2]. Adopting best practices within the constraints of this methodology is necessary to allow uniform and unbiased determination of atom positions and depth profiles. Although the ultimate sensitivity of APT is determined by counting statistics, it is well known that counting statistics alone do not fully account for accuracy limitations. The free parameters available within the reconstruction process are often dominant in terms of total observed error.

During this presentation, a number of examples will be shown of APT applied to the analysis of dopant distributions in relevant structures. The focus will be ion implanted structures with discussion of best practice approaches to minimize error and remove bias by the practitioner. Material structures include a series of NIST Standard Reference Material implants into silicon [3] and additional implants into GaN-based materials.

[1] T.F. Kelly and D.J. Larson, *Annual Reviews of Materials Research* 42 (2012) 1.

[2] P. Bas et al., *Surf. Sci.* 87/88 (1995) 298.

[3] R.R. Greenberg et al., *Radioanal. Nucl. Chem,* 245 (2000) 57.

4:40pm **PS+AP+SE-ThA8 Optical Emission Spectroscopy to Determine Plasma Parameters in an Oxygen Inductively Coupled Plasma**, ***Nathaniel Ly***, *J. Boffard, C.C. Lin, A.E. Wendt,* University of Wisconsin - Madison*, S. Radovanov, H. Persing, A. Likhanskii*, Applied Materials, Inc.

The success of ion implantation to precisely modify substrate properties requires control of the incident ion energies to achieve the desired depth of the implanted ions. Oxygen plasmas generally contain both O^+ and O_2^+ positive ions, and in plasma immersion ion implantation (PIII) of oxygen, the two will produce different concentration depth profiles due to their different energy/mass ratios. Predicting the overall profile thus requires knowledge of the relative fluxes of the two ion species. Motivated by the long term goal of a robust predictive model, here we combine experiment and numerical simulation to investigate the feasibility of using non-invasive optical emission spectroscopy (OES) to monitor plasma parameters in an oxygen inductively-coupled plasma. Initial experiments made use of a small admixture of argon with the oxygen to take advantage of established techniques involving argon OES. In addition to recording argon emissions, measurements of multiple O, O_2, O^+, and O_2^+ emission intensities were made as a function of pressure (1-30 mTorr) and power (500-2000 W). An emission model makes use of available electron impact excitation cross sections for argon and atomic and molecular oxygen to relate measured emission spectra to corresponding plasma parameters, including electron temperature and the dissociation fraction of the neutral oxygen. Data taken while as a function of the percentage of argon in the Ar/O_2 mixture showed that even a very small admixture of argon significantly affected the oxygen plasma properties, and more recent experiments have thus focused on oxygen OES in a pure oxygen plasma. The CRTRS 2D/3D plasma code self-consistently and semi-implicitly solves for ICP power deposition and uses Poisson's equation to solve for the electrostatic potential and dynamics of electrons and ions in the drift-diffusion approximation (or full momentum equations). The code also solves for the electron temperature, and generation and quenching of excited states as well as their dynamics. The experimental results are used in combination with simulation predictions to understand the dependence of plasma parameters, including the relative fluxes of O^+ and O_2^+, on the operating parameters.

The authors acknowledge support from NSF grant PHY-1068670.

5:00pm **PS+AP+SE-ThA9 Adhesion Improvement of Carbon Nitride Coatings on Steel Surfaces by Metal Ion Implantation using HiPIMS**, ***Konstantinos Bakoglidis***, *G. Greczynski, S. Schmidt, L. Hultman*, Linkoping University, Sweden

Carbon based thin films are materials with low friction and wear resistance. Deposition of C based thin films as coatings on steel substrates can enhance the tribological performance of steel surfaces. Adhesion of magnetron sputtered C based coatings on steel substrates is, however, often

insufficient, leading to film delamination or flaking after the deposition. Adhesion is essential when such films are exploited in tribological applications and can be improved by using ion etching of the steel surface prior to film deposition. Several ion etching techniques are used, among them metal ion etching, for ion implantation in order to prepare the steel surface for the C film deposition. Moreover, high power impulse magnetron sputtering (HiPIMS) offers high metal ionization conditions and effectively enhances ion implantation into the steel subsurface. In this study, we used four different metal targets, namely Al, Cr, Zr, W, in HiPIMS mode in Ar-based plasma with a pressure of 200 mPa, and under a negative applied bias voltage of 900 V, which was synchronized with the cathode pulse. All targets were operated with an energy per pulse of 15 J, with pulse width of 200 µs, an etching time of 30 s, while the frequency was set at 100 Hz. A carbon nitride (CN_x) thin film was deposited after each etching step, using a graphite target in DC mode, operated at 1400 W, in a N_2/Ar gas mixture with a ratio of 0.16, and at a temperature of 150 °C, while the pressure was kept constant at 400 mPa. In all cases except Zr, a thin metal interlayer was obtained, with thicknesses < 20 nm, while adhesion of CN_x films on steel surface was dramatically improved when W ions were used for the pre-treatment phase.

Plasma Science and Technology
Room: 210A - Session PS-ThA

Plasma Sources
Moderator: Cheng-Che Hsu, National Taiwan University

2:20pm **PS-ThA1 Control of Electron Heating and Ion Energy Distributions in Capacitive Plasmas by Voltage Waveform Tailoring based on a Novel Power Supply and Impedance Matching**, ***Birk Berger***, *J. Franek, St. Brandt,* West Virginia University, *M. Liese, M. Barthel,* Barthel HF-Technik GmbH, Germany, *E. Schuengel, M. Koepke, J. Schulze*, West Virginia University

We present a novel radio-frequency (RF) power supply and impedance matching to drive technological plasmas with customized voltage waveforms. It is based on a system of phase-locked RF generators that output single frequency voltage waveforms corresponding to multiple consecutive harmonics of a fundamental frequency. These signals are matched individually and combined to drive an RF plasma. Electrical filters are used to prevent parasitic interactions between the matching branches. By adjusting the harmonics' phases and voltage amplitudes individually any voltage waveform can be realized as a customized finite Fourier series. This RF supply system is easily adaptable to any technological plasma for industrial applications and allows the commercial utilization of process optimization based on voltage waveform tailoring for the first time. Here, this system is tested on a capacitive discharge based on three consecutive harmonics of 13.56 MHz in Argon with an admixture of Neon as tracer gas for Phase Resolved Optical Emission Spectroscopy (PROES). Measurements were performed for gap lengths of 30mm and 40mm, different pressures (p=3, 5, 200Pa) and varying applied voltages (V=120, 210V). According to the Electrical Asymmetry Effect, tuning the phases between the applied harmonics results in an electrical control of the DC self-bias and the mean ion energy at almost constant ion flux. A comparison with the reference case of an electrically asymmetric dual-frequency discharge reveals that using more than two consecutive harmonics significantly enlarges the control range of the mean ion energy. Additionally, the effect of tuning the phases on the electron heating and sheath dynamics within one low frequency cycle is investigated using PROES and correlated with changes of ion energy distributions at the electrodes.

2:40pm **PS-ThA2 Spectroscopic and Beam Current Characterisation of an RF Excited Argon Plasma Cathode Electron Beam Gun for Material Processing Applications**, ***Sofia del Pozo,*** TWI Ltd. and Brunel University, United Kingdom of Great Britain and Northern Ireland, *C.N. Ribton,* TWI Ltd., United Kingdom of Great Britain and Northern Ireland, *D.R. Smith*, Brunel University

Details are given of a design of a novel RF excited plasma cathode gun that generates electron beams (EBs) for material processing applications including additive manufacturing, welding and cutting. Plasma EB sources offer solutions to the main problems with conventional electron beam guns, which use a thermionic cathode. Cathode wear from thermal cycling or ion bombardment is eliminated. EB power can be controlled by RF power modulation, which avoids the need for a grid electrode, and as a result reduces beam aberration. This technology has generated interest from various sectors of industry including additive manufacturing where rapid printing would be possible due to the high power provided by the electron beam, and at the same time fast beam pulsing can control material melting.

In this work, EBs were generated at accelerating potentials between 30 kV and 60 kV with beam powers of up to 1kW. The experimental setup allowed carrying out optical emission spectroscopy measurements simultaneously with beam current measurements.

A capacitively coupled plasma was generated in a cylindrical quartz chamber with 14 mm inner diameter. An RF power signal of 20 to 50 W at 84 MHz was applied between electrodes separated by 25 to 80 mm. Electrons were extracted from the plasma chamber to the vacuum chamber (at about 10^{-5} mbar) through an aperture (0.8 to 1.2 mm diameter) at the end of the plasma chamber by applying an accelerating voltage. Typically argon was used but EBs were also generated using krypton, helium and air. The pressure in the plasma chamber was controlled in the range 0.1 mbar to 1.5 mbar.

Optical emission spectroscopy measurements have been carried out in order to optimise plasma parameters for higher electron emission. This plasma diagnosis technique was selected as it is non-intrusive and allows estimation of important plasma parameters such as electron density and temperature. The spectra were correlated with electron emission. Ar – II lines were found to be much intense than Ar – I lines in those plasmas of higher electron emission. It was observed that the electron beam power was increased as the plasma chamber pressure decreased in one of the plasma chamber geometries. At any one plasma pressure, the beam power increased with RF power.

Further work is currently being carried out in order to increase the power of the electron beams generated. This includes revised plasma chamber designs and particle in cell simulation of the argon plasma.

3:00pm **PS-ThA3 Around the World of RF-Plasma Generation: A Brief Tour in 80 (half) Minutes**, ***Neil Benjamin***, Lam Research Corporation **INVITED**

This paper starts with a review of historical progress to reach the present day, when it is virtually universal to use RF excited plasmas to process semiconductor materials. This may extend to hundreds of process steps as Deposition, Etching, Stripping, Cleaning and Surface treatments are all in the RF-plasma repertoire. In order to do so, multiple factors and timelines have had to converge, including:

I. Electronics development, specifically RF technology and devices.

II. Plasma Technology A.K.A. Gaseous Electronics, specifically Dry Processing as applied to: Semiconductors, Flat panel displays, P-V solar panels, MEMs devices etc.

It is less than 70 years since the invention of active solid state electronics in 1947, but the semiconductor industry is now mature and consolidated while continuing to advance according to Moore's law. In the same period RF delivery systems have also progressed from high power vacuum tubes/valves to solid state devices in the 1980s. Most such RF systems use 50Ω transmission lines (for I.S.M.) so that matching networks are used to optimize power transfer to the antenna load impedance. Plasma technology use for semiconductor production did not start until the late 1960s / early 70s. In particular, despite the engineering complications of dealing with RF excitation, RF plasmas became popular because of their suitability for use with dielectric materials, and ameliorating the potential for damage caused by passing DC currents through delicate devices during manufacture.

In the second half of the paper we consider that while the technology involved in plasma processing has remained basically the same for nigh on 50 years, the demands on RF performance, control and consistency have escalated beyond all recognition. I will address some typical RF-plasma issues with examples taken from the current state of the art that continue to challenge us. These include igniting and delivering RF into the changing load impedance of a transient plasma, whether due to instability or by design. Another is dealing with the problem of stable and consistent excitation when there are multiple frequencies present either due to multiple source frequencies or due to the plasma generation of harmonics and mixing products. I will discuss how we achieve stable performance in terms of both uniformity and tool matching, in part by using sensor based control schemes. The question we must answer going forward is whether we can maintain or indeed improve this level of precision and performance, but do so ever more cost effectively.

4:00pm **PS-ThA6 Electron Beam Generated Plasmas Produced in Fluorine-Containing Gases: Characterization of Plasma-Surface Interactions**, ***Scott Walton***, *D.R. Boris,* US Naval Research Laboratory, *R.F. Fernsler,* Sotera Defense Solutions, Inc., *S.C. Hernández, Tz.B. Petrova, G.M. Petrov*, US Naval Research Laboratory

Electron beam generated plasmas are characterized by high plasma densities (> 10^{10} 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 characterizing the flux of species incident to substrates located adjacent to magnetically collimated electron beam generated plasmas produced in fluorine-containing gases (e.g. SF_6, C_xF_y, etc). In particular, the type and energy of the ions at the substrate surface are measured as function of relative gas concentration and substrate-to-beam distance. These results are complimented by bulk plasma measurements and modeling and then discussed in terms of the changes in surface directed ion flux caused by changes in electron temperature and density, and electronegativity associated with the introduction of attaching gases to very low T_e plasmas. This work is supported by the Naval Research Laboratory Base Program.

4:20pm **PS-ThA7 Electron Beam Generated Plasmas Produced in Fluorine-Containing Gases: Characterizing Plasma Parameters**, ***David Boris**, G.M. Petrov,* Naval Research Laboratory*, R.F. Fernsler,* Sotera Defense Solutions*, Tz.B. Petrova, S.G. Walton*, Naval Research Laboratory

Electron beam generated plasmas are characterized by high plasma density (>10^{10} cm^{-3}), and very low electron temperatures (<1 eV) making them well suited to next generation processing techniques where high fluxes of low energy ions are desired. In this work, we focus on the characteristics these plasmas in fluorine containing chemistries (SF_6, C_xF_y), due to their relevance to industrial etching applications. In particular we focus on the effect of dilute fluorine gas mixtures on the electron density, total plasma density, electronegativity, and electron temperature. These parameters are measured using a suite of probes, with plasma parameters calculated using an NRL developed Langmuir probe model which is particularly useful in complex multi-component plasmas. The results are then compared with a one-dimensional steady-state hydrodynamic model of electron beam generated Ar-SF_6 plasmas at low pressure in a constant magnetic field.

This work supported by the Naval Research Laboratory Base Program

4:40pm **PS-ThA8 Microwave Plasma Source Technologies: A Fifty Year Evolution from Unwanted Discharges to Free Radical Sources, to Low Pressure and Temperature Plasma Processing, to Gem Quality Diamond Synthesis**, ***Jes Asmussen***, Michigan State University **INVITED**

Opportunities to create, to experiment with and to apply microwave plasmas occurred after world war II when high power microwave sources became commercially available. The first applications of microwave plasmas used a small, micro plasma - like discharge as a harmonic generator, i.e. these plasmas were used to generate even higher frequency electromagnetic radiation. As the understanding of how to efficiently create and maintain a discharge improved, microwave plasma sources, as they were identified at that time, were applied to numerous high and low pressure applications such as down stream and in - plasma free radical sources for thin film deposition, etching and more generally to a large variety of plasma surface treatments. Under the influence of these applications, microwave applicator and plasma source technologies rapidly evolved and became more application specialized. Initially a plasma discharge scale up was identified as a challenge, but the ability to produce large, high density microwave discharges was demonstrated. Completely new subclasses of microwave discharges, such as electron cyclotron resonance (ECR) discharges, were identified. Eventually applications, such as microwave plasma - assisted synthesis of diamond, created important new microwave plasma technologies. Certainly over the past fifty years microwave plasma sources have evolved into an important and diverse group of technologies that have broad range of material processing applications.

In this presentation, the historical evolution of microwave plasma source technologies will be briefly reviewed. The current diverse group of the technologies now known as microwave plasma source technologies will be organized into subclasses. The physics and the methods of efficiently coupling microwave energy to both high and low pressure discharges will be identified and compared. The state - of - the - art applications such as single crystal diamond synthesis and ECR discharges will be reviewed. Finally the current microwave plasma source technologies will be compared with the more common, lower frequency excited capacitive and inductive plasma sources.

5:20pm **PS-ThA10 Insights to Scaling Remote Plasma Sources Sustained in NF_3 Mixtures**, ***Shuo Huang***, University of Michigan*, V. Volynets, S. Lee, I.-C. Song, S. Lu,* Samsung Electronics Co., Ltd., Republic of Korea*, J.R. Hamilton, J. Tennyson,* University College London, UK*, M.J. Kushner*, University of Michigan

Remote plasma sources (RPS) are used in microelectronics fabrication to produce fluxes of radicals for etching and surface passivation in the absence of damage to devices that may occur by charging and energetic ion bombardment. RPS reactors use distance, grids or other discriminating barriers to reduce or eliminate charged particle fluxes from reaching the surface of the material being treated. Nitrogen trifluoride (NF_3) is often used in RPS due to the efficiency with which F atoms are produced by dissociative attachment. RPS sustained in NF_3 gas mixtures, such as $Ar/NF_3/O_2$ increases the variety of reactive species produced, for example, N_xO_y. For certain applications it may be desirable to separately optimize, for example, F atom fluxes; and O atoms, or N_xO_y. This separate optimization could, in principle, be performed using pulsed power or pulsed gas sources. In this paper, we report on a computational investigation of RPS sustained in different NF_3 containing gas mixtures using pulsed power for low-damage plasma etching applications. Two modelling approaches were used – global modelling to investigate fundamental reaction mechanisms and 2-dimensional modelling to address the spatial dynamics of flow. A reaction mechanism was developed for plasmas sustained in mixtures containing $Ar/NF_3/N_2/O_2$. Cross sections for NF_x were generated using ab initio computational techniques based on the molecular R-matrix method. Results for RPS produced by both continuous wave power and pulsed power will be discussed, and comparisons made to experiments.

Selective Deposition as an Enabler of Self-Alignment Focus Topic
Room: 210F - Session SD+AS+EM+PS-ThA

Process Development for Selective Deposition and Self-aligned Patterning
Moderator: John Ekerdt, The University of Texas at Austin, Chuck Winter, Wayne State University

2:20pm **SD+AS+EM+PS-ThA1 Surface Chemistry Related to Selective Deposition**, ***Suvi Haukka***, ASM Microchemistry Ltd., Finland*, J.W. Maes*, ASM Belgium **INVITED**

The shrinking device dimensions in semiconductor manufacturing call for new innovative processing approaches. One of these considered is selective deposition which has gained increasing interest among semiconductor manufacturers today. Selective deposition would be highly beneficial in various ways, for instance, it would allow a decrease in lithography and etch steps reducing the cost of processing and enable enhanced scaling in narrow structures making bottom up fill possible. Chemical vapor deposition (CVD) and especially atomic layer deposition (ALD) as very surface sensitive techniques are considered enabling techniques.

Selective deposition typically deals with a selective deposition method where, for instance, a metal layer is selectively deposited on metal surface over dielectric surface, or a dielectric layer is selectively deposited on hydrophilic polymer over a more hydrophobic polymer. In most of the selective deposition schemes of today the passivation is used for the surface on which no deposition is desired. The most known method is to use SAM´s (self-assembled monolayers) which are silicon compounds with long carbon chains. Besides the SAM passivation of surfaces also the clever selection of precursors with built-in selectivity in certain process conditions could be applied.

In this paper, the chemistry challenges in the various selective deposition approaches and passivation means are reviewed. In addition, results from the selective deposition of metal on metal over dielectric surface in a Cu capping application and from selective strengthening of DSA (direct self-assembly) layers are presented.

3:00pm **SD+AS+EM+PS-ThA3 Selective Deposition - The New Patterning Paradigm?**, ***Florian Gstrein***, Intel Corporation **INVITED**

Top-down patterning techniques based on optical lithography have made consumer electronics ever more powerful, ubiquitous and affordable. This is largely due to the ability of lithographic techniques to transfer trillions of mask features to wafers at defect densities approaching virtually zero in high-volume manufacturing. While the resolution of optical lithography tools is typically considered to be the main challenge for continued device scaling, it is actually accurate pattern placement, which has emerged as the biggest concern. Novel bottom-up patterning approaches such as selective deposition are needed to overcome shortcomings in pattern placement accuracy.

The talk will first outline the challenges patterning processes based on 193i pitch division and EUV lithography face in terms of alignment accuracy and how complementary patterning techniques such as selective deposition can reduce pattern placement errors. One of the great challenges of selective deposition is defect mitigation, especially as the sensitivity to killer defects increases as device dimensions scale. Defect mitigation requires a fundamental understanding of the chemical selectivity of surfaces. While molecules can recognize chemical functionality on a surface, selective deposition processes based on atomic layer deposition (ALD) or chemical vapor deposition (CVD) are exceedingly rare and largely limited to specific

precursors and substrates. For metal deposition, inherent selectivity was achieved through judicious precursor ligand design. Experimental results will be presented in the context of a theoretical investigations aimed at calculating the kinetic barriers that govern the selectivity of metal deposition. The use of self-assembled monolayers (SAMs) as passivants and/or blocking layers for subsequent deposition is an attractive way of overcoming the non-selectivity of many CVD or ALD processes. Here, the critical parameters for selective blocking are choice of the terminal group, surface termination, carbon chain length, and proper precursor choice. Using SAMs, selective deposition of dielectrics with respect to a variety of surfaces was achieved. The talk will conclude with our vision of how defects can be mitigated: It comprises a fundamental understanding of the chemical nature of the surface, precursors with high kinetic barriers for defect formation, passivation of defect nucleation sites, and the removal of defects post deposition. Selective deposition, if properly resourced and developed, can provide powerful means to future scaling and is one way of ensuring that patterning will continue to support Moore's Law in the foreseeable future.

4:00pm **SD+AS+EM+PS-ThA6 Area-Selective Molecular Layer Deposition: Enhanced Selectivity via Selective Etching**, ***Richard Closser***, *D.S. Bergsman, F.H. Minaye Hashemi, S.F. Bent*, Stanford University

Recent developments in electronic devices are pushing toward smaller and smaller features of both metal and dielectric patterns, along with a desire to produce selectively deposited organic thin films on such patterns. Techniques that allow for a high degree of control over the thickness and conformality of organic thin films, such as molecular layer deposition (MLD), are ideal candidates to meet these selective deposition requirements. Using MLD, several types of thin film polymers can be deposited with angstrom-level control due to the sequential, self-limiting surface reactions resulting in monomer-by-monomer growth. Selectivity in the MLD polymer growth is then achieved by utilizing the chemical functionally between the solid substrate surface and the gas phase monomer precursors.

Previously, we have shown the ability to selectively deposit thin film polymers by MLD onto pre-patterned metal and dielectric substrates by utilizing a blocking layer of octadecylphosphonic acid (ODPA) self-assembled monolayers (SAMs) that deposits onto metals more readily than onto dielectric films. Although this process can prevent MLD for up to 6 nm of deposition, selectivity of polymer growth is lost for thicker films, and therefore we are exploring new methods for increasing the MLD selectivity. For the current studies, ODPA SAM is deposited onto a patterned metal/dielectric (Cu on SiO_2) substrate to act as the MLD blocking layer. Once the SAM is fully deposited, polyurea films are grown onto the substrate by MLD to a desired thickness which can be controlled by the number of monomer dose cycles used. An acid etchant is then used to remove the surface oxide of the metal along with the SAM layer while leaving intact the polymer film deposited onto the dielectric. X-ray photoelectron spectroscopy, Auger electron spectroscopy, and ellipsometry measurements show that this process removes undesired MLD film that was deposited on the metal. Studies on patterned substrates confirm selective polymer film growth onto the dielectric over the metal. The etchant removal technique thus increases the selectivity of MLD growth by more than an order of magnitude when compared to the SAM blocking layer alone. Due to the increased selectivity with the etching based process, selective deposition of MLD films as thick as 12 nm have been demonstrated. Atomic force microscopy results show slight surface roughening due to etching while the bulk of the metal/dielectric pattern remains intact. This increase in MLD selectivity should allow for novel applications of selective polymer film deposition.

4:20pm **SD+AS+EM+PS-ThA7 Nucleation and Steady State ALD of Metallic Tin Using $SnCl_4$ and a Silyl Pyrazine Reducing Agent**, ***Eric Stevens***, *M.B. Mousa, G.N. Parsons*, North Carolina State University

Metal atomic layer deposition (ALD) processes are typically limited to noble, high work-function metals where uniform nucleation and conformal growth can be problematic. Recent work suggests that 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine (DHP) could be an effective reducing agent for deposition of metals with highly negative electrochemical potentials. This work investigates DHP as a potential reducing agent for tin metal ALD using tin (IV) chloride ($SnCl_4$).

Experiments were carried out in a custom-built, hot-wall reactor using N_2 carrier gas, an operating pressure of 1.3 Torr, and temperatures between 130 and 170°C. The DHP source was heated to 70°C to maintain a vapor pressure ~1.2 Torr. Initial films were deposited at 130°C on silicon using a $SnCl_4/N_2/DHP/N_2$ exposure sequence of 4/50/10/50 seconds, then analyzed ex-situ by X-ray photoelectron spectroscopy (XPS) with Ar depth profiling. In sputtering deeper into the film, XPS exhibited both Sn-Sn and Sn-O peaks at 485 and 486.7 eV, respectively, where a decrease in Sn-O and an increase in Sn-Sn peak intensities suggests native oxidation of the film upon exposure to air. Furthermore, 7% Cl and 19% N were found in the films after sputtering, presumably from an incomplete reaction and/or incorporation of reaction byproducts.

To better understand surface reactions and growth mechanisms, we characterized the ALD process at 130, 150, and 170°C using *in situ* quadrupole mass spectrometry (QMS) and quartz crystal microbalance (QCM). QCM analysis at 130 and 150°C showed continued growth with extended exposures, consistent with non-ALD growth. Deposition at 170 °C was more repeatable and more closely approached surface saturation. At 170°C, QCM showed a clear mass increase during the $SnCl_4$ dose and a corresponding mass decrease during the DHP dose, consistent with DHP removing Cl and reducing the Sn-Cl surface. Moreover, the QMS results showed peaks exclusively during DHP doses at m/z values of 80 (pyrazine) and 65, 93, 95 (trimethylsilyl chloride), which are the most probable byproducts of DHP reacting with a chlorinated surface.

Using gold-coated QCM crystals at 170°C, Sn growth proceeds slowly for the first ~150 ALD cycles, whereas growth on QCM crystals previously coated with Sn show a more rapid transition to steady-state growth (<20 cycles). We are currently investigating the nucleation on different substrates and how process conditions can be tuned to achieve selective deposition. Understanding the surface reaction and growth mechanisms of tin metal deposition using DHP could provide a foundation for deposition of metal thin-films that were previously unattainable.

4:40pm **SD+AS+EM+PS-ThA8 Determination of the Minimum Saturating Dose during Atomic Layer Deposition of Alumina and Titania on Si(100) and Si(100)-H**, *D. Dick*, University of Texas at Dallas, ***Joshua Ballard***, *J. Randall*, Zyvex Labs, *Y.J. Chabal*, University of Texas at Dallas

Atomic layer deposition (ALD) has become an important process step in semiconductor manufacturing, where the self-limiting nature of each step of the process permits atomic scale control over the ultimate layer thickness in addition to relatively fast processing with high pressure reactors. However, it has been shown that ALD can be used to selectively deposit material onto patterned surfaces, requiring not only saturation of each deposition cycle in desired areas but also suppression of deposition in those areas where it is undesirable. One mechanism for improving practical selectivity would be to find the minimum exposure that is saturates the growth where desired in order to avoid excess overall reaction probability in areas where inhibited growth is preferred.

To investigate this, we have examined the deposition in vacuum ("UHV ALD") of Al_2O_3 and TiO_2 with TMA and $TiCl_4$, respectively, on both hydrophobic, H-terminated Si(100) surfaces and hydrophilic OH-terminated Si(100) surfaces prepared by H_2O exposure of clean Si(100)-(2x1) surfaces. Surface reactions and relative coverages are determined by in-situ IR spectroscopy, and ex-situ XPS. We find that good selectivity can be achieved at 150ºC. Preliminary data and calculations also suggest that an initial wetting layer of TMA on clean Si(100) promotes subsequent growth of TiO_2 or other high-k dielectrics. Finally, we will discuss how these findings have made it possible to develop a full multi-cycle process for a custom low-pressure ALD system equipped with scanning tunneling microscopy and atomic force microscopy.

5:00pm **SD+AS+EM+PS-ThA9 Selective Growth of GeSbTe Phase-Changing Materials Utilizing Self-Aligned Confined Structure**, ***ByungJoon Choi***, Seoul National University of Science and Technology, Republic of Korea, *T. Eom, C.S. Hwang*, Seoul National University, Republic of Korea

GST Phase changing material, typically GeTe–Sb_2Te_3 pseudo-binary solid solution, has been extensively studied for rewritable digital versatile optical disks or phase change random access memory (PcRAM), on account of the drastic change of its optical reflectivity or electrical resistivity between amorphous and crystalline phases. As the device size of PcRAM is scaled down, GST materials should be confined into the contact-plug for reducing its programming current, which cannot be achieved by any physical deposition method.

Among the various metal-organic (MO) precursors, the combination of $Ge(iBu)_4$, $Sb(iPr)_3$ and $Te(iPr)_2$ has been extensively studied for plasma enhanced chemical vapor depostion or its variant methods with plasma-activated H_2 gas as a reducing agent of the MO-precursors. Plasma-enhanced pulsed CVD was attempted using the precursor pulse sequence consisting of Sb–Te–Ge–Te cycles (each elemental cycle is composed of precursor injection and Ar + H_2 plasma reduction steps). The chemical composition of the films was appropriately controlled by the cycle ratio and sequence of each precursor pulse. The linear growth with the number of cycles was shown, and the GPC (growth-per-cycle, i. e. growth rate) was determined to be 0.73 nm/super-cycle from the slope at a wafer temperature of 200˚C.

Strong substrate dependency can be utilized in the selective growth of GST material on a TiN contact-plug formed in the SiO_2 inter-layer dielectric (ILD). Higher selectivity (difference of GPC) between TiN contact-plug and SiO_2 ILD layer was achieved by pulsed CVD with increasing the amount of $Te(iPr)_2$ injection. The reason for the selective growth was believed to have originated from the adverse interference of the residual gas (unreacted $Te(iPr)_2$ or its derivatives) to the chemical adsorption of Sb nuclei on the SiO_2 surface, which functions as a nucleation site for further GST growth. It was reported that amide-based Ge precursors also showed strong selectivity at a particular temperature, enabling Sb and Te precursors to be chemisorbed on the Ge seed layer, which could be utilized for selective growth of GST.

The most feasible explanation for the substrate-dependent growth behavior of the GST film is the electron donation from the substrate, which would enhance the precursor decomposition and removal of ligands from the adsorbed precursor molecules. The nucleation and growth behaviors of the GST films were studied on Si substrates with various nucleation or buffer layers. It turned out that the types of substrates have a crucial impact on the nucleation behaviors and the chemical composition of the film.

5:20pm **SD+AS+EM+PS-ThA10 Toward an All- Vapor Process for Area Selective Atomic Layer Deposition**, ***FatemehSadat Hashemi***, *S.F. Bent*, Stanford University

Modern electronic devices containing planar and 3-D structures utilize a number of metal/dielectric patterns in both the front and back end. The scaling of next generation electronic devices makes achieving these patterns increasingly difficult and motivates the development of novel processing methods. One such method−area selective deposition−has the opportunity to play an important role in significantly reducing process complexities associated with current top-down fabrication of patterned structures by eliminating some of the deposition and etching steps that are time-consuming and expensive.

Atomic layer deposition (ALD) is a good choice for area selective deposition because its chemical specificity provides a means to achieve selectivity on a spatially patterned substrate. Area selective ALD, reported previously by several groups, requires improvements for the process to be compatible with current device fabrication goals. Most previous studies of area selective ALD have achieved deposited thicknesses on the order of only a few nanometers and the selectivity was generally obtained by passivation of the surface using self-assembled monolayers (SAMs) in the regions where ALD was not desired. Existing methods are usually performed by dipping the substrates into a solution containing the SAM-forming molecules for several hours. A more desirable all-vapor process would require vapor delivery of the SAMs. This method would provide better SAM coverage on porous or three-dimensional structures, potentially decreasing the required deposition time for the passivation layer, and allowing the SAM passivation step to be integrated with the rest of the ALD process.

In this work, we investigate area selective dielectric-on-dielectric deposition by selectively depositing organic alkanethiol SAM as the blocking layer on metal parts of a metal/dielectric (Cu/SiO_2) pattern. We compare area-selective ALD achieved by introduction of the thiolate SAM in both the solution and vapor phase. We show that while in both cases the SAM can prevent subsequent deposition of metal oxide dielectric films via ALD, vapor deposition provides stronger passivation in a shorter exposure process on the metal. We also report results on regenerating the thiol SAM protecting layer from the vapor phase between ALD cycles and show that this approach is effective in improving the blocking properties of the SAM on Cu. This strategy provides the ability to significantly improve selective deposition of dielectrics. Moreover, it is a significant step toward an all-vapor process for area selective deposition, opening up the possibility for new applications in next generation electronic devices.

5:40pm **SD+AS+EM+PS-ThA11 Selective Deposition of ALD Metal oxides and Metal Thin Films by Fab-Friendly Surface Treatments**, ***Kandabara Tapily***, *K.-H. Yu, S. Consiglio, R. Clark, D. O'Meara, C. Wajda, G. Leusink*, TEL Technology Center, America, LLC

For the last 5 decades, the semiconductor industry has relied on the continued scaling down of the device feature size in order to improve performance and increase bit density according to Moore's law. However, with the delay in implementation of extreme ultraviolet lithography (EUV) in high volume manufacturing,[1] patterning beyond the 14 nm technology node is getting extremely difficult to manage due to the overlay control and the increase in manufacturing cost due to multi-layer alignments. In order to keep reducing the device feature size, new patterning solutions are needed such as selective deposition and selective etching of materials. Atomic layer deposition (ALD) has emerged as one of the leading film deposition techniques as a result of the semiconductor device scaling.[2] ALD provides excellent film control, uniformity and high conformality. ALD is highly surface reaction driven and it is possible to modify the substrate surface to activate or deactivate growth on selected area hence selective-area ALD (SA-ALD). Selective-area ALD can simplify and reduce the high manufacturing cost associated with highly aggressive patterning schemes by eliminating certain lithography steps. Thin films can now be selectively deposited or removed from a desired area. Most selective-area ALD studies in the literature are conducted with the use of self-assembled monolayers (SAMs) in order to deactivate or activate growth on certain areas.[3-5] SAMs are thin organic films that form spontaneously in tightly packed oriented molecules on solid surfaces. A key enabler of SAMs is the ability to turn these organic layers into patterned layers. However, thermal stability and the slow formation process into well packed layer are some of the major drawbacks of SAMs.[5]

In this study, a non SAMs based approach was used to inhibit ALD growth of metals and metal oxides. Using different surface treatments, it was observed the growth of the ALD thin films can be modulated, see Fig.1 and Fig.2 respectively. ALD Al_2O_3 growth was suppressed by a combination of the vapor HF and cyclical low temperature plasma hydrogen treatment and deposition. Additionally, ALD TaN growth was also inhibited by the use of a combination trimethylsilane (TMS) and dimethylamine (DMA) treatment of the surface prior to ALD deposition.

Reference

1. J. Beynet, et al, *Proc. SPIE*, 7520, 75201J (2009).

2. S. M. George, *Chem. Rev.***110**, 111 (2010).

3. ChaMarra K et al. *Nanotechnol*,***3***, 114 (2012).

4. J. C. Love et al., *Chem. Rev.*,**105**, 1103 (2005).

5. A. J. M. Mackus et al, *Nanoscale*, **6**, 10941 (2014).

Surface Modification of Materials by Plasmas for Medical Purposes Focus Topic
Room: 211D - Session SM+AS+BI+PS-ThA

Plasma Processing of Biomaterials and Biological Systems

Moderator: David Graves, University of California, Berkeley, Jean-Michel Pouvesle, GREMI CNRS/Université d'Orléans

2:20pm **SM+AS+BI+PS-ThA1 Matching Plasma Sources with Intended Biomedical Outcomes: Open Questions in Modeling of Plasma Surface Interactions**, *W. Tian,* University of Michigan*, S.A. Norberg,* US Military Academy - West Point*, A.M. Lietz,* University of Michigan*, N.Yu. Babaeva,* Joint Institute for High Temperatures*, **Mark Kushner***, University of Michigan **INVITED**

Plasma surface modification of materials for biomedical applications typically involves atmospheric pressure plasmas in the form of dielectric barrier discharges (DBDs) or atmospheric pressure plasma jets (APPJs). In many cases, APPJs operate similarly to DBDs with an ionization wave (IW) propagating through a rare-gas dominated gas channel. The intersection of the IW with the surface being treated, for example tissue, in both DBDs and APPJ produces locally large fluxes of ions, UV/VUV photons and electric fields onto the surface. These fluxes are collectively *hard fluxes* due to the higher levels of activation energy they represent. Remote DBDs and APPJs where the plasma plume does not intersect the surface produce *soft fluxes*, dominated by neutral reactants. The character and ratios of *hard-to-soft fluxes* and their compositions are functions of flow dynamics, ambient conditions (e.g., humidity) and pulse power waveforms. In many biomedical applications, the tissue is covered by a liquid (or the intended surface is liquid as in plasma activated water). In these cases, plasma produced activation energy, radicals and ions must penetrate through the plasma-liquid interface, where liquid phase mechanisms then determine the reactants to the tissue. From one perspective, significant advances have been made in modeling these processes and furthering our understanding. From another perspective, there are still significant open questions that models need to address, including the manner of coupling of the gas phase plasma and liquid, gas induced fluid dynamics, long term evolution of the liquid chemistry, reactions at the surface of the tissue and control schemes to minimize variability. A brief overview of progress in modeling plasma modification of biomaterials will be provided followed by examples of the authors' modeling works for APPJs and DBDs intersecting with model tissues and liquids.

3:00pm **SM+AS+BI+PS-ThA3 Plasma Processing of Biomimetic and Sintered Calcium Phosphates for Bone Regeneration and Repair**, ***Cristina Canal***, Technical University of Catalonia, Spain **INVITED**

Large bone defects caused by trauma, osteoporotic fractures, infection and tumour or cysts resection pose a great clinical and socio economic problem. Bone grafting materials respond to the need generated by over 2 million bone grafting procedures that are performed every year worldwide. As an alternative to autografts or xenografts, different biomaterials have been proposed, yet with partial success since different aspects remain yet to be improved.

In this context, the use of low pressure (LP) and atmospheric pressure (AP) plasmas opens new opportunities in the field of bone biomaterials. It is the aim of this talk to provide an overview on the strategies undertaken in our group to enhance diverse features of bone biomaterials and to enhance bone therapies.

The examples discussed here include biomimetic hydroxyapatite (HA) and β-tricalcium phosphate (β -TCP) as the most clinically used calcium phosphate (CaP) ceramics for bone regeneration. Some of the points of improvement include increasing their mechanical strength, or using them as local dosage forms for the delivery of drugs, to aid in different therapies, such as combating infection or fighting cancer.

For instance, we have investigated LP plasmas with the aim of expanding the use of biomimetic CaPs to load-bearing sites. Although composites have been defined, their performance is not yet optimal, possibly due to insufficient adhesion between the matrix and the reinforcing agent. Oxygen and argon plasmas have been employed in the surface modification of polylactide fibers to improve the adhesion at the interface between them and biomimetic CaPs with interesting results.

In a different approach we have focused on modulating drug delivery from bone biomaterials. Both AP and LP plasmas are of interest with views on different medical applications and in the design of advanced biomaterials with controlled drug release properties. Different strategies are considered with that aim, such as using either plasma functionalization with AP plasma jet to modulate the interactions of the drug with the CaP surface or employing LP plasma polymerization on CaP scaffolds as a strategy to control the drug release. Lastly, AP plasmas are in the limelight due to their wide potential in the medical field, and here we will discuss some recent findings for application in bone therapies and regeneration.

Acknowledgements

Spanish Government is acknowledged for support through Project MAT2012-38438-C03-01, co-funded by the EU through European Regional Development Funds, and Ramon y Cajal fellowship of CC. The European Commission is also acknowledged through funding in FP7/2007-2013 under the Reborne project (no. 241879).

4:00pm **SM+AS+BI+PS-ThA6 Plasma Processing of Biomaterials and Biomedical Devices**, *H.J. Griesser, T.D. Michl, S.S. Griesser, M. Jasieniak, H.H. Mon,* ***Bryan Coad***, University of South Australia **INVITED**

Gas plasmas have attracted considerable attention over more than 40 years as a convenient method for changing the surface chemical composition of biomaterials and thereby alter and control the interfacial interactions between biomedical devices and contacting "biology" such as protein solutions, blood, cells and tissue, and bacterial biofilm growth. Plasma technologies are already in use on a large industrial scale in several biomedical device companies; for example 30-day contact lenses use a thin plasma coating to confer wettability and low fouling to silicone-based contact lens materials. Bio-interfacial interactions are very short range, and hence it is sufficient to apply ultrathin coatings (< 20 nm thick). Plasma techniques are ideally suited because process control is straightforward and the resultant surface modifications or coatings tend to have a high degree of uniformity and reproducibility compared with other, solution based coating methods. On the other hand, the complex chemical composition of plasma gas phases prevents fine control of chemistry to the extent achievable by conventional chemical approaches. Detailed surface analysis is essential.

Plasma approaches are useful to produce coatings designed to combat the problem of bacterial and fungal biofilm growth on biomedical devices, which leads to infections and delayed healing. One approach is the use of organochlorine plasma polymer coatings, which are highly effective at contact killing. Other, cytocompatible approaches comprise the use of plasma polymer coatings that release NO or available antibiotics such as levofloxacin. A different approach entails the covalent immobilization of a monolayer of antimicrobial molecules onto a thin plasma polymer interlayer whose function is to provide good adhesion and reactive surface chemical groups that can be used to attach antibiotics. Such covalently grafted monolayers have given excellent deterrence of attachment and biofilm formation of bacteria and pathogenic fungi.

4:40pm **SM+AS+BI+PS-ThA8 Organs on a Chip – Biointerfaces in Stem Cell Research**, ***Kevin Healy***, University of California at Berkeley **INVITED**

Highly regulated signals in the stem cell microenvironment such as ligand adhesion density, matrix stiffness and architecture, and growth factor presentation and concentration have been implicated in modulating stem cell differentiation, maturation, tissue formation, and ultimately function. My group has developed a range of materials systems and devices to study and control stem cell function and their self-organization into three-dimensional microtissues (e.g., 'organs on a chip'). These systems are being developed for screening molecular therapies and patient specific medicine via *in vitro* disease specific tissue models. Examples of how biointerface science is important in these applications will be highlighted. The benefits of our approach include: 1) robust and reproducible platform embodies precision microengineering to create better microtissue environments; 2) precise delivery of molecules (e.g., drugs) in a computationally predictable manner; 3) ability to model human cardiomyopathy; and, 4) cost efficient and high content characterization of cardiac tissue drug response.

5:20pm **SM+AS+BI+PS-ThA10 Effect of the Radical Species for Gene Transfection by Discharge Plasma Irradiation**, ***Yoshihisa Ikeda***, *M. Jinno*, Ehime University, Japan

Gene transfection is a technique of deliberately introducing nucleic acids into cells in order to give them specific characteristics. In practice, this can be achieved in three different ways: chemical method, physical method and the viral vector method.

One of the physical methods that uses discharge plasma irradiation was invented by Satoh, who is one of the authors, and his group in 2002. Since this technique is free from adverse effect associated with viruses, there are no risks as the others mentioned above. The plasma irradiation on genes and cells induces the transfection process in which the genes and cells are exposed to discharge current, charged particles and chemically reactive species.

The authors investigated the factors for plasma gene transfection by changing protocols and looked at the time periods the factors become effective. The results is that transfection rate drops to 1/10 of the standard protocol when the charged particles and chemically reactive species genes are washed out from the wells by PBS solution 60s after plasma irradiation. Since the life times of the charged particles delivered from plasma to the plasmid solution is less than 60s, the direct effect of the charged particles causing transfection finishes before wash out process. This means that nearly 1/10 of transfections occur during plasma irradiation and that the last 9/10 of transfections occur after plasma irradiation is stopped. This second stage transfection is mainly caused by the residual chemically reactive species, however, plasma irradiation stress to cells and plasmids also induces transfection., i.e. possibly charging effect and oxidation stress induce bio-chemical process of the cells in addition to the chemical reactions on the cell membrane and plasmid induced by chemically reactive species such as radicals.

5:40pm **SM+AS+BI+PS-ThA11 Nonlinear Optical Spectroscopic Observation of Plasma-Treated Bio-Specimen**, ***Kenji Ishikawa***, *R. Furuta, K. Takeda,* Nagoya University, Japan, *T. Nomura, T. Ohta,* Meijo University, Japan, *H. Hashizume, H. Kondo,* Nagoya University, Japan, *M. Ito,* Meijo University, Japan, *M. Sekine, M. Hori*, Nagoya University, Japan

Applications of nonequilibrium atmospheric pressure plasma (NEAPP) to the medical field have been reported in recent years. However, a mechanism of interactions between NEAPP and living cells has not been yet elucidated comprehensively. Our strategy for elucidation of plasma-biomaterial interactions is to observe reactions *in situ* at real time. By applying nonlinear optical spectroscopic techniques, the vibrational sum-frequency-generation (SFG) and multiplex coherent anti-Stokes Raman scattering (CARS) microscopy, which are a beneficial tool for addressing best sensitivity at surface and interface, have been used in this study. By using SFG, we have explored topmost surface modification after the interaction between plasma and biopolymeric materials. For the NEAPP-induced reactions on budding yeasts as an eukaryotic cell model, a two-dimensional mapping of budding yeasts treated by the plasma using the CARS microscopy was observed with fluorescence label-free contrasts of chemical vibrational nature. The biomedical imaging of cell membranes, intracellular organelles, nucleus and so forth, was revealed to decompose intracellular membrane by exposure of plasma-generated chemically reactive species, especially for induction of lipid peroxidation. These results will be useful for understanding the plasma induced reactions in the plasma medicine.

Thin Film
Room: 114 - Session TF+PS-ThA

Thin Film Permeation Barriers and Membranes
Moderator: Mariadriana Creatore, Eindhoven University of Technology, Netherlands

2:20pm **TF+PS-ThA1 Synthesis, Characterisation and Engineering of Moisture Barrier Films Deposited in a Roll-to-Roll High Current Dielectric Barrier Discharge**, ***Hindrik de Vries***, FOM institute DIFFER, Netherlands **INVITED**

Atmospheric pressure plasma enhanced chemical vapor deposition (AP-PECVD) is a new and rapidly evolving technology having clear benefits in terms of equipment costs, footprint size and possibilities for in-line processing. The excellent scalability of the dielectric barrier discharge combined with the possibility to generate non-thermal plasma in low-cost helium free gas mixtures, are essential requirements for large scale processing of functional films on web-rolled substrates.

In this work a cylindrical drum shaped DBD reactor configuration was implemented to facilitate roll-to-roll processing. We performed a systematic study of the discharge physics investigated by fast ICCD camera and voltage-current waveforms and we comprehensively analyzed the silica-like films deposited under barrier deposition conditions using AFM, XPS, SE and FTIR.

The time evolution of the atmospheric discharge was studied in 2 orthogonal directions of the cylindrical electrode geometry showing a glow-like discharge character. Detailed AFM morphology study and surface statistical analysis of the silica growth dynamics was carried out. The microstructure of the silica layers was studied using polarized ATR-FTIR and linked to the water vapor transmission rate (WVTR). The remarkable power law scaling between WVTR and film thickness was tentatively explained by the percolating nature of the moisture transport through the films. Based on this hypothesis, different approaches were investigated towards (bi-)layer architectures using AP-PECVD as well as other deposition techniques. Such a bi-layer architecture typically consists of a first porous silica layers that is subsequently covered by a dense silica capping layer.

In this contribution we will focus on the processing of silica bi-layers synthesized in different deposition regimes. The process conditions of the layers will be discussed in the frame of different scaling parameters like the energy spent per precursor molecule and the local deposition rate. Gas permeation properties were characterized by Technolox Deltaperm and calcium test. It was shown that AP-PECVD grown silica thin films of less than 30 nm deposited on a porous silica layer can yield excellent overall moisture barrier values (WVTR) typically $\sim 6*10^{-4}$ g/m^2 day at 40ºC, 90%RH accelerated ageing conditions.

3:00pm **TF+PS-ThA3 Investigation on Nano-Porosity in Moisture Permeation Barrier Layers by Electrochemical Impedance Spectroscopy**, ***Alberto Perrotta***, Eindhoven University of Technology, Netherlands, *S.J. Garcia Espallargas*, Delft University of Technology, Netherlands, *J.J. Michels*, Max Planck Institute for Polymer Research, Germany, *M. Creatore*, Eindhoven University of Technology, Netherlands

High-tech devices relying on organic semiconductors require device encapsulation against moisture and oxygen permeation, which would otherwise negatively affect the device opto-electrical performance.

The water permeation in inorganic moisture barriers has been shown to occur through macro-scale defects/pinholes (ranging from tens of nms to several µms) and nano-pores, down to sizes approaching the water kinetic diameter (0.27 nm). Both permeation paths can be identified by the calcium test, which allows discerning between the effective water vapor transmission rate (WVTR) and the intrinsic WVTR, the latter solely attributed to the permeation through the nano-porosity characterizing the bulk of the barrier layer. Recently [1], we have shown that ellipsometric porosimetry (EP) is a valid method to classify and quantify the nano-porosity content of inorganic barriers and a correlation has been found between their relative pore content and intrinsic WVTR values [1]. However, no information can be retrieved on the macro-scale defects nor on the kinetics of water permeation through the barrier, both essential elements in assessing the quality of the barrier layer.

In this study, electrochemical impedance spectroscopy (EIS) is demonstrated as a sensitive method to obtain quantitative information on both nano-porosity and macro-scale defects, complementing the barrier property characterization obtained by means of EP and calcium test.

EIS analysis is carried out on thin SiO_2 barrier layers deposited by plasma enhanced-CVD. The layer capacitance has been determined by modelling the impedance data with the proper equivalent circuit and the change of the capacitance upon water permeation has been followed. The Brasher-Kingsbury equation has been successfully applied and water uptake in the range of 0.8-4% have been found, in agreement with the nano-porosity content inferred by EP. A good linear correlation between the nano-porosity and the values of the electrical components used in the fitting procedure of the EIS data has been obtained, suggesting the direct calculation of open nano-porosity from an EIS fit. Furthermore, the kinetics of water permeation can be followed by EIS: the water diffusivity for the SiO_2 layers has been determined and found in agreement with literature values. Moreover, differently from ellipsometry-based techniques, EIS data are shown to be sensitive to the presence of local macro-defects, inferring its possible use for the prediction of the barrier performance with the calcium test.

[1] A. Perrotta *et al.*, Microporous Mesoporous Mat., 188 (2014) 163-171

4:00pm **TF+PS-ThA6 Thin-film Dielectrics for Chronic Nonhermetic Encapsulation of Electrically Active Neural Implants**, ***Stuart Cogan***, The University of Texas at Dallas **INVITED**

The needs of emerging clinical applications of neural stimulation and recording in the treatment of many diseases and disorders are driving a reduction in the size of implanted devices and the development of strategies to manage the large number of electrical interconnects between implanted electrodes and control electronics. The requirements for large numbers of electrodes, exceeding many hundreds for vision prostheses, and the ability to interface with nerves that may be as small as 100 microns in diameter, precludes the use of conventional packaging with hermetically sealed metal or ceramic cans. One of the few practical alternatives to hermetically sealed enclosures is the use of thin-film dielectrics, possibly combined with polymer over-layers. Besides the need for these thin-film coatings to provide effective passivation against corrosion, they also serve a multifunctional role providing adhesion between polymer and metal layers in flexible devices, providing a biocompatible interface to neural tissue and in some devices, providing a surface for functionalization with bioactive molecules. Conventional passivation materials such as silicon dioxide and silicon nitride are prone to corrosion *in vivo* and recent experience with polymer encapsulation such as Parylene-C suggests that this otherwise excellent barrier layer may fail after chronic implantation for more than about one year. The implanted electronics on these devices operates typically at 3 V or higher and neural stimulation involves pulsatile currents that may also induce unexpected failures at interfaces. In this context, other thin-film materials such as amorphous silicon carbide (a-SiC), ultra-nanocrystalline diamond (UNCD), and atomic-layer-deposition (ALD) Al_2O_3 are being investigated as alternative passivation materials that can provide chronic protection of active implants. A discussion of the physical and chemical requirements for these materials and results reported to date is presented. Emphasis is placed on understanding the constraints of the application including processing compatibility with temperature-sensitive substrates, the need for conformal coatings, and appropriate test methodologies to validate predictions of chronic *in vivo* lifetimes. Early results are promising with some combinations of thin-film and polymer encapsulation exhibiting excellent stability and biocompatibility. Of particular interest, are the relative roles and importance of interfacial properties and bulk barrier properties in achieve long-term chronic passivation of implanted active devices.

4:40pm **TF+PS-ThA8 Atmospheric Pressure Roll-to-Roll Plasma Enhanced CVD of High Quality Silica-like Bi-layer Moisture Barrier Films: The Influence of Input Energy**, ***Fiona Elam***, FUJIFILM Manufacturing Europe B.V., Netherlands, *A. Meshkova, S.A. Starostin,* DIFFER, Netherlands, *J.B. Bouwstra,* FUJIFILM Manufacturing Europe B.V., Netherlands, *M.C.M. van de Sanden, H.W. de Vries*, DIFFER, Netherlands

Atmospheric Pressure-Plasma Enhanced Chemical Vapour Deposition (AP-PECVD) is a new enabling technology that can be easily integrated into many existing manufacturing systems to facilitate the mass production of functional films. To date, roll-to-roll AP-PECVD has been successfully used to produce ultra-smooth, dense, 100 nm single layer silica-like thin films that demonstrate good water vapour barrier performance, therefore showing particular promise as a technique in the field of protective layer synthesis for flexible organic solar cells. However, this technology is only viable for moisture barrier production if high quality films can be manufactured at high throughput and at low cost. The generation of bi-layer silica-like thin films comprising a 'dense layer' synthesised using very low precursor gas flows deposited on top of a 'porous layer' synthesised at a high deposition rate, could provide one potential solution to this scientific challenge.

A glow-like AP dielectric barrier discharge in a roll-to-roll set-up was used to deposit a series of ~90 nm bi-layer silica-like thin films composed of a ~60 nm 'porous layer' and ~30 nm 'dense layer' onto a polyethylene 2,6

naphthalate substrate by means of AP-PECVD. Tetraethyl orthosilicate (TEOS) was used as the precursor gas, together with a mixture of nitrogen, oxygen and argon. In each case, the deposition conditions for the 'porous layer' were kept constant, while the conditions for the synthesis of the 'dense layer' were varied in order to study the effect of increased input energy per precursor gas molecule (~6 – 70 keV/TEOS molecule) on the chemical composition and porosity of the 'dense layer' and hence, the influence of this 30 nm layer on the moisture barrier performance of the overall film.

Each film was characterised in terms of its water vapour transmission rate, its chemical composition (*s*-, *p*- and *un*-polarised Attenuated Total Reflectance-Fourier Transform Infrared spectroscopy and X-ray Photoelectron Spectroscopy) and its morphology (Atomic Force Microscopy) as a function of the input energy per precursor gas molecule during the 'dense layer' deposition. The analysis provided valuable information concerning the structure of the silica network within each 'dense layer', and hence the influence of input energy per precursor gas molecule on the ultimate film quality.

The ~90 nm bi-layer silica-like thin films were seen to exhibit water vapour transmission rates of at least 6.2×10^{-4} g m^{-2} day^{-1} (at 40ºC, 90% RH), illustrating that it is possible to produce exceptionally high quality moisture barrier films using the presented bi-layer approach in a roll-to-roll AP-PECVD set-up.

5:00pm **TF+PS-ThA9 Use of Aluminum Oxide as a Permeation Barrier for Producing Thin Films on Aluminum Substrates**, ***James Provo***, Consultant, J. L. Provo Consulting

Aluminum has desirable thermal properties (i.e. conductivity, diffusivity and specific heat), electrical and optical properties of resistivity and reflectivity, and the characteristic of being non-magnetic and having a low atomic weight (26.98 g-atoms), but because of its low melting point (660°C) and ability as a reactive metal to alloy with most metals, it has been ignored as a substrate for use in processing thin films. The author, proposed a simple solution to this problem, by putting a permeation barrier of (Al_2O_3) onto the surface of Al substrates, by using a standard oxidation process of the surface (i.e., anodization), before additional film deposition of reactive metals at temperatures up to 500°C for 1 hour, without the formation of alloys or inter-metallic compounds that would affect the properties of the Al substrates. The chromic acid anodization used (MIL-A-8625) produced a film barrier of ~ 10k Å of alumina. The fact that refractory Al_2O_3 can inhibit the reaction of metals with Al at temperatures below 500°C suggests that Al is a satisfactory substrate if properly oxidized prior to film deposition. To prove this concept, thin film samples of Cr, Mo, Er, Sc, Ti, and Zr were prepared on anodized Al substrates and studied by Auger/ argon sputter surface analysis to determine any film substrate interactions. In addition, a thin film of (ErD_2) on an anodized aluminum substrate was studied with and without the alumina permeation barrier. Films for study were prepared on 1.27 cm O.D. high purity Al substrates with ~ 5k Å of the metals studied after anodization. Substrates were weighed, cleaned, and vacuum fired at 500°C prior to use. The aluminum substrates were deposited with the metals studied, using standard electron beam evaporation techniques, and after film deposition the erbium film was hydride with D_2 gas using a standard air-exposure hydriding technique. All processing was conducted in an all metal ion pumped high vacuum system. Results showed that e-beam deposition of all films studied onto Al substrates could be successfully performed, if a permeation barrier of Al_2O_3 from (5-10)k Å was made prior to thin film deposition up to temperatures of 500°C for 1 hour. Dihydrides, can also be successfully produced with full gas/metal atomic ratios of ~ 2.0 as evidenced by the (ErD_2) thin films produced. Thus the use of a simple permeation barrier of Al_2O_3 on Al substrates prior to additional metal film deposition, was proven to be a successful method of producing both thin metal and hydride films of various types for many applications without the formation of alloys or inter-metallic compounds that would affect substrate properties.

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

Plasma Science and Technology Poster Session

PS-ThP1 Effect of Embedded Radio Frequency Pulsing for Selective Etching of SiO_2 Contact Hole using $Ar/C_4F_8/O_2$ Gas Mixture in the 60/2 MHz Dual-frequency Capacitively Coupled Plasma System, ***Namhun Kim***, Samsung Electronics, Republic of Korea, *G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

The characteristics of embedded pulse plasma using 60 MHz radio frequency as the source power and 2 MHz radio frequency as the bias power were investigated for the etching of SiO_2 masked with an amorphous carbon layer (ACL) using an $Ar/C_4F_8/O_2$ gas mixture. Especially, the effects of the different pulse duty ratio of the embedded dual-frequency pulsing between source power and bias power on the characteristics on the plasma and SiO_2 etching were investigated. The experiment was conducted by varying the source duty percentage from 90 to 30% while bias duty percentage was fixed at 50%. Among the different duty ratios, the source duty percentage of 60% with the bias duty percentage of 50% exhibited the best results in terms of etch profile and etch selectivity. The change of the etch characteristics by varying the duty ratios between the source power and bias power was believed to be related to the different characteristics of gas dissociation, fluorocarbon passivation, and ion bombardment observed during the different source/bias pulse on/off combinations. In addition, the instantaneous high electron temperature peak observed during each initiation of the source pulse-on period appeared to affect the etch characteristics by significant gas dissociation. The optimum point for the SiO_2 etching with the source/bias pulsed dual-frequency capacitively coupled plasma system was obtained by avoiding this instant high electron temperature peak while both the source power and bias power were pulsed almost together, therefore, by an embedded RF pulsing.

PS-ThP2 Synthesis of B_4C And In Situ B_4C / ZrB_2 From Sugar Based Precursor, ***Abdullah Selim Parlakyigit***, *E. Aktan, C. Ergun*, Istanbul Technical University, Turkey

Boron carbide (B_4C) is one of the hardest materials and therefore commonly used for a variety of applications including armor plating, blasting nozzles and mechanical seal faces, as well as for grinding and cutting tools. Conventional production methods of B_4C, such as carbothermal reduction in industrial scale requires high investment and high operating costs, inhomogeneous resultant material, etc.

Zirconium diboride (ZrB_2) is a highly covalent refractory ceramic material which is considered as an ultra-high temperature ceramic (UHTC) with a melting point of 3246 °C. ZrB_2 with its relatively low density of ~6.09 g/cm^3 and good high temperature strength has a potential to be used for high temperature aerospace applications.

In the present study, a method based on sulfuric acid dehydration of sugar was developed to synthesis a precursor material, which can yield B_4C and in situ B_4C/ ZrB_2 composites at much lower temperatures compared to traditional carbothermal methods. The precursor material was heat treated at the temperatures between 1000 and 1600°C under inert atmosphere and characterized by XRD, SEM and FTIR.

PS-ThP3 High Power Pulsed Magnetron Sputtering: A Way to Broaden Industrial Implementation, ***Jake McLain***, *P. Raman, I.A. Shchelkanov*, Center for Plasma Material Interactions, University of Illinois, USA, *S. Armstrong*, Kurt J. Lesker Company, *D.N. Ruzic*, Center for Plasma Material Interactions, University of Illinois, USA

High Power Pulsed Magnetron Sputtering (HPPMS) is a magnetron sputtering technique that utilizes high peak power pulses applied to the sputtering target. HPPMS is capable of producing a much higher fraction of sputtered material ions, though has the major drawback of intrinsically low deposition rates for all materials. The low deposition rate is a byproduct of the “return effect”, seen in systems that have high amounts of sputtered ions. [1]. HPPMS provides better film quality, and in some cases enables unique deposition processes. [2] Despite the characteristic better film quality, the inherently low deposition rates obstruct wide industrial implementation.

Center for Plasma Material Interactions (CPMI) has developed the “ε” magnet pack, which is capable of HPPMS deposition rates comparable to DC Magnetron Sputtering (dcMS) deposition rates at 500W and 10mTorr. [3] To achieve that high deposition rate, the “ε” magnetic configuration implements a field topology referred to as “opened field lines”.

All previous research was done in cylindrically symmetric configurations, but most large- scale industrial tools utilize liner magnetrons of up to several meters long. This work is dedicated to the development of a rectangular magnet pack compatible with commercially available magnetrons, in order to provide higher deposition rates of HPPMS in a wider range of technological processes. Electron confinement is discussed in detail, and the sputtering rate from the rectangular pack at different cathode-substrate distances in a HPPMS discharge is modeled.

[1] L. Meng, H. Yu, M. M. Szott, J. T. McLain, and D. N. Ruzic, J. Appl. Phys. 115, 223301 (2014).

[2] J. Alami, K. Sarakinos, G. Mark, and M. Wuttig, Appl. Phys. Lett. 89, 154104 (2006).

[3] P. Raman, I. Shchelkanov, J. McLain, and D. N. Ruzic, J. Vac. Sci. Technol. A 33, 031304 (2015).

PS-ThP4 Non-thermal Plasma Synthesis of Hollow Silicon Carbide Nanoparticles, ***Devin Coleman***, *T. Lopez, O. Yasar-Inceolgu, L. Mangolini*, University of California - Riverside

The synthesis of beta-phase silicon carbide nanoparticles exhibiting a hollow core-shell morphology is demonstrated by means of a two-step non-thermal plasma method.[1] Crystalline silicon nanoparticles are nucleated from silane precursor gas in a non-thermal plasma reactor similar to the one described in [2] and injected into a secondary methane-containing plasma reactor, where they are carbonized to form beta-phase silicon carbide nanoshells. An analytical solution of the 1D diffusion equation in spherical coordinates, as well as the lattice volume expansion from silicon to silicon carbide are used to explain the formation of the interior void. This provides an alternative to previously reported results, which invoke the nanoscale Kirkendall effect to explain the void formation by means of fast out-diffusion of the core element.[3] Further consideration of the system kinetics indicates interactions with the ionized gas leads to particle superheating, allowing for the diffusion of carbon into the silicon matrix and nucleation of beta-phase silicon carbide to occur during the short residence time of the particles in the system. This work expands upon the materials achievable by non-thermal plasma synthesis and reinforces its potential as an industrial materials processing method. Furthermore, it suggests that such systems offer the capability to engineer particle morphology.

References:

[1] Hollow silicon carbide nanoparticles from a non-thermal plasma process. D. Coleman, T. Lopez, O. Yasar-Inceoglu, and L. Mangolini. J. Appl. Phys. In press (2015).

[2] Silicon nanocrystal production through non-thermal plasma synthesis: a comparative study between silicon tetrachloride and silane precursors. O. Yasar-Inceoglu, T. Lopez, E. Farshihagro, and L. Mangolini, Nanotechnology 23, 255604 (2012).

[3] Formation of Hollow Nanocrystals Through the Nanoscale Kirkendall Effect. Y. Yin, R. M. Rioux, C. K. Erdonmez, S. Hughes, G. A. Somorjai, and A. P. Alivisatos, Science 304, 711 (2004).

PS-ThP5 Finite Element Modeling of Surface Wave Plasmas Excited by Microwave Slot Antennas for Processing of Thin Film Materials, ***Pawel Piotrowicz***, University of Illinois, *D. Alman, B. Jurczyk*, Starfire Industries, *M. Stowell*, Applied Materials, *I. Schelkanov*, University of Illinois, *D. Curreli*, University of Illinois at Urbana Champaign, *D.N. Ruzic*, University of Illinois

Plasmas generated by microwave excitation offer multiple advantages to thin film processing over lower frequency and DC discharges. Typical microwave discharges create plasmas with higher densities of electrons, lower average electron temperatures, and lower sheath voltages. The decreased ion energies and higher densities respectively offer less ion-induced damage to the thin film and higher deposition rates. These advantages can provide a processing technique to grow high quality crystalline thin films with low density of intrinsic defects.

However, on smaller scale devices, microwave discharges have not been used in industry, due to the difficulty in creating a uniform plasma density. The finite element model describes surface wave plasmas generated by a microwave slot antenna. The plasma is modeled as a dielectric medium with variable plasma density. Dielectric properties of the plasma are derived from a cold plasma dispersion relation. This approach provides a simple model to predict plasma density based on power deposition throughout the dielectric material, which can be used to optimize antenna design for uniform plasma generation.

PS-ThP6 Instantaneous Generation of Many Flaked Particles in Mass-Production Plasma Etching Equipment, ***Yuji Kasashima***, National Institute of Advanced Industrial Science and Technology (AIST), Japan

The mechanism of instantaneous generation of many flaked particles is investigated in mass-production plasma etching equipment. The results indicate that the deposited films are severely damaged and flaked off as many particles when an inner wall potential (floating potential) changes instantaneously and the electric field stress works as an impulsive force.

Particle contamination in plasma etching equipment significantly lowers production yield and overall equipment efficiency. In plasma etching, etching reaction products adhere to the inner chamber walls, gradually forming films as wafers are processed. Particles are generated by flaking of the deposited films due to electric field stress. In mass-production line, serious contamination caused by many particles sometimes suddenly occurs.

The experimental apparatus is the mass-production reactive ion etching equipment which can generate capacitively coupled plasma discharge. The etching process sequence and equipment parameters are similar to those used in actual manufacturing facilities. This study uses a titanium etching process that often causes significant particle contamination in mass-production equipment.

Flaked particles are detected by the in situ particle monitoring system. A sheet-shaped laser beam is introduced in a plane parallel to the wafer in the processing chamber at a distance of 4 mm from the ground electrode. The light scattered by particles is measured using an image-intensified charge-coupled device camera. The viewing port style plasma probe (VP-Probe) can detect a transient change in the floating potential formed on the inner surface of the chamber.

In this experiment, electrostatic chuck voltage much higher than usual is supplied to induce micro-arc discharge at the back of wafer. Many particles are detected simultaneously with the abrupt increase in the amplitude of VP-Probe caused by the micro-arc discharge. The arcing at backside of the wafer and many particles from the ground electrode occur simultaneously. That is, these phenomena occur at the same time despite in different parts of the chamber. The large and rapid change in the inner wall potential due to the arcing can make the electric field stress acting on the deposited film work as an impulsive force, generating numerous flaked particles suddenly.

Accordingly, the results reveal that the floating potential on the inner chamber wall changing rapidly and markedly causes many flaked particles because the deposited films are strongly damaged by the impulsive force of electric field stress. This mechanism can occur on not only a ground electrode but also a chamber walls, and lead to serious contamination.

PS-ThP7 Plasma Chemical Transport of Borazine for 2D Atomic Layer Growth of Hexagonal Boron Nitride, ***Takeshi Kitajima***, *T. Nakano*, National Defense Academy of Japan

Hexagonal Boron Nitride (h-BN) is interested because of its similar 2 dimensional crystal feature to Graphene.

The stack of h-BN with Graphene has less lattice mismatch compared to the other dielectric materials.

Mechanical exfoliation and stacking of h-BN with Graphene is examined and presented a novel transistor characteristics[1]. Chemical vapor deposition schemes are desired for the future mass production of the devices.

CVD growth of h-BN film on Cu or Ni is shown by several groups using Borazine as the source of BN under high temperature atmospheric conditions[2].

In this study, we introduced a new plasma induced chemical transport technique[3] of Borazine to the growth of h-BN for expanding the process window.

The experimental apparatus of the plasma chemical transport consists of the growth chamber and the plasma chamber (Fig.1). The growth chamber has a manipulator with a Mo sample heater. The plasma chamber has inner type 9 turn coil for inductive coupling of 100 MHz RF power. On the side of the coil, Borazine powder is placed to be vaporized by the hydrogen plasma exposure. The pressure of the plasma is 30 Pa. The Borazine vapor and the hydrogen radicals are transported to the growth chamber through 2 mm orifice which suppresses the ion exposure to the sample surface. The growth temperature ranges 560C to 1000C.

The optical microscope image of the film (Fig.2) shows the BN related clusters are locally produced on 560C sample while 1000C sample shows many graphene patches generated from excess carbons from the plasma source. The atomic concentration of the sample (Fig.3) shows the B and N concentration is highest (16 and 12 %) at 560C, and decreases to 3 and 2 % at 730C. Therefore, BN precursors can deposit on Cu surface only at lower sample temperature. This is also confirmed by the Atomic Force Microscope image of the sample (Fig.4). The image shows the 560C sample is covered with BN related polymer islands about a few tens of nm in width. The islands disappear as the growth temperature increases and the terrace of the Cu is emphasized.

The results show that BN growth on Cu with low pressure plasma induced chemical transport of Borazine is only possible at relatively low sample temperature. The 2 dimensional BN film growth is required to start from the BN polymer growth at lower temperature. We expect the BN polymer should be annealed at higher temperature around 1000C and be converted to 2 dimensional atomic layer.

1. I. Meric, *et.al.IEDM*, (2010) 23.2

2. S. Yumeng, *et.al. Nano Letters* 10, 4134 (2010)

3. H. Ohmi et al., *J. Appl. Phys.* 102, 023302 (2007)

PS-ThP9 A Low Cost Microplasma Generation Device for Detection of Volatile Organic Compounds Using Plasma Emission Spectroscopy, ***Po-Wei Ye***, *C.C. Hsu*, National Taiwan University, Taiwan, Republic of China

A low-cost and portable dielectric-barrier-discharge-type microplasma generation device (MGD) and the use of this MGD to detector volatile organic compounds are presented. This MGD was made of double-side copper laminate (CCL) and the MGD electrode patterns were defined using the toner-transfer method. Which enables defining the patterns with resolution down to approximately 150 mm without the need of using cleanroom facilitates. Using this MGD with a specially designed electrode arrangement, an applied voltage of 20 kHz and 500 Vrms is sufficient to ignite and sustain stable plasmas in an Argon-rich atmosphere. When the plasma is ignited in Argon atmosphere with a controlled amount of organic compounds addition, carbon-related optical emissions, namely CH(430.29nm) and C2(513.5nm), are observed using a spectrometer. With this MGD, the detection limit for methanol, ethanol, and acetone are 248 48, and208ppm, respectively. A nearly linear calibration curve can be obtained for ethanol with a concentration range from 50 to 1000 ppm.

PS-ThP10 The Development of a Pin-to-Droplet Plasma Generation Device for Detection of Metallic Ions in Aqueous Solutions, ***Min-Chun Chen***, *C.C. Hsu*, National Taiwan University, Taiwan, Republic of China

This work presents a simple set-up and potentially portable plasma generation device for the detection of metallic ions by optical emission spectrometry. This device consists of a needle-type power electrode and a droplet on a metal plate as the ground electrode. With a precisely control of the pin-to-droplet distance of 0.1 to 0.3 mm, the plasma can be ignited with a 2 kV DC voltage in ambient air without the need of any purging gases. . With this device, detection of metallic ions in aqueous solutions can be performed by analyzing the plasma emission spectroscopy with a sample amount as small as 5 µL. Na, Li and K ions with a concentration as low as 20, 70, and 400 µg/L, respectively, can be detected. This detection limit can be significantly decreased when the metallic ions are dissolved in acid such as HNO_3 or HCl. The sensitivity for optical emission spectrometry of different metallic ion is Na>Li>K>Cu>Zn. A linear calibration curve with a concentration between 2 and 2000 mg/L for Na ion by correlating the normalized metallic emission intensities and the concentration has been established. Finally, the potential using this device as a battery-powered and portable analytical tool will be discussed.

PS-ThP12 Simulation of Deep Silicon Etching under Cryogenic ICP $SF_6/O_2/Ar$ Plasma Mixture using multi-Scale Approach, *Y. Haidar*, ***Ahmed Rhallabi***, *A. Pateau, A. Mokrani,* Université de Nantes, France, *F. Taher*, Université Libanaise, Lebanon

SF_6 based plasma is widely used in the dry etching of silicon. In many new devices manufacturing such as Systems in Packages (SIP) or Micro-Electro-Mechanical Systems (MEEMS), deep etching of silicon without any local morphological defects like bowing, undercut or trenching is required. Cryogenic silicon etching is used by adding oxygen in order to inhibit the sidewall etching and then improve the silicon etch anisotropy. The fraction of oxygen in $SF_6/O_2/Ar$ plasma mixture is one of the critical parameters in the control of this process.

In order to know more about the plasma surface interaction in cryogenic ICP silicon etching process, we have developed silicon etching simulator. The model is composed of three modules: plasma kinetic model, sheath model and etching model. The plasma kinetic model is based on the 0D global approach which allows the calculation of the average densities and fluxes of neutral and ion species as well as the electron density and temperature in ICP $SF_6/O_2/Ar$ plasma mixture versus the ICP machine parameters. Such output parameters are introduced as input parameters in the sheath model and silicon etching model. Cellular Monte-Carlo method is used to describe the plasma surface interactions in a probabilistic way for silicon etching trough the mask.

The aim of this work is to validate the set of simulation and show the influence of some input parameters (Rf power, pressure, gas flow rates and bias voltage) on the etching processes.

Particular attention is paid on the study of the effect of the oxygen fraction on the evolution of both the $SF_6/O_2/Ar$ plasma kinetic and the silicon etch profile trough the mask. The simulations results show that up to 10% of O_2, diminution of the undercut characterized by the surface etching under the mask is observed while beyond this value, the etching rate is considerably decreased. This is due to the domination of the passivation process by oxygen on the silicon trench bottom.

PS-ThP13 Two Dimentional Visualization of Oxidation Effect of Scalable DBD Plasma Irradiation using KI-starch Solution, *K. Koga, T. Amano,* ***Thapanut Sarinont****,* Kyushu University, Japan*, T. Kawasaki,* Nippon Bunri University, Japan*, G. Uchida,* Osaka University, Japan*, H. Seo, N. Itagaki, M. Shiratani, Y. Nakatsu, A. Tanaka*, Kyushu University, Japan

Biomedical applications of plasmas have been extensively explored by applying various plasma sources such as corona discharges, dielectric barrier discharges (DBD), gliding arc, and spark discharges. Quantitative evaluation of oxidation effect of these plasma sources is crucial to select one of the sources appropriate to an application, because most applications employ the oxidation effect. Here we have assessed the oxidation effect of our scalable DBD plasmas using KI-starch solution, the color of which changes from transparent to purple by the oxidation of I^- to I_2 [1]. Experiments were conducted using the scalable DBD device of 40x44 mm^2 in discharge area [2, 3]. 360 μl of solution of 0.5 % potassium iodide and 0.5 % starch was put in each well of a 96 well plate. The well plate was set at 3-10 mm below the electrode and then the solution was irradiated by the discharge plasma. The discharge voltage and current were 9.2 kV and 0.2 A. The discharge duration was 15 s. After the plasma irradiation absorbance at 560 nm of the solution in each well was measured with a plate reader (BioTeK Synergy HT). Two dimensional spatial profiles (71x54 mm^2 in area) of the oxidation effect was obtained by one plasma irradiation experiment. At y= 3 mm below the electrodes the absorbance is nearly constant of 2.6 O.D. under the electrode area, while it sharply decreases to 0.1 O.D. at x= 9 mm outside from the electrode edge x= 0 mm. At y= 10 mm, the absorbance is 2.6 O.D. at the center of the electrodes and gradually decreases even under the electrode area with increasing the distance from the center. It becomes 0.04 O.D. at x= 9 mm. Nonthermal air plasma provides ROS, RNS, charged species and photons to the well plate. Among these species, ROS and charged species are important oxidation species based on the experimental results.

This work was partly supported by KAKENHI Grant Numbers 24108009 and 24340143.

[1] T. Kawasaki, et al., IEEE Trans. Plasma Sci. 42, 2482 (2014).

[2] T. Sarinont, et al., JPS Conf. Proc. 1, 015078 (2014).

[3] S. Kitazaki, et al., Curr. Appl. Phys., 14, S149 (2014).

PS-ThP14 Sensitivity Enhancement of RF Plasma Etch Endpoint Detection With K-means Cluster Analysis*,* ***Honyoung Lee****, H. Jang, H. Lee, H. Chae*, Sungkyunkwan University, Republic of Korea

Plasma etch endpoint detection (EPD) of SiO2 and PR layer is demonstrated by plasma impedance monitoring in this work. Plasma etching process is the core process for making fine pattern devices in semiconductor fabrication, and the etching endpoint detection is one of the essential FDC (Fault Detection and Classification) for yield management and mass production. In general, Optical emission spectrocopy (OES) has been used to detect endpoint because OES can be a simple, non-invasive and real-time plasma monitoring tool. In OES, the trend of a few sensitive wavelengths is traced. However, in case of small-open area etch endpoint detection (ex. contact etch), it is at the boundary of the detection limit because of weak signal intensities of reaction reactants and products. Furthemore, the various materials covering the wafer such as photoresist (PR), dielectric materials, and metals make the analysis of OES signals complicated.In this study, full spectra of optical emission signals were collected and the data were analyzed by a data-mining approach, modified K-means cluster analysis. The K-means cluster analysis is modified suitably to analyze a thousand of wavelength variables from OES. This technique can improve the sensitivity of EPD for small area oxide layer etching processes: smaller than 2.0 % oxide area. This technique is expected to be applied to various plasma monitoring applications including fault detections as well as EPD.

PS-ThP15 The Study on the Etching Characteristics of the High Aspect Ratio Amorphous Carbon Layer(ACL), ***Yonghyun Kwon****, Z.H. Gang, K.S. Shin,* Samsung Electronics Co., LTD., Republic of Korea*, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

High aspect ratio etch is the key process step in the fabrication of vertically stacked(3D) memory, which is currently the most promising approach for ultra high density and high performance data storage applications. Superior hole dry etch capability, such as wide aspect ratio coverage, good vertical profile control, short throughput, etc, determines the satisfying vertical extendibility, memory cell performance and yield of the 3D memory. The hole etch usually takes a long process time(e.g., >1000 s). Therefore, a fine patterned thick(e.g.,>10um) hard mask must be required. Amorphous carbon layer(ACL) is a proper hard mask material due to its advantageous properties such as high selectivity, ease of deposition and removal and fine profile controllability. In this study, the control knob of thick ACL etch is investigated and solutions for high aspect ratio ACL etch is proposed. By reviewing the scanning electron microscopy(SEM) image after ACL de-capsulation, major/minor axis and the angle is investigated, and ACL tilting and distortion is observed at the aspect ratio 17. A model of ACL tilting induced by wafer warpage and sheath tilting, and ACL distortion formation due to non-uniform indirect ion scattering and by-product deposition is proposed. In addition, possible solutions for improving the ACL tilting and distortion by tuning the bias power, pulse and COS gas flow rate is discussed.

PS-ThP16 Carbon Dioxide and Methane Conversion Using Low Cost Microplasma Generation Devices, ***Yu-Hsin Huang****, C.C. Hsu, C.M. Wang*, National Taiwan University, Taiwan, Republic of China

Microplasmas offer great potential in gas conversion. In this work, we present the use of a low cost microplasma generation device (MGD) for carbon dioxide and methane conversion. This MGD was made of double-side copper laminate (CCL) and the MGD electrode patterns were defined using the toner-transfer method, which does not require the use of cleanroom facilitates. Two types of system arrangements are tested. In the first arrangement, a MGD was placed in a closed controlled volume with the gas flowing into the system. In the second arrangement, the MGD was integrated with flow channels fabricated on Polydimethylsiloxane (PDMS) devices, which allows for effective plasma-treated gas interaction. With the second arrangement, the conversion of CO_2 was tested at the conditions of 10 KHz and 2.7 KVpp applied voltage, which yields the formation of CO as high as 40000 ppm, which is nearly seven times higher than that obtained using the first arrangement. We will also show the use of these systems to perform the conversion of CH_4 into higher hydrocarbons. Finally, we will discuss the potential using this system for industrial manufacturing processes as a novel platform for gas conversion.

PS-ThP17 A MEMS Approach to Making Quantitative Measurements of IIEE Yields in the Presence of Moderate Electric Fields, ***Keith Hernandez****, A. Press, D. Urrabazo, M.J. Goeckner, L.J. Overzet*, University of Texas at Dallas

Semiconductor MEMs mechanical switches are prone to failure due to electrical breakdown across gaps between contacts. Electrical breakdown is characterized by Paschen's curve which is a function of both ion induced electron emission (IIEE) yield, electrode spacing, pressure and gas type. Paschen's curve also applies to low frequency microdischarges where the IIEE is one important mechanism of electron emission. Despite the widespread impact of the electrical breakdown phenomenon, few direct measurements of IIEE yield from semiconductors exist. In addition, the semiconductor IIEE yield data currently available do not pertain to practical MEMS or DC microdischarge applications, since the measurements were made on atomically clean and electric field free surfaces. The electric field free aspect of the previous measurements is the result of the macroscopic scale of the electron detection system. To address this issue, we have designed and begun the fabrication of a microfabricated electron detection system (mEDS). This system consists of the basic components of a current-based electron detection system: Electron suppressor- to prevent electrons from escaping collection, an electron collector and sample. A guard layer was also introduced in between the electron suppressor and collector to mitigate leakage current. Unlike previously designed electron detection systems, this device is capable of imposing a controllable uniform electric field (up to 10 V/um). Thus, by integrating the mEDS with an ion source we will have the ability to make IIEE yield measurements under varying electric field conditions. Thus, measurements of field enhanced IIEE and/or ion enhanced field emission become possible. In addition, this mEDS structure can be built on to any substrate that can withstand 250 ^{0}C and high vacuum. This poster will present the design, modeling and fabrication involved in bringing the mEDS to fruition.

Acknowledgement: This material is based upon work supported by the Department of Energy under Award Number DE-SC-0009308.

PS-ThP18 Spectroscopic Investigation of Hydrocarbon Plasmas for Coating Applications, ***Sarah Siepa,*** Ruhr-University Bochum, Germany, *S. Grosse, M. Guenther,* Robert Bosch GmbH, Germany, *A. von Keudell*, Ruhr-University Bochum, Germany

Diamond-like carbon (DLC) is widely used in coating applications, e.g. as wear-resistant coating on automotive components. One of the common technologies to deposit such layers is by using hydrocarbon plasmas with feed gases such as methane or acetylene. In order to better understand the coating process and to be able to tailor the plasma to the optimum conditions for the specific components, various diagnostic methods are applied to an industrial-scale plasma reactor. Besides probe measurements and Quadrupole Mass Spectrometry (QMS), Optical Emission Spectroscopy (OES) is used. OES investigations have the advantage of being easily applicable even under industrial conditions, where access to the plasma is often limited and homogeneity requires the use of a non-disturbing diagnostic technique. From the spectroscopic measurements and the corresponding model, the excitation dynamics of the plasma is investigated. The plasma parameters electron density and temperature (mean energy) can be determined as a function of input parameters such as pressure, power and gas flow.

PS-ThP19 From Plasma Reactor to Surface Level: Linking Plasma with Feature Profile Simulations, ***Sebastian Mohr***, *A. Dzarasova,* Quantemol Ltd., UK*, D. Tsamados, V. Deshpande, M. Oulmane,* Synopsys LLC, Switzerland*, J. Tennyson*, University College London, UK

Competitiveness in semiconductors industry is based on the ability to quickly integrate advanced technologies in products and optimise manufacturing processes. Only a coherent preparation of these processes allows companies to design successful products. One of the most important steps in the production of semiconductors is the treatment of surfaces by means of plasma processing. The resulting surface profiles usually depend on process parameters such as power or pressure in a non-linear way and are hard to predict. Simulations of plasmas on reactor scale and feature scale modelling of the surface reactions are an alternative to trial and error, saving costs and providing insights in the physical processes. Such simulations require solid input data. In case of plasma simulations, the process parameters are needed; Feature scale models require the flux distributions of particles to the processed surfaces. These flux distributions must be obtained either experimentally, which is not always possible and reliable. Or they are taken from simulations, which requires the output from the plasma simulation to be compatible with the input for the feature scale model. We aim to simplify these investigations by linking two software packages: Quantemol-VT (Q-VT) by Quantemol Ltd. and Sentaurus Topography 3D by Synopsys. Q-VT is a 2D plasma simulation tool, based on the Hybrid Plasma Equipment Model (HPEM) by Mark Kushner [1], which allows the simulation of plasmas in industrial tools on reactor scale level for a wide range of process parameters. The graphical interface of Q-VT allows for an easy setup of HPEM simulations for diverse chamber designs. As a result, Q-VT produces flux distributions of species relevant for surface reactions as a function of both the energy and the angle. These distributions are used as input for Sentaurus Topography 3D, a three dimensional TCAD feature scale etching and deposition simulator for plasma processes used in semiconductor manufacturing: PMC (particle Monte-Carlo) module which is controlled by a set of user-defined surface reactions simulates different phenomena such as adsorption and re-emission, ion reflection, ion-enhanced chemical and physical sputtering, and re-deposition of reaction products, predicting different effects of interest such as micro loading, bowing, micro trenching etc. Linking these two simulations allows comprehensive studies of surface profiles without any additional steps. The validation of the linked tools is currently under progress by comparing its results with published data on common surface processes. First results will be presented.

[1] M J Kushner, *J. Phys. D: Appl. Phys.* **42,** 194013 (2009)

PS-ThP20 Atomic Layer Etching of SiO_2 Using Self-Limited Fluorocarbon Films, ***Sanbir Kaler****, Q. Lou, V.M. Donnelly, J. Economou*, University of Houston

Atomic Layer Etching (ALEt) with monolayer accuracy is a critical requirement for advancing nanoscience and nanotechnology. Current plasma etching techniques do not have the level of control or damage-free nature that is needed for patterning delicate sub-10 nm structures with uniform etching rates and higher selectivities. Here we present beam studies of ALEt of SiO_2. Substrates consisting of thin layers of SiO_2 on Si are placed in an ultrahigh vacuum (UHV) chamber, cleaned with an oxygen plasma beam, and then exposed first to a beam of species effusing from a C_4F_8 plasma, followed by bombardment by an Ar^+ beam. The C_4F_8 plasma beam deposits a fluorocarbon (FC) film and the Ar^+ beam removes the film along with a small amount of SiO_2. The process is then repeated. Multiple times between each step, the sample is moved under vacuum to another UHV chamber equipped with x-ray photoelectron spectroscopy (XPS). Changes in FC film thickness and composition are measured as a function of exposure time to the C_4F_8 plasma beam. Similarly, changes are measured in the FC film and SiO_2 film thickness and composition as a function of Ar^+ beam exposure time. The FC film first deposits rapidly, then nearly saturates at a thickness of 0.8 nm and then continues to grow at a much slower steady rate. Stopping at this saturation FC film thickness and exposing the sample to a ~120 eV Ar^+ beam removes 0.08 nm of SiO_2, concomitant with the loss of CF_3 and CF_2 moities (but not of C and F), and then continues to sputter SiO_2 at a much slower rate. The 7:1 F:C ratio observed after 0.8 nm FC film deposition is much higher than the F:C ratio computed from a peak fit of the C(1s) high resolution spectrum (1.3:1), indicating that most of the F is bound in the SiO_2 film. Further details and mechanisms for the ALEt process will be presented.

PS-ThP21 Amorphous Hydrogenated Boron Carbide: A New Color in the Materials Palette for Multiple Patterning*, M.M. Paquette,* ***Bradley Nordell****, T.D. Nguyen, S. Dhungana, A.N. Caruso,* University of Missouri-Kansas City, *W.A. Lanford,* University at Albany-SUNY*, P. Henry, S.W. King*, Intel Corporation

Advanced metal interconnect patterning schemes require a number of materials with specific characteristics and unique etch properties. Currently, many such materials fall within the Si/O/C/N/H phase diagram, and it is becoming increasingly difficult to achieve adequate etch selectivity. Amorphous hydrogenated boron carbide (a-B_xC:H_y) is a unique material with appealing properties for a variety of interconnect applications including a low dielectric constant and excellent mechanical properties. Importantly, because it breaks away from the Si/O/C/N/H stoichiometry, it offers unique etch chemistries, and may therefore represent an important addition to the multiple patterning tool box. We investigate the wet and dry etch behaviors of a-B_xC:H_y films of varying atomic composition and density in comparison with those of silicon-based oxides, nitrides, and carbides.

PS-ThP22 Properties of a Magnetic Neutral-Loop Discharge Plasma*,* ***Weiyi Li****, S. Kim, J. Blatz,* University of Wisconsin-Madison*, Y. Nishi,* Stanford University, *J.L. Shohet*, University of Wisconsin-Madison

Since Uchida[1] invented the magnetic neutral loop discharge (NLD) plasma in 1994, this technique has been investigated by various approaches. This work utilizes an NLD plasma reactor using a stainless-steel vacuum chamber, instead of the more commonly used quartz chamber in previous work .

The cylindrical vacuum chamber is placed in the middle of three sets of magnet coils. With DC currents flowing in opposite direction in the middle set compared with the ends sets of coils, a circular path on which the magnetic field is zero, *i.e*. a 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 through a quartz window on one end of the chamber with a spiral antenna. The reactor can be operated in three modes, (1) ICP mode when there are no currents in the magnet coils, (2) NLD mode when there is an oppositely directed DC current in the middle magnet coils and the current in the middle is weaker than the currents on the sides, or (3) Enhanced-ICP (E-ICP) mode when current in the middle coils is stronger than currents on the sides. In NLD mode, the plasma was observed to be brighter near the NL than along the axis of the vacuum chamber. In the E-ICP mode, the plasma was observed as bright ball-shape on the axis. This difference was further confirmed with two measurements: The optical spectrum using an OceanOptics spectrometer and the density and temperature using a Langmuir probe. By adjusting the ratio of the DC currents flowing in the magnet 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).

This work has been supported by the Semiconductor Research Corporation under Contract No. 2012-KJ-2359 and by the National Science Foundation under Grant CBET-1066231.

[1] T. Uchida, "Application of radio-frequency discharged plasma produced in closed magnetic neutral line for plasma processing," *Japanese Journal of Applied Physics,* vol. 33, pp. L43-L44, 1994.

PS-ThP23 Impact of Charge Separation Grid Design on Wafer Level Device Performance in an Advanced Plasma Asher, *H-A. Phan-Vu,* ***Shawming Ma***, Mattson Technology

Tradition plasma asher design depends on the grid, or baffle between source and wafer to separate ionized species from activated neutral so more activated neutral is preferred to reach wafer surface to react with photoresist. However, the more you separate the neutral species, the lower the ash rate in general due to loss mechanism during the separation process. In addition, the grid design also controls the ash rate uniformity and affects many other critical device parameters to the final device wafer performance. Therefore, it is extremely important to choose the correct design to the right process application. This paper discussed the impact of advanced plasma

asher grid design on the device performance in process uniformity and device response. It is found that grid materials are critical to reduce the ionized species to reach the wafer surface with the conductive grounded grid to be the best for ionized species separation. In addition, the conductive grounded double grid design can not only have better particle and defect performance but also remove any possible UV impact on device from strong UV generated from high ash rate high power recipes. This has contributed to better yield in the production environment down to 10nm technology node.

PS-ThP24 Fluorophore based Sensor for Oxygen Radicals in Processing Plasmas, *F. Choudhury, G. Sabat, M. Sussman,* University of Wisconsin-Madison, *Y. Nishi,* Stanford University, ***J. Leon Shohet***, University of Wisconsin-Madison

A high concentration of free-radicals is present in many processing plasmas, which affects the processing conditions and the properties of materials exposed to the plasma. Determining the types and concentrations of such free radicals is critical in order to determine their effects on the materials being processed. Current methods for detecting free radicals in a plasma require multiple expensive and bulky instruments, complex setups and often, modifications to the plasma reactor. This work presents a simple technique that detects reactive-oxygen radicals incident on a surface from a plasma. The measurements are made using a fluorophore dye (Alexa 488) that selectively reacts with oxygen radicals. It is commonly used in biological and cellular systems for assay labeling in liquids. Using fluorometric analysis, it was found that the fluorophore reacts with oxygen radicals incident from the plasma which is indicated by degradation of its fluorescence. The results show that the fluorescence degrades for about 60 seconds and reaches a constant fluorescence value after which little degradation is observed for longer exposure times. As plasma power was increased, the quenching of the fluorescence significantly increased as expected, because the radicals have higher energies as microwave power was increased. Although they are commonly used in liquid form, the dye can also be immobilized on a surface using an appropriate volatile solvent. Both immobilized and liquid fluorophores were used and the results indicate that both states function effectively under vacuum conditions. The immobilized dye can be ‘painted’ on a surface and the radical density incident on the surface can be inferred from fluorometric analysis. The immobilized technique can be very useful for many plasma applications - especially when used under vacuum since it prevents the dye from evaporating.

This work has been supported by the Semiconductor Research Corporation under Contract No. 2012-KJ-2359 and the National Science Foundation under Grant No. CBET-1066231.

PS-ThP26 Capacitively Coupled Indirect Plasma Discharge - 2 Dimensional Fluid Model Simulation Study, ***Pei-Siou Luo**, T.Y. Chang,* National Tsing Hua University, *K.C. Leou*, National Tsing Hua University, Taiwan, Republic of China

Capacitively coupled indirect plasma (CCIP) where a grounded mesh is placed between the two electrodes of a conventional CCP have gain a great deal of interests recently for applications where uniform radicals generated by the plasma are needed for material processing while harmful energetic ions or high energy photons should be minimized. In this study, a rf (13.56 MHz) CCIP Ar/H2 discharge has been investigated by numerical simulation based on fluid model, with 12

species and 28 gas phase reactions. Simulation results show that plasma density, as well as the number densities and fluxes of H, important reactive species for applications, increase with rf power, as expected. Simulation Results show that, as a result of the grounded mesh/grid that separating the two chambers, the flux of both ionic and reactive neutral species drop significantly, by a factor of ~1/1000 - 1/10000, from the top main chamber to the bottom drift chamber. More importantly, the plasma density also decreases significantly and the resulting plasma potential in the bottom chamber is only ~10% of that in the top main chamber. This, in term, implies that the ion energy flux incident on the grounded bottom electrode should be minimal, and thus damage to the wafer surface due to ion bombardment can be significantly reduced. Detailed simulation results will be presented.

*Work supported by the National Science Council of ROC.

PS-ThP27 Plasma Simulations with Adaptive Mesh Refinement and Hybrid Kinetic-Fluid Models, ***Vladimir Kolobov**, R.R. Arslanbekov*, CFD Research Corporation

This paper describes the development of plasma simulation tool using adaptive kinetic-fluid models for modern heterogeneous computing systems. The new tool will have a) ability to dynamically switch between fluid and kinetic approaches, b) robust mesh generation and adaptive mesh refinement algorithms, c) implicit solvers adapted for massively parallel CPU-GPU systems.

For gas dynamics in mixed rarefied-continuum regimes, our Unified Flow Solver (UFS) combines a tree-based algorithm of Adaptive Mesh Refinement (AMR) with cell-by-cell selection of kinetic (Boltzmann) and fluid (Navier-Stokes) solvers [1]. This Adaptive Mesh *and* Algorithm Refinement (AMAR) methodology provides the highest level of adaptation to the solution being computed. The kinetic module in UFS can solve kinetic equations by either the Discrete Velocity Method (DVM) [2] or by the statistical particle methods (such as Direct Simulation Monte Carlo (DSMC)) [3]. We have ported the kinetic solvers to Graphics Processing Units (GPU) and demonstrated double digit speedups on single GPU and good multi-GPU scaling [4].

The extension of AMAR to plasma simulations poses extra challenges due to disparity of electron and ion/neutral masses [5]. In this paper, we will show examples of plasma simulations with AMR capabilities using multi-fluid plasma models and describe the implementation of an implicit electrostatic Particle in Cell with Monte Carlo Collisions (PIC-MCC) module. The capabilities of the new PIC-MCC module will be demonstrated for positive column of DC discharges in weakly-collisional regime. We will describe algorithms for porting the PIC-MCC module to GPU and evaluate acceleration that can be achieved. Finally, we will discuss physics-based criteria for the kinetic-fluid decomposition for hybrid plasma simulations.

---

[1] V.I. Kolobov, R.R. Arslanbekov, V.V. Aristov, A.A. Frolova, S.A. Zabelok, Unified solver for rarefied and continuum flows with adaptive mesh and algorithm refinement, J. Comput. Phys. **223** (2007) 589

[2] R.R. Arslanbekov, V.I. Kolobov, and A.A. Frolova, Kinetic Solvers with Adaptive Mesh in Phase Space, Phys. Rev. E **88** (2013) 063301

[3] R.R. Arslanbekov, V.I. Kolobov, J. Burt, E. Josyula, Direct Simulation Monte Carlo with Octree Cartesian Mesh, AIAA 2012-2990

[4] S.A. Zabelok, R.R. Arslanbekov, and V.I. Kolobov, Adaptive Kinetic-Fluid Solvers for Heterogeneous Computing Architectures, http://arxiv.org/abs/1503.00707

[5] V.I. Kolobov and R.R. Arslanbekov, Towards Adaptive Kinetic-Fluid Simulations of Weakly Ionized Plasmas, J. Comput. Phys. **231** (2012) 839

PS-ThP28 Meshed Shielding Grid Added Electron Beam Excited Plasma Apparatus for Neutral Nitriding of Precision Components, ***Petros Abraha***, Meijo University, Japan

In this research, a customized equipment that utilizes electron beam gun and processing chamber with a meshed shielding grid that comprises of a discharge region, acceleration region and processing region is used to perform diffusion based nitriding treatment of steel components.

The electron beam gun starts discharge when an argon gas is introduced into the discharge region, and DC voltage is applied between the heated cathode and the discharge electrode. Argon is then ionized resulting in a large number of electrons in the discharge region. The electrons are then accelerated by the acceleration voltage Va applied between the discharge electrode and the anode. The generated electron beams are delivered into the processing chamber to produce nitrogen plasma. The plasma nitriding apparatus includes a meshed electrode mounted on the stage and electrically insulated from the processing chamber. The meshed shielding grid is made of stainless and formed into a cylindrical shape. The metal mesh is formed of a wire which has a diameter of 0.16 mm and having 40 meshes per inch. The sample to be treated is placed in the meshed electrode. The plasma nitriding apparatus includes a DC power supply device that bias the sample to a positive potential higher than the plasma potential at the location where the sample is set within the meshed shielding grid. The plasma nitriding apparatus also includes DC power supply that biases the meshed shielding grid to a negative potential.

The results of the nitrided samples, within the meshed shielding grid, for 3, 6, and 12 hours show that the treated surfaces were without any compound layer but composed of only diffusion layer whereby the measured thicknesses were about 45 μm, 65 μm and 90 μm respectively. For comparison, samples were treated under the same conditions but without the meshed shielding grid. The results reveal that in addition to the diffusion layer of about the same thickness, a 5 μm thick compound layer was formed in all three samples. This confirms that the meshed shielding grid is effective in diffusion based nitriding.

PS-ThP29 Deposition of Silicon Nitride Coatings by Pulser Laser Deposition Technique, ***Johans Restrepo***, Universidad Nacional Autonoma de Mexico, *E. Camps,* Instituto Nacional De Investigaciones Nucleares, Mexico, *S. Muhl*, Universidad Nacional Autonoma de Mexico

The Silicon Nitride present problems to be deposited by Pulsed Laser Deposition (PLD) Technique using a pure nitrogen atmosphere and silicon

target because the low nitrogen reactivity produce a partial oxidation during the deposition such as the oxygen amount reach values around to 20at%. The aim of this research was deposited silicon nitride at different nitrogen pressure and energy density to found the deposition parameters to reduce the oxygen included on the coatings. The coating were characterized by perfilometry, Routherford Back Scattering (RBS), Raman Spectroscopy, UV-bis Spectroscopy and Nanoindentation while the Plasma properties were characterized by Langmuir probe and Optical Emission Spectroscopy (OES). The OES results showed that the maximum nitrogen activity is reached at $4x10^{-3}$mbar (N_2^+ 391.4nm) and decrease at the nitrogen pressure increase. The average ion kinetic energy and the plasma density decrease from 120 to 100eV and $3.26x10^{13}$ to $4.89x10^{11}$ ion/cm^3 at nitrogen pressure of $4x10^{-3}$ and $6x10^{-2}$ mbar respectively.

2D Materials Focus Topic
Room: 212C - Session 2D+EM+IS+NS+PS+SP+SS-FrM

Surface Chemistry of 2D Materials: Functionalization, Membranes, Sensors
Moderator: Peter Sutter, University of Nebraska - Lincoln, Judy Cha, Yale University

8:20am **2D+EM+IS+NS+PS+SP+SS-FrM1 Chemically Modifying Graphene for Surface Functionality**, ***Paul Sheehan****, S. Tsoi, S.C. Hernández, S.G. Walton, T.L. Reinecke, K.E. Whitener, J.T. Robinson,* Naval Research Laboratory*, R. Stine*, Nova Research

Graphene has many superlative properties that may be tailored for specific applications, or even enhanced, through chemical functionalization. Chemical functionalization dramatically changes almost every critical property of graphene, changing it from opaque to transparent, from diamagnetic to ferromagnetic, from electron rich or electron poor, from electrically conducting to insulating (and back again!). This extensive control suggests that chemically modified graphene may aid applications from flexible sensors to surface engineering. I will discuss how stacks of 2D materials can control the dominant surface forces—van der Waals,[1] acid-base interactions, electrostatic interactions, etc.—and so surpass conventional methods of preparing surfaces with, for example, self-assembled monolayers. I will also briefly address goals as diverse as biosensing[2] or sloughing off chemical warfare agents.[3]

[1] ACS Nano, **2014**, *8* (12), pp 12410–12417

[2] BioTechniques, Vol. 57, No. 1, July 2014, pp. 21–30

[3] ACS Nano. 2013 Jun 25;7(6):4746-55.

8:40am **2D+EM+IS+NS+PS+SP+SS-FrM2 Structural Phase Stability Control of Monolayer $MoTe_2$ with Adsorbed Atoms and Molecules**, ***Yao Zhou****, E.J. Reed*, Stanford University

Of the Mo- and W- dichalcogenide monolayers, $MoTe_2$ is particularly interesting because it exhibits a small energy difference (approximately 31 meV per $MoTe_2$) between its semiconducting 2H phase and metallic 1T' crystal structures. This feature makes it particularly interesting for potential phase change applications.

We study the adsorption of some common atoms and molecules onto monolayer $MoTe_2$ and the potential for adsorption to induce a phase change between the semiconducting 2H and metallic 1T' crystal structures of the monolayer. Using density functional theory with spin orbit and van der Waals energy contributions, we determined the most energetically favorable adsorption positions and orientations on the two phases of monolayer $MoTe_2$. We then obtained the formation energies for these adsorption reactions and found that atomic adsorption generally favors 1T' metallic phases while molecular adsorption favors semiconducting 2H phases. A possible application of this work may be the chemical stabilization of a preferred phase during the growth process.

Further, we consider the $Mo_xW_{1-x}Te_2$ alloy monolayers that exhibit even smaller energy difference between phases. Our calculations indicate that it may be possible to engineer an alloy ($0<x<0.5$) such that specific molecules will induce a phase change to 1T' while other molecules studied stabilize the 2H phase, which suggests that alloying may provide some molecular selectivity. This potentially provides the basis for molecular sensing applications due to the large electronic contrast between 2H and 1T' phases.

9:00am **2D+EM+IS+NS+PS+SP+SS-FrM3 Selective Nanochemistry on Graphene/Silicon Carbide: Substrate Functionalization and Polycyclic Aromatic Hydrocarbons Formation**, ***Patrick Soukiassian***, CEA, France **INVITED**

Graphene & silicon carbide (SiC) are advanced semiconductors having figures of merit scaling well above those of well-established ones [1,2]. Understanding/mediating SiC and graphene surfaces & interfaces properties are of central importance toward functionalization and applications. As a 2D material, graphene is a single atomic layer of carbon atoms in a *sp2* bonding configuration. Therefore, functionalization remains challenging since interacting too strongly with the graphene atomic layer may change its bonding configuration and properties. Instead, interacting with the SiC substrate offers an alternative approach. The 1st case of hydrogen-induced metallization of a semiconductor surface has been shown for a 3C-SiC(001) surface [3]. Here, combining investigations using advanced experimental techniques such as STM/STS, vibrational & 3rd generation synchrotron radiation-based photoelectron spectroscopies together with state-of-art calculations will be presented and discussed. It includes: i) the 1st evidence of H/D-induced nanotunnel opening at a semiconductor sub-surface shown here for SiC [4]. Depending on H coverage, these nanotunnels could either be metallic or semiconducting. Dangling bonds generated inside the nanotunnels offer a promising template to capture atoms or molecules. These features open nano-tailoring capabilities towards advanced applications in electronics, chemistry, storage, sensors or biotechnology. Understanding & controlling such a mechanism open routes towards selective surface/interface functionalization of epitaxial graphene [4]. ii) The role of H interaction with graphene on SiC dust grains in polycyclic aromatic hydrocarbons (PAH) formation in the interstellar space with a possible route toward prebiotic roots of life in the universe [5].

1–W. Lu, P. Soukiassian, J. Boeckl "*Graphene: fundamentals and functionalities*" **MRS Bull. 37**, 1119 (2012)

2–P. Soukiassian "*Will graphene be the material of the 21th century?*" **MRS Bull. 37**, 1321 (2012)

3-V. Derycke, P. Soukiassian, F. Amy, Y.J Chabal, M. D'angelo, H. Enriquez, M. Silly, "*Nanochemistry at the atomic scale revealed in hydrogen-induced semiconductor surface metallization*", **Nature Mat.2**, 253 (2003)

4–P. Soukiassian, E. Wimmer, E. Celasco, Cl. Giallombardo, S. Bonanni, L. Vattuone, L. Savio, A. Tejeda, M. Silly, M. D'angelo, F. Sirotti, M. Rocca "*Hydrogen-induced nanotunnel opening within semiconductor subsurface*" **Nature Com. 4**, 2800 (2013)

5–P. Merino, M. Švec, J.I. Martinez,P. Jelinek, P. Lacovig, M. Dalmiglio, S. Lizzit, P. Soukiassian, J. Cernicharo, J.A. Martin-Gago "*Graphene etching on SiC grains as a path to interstellar PAHs' formation*" **Nature Com. 5**, 3054 (2014)

9:40am **2D+EM+IS+NS+PS+SP+SS-FrM5 Intrinsic Wettability of Graphene**, ***Haitao Liu***, Department of Chemistry, University of Pittsburgh

Graphene and graphite are long believed to be hydrophobic. Here we show that a clean graphitic surface is in fact mildly hydrophilic [1]. We find that an as-prepared graphene sample is hydrophilic with a water contact angle of ca. 40°. Upon exposure to ambient air, the water contact angle gradually increased to ca. 60° within 20 min and plateaued at ca. 80° after 1 day. Infrared (IR) spectroscopy and X-ray photoelectron spectroscopy (XPS) showed that airborne hydrocarbon adsorbed onto the graphene surface during this process. Both thermal annealing and controlled UV/O_3 treatment removed the hydrocarbon contaminants, which was accompanied by a concurrent decrease in the water contact angle. Our findings show that graphene is more hydrophilic than previously believed and suggest that the reported hydrophobic nature of graphene is due to unintentional hydrocarbon contamination from ambient air.

Reference

[1] Zhiting Li; et al.; Nature Materials, 12, 925-931, (2013)

10:00am **2D+EM+IS+NS+PS+SP+SS-FrM6 Au-doped Graphene As a Promising Electrocatalyst for the Oxygen Reduction Reaction in Hydrogen Fuel Cells: Prediction from First Principles**, ***Sergey Stolbov***, University of Central Florida*, M. Alcantara Ortigoza*, Tuskegee University

One of the main obstacles hindering large scale practical application of hydrogen fuel cells is a prohibited cost of the Pt (or Pt-based) catalysts for the oxygen reduction reaction (ORR) on the fuel cell cathode. In this work, we consider Au-doped graphene as an alternative to Pt for facilitating ORR. Our first-principles calculations show that Au atoms incorporated into graphene di-vacancies form a thermodynamically and electrochemically stable structure. Furthermore, calculation of the binding energies of the ORR intermediates reveals that Au-C bonding makes the C atoms neighboring to Au optimally reactive for ORR. The calculated ORR free energy diagrams suggest that the Au-graphene structures have an ORR onset potential as high as that of Pt. We also demonstrate that the linear relation among the binding energy of the reaction intermediates assumed in a number of works on computational high-throughput material screening does not hold, at least for this none purely transition-metal material.

10:20am **2D+EM+IS+NS+PS+SP+SS-FrM7 Spontaneous Deposition of Palladium Nanoparticles on Graphene through Redox Reaction**, ***Xiaorui Zhang****, W. Ooki, Y.R. Kosaka, T. Kondo, J. Nakamura*, University of Tsukuba, Japan

Due to its unique properties such as huge surface area and excellent conductivity, graphene becomes great interesting for supporting noble metal catalysts. Some noble metals such as palladium, platinum, gold nanoparticles was reported to be able to spontaneous deposition on as-synthesized reduced graphene oxide with external reducing agent-free

recently. Yet the mechanism of spontaneous deposition of metals on graphene has not been clarified until now. In the present research, we spontaneously deposited palladium nanoparticles on as-synthesized reduced graphene oxide in H_2O medium without external reducing agent. It was found that the deposited amount of palladium varied with pH, meanwhile, the bivalent Pd^{2+} precursor was reduced to metallic palladium, and graphene was oxidized simultaneously with an increasing of its oxygen functional groups. The atomic ratio of the deposited Pd and the increased O in rGO located in a range from 1 to 2. As reducing agent-free, the mechanism on spontaneous redox deposition of metal nanoparticles on graphene was proposed, firstly, an efficient adsorption of metal precursor on graphene is a prerequisite which is determined by their electrical charges and adjusted by pH. Secondly, a positive galvanic potential between metal precursor and graphene is necessary for metal spontaneous deposition.

10:40am **2D+EM+IS+NS+PS+SP+SS-FrM8 Gradient Electrochemical Response of Template Synthesized Thickness Sorted MoS_2 Nanosheets for Cellular Level Free Radical Detection**, ***Ankur Gupta***, *T. Selvan, S. Das, S. Seal*, University of Central Florida

The human body is a complex system capable of defending in adverse conditions. A classic example of such complex process is balanced equilibrium production between pro-oxidant and antioxidant in cells. However, when this equilibrium is disturbed, production of free radicals such as superoxide and nitric oxide strengthen, and causes serious cellular damages. Furthermore, myeloperoxidase (MPO) is released during the oxidative burst. This MPO combines with hydrogen peroxide (H_2O_2) and Cl^- and generate hypochlorous acid (HOCl). This is a short-lived and powerful diffusible oxidant strong oxidizer and could react with O^{2-} to produce $OH^.$. Therefore, in physiological condition HOCl has a major role as a potent microbicidal agent in the immune defense; however, during the oxidative burst HOCl not only damage healthy tissue and generate radicals that are extremely reactive. Therefore, monitoring of the production of free radicals at the cellular level is important for diagnostic purpose. Over past years, several material have been used to develop sensors for free radical detection such as cerium oxide nanoparticles, MoS_2 nanosheets and nanoparticles. However, detection of free radicals at cellular level is still a challenge.

In this attempt, layered molybdenum disulfide (MoS_2) were synthesized via hydrothermal method. SBA-15 polymer template were utilized during hydrothermal process to grow MoS_2 around it to develop porosity. After the hydrothermal synthesis and washing, polymer template was removed by dissolving it in isopropanol which leaves high surface area layered MoS_2 crystal. Wet chemical exfoliation of MoS_2 were carried out in aqueous solution of Pluronic^{Ô} F-127 having hydrophobic and hydrophilic chains. Pluronic^{Ô} F-127 was used to bring down the buoyant density of MoS_2. Non-templated nanosheets were synthesized as control. The exfoliated solution were centrifuged at 3000 rpm to remove large particle and supernatant was collected for density gradient ultracentrifugation (DGU). Separation of different thickness layers is carried out by DGU. Thickness sort MoS2 nanosheets were characterized using AFM, XPS, HRTEM, Raman and UV-Vis spectroscopy for structural and chemical analysis. XPS, HETEM and EFTEM analysis of nanosheets have illustrate the sulfur deficiency at the edges of the nanosheets. MoS2 nanosheets were deposited on glassy carbon electrode for cyclic-voltammetry and chronoamperometry measurements. Higher sensitivity and repeatability were demonstrated by nanosheets prepared via template method as compared to control for reactive oxygen and nitrogen species, and HOCl.

11:00am **2D+EM+IS+NS+PS+SP+SS-FrM9 Methanol Synthesis on Defect-Laden Single-Layer MoS_2 Supported on Cu(111): Results of a First Principles Study**, *D. Le*, ***Takat B. Rawal***, *T.S. Rahman*, University of Central Florida

Despite being found to be the preferred structure in single layer MoS_2, the sulfur vacancy row does not facilitate alcohol synthesis from syngas [1] because its narrow size limits adsorption, diffusion, and formation of possible intermediates. On the Cu(111) surface, strong interactions between MoS_2 and Cu are expected to reduce the corrugations caused by sulfur vacancy rows, resulting in a larger exposure of vacancies to adsorbates which could enhance the catalytic activity of the row towards alcohol synthesis from syngas. Based on the results of our density functional theory (DFT) simulations utilizing the DFT-D3 correction for accounting the van der Waals interactions, we show that: (1) there is a significant charge transfer from the Cu(111) surface to MoS_2, enhancing its catalytic properties, (2) the binding energies of CO and dissociated H_2 increase by 0.3 eV in comparison to that on unsupported MoS_2, indicating stronger interactions, and (3) the barriers for forming intermediate species in alcohol synthesis process reduce significantly in comparison to that on unsupported MoS_2. On the basis of these energetics, we conclude the Cu(111) substrate promotes methanol synthesis from syn gas on single-layer MoS_2 with a vacancy row. We will also present the energetic pathways for the formations of other reaction products such as methane, formaldehyde, and water, as well as that of (the reverse) water gas-shift reaction.

[1] D. Le, T. B. Rawal, and T. S. Rahman, *J. Phys. Chem. C***118**, 5346 (2014).

*This work is supported in part by the U.S. Department of Energy under grant DE-FG02-07ER15842

11:20am **2D+EM+IS+NS+PS+SP+SS-FrM10 The Happy Marriage of Graphene and Germanium: Graphene Achieves Exceptional Conductivity and Protects Germanium from Oxidizing**, ***Richard Rojas Delgado***, University of Wisconsin-Madison, *F. Cavallo*, University of New Mexico, *R.M. Jacobberger, J.R. Sanchez Perez, D. Schroeder, M.A. Eriksson, M.S. Arnold, M.G. Lagally*, University of Wisconsin-Madison

The properties of graphene (G) make it an outstanding candidate for electronic-device applications, especially those that require no band gap but a high conductance. The conductance, involving both carrier mobility and carrier concentration, will depend critically on the substrate to which G is transferred. We demonstrate an exceptionally high conductance for G transferred to Ge(001) and provide an understanding of the mechanism.[1] Essential in this understanding is an interfacial chemistry consisting of Ge oxide and suboxide layers that provide the necessary charges to dope the graphene sheet, and whose chemical behavior is such that one can obtain long-term stability in the conductance. In contrast, when high-quality G is grown directly on Ge (100), (111), or (110), the conductance is unexceptional, but oxidation of the surface is significantly delayed and slowed, relative to both clean Ge and Ge with G transferred to its surface . [2,3] We fabricate Hall bars in G transferred to Ge and G grown using atmospheric-pressure CVD with methane precursors . X-ray photoelectron spectroscopy (XPS) is used to investigate the oxide in all stages of the measurements. The sheet resistance and Hall effect are measured from 300K to 10K for transferred and grown samples. Values of mobility and carrier concentration are extracted. It appears we have reached the highest combination of mobility and carrier concentration in graphene (suspended or supported) for temperatures from 10 to 300K. The implication is that the primary mechanisms for scattering charge in the G, roughness and a non-uniform electrostatic potential due to fixed charges, have limited effect when the substrate is oxidized Ge. Finally the subsequent oxidation kinetics of Ge (001) are compared for graphene directly grown on Ge and for graphene transferred to Ge. XPS shows that for graphene grown on Ge(001) the interface is oxide-free and remains so over long periods of time. For graphene transferred to Ge(001) the interface contains stoichiometric and substoichiometric oxides. The thickness of these oxides increases with time, but quite slowly. Using spatially resolved XPS, we propose a model of diffusion limited oxidation initiated at edges of the graphene.

Research supported by DOE.

[1]Cavallo, Francesca, et al. "Exceptional Charge Transport Properties of Graphene on Germanium." *ACS nano* 8.10 (2014): 10237-10245.

[2] R. M. Jacobberger, et al. "*Oriented Bottom-Up Growth of Armchair Graphene Nanoribbons on Germanium." Nature Comm*., under review.

[3] R. Rojas, et. al "Passivation of Ge by Graphene.", in process.

Plasma Science and Technology
Room: 210A - Session PS+SE-FrM

Atmospheric Pressure Plasma Processing II
Moderator: Souvik Ghosh, Case Western Reserve University

9:00am **PS+SE-FrM3 Scaling Atmospheric Pressure Plasma Sources for Manufacturing-Scale Applications**, ***Steven Shannon***, North Carolina State University **INVITED**

Material processing using plasmas at atmospheric pressure presents one of the great areas of future growth for the Plasma Science and Technology Division of the AVS. Extension of plasma processing to atmospheric pressures (and ironically eliminating the need for "vacuum") provides two key advantages in processing. The first is the reduced cost and increased throughput that could be realized in equipment that does not require high vacuum design, load locks, etc. The second, and more significant, are the new applications that plasma science can now contribute to including water treatment, soft materials processing, processing of non-vacuum-friendly materials, and medicine.

Atmospheric plasma systems for manufacturing have the same high volume integration challenges that low pressure plasma systems do. These are scalability and throughput. These systems need to be able to process large areas (or volumes, depending on the application). This throughput scaling

presents a challenge especially when some level of homogeneity in process both within a sample and from sample to sample are required. Maintaining this process uniformity over a large area is further complicated by the need to maintain a high rate of reactive specie production, especially when the standard solution of "turn up the power" results in typically undesirable instability and heating in these higher pressure discharges.

At NCSU, researchers have developed an atmospheric plasma source that seeks to address these scale-up concerns of size and reactant production. This coaxially driven source can be driven in the VHF range of frequencies (60MHz - 200MHz, with 162MHz used in the work shown here) with a plurality of feed gases not requiring noble gas dilution. The VHF heating combined with source circuit design produce a volume glow with power densities ranging from $1W/cm^3$ to $20W/cm^3$. The unique source design enables operation of an RF driven / DC grounded electrode that enables delivery of gas and liquid precursors through the electrode surface. This enables the introduction of liquid precursors into the active plasma region while maintaining a stable volume glow. Multiple sources can be run in parallel for larger volume operation, and scalability has been demonstrated. Reactive specie production has been quantified for air plasmas and water plasmas (with water delivery from the powered electrode). The water electrode configuration yields OH concentrations over $10^{15}/cm^3$ in the active plasma region.

.

This work is supported by the NSF I/UCRC program through the Center for Lasers and Plasmas in Advanced Manufacturing, the NCSU Chancellor's Innovation Fund, and Advanced Energy Inc.

9:40am **PS+SE-FrM5 Improving of Harvest Period and Crop Yield of *Arabidopsis Thaliana L.* using Nonthermal Atmospheric Air Plasma**, ***Kazunori Koga***, *T. Sarinont, T. Amano, H. Seo, N. Itagaki, M. Shiratani*, Kyushu University, Japan

Nonthermal atmospheric plasmas have been widely used for biomedical applications [1-3]. Growth enhancement of plants is one of the important applications of such plasmas. Here we have studied effects of atmospheric air plasma irradiation to seeds of *Arabidopsis thaliana L.* on the harvest period and crop yield. Experiments were carried out using a scalable DBD device [2, 3]. The device consisted of 20 electrodes of a stainless rod of 1 mm in outer diameter and 60 mm in length covered with a ceramic tube of 2 mm in outer diameter. The discharge voltage and current were 9.2 kV and 0.2 A. 20 seeds of *Arabidopsis thaliana L.* were set 3 mm below the electrodes. After 3 minutes plasma irradiation, they were grown on rockwool until the harvest stage. The harvest period is defined as time from the beginning of cultivation to the first seed production. To evaluate the growth enhancement ability of the plasma irradiation, the area of two primary leaves of eight plants, namely 16 leaves, was measured every three days. The whole experiment was repeated 3 times with similar results. Data were analyzed by two-way analysis of variance. The harvest period without and with plasma irradiation are 71.31±5.63 and 66.53±3.82 days. The seed weight without and with plasma irradiation are 0.0201±0.0024, 0.0225±0.0016 mg/seed. The leaf area after 28 days from the beginning of cultivation without and with plasma irradiation are $0.049\pm0.011\ cm^2$ and $0.064\pm0.014\ cm^2$. These measured values without and with plasma irradiation are statistically significance different at $\alpha= 0.05$ ($P< 0.05$). Plasma irradiation brings about 7% shorter harvest period, 12% higher seed weights and 30% larger primary leaves, compared to those without plasma irradiation. Thus, plasma irradiation to seeds is a cost effective and environmental friendly method for improving of harvest period and crop yield of plants. The growth enhancement mechanism will be discussed in the presentation.

[1] J. Raiser and M. Zenker, J. Phys. D, **39**, 3520 (2006).

[2] T. Sarinont, et al., JPS Conf. Proc. **1**, 015078 (2014).

[3] S. Kitazaki, et al., Curr. Appl. Phys., **14**, S149 (2014).

10:00am **PS+SE-FrM6 Numerical Modelling of Atmospheric Pulsed Streamers over Water; Electrodynamics at the Interface**, ***Alex Lindsay***, *S. Shannon,* North Carolina State University, *D.B. Graves*, University of California at Berkeley

There is significant interest in characterizing interactions between atmospheric plasmas and water for applications in medicine, water decontamination, distributed farming, etc. In one particular example members of the community are investigating replacement of invasive electroporation for drug delivery and gene therapy with low-power atmospheric plasma devices. Although the mechanism by which electric fields create conductive pathways for drug delivery into cells is generally known, the mechanism by which plasmas create those liquid-phase electric fields is an active area of research. Pioneering work in [1] has done much to advance our understanding, but more work remains. We wish to present modeling tools that are open to the community in the hope that this will enhance development of the tools, scrutiny and reproducibility of numerical results, and the pace at which plasma-liquid research is conducted. By developing open community tools, we hope to reduce the time-waste that comes from different groups re-inventing the wheel to study similar phenomena. With those motivations, we consider both finite-volume and finite-element discretizations of the Poisson and continuity equations governing electrodynamics in the gas and liquid phases. For a first pass, a local-field approximation is used to study streamer propagation in a point-to-plane configuration with water serving as the planar electrode. Different methods for stabilization (e.g. inconsistent vs. consistent, streamline and/or crosswind) as well as markers for mesh adaption (potential, electron density curvatures) are considered.

[1] Babaeva et. al. J. Phys. D: Appl. Phys. 47 (2014) 235201

10:20am **PS+SE-FrM7 Application of Atmospheric Pressure Plasma treatment on Carbon Fiber Reinforced Plastics for Adhesive Bonding**, ***Timo Hofmann***, *J. Schäfer,* Bundeswehr Research Institute for Material, Fuels and Lubricants, Germany, *T. Löbel,* German Aerospace Center (DLR), *T. Meer,* Airbus Group Innovations, *J. Rehbein, J. Holtmannspötter*, Bundeswehr Research Institute for Material, Fuels and Lubricants, Germany

The demand for environmentally friendly means of transportation has led to a strong increase in the use of carbon fiber reinforced plastics (CFRPs). Joining of CFRP structures is currently performed using rivets and bolts. In order to exploit further weight-saving potential, the usage of adhesive bonding is investigated.

An important key factor for the success of adhesive bonding is the surface pre-treatment of the adherents. In this contribution, CFRP surfaces were treated using Atmospheric pressure plasma jet (APPJ) as a method to clean the samples and to improve adhesion by creating surface functional groups.

We present a detailed investigation of the surface morphology and the composition of CFRPs before and after treatment with APPJ. The CFRP surfaces were examined using a combination of Field-Emission Scanning Electron Microscopy (FE-SEM), Atomic Force Microscopy (AFM), Energy-Dispersive X-ray spectroscopy (EDX), and X-Ray Photoelectron Spectroscopy (XPS). Destructive tests were carried out to determine the adhesive strength and the failure mode as a function of APPJ.

We demonstrate that APPJ-processes can be used to form structural and long term stable bonds. Our results show that through the combination of analytical techniques and destructive tests it is possible to develop an understanding of the processes at the surface and to optimize the plasma treatment process.

10:40am **PS+SE-FrM8 Atmospheric Plasma Deposition of Transparent Organosilicate Multifunctional Coatings on Plastics in Air**, ***Siming Dong***, *Z. Zhao, R.H. Dauskardt*, Stanford University

Atmospheric plasma deposition is a versatile coating process that enables deposition on large and/or complex shapes in air. The low temperature plasma and solvent free process allows deposition on, and simultaneous functionalization of plastic substrates in a single step. Building on our previous studies, we demonstrate a highly efficient deposition method using two precursors, an inorganic tetraethoxysilane (TEOS) and an organic 1, 5-cyclooctadiene (CYC), to deposit multi-layer organosilicate transparent coatings on poly methyl methacrylate (PMMA) and silicon (Si) substrates with atmospheric plasma deposition in air. The coatings deposition rate, transparency, chemical composition and adhesion with the PMMA substrate were investigated. Using only the TEOS precursor, high density and elastic modulus coatings were deposited on PMMA but with poor adhesion. The addition of the organic CYC precursor allowed controlled incorporation of organic components into the coating molecular network which significantly improved adhesion. The deposition rate increased from ~65 nm/min for the single precursor to ~130 nm/min for the two precursor process. The coatings exhibited ~100% transmittance in the visible wavelength range. FTIR and Raman spectroscopy of the coatings showed that the organic component $(\text{-C-C-})_n$ in the coatings can be incorporated to form an organosilicate molecular network. This incorporation increased the coating deposition rate and also resulted in mechanical plasticity in the coatings. The adhesion of coatings with PMMA increased from $\sim 2\ J/m^2$ to $\sim 10\ J/m^2$ and the Young's modulus ranged from 22GPa to 34GPa. Coatings structures including composition and coating thickness to achieve optimized hardness and adhesive properties are reported.

11:00am **PS+SE-FrM9 Atmospheric Plasma Deposition of Anti-Reflection Coatings on Silicon in Open Air**, ***Michael Hovish***, *R.H. Dauskardt*, Stanford University

For many modern energy and sensing applications, multilayer optical coatings are an effective way to dramatically improve light collection.

Traditionally, such multilayer coatings are deposited on hard substrates using vacuum depositions. Furthermore, traditional vacuum techniques are not easily scalable, due to high costs and poor integration into the manufacturing scheme. Atmospheric plasma deposition has received attention in materials processing due to the ability to deposit functional coatings at room temperature and in open air. Room temperature operation allows for a dynamic range of substrates, both organic and inorganic. In addition to these qualities, atmospheric plasma deposition is a solvent free technique, making it a competitive alternative to sol-gel methods. In our research program, we have successfully shown several material systems which are amenable to atmospheric plasma deposition, including multifunctional organosilicate and metal oxide films. In particular, the solvent-free deposition of metal oxide films at atmospheric pressure and near room temperature provides an attractive platform for the design and fabrication of optical coatings.

We have employed atmospheric plasma to deposit thin, anti-reflection coatings on silicon. Both TaO_x and TiO_x films were investigated as candidates for single layer anti-reflection coatings. Films were optimized for low reflection within the visible wavelengths of light. High purity helium gas was used to transport either tantalum ethoxide or titanium ethoxide vapor into the afterglow of a helium-nitrogen plasma. A high temperature precursor delivery system was used to prevent the condensation of precursor vapors en route to the afterglow. Within the afterglow, the metal-organic compounds undergo molecular fragmentation and redistribution onto the substrate. Deposition rates, chemical compositions, optical properties, and adhesion energies to the substrate were investigated as a function of plasma power and gas composition. Spectral reflectance at 10° from normal was measured to determine the anti-reflection properties of the coatings. Atmospheric plasma deposited films on silicon show excellent anti-reflection properties, with less than 3% reflection loss near 550 nm.

11:20am **PS+SE-FrM10 Polymer Thin Film Deposition using Atmospheric Pressure Single Plasma Jet or Plasma Jet Array from a Plasma Gun Device**, ***Céline Vivien***, IEMN CNRS/Université Lille 1, France, *E. Robert, J.-M. Pouvesle*, GREMI CNRS/Université d'Orléans, France

Plasma Enhanced Chemical Vapour Deposition (PECVD) processes have been used for decades for surface processing in a wide range of industrial applications like semiconductor films, low-k films, barrier diffusion. Thin film deposition is especially of high interest for biomedical applications for the production of protective coatings, adhesion layers, hydrophilic or hydrophobic layers. Up to now, most of used processes are usually realized under low pressure. Actually, there is a great and increasing interest in the development of plasma sources operating at atmospheric pressure. The present work deals with plasma polymerisation of TMDSO and HMDSO with a Dielectric Barrier Discharge plasma jet at atmospheric pressure, the Plasma Gun developed in GREMI. Depending on parameters like voltage, frequency, carrier gas and monomer injection, the deposited polymer appears either as a gel-like coating or a transparent film with fringes. Deposits are characterized by Fourier Transformed IRspectroscopy and contact angle measurements. The precursor used was introduced in both liquid or gaseous state, in case TMDSO and only gaseous state in case of HMDSO. The liquid flow rate was regulated by a peristaltic pump (Ismatec) while the vapour flow was ensured by bubbling nitrogen or oxygen with a fixed flow rate of 10 sccm. Microscope slides and polished Silicon wafer (100) were used as substrates. The polymerized coatings have been obtained at frequencies between 500Hz and 4 kHz, for applied voltages between 14 and 20 kV and exposure times from 1 to 10 minutes. The deposition were realized with plasma tube edge-to-substrate distances ranging from 3 to 12 mm. Profilometer measurements revealed thicknesses comprised between 500 nm and 1.5 µm at the middle of the deposit. Deposited films analyses clearly show the efficiency of this atmospheric plasma-type TMDSO and HMDSO polymerisation and their similarity with those usually realized under low pressure RPECVD. The most interesting deposited films are obtained when the monomer is introduced under gaseous state, the samples clearly showing a better homogeneity. The influence of the transport gas is not evidenced. More experiments and analyses need to be achieved to complete these preliminary results. It must be stressed that multi-spot deposition has been obtained from plasma multi-jet delivered by a single Plasma Gun.

11:40am **PS+SE-FrM11 XPS to Investigating Spatial and Temporal Modification of Polymeric Platforms for Micro-Fluidic Devices**, ***Marshal Dhayal***, CSIR Centre for Cellular and Molecular Biology (CCMB), India

Spatial and temporal changes in surface chemical composition silicon (Si), carbon (C) and oxygen (O) of polydimethyl siloxane 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 polydimethyl siloxane were calculated and were compared to experimentally obtained ratio for Si/C/O obtained from untreated and plasma treated surfaces used for micro-fluidic devices. The contact angle measurements have shown that 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 polydimethyl siloxane surface as hydrophilic in nature for micro fluidic application. The surface chemistry of PEG-functionalized polydimethyl siloxane 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 polydimethyl siloxane base micro fluidic devices. The effect of different pH of the fluids on the fluid velocity in polydimethyl siloxane -based micro channel was also studied.

Plasma Science and Technology
Room: 210B - Session PS+SS+TF-FrM

Atomic Layer Etching (ALE) and Low-Damage Processes II
Moderator: Toshihisa Nozawa, Tokyo Electron Ltd.

8:20am **PS+SS+TF-FrM1 Atomic Layer Etching of Silicon Dioxide to Enable Self-aligned Contact Integration**, *B. Finch, H. Singh*, ***Eric Hudson***, Lam Research Corporation **INVITED**

CMOS devices have continued to scale dimensionally following the implementation of FinFET transistors. Self-alignment of the source and drain contact to the gate has been presented as an integration solution starting at the 22nm technology node[1]. This self-aligned contact (SAC) integration creates additional challenges and constraints on the etch process for the 10 nm node and beyond. Due to smaller feature dimensions, lithography overlay, and full contact wrap-around of the transistor fins, unprecedented etch precision is now required.

A novel approach for SAC oxide etching has been developed which addresses the many tradeoffs of this application using a directional atomic layer etch process (ALE) as reported by Hudson et al[2]. Key trade-offs to enable contact etching capability of CDs as small as 10 nm include SAC spacer loss, lack of profile control, and contact not-opens. This cyclic SiO_2 ALE process repeats discrete unit process steps of fluorocarbon deposition and ion bombardment to achieve high selectivity of SiO_2 to Si_3N_4 while simultaneously addressing these tradeoffs. Oxide removal rates can be precisely controlled with minimal removal of Si_3N_4 films, enabling a highly selective etch process. Anisotropic, directional etch behavior superior to traditional SiO2 etch is enabled, creating vertical oxide profiles. This capability is highly desirable for SAC etch applications as it maintains the integrity of the gate electrode spacer during etch. Experimental results showing the ability of this oxide ALE process to eliminate tradeoffs is presented

[1] C. Auth, et al, "A 22 nm high performance and low-power CMOS technology featuring fully-depleted tri-gate transistors, self-aligned contacts and high density MIM capacitors," accepted in VLSI Symp. Tech. Dig., Jun. 2012.

[2] E. Hudson, et al, "Highly Selective Atomic Layer Etching of Silicon Dioxide Using Fluorocarbons," accepted in AVS 61st International Symp. & Exhibition, Nov. 2014.

9:00am **PS+SS+TF-FrM3 High Performance Self Align Contact Etching with Newly developed Quasi-ALE**, ***Akihiro Tsuji***, Tokyo Electron Miyagi Limited, Japan, *M. Tabata, H. Watanabe, T. Katsunuma*, Tokyo Electron Miyagi Limited, *M. Honda*, Tokyo Electron Miyagi Limited, Japan

The Self-Aligned Contact (SAC) process has been widely adopted to achieve aligned narrow contacts between electrodes as the pitch shrinkage has progressed with the miniaturization of devices in high-scale integration. In SAC fabrication, it is important to achieve high selectivity of the interlayer insulator (SiO_2) over an etch stop film (SiN) to improve insulation tolerance between the contact plug and the wiring. Such high-selective etch processes have been realized by depositing fluorocarbon (FC) film selectively on the SiN film by using the composition difference between SiO_2 and SiN with fluorocarbon plasma, which protects SiN surface during SiO_2 etch. In order to minimize SiN loss, a balance of FC film thickness and the penetration depth of the ion energy on SiN become significant [1,2]. When trying to achieve improved SiN loss reduction, reducing ion energy is one effective solution, but a balance of ion energy flux and FC radical flux ($E_i \Gamma_i / \Gamma_{CF}$) breaks down, resulting in an excess amount of deposition, causing etch stop to occur. This is caused by the

limited control margin of the ion energy flux over the FC radical flux ratio using conventional processes.

Atomic Layer Etching (ALE) concept has attracted great attention in recent years for its precise fabrication potential at the atomic level and its ability to solve this issue [3,4]. ALE method enables clear separation of ion energy flux and FC radical flux supply by controlling $E_i\ \Gamma_i\ /\ \Gamma_{CF}$ dynamically using a new parameter of flux ratio respective to step time. Furthermore, specific control of the surface condition at each cycle is expected to be effective for precise fabrication. This report discusses the application of the ALE concept in the SAC process as a Quasi-ALE scheme with consideration for implementation to volume production. This scheme realized a dramatic improvement of SiO_2 etch performance with substantial reduction of SiN loss. Further analysis of the surface condition by XPS, SIMS, HR-RBS helped determine the mechanism of selectivity enhancement. Quasi-ALE technology is a promising weapon, corresponding to leading-edge processes of various fabrication requirements along with the miniaturization of devices, towards 10nm and beyond.

Reference

[1] T.Tatsumi, M.Sekine et al. JVST B 18(4), 2000

[2] M.Matsui, M.Sekine et al. JVST A 19(4), 2001

[3] D.Metzler, G.S.Oehrlein et al. JVST A 32(2), 2014

[4] M. Honda, AVS 61th Int. Symp. & Exhibit. (2014)

9:20am **PS+SS+TF-FrM4 Fluorocarbon Based Atomic Layer Etching of Si_3N_4 and Selectivity of SiO_2 over Si_3N_4**, ***Chen Li***, *D. Metzler, G.S. Oehrlein,* University of Maryland, College Park*, C.S. Lai, M. Danek, E.A. Hudson, A. Dulkin*, Lam Research Corporation

Angstrom-level plasma etching precision is required by semiconductor manufacturing for the sub-14 nm technology node. Atomic layer etching (ALE), achieved by a series of self-limiting cycles, can precisely control the amount of reactant available and resulting etching depths. Recently, controlled etching of SiO_2 at the Angstrom-level based on steady-state Ar plasma, periodic injection of a defined number of fluorocarbon (FC) molecules, and synchronized plasma-based Ar^+ ion bombardment has been demonstrated [1,2]. This novel ALE approach is achieved by deposition of a thin (several Angstroms) reactive FC layer on the material surface using pulsed FC flow. Subsequent low energy Ar^+ ion bombardment removes the FC layer along with SiO_2 from the surface. The ion energies were selected to allow only chemical enhanced etching to take place without any physical sputtering, which enables a self-limited SiO_2 removal. We report on controlled etching of Si_3N_4 and SiO_2 layers of the order of one to several Angstroms using this cyclic ALE approach. The work was performed in an inductively coupled plasma reactor. Using SiO_2-Si_3N_4-SiO_2 multi-layer stacks on a Si substrate enabled precise evaluation of selectivity, self-limitation, and modification by *in situ* real time ellipsometry. Si_3N_4 etching and etch selectivity of SiO_2 over Si_3N_4 were studied and evaluated with regard to the dependence on FC surface coverage, precursor selection, ion energy, and etch step length. Surface chemistries of SiO_2 and Si_3N_4 were investigated by vacuum transferred x-ray photoemission spectroscopy (XPS) at each stage of the ALE process. The choice of precursor can have a significant impact on the surface chemistry and therefore the chemically enhanced etching characteristics.

The authors gratefully acknowledge financial support of this work from National Science Foundation (CBET-1134273) and Lam Research Corporation.

References:

[1] D. Metzler, R. Bruce, S. Engelmann, E. A. Joseph, and G. S. Oehrlein, "Fluorocarbon assisted atomic layer etching of SiO_2 using cyclic Ar/C_4F_8 plasma", J Vac Sci Technol A 32, 020603 (2014)

[2] E. Hudson, V. Vidyarthi, R. Bhowmick, R. Bise, H.J. Shin, G. Delgadino, B. Jariwala, D. Lambert, S. Deshmukh, "Highly selective etching of Silicon Dioxide Using Fluorocarbons"; AVS 61st International Symposium & Exhibition (2014);

9:40am **PS+SS+TF-FrM5 Chamber Wall Effect for Fluorocarbon Assisted Atomic Layer Etching of SiO_2 Using Cyclic Ar/C_4F_8 Plasma**, ***Masatoshi Kawakami,*** Hitachi High-Technologies, Japan*, D. Metzler, C. Li, G.S. Oehrlein*, University of Maryland, College Park

The requirement for atomic scale etching is becoming more important with increasing miniaturization of semiconductor devices. A novel approach for oxide etching has been developed by Metzler et al [1]. Controlled etching of SiO_2 at the angstrom-level is based on steady-state Ar plasma and deposition of a thin reactive fluorocarbon layer enabled by precise, periodic C_4F_8 injection. High process stability is necessary for the success of this method and its use in mass production. Chamber wall interactions are crucial to the stability of this process. In this research, we studied the influence of chamber wall temperature and chamber wall chemical state on ALE process performance. The experiments were conducted in an inductively coupled plasma system excited at 13.56 MHz. The temperature of the quartz coupling window was measured with an infrared temperature sensor. *In situ* real time ellipsometry allows for film thickness measurements during the process. Plasma gas-phase chemistry was characterized by optical emission spectroscopy. We conducted the cyclic Ar/C_4F_8 SiO_2 ALE process using different initial chamber temperature, and chamber wall polymer coverage condition. It was found that although the polymer film thickness deposited in each cycle is constant, the etching behavior changed, likely related to a change in depositing species. Chamber wall temperature shows a clear effect on the CO and SiF emission and their relative ratio. When the surface of the quartz coupling window started to be covered by a fluorocarbon film, the overall CO and SiF intensity decreased while the CO/SiF emission peak ratio did not change. The relationship to observed etching behavior will be discussed.

The authors gratefully acknowledge financial support of this work from National Science Foundation (CBET-1134273) and US Department of Energy (DE-SC0001939).

References:

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

10:00am **PS+SS+TF-FrM6 Potential Solutions for Atomic Precision Etching**, ***Olivier Joubert***, LTM-CNRS, France*, E. Despiau-Pujo,* LTM, France*, G. Cunge,* LTM - CEA/LETI, France*, L. Vallier, J. Dubois, A. Tavernier,* Univ. Grenoble Alpes-CNRS-CEA/Minatec-LTM, France*, O. Luere, S. Banna, Y. Zhang*, Applied Materials **INVITED**

The continuous downscaling of device dimensions and introduction of new transistor architectures such as FDSOI or FINFEts transistors is bringing up new challenges for plasma etching technologies. For the gate transistor for example, future technological nodes require patterning capabilities in a range of dimension going below 10 nm. Extremely thin layers (less than 1nm) of materials are now involved in the stacks of materials to pattern requiring in some cases an etch precision better than 1 nm. In other words, the etch selectivity and physical/ chemical damage induced by the plasma must be controlled in a way such as the plasma can stop in a layer of materials as thin as 1nm without damaging the underlayers or the substrate material. Such a precision in processes becomes difficult to reach with the state of the art plasma technologies.

In this presentation, we will describe two plasma technologies that could potentially reach that goal.

A new Technology is the so-called "Thin Layer Etching" technology. In the first step of the TLE technology, H2 or He Ions produced by a capacitive plasma induce modification of silicon based materials while in a second step the modified material is removed in an all dry NF3/NH3 remote plasma that form volatile products with the modified silicon based materials. Performance achieved by TLE for nitride spacer etching will be shown and compared to conventional ICP results.

Fast gas pulsing technology could also be a promising way to form ultra-thin reactive layer during plasma processing, allowing atomic precision etching to be achieved. This concept will be explained and discussed based on preliminary result of silicon etching in chlorine plasmas using atomistic simulation.

10:40am **PS+SS+TF-FrM8 Molecular Dynamics Simulations of Atomic Layer Etching by Low Energy Ions***, **Jun-Chieh Wang**, S. Rauf, J.A. Kenney, L. Dorf, K.S. Collins*, Applied Materials Inc.

In the semiconductor industry, the use of atomic layer etching (ALE) makes it feasible to accurately control the critical dimensions to nanometer level or smaller. In ALE, the target substrate is first exposed to a reactive gas that passivates the surface, which is then followed by ion bombardment with energy below the sputtering threshold. It is critical to precisely control the ion energy and flux during the etching process to remove the topmost layer of the passivated surface without damaging the underlying substrate. Once the passivation layer is removed, the etch process stops. The passivation and etching steps are repeated until one has etched to the desired thickness. In contrast to conventional plasma etch processes, microfabrication using ALE promises high selectivity and low damage to the substrate.

In this presentation, we discuss the properties of ALE using results from molecular dynamics (MD) simulations. The simulation procedure is conceptually similar to those described in previous publications [1,2]. In this study, a crystalline Si(100)-(2x1) or amorphous surface (made by low energy Ar^+ ion bombardment) was generated and equilibrated at room temperature. The bottom layers were fixed in space, and the periodic boundary conditions were applied laterally to remove the boundary effect. The ions are modeled as energetic neutrals. The surface was passivated by repeated bombardment with low energy Cl atoms at normal incident, which was followed by Ar^+ or Cl^+ ion bombardment to remove the passivation

topmost layers. The Berendsen scheme is used between ion/neutral impacts to remove the energy from the surface region and cool the surface layer to room temperature. The Stillinger Weber (SW) type potentials are used for Si-Si, Si-Cl and Cl-Cl interactions. The Ar-Si and Ar-Cl interactions were modeled using Moliere potentials. The leap-frog form of Verlet algorithm was used to numerically integrate the Newton's equation of motion. The MD is applied to study several variants of the ALE process. The fundamental properties of Si etching are also investigated for both bare and Cl-passivated Si surfaces with several ions including Ar^+, Cl^+ and Cl_2^+. These fundamental studies are used to interpret our layer-by-layer ALE experiments in our laboratory.

Reference

[1] N. A. Kubota, D. J. Economou and S. J. Plimpton, J. Appl. Phys. 83, 4055 (1998).

[2] B. A. Helmer and D. B. Graves, J. Vac. Sci. Technol. A. 16, 3502 (1998).

11:00am **PS+SS+TF-FrM9 Atomic Layer Etching of InGaAs using Cl_2/Ar Ion Beam**, ***Jinwoo Park***, *D.H. Yun, H.S. Kim, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

Atomic layer etching can be one of next-generation etching techniques that can be applied to various materials including III-V compounds semiconducting materials such as indium-gallium arsenide (InGaAs) which is a great potential material due to the high carrier mobility for nano-scale devices. In this study, the atomic layer etching characteristics of InGaAs has been investigated using chlorine as adsorption gas and low energy Ar ion for desorption during the etch cycle to control the etch depth precisely and to minimize the surface damage of the material. For the chlorine adsorption, chlorine radical was adsorbed on the InGaAs surface and, during the desorption, the chlorine adsorbed InGaAs was removed by the Ar ion with the energy of about 20eV. By using the atomic layer etching technique, the controlled InGaAs etch depth per cycle and very high etch selectivity of InGaAs over dielectric materials such as silicon dioxide and hafnium dioxide could be obtained. The surface roughness of etched InGaAs characterized by atomic force microscopy was similar to that of un-etched InGaAs at the atomic layer etching condition.

11:20am **PS+SS+TF-FrM10 InGaN Quantum Nanodisks Fabrication by Bio-Template and Neutral Beam Etching**, ***Yi-Chun Lai***, National Chiao Tung University, Taiwan, Republic of China, *A. Higo, C. Thomas, C.Y. Lee, T. Tanikawa, K. Shojiki, S. Kuboya, R. Katayama*, Tohoku University, Japan, *T. Kiba*, Hokkaido University, Japan, *I. Yamashita*, Nara Institute of Science and Technology, Japan, *A. Murayama*, Hokkaido University, Japan, *P.Yu. Yu*, National Chiao Tung University, Taiwan, Republic of China, *S. Samukawa*, Tohoku University

III-N quantum dots (QDs) gain media have generated great interest because of their desirable properties such as low threshold and temperature independence due to the discrete nature of the density of states. A uniform and high-density two-dimensional (2D) array of an isolated QD structure is required when considering applications in visible wavelength such as white LED. In general, size distribution, uniformity, and high-density are trade-offs when using a conventional self-assembly method; therefore, we have developed a technique that integrates a bio-template with neutral beam etching (NBE) process.

In this work, quantum nanodisks (QNDs) were fabricated from InGaN/GaN single quantum well (SQW) by using a bio-template and NBE. We developed a damage-less, top-down fabrication process for achieving high density of QNDs such as 2×10^{11} cm^{-2} embedded in 10 nm in diameter and 20 nm high nanopillars. The fabricated QNDs have great potential for fabricating quantum optoelectronic devices because of controllable diameter and thickness.

The InGaN/GaN SQW wafer was grown on a 2-inch c-plane sapphire substrate by metal-organic vapor phase epitaxy (MOVPE). The structure consisted of a 1μm-thick GaN buffer layer, 3nm-thick $In_{0.1}$GaN and a 10nm-thick GaN capping layer. We used ferritins modified with polyethylene glycol (PEG ferritins) that include a metal oxide core for the etching mask. Oxygen annealing in vacuum was used to remove the ferritin protein shell at 350˚C, at chamber pressure of 32 Pa. Therefore the 7 nm diameter iron core was remained on the surface. Then hydrogen radial treatment, hydrogen passivation and NBE etching process were performed. At first, hydrogen radical treatment was realized to remove the surface oxide at chamber pressure of 32 Pa at 350˚C. Subsequently, hydrogen passivation was done to avoid any re-oxidation during the process. Finally, SQW was etched completely to form nanopillars using 40 sccm Cl_2 at a chamber pressure of 0.1 Pa, with a substrate temperature of 100˚C, ICP power of 800 W and bottom electrode bias power of 10W. As a result, InGaN/GaN 10 nm in diameter and 20 nm high nanopillars could be fabricated. The etching profile was confirmed by Transmission electron microscopy (TEM).

After etching, we measured the photoluminescence (PL) and time-resolved PL (TRPL) to observe the quantum confinement energy levels. According to the PL measurements, we found an energy shift of 1.25 eV, from 2.9eV for SQWs to 2.75eV for QNDs. Although these measurements are still on-going now, we will clearly analyze and discuss the phenomena related to this shift in energy in the near future.

11:40am **PS+SS+TF-FrM11 Towards a Nanoscale Plasma Etching Precision: Molecular Dynamics Simulations of Si-Cl Interactions**, ***Paulin Brichon***, Univ. Grenoble Alpes-CNRS-CEA/Minatec-LTM,38000 Grenoble-France, *E. Despiau-Pujo*, LTM, France, *O. Mourey*, Univ. Grenoble Alpes-CNRS-CEA/Minatec-LTM,38000 Grenoble-France, *G. Cunge*, LTM - CEA/LETI, France, *O. Joubert*, Univ. Grenoble Alpes-CNRS-CEA, France

Due to high ion bombardment energies and significant fragmentation rates, conventional CW plasma processes are not able to selectively etch ultrathin films without damaging the active layers of advanced nanoelectronic devices (FDSOI, FinFET). In order to achieve uniform and damage-free etching of sub-nm-thick materials, one alternative is to lower the electron temperature (T_e) of the plasma. This can be achieved temporally by pulsing the plasma (i.e. switching on and off the RF source power), which introduces two additional parameters to tune an etching process, the pulsation frequency and the duty cycle (DC). Pulsed-plasma discharges exhibit lower average ion energies (E_i~5-10eV); their chemical reactivity (or dissociation rate) can also be controlled by varying the DC. Another alternative is to lower T_e spatially, by segregating the electron heating region far from the wafer. These low-T_e plasmas are characterized by very low E_i (E_i<5eV) and high radical densities.

With lower E_i and controllable reactivity, these plasmas are promising to etch sub-nm-thick stacked materials. However, the interactions between reactive plasmas and surfaces are so complex that the efficient development of new processes can require numerical simulations. Therefore, we develop Molecular Dynamics (MD) simulations to understand the impact of various plasma technologies on the interactions between ultrathin Si films and Cl_2 plasmas under a wide range of plasma conditions. They help to understand the precise role of E_i in plasma-surface interactions, the relationship between the flux/energy of reactive species bombarding the surface and its structural/chemical modifications.

In this study, MD simulations - coupled with experiments - are performed to quantify modifications (plasma-induced damage, etch rate) of Si films after exposition to various Cl_2 plasma conditions, simulated by bombarding the substrate with both ion and neutral species. All simulations show the formation of a stable $SiCl_x$ reactive layer and a constant etch yield (EY) at steady state. The key plasma parameter to control the etching of ultrathin Si layers is E_i, which lowers both the damaged layer thickness and EY when it is decreased. The neutral-to-ion flux ratio (Γ) is the 2nd key parameter: its increase reduces the damaged layer thickness while the etch rate grows. While maintaining Γ constant, the neutral dissociation rate and the ion composition do not influence significantly the etching process. Etching simulations of a simple Si pattern are then compared to the etching of blanket silicon, focusing on phenomena such as ion channeling, passivation/damage of pattern sidewalls and top pattern erosion.

Authors Index

Bold page numbers indicate the presenter

— A —

Abraha, P.: PS-ThP28, **54**
Abuzairi, T.: SM+AS+BI+PS-ThM5, 38
Agarwal, A.: PS+SS+TF-WeM12, 30; PS2-TuA3, **23**; PS-MoA5, 13
Agarwal, S.: PS+EM-MoA8, 11
Ahlgren, M.: SE+PS-TuA7, 25
Aktan, E.: PS-ThP2, 50
Al-Bataineh, S.: SE+PS+SM-TuM2, **18**
Alcantara Ortigoza, M.: 2D+EM+IS+NS+PS+SP+SS-FrM6, 56
Alman, D.: PS-ThP5, 50
Altieri, N.D.: PS1-TuA11, 22; PS1-TuA7, **21**
Alvarez, D.: EM+NS+PS-MoA7, 10; EM+NS+PS-MoA8, **10**
Alverez, D.: EM+NS+PS-MoM4, 3
Amano, T.: PS+SE-FrM5, 58; PS-ThP13, 52
Ande, C.K.: PS+TF-WeA7, 34
Anders, A.: PS+2D+SE-WeM5, 27
Anderson, C.: PS+BI+SM-TuM11, 15
Archambault-Caron, M.: PS+SE-MoM9, 6
Armstrong, S.: PS-ThP3, 50; SE+PS-TuA2, 25
Arnold, J.C.: PS1-TuA8, 21; PS1-TuA9, 22; PS-TuM1, **16**; PS-TuM5, 17; PS-TuM6, 17
Arnold, M.S.: 2D+EM+IS+NS+PS+SP+SS-FrM10, 57
Arslanbekov, R.R.: PS-ThP27, 54
Arvet, C.: PS+SS+TF-WeM4, 29; PS-MoM1, 6
Ashfold, M.N.R.: PS+2D+SE-WeM3, **27**
Asmussen, J.: PS+TF-WeA12, 35; PS-ThA8, **44**
Awakowicz, P.: PS+TF-WeA9, **35**
Azcatl, A.: PS+2D+SE-WeM12, **28**

— B —

Babaeva, N.Yu.: SM+AS+BI+PS-ThA1, 46
Baklanov, M.: PS-TuM12, 17
Bakoglidis, K.D.: PS+AP+SE-ThA9, **42**
Ballard, J.: SD+AS+EM+PS-ThA8, **45**
Baneton, J.: PS+EM-MoA9, **11**
Banna, S.: PS+SS+TF-FrM6, 60
Barankova, H.: SE+PS+SM-TuM5, 19
Bardos, L.: SE+PS+SM-TuM5, **19**
Barnola, S.: PS+SS+TF-WeM4, 29; PS-MoM1, **6**
Barthel, M.: PS-ThA1, 43
Bartis, E.A.J.: PS+BI+SM-TuM11, 15; PS+SE-MoM5, 5
Bayer, B.C.: PS+2D-ThM3, 37
Beams, R.: 2D+EM+NS+PS+SP+SS+TF-MoM4, 1
Beier, O.: SE+PS+SM-TuM3, 18
Beique, G.: PS-TuM3, 16
Bekman, H.H.P.Th.: PS-TuM13, **18**
Belen, J.: PS2-TuA11, 24
Bellido-Gonzalez, V.: PS+TF-WeA4, 34
Benjamin, N.: PS-ThA3, **43**
Benson, R.: PS-MoM4, 7
Bent, S.F.: SD+AS+EM+PS-ThA10, 46; SD+AS+EM+PS-ThA6, 45
Berger, B.: PS-ThA1, **43**
Bergsman, D.S.: SD+AS+EM+PS-ThA6, 45
Bermudez, V.M.: 2D+EM+NS+PS+SP+SS+TF-MoM1, 1
Bhattacharjee, S.: SM+AS+BI+PS-ThM5, 38
Bilici, M.A.: PS+SE-MoM8, **5**
Biolsi, P.: PS-TuM3, 16
Blatz, J.: PS-ThP22, 53
Blechle, J.M.: PS-MoA3, **12**
Bluck, T.: SE+PS-TuA11, 26
Boffard, J.: PS+AP+SE-ThA8, 42; PS-MoA6, 13
Bol, A.A.: TF+EM+NS+PS+SM-ThM12, 41; TF+EM+NS+PS+SM-ThM6, 40
Bolt, R.J.: PS-TuM13, 18
Booth, J.-P.: PS+2D-ThM1, 37; PS2-TuA3, 23; PS-MoA10, 14; PS-MoA5, **13**
Boris, D.R.: PS+SS+TF-WeM12, 30; PS-ThA6, 43; PS-ThA7, **44**
Borros, S.: SM+AS+BI+PS-ThM10, **39**
Bosch, R.H.E.C.: PS+TF-WeA7, **34**
Bottoms, W.R.: EM+MN+PS-TuA1, **20**
Boufnichel, M.: PS1-TuA3, 20
Bourke, P.: PS+BI+SM-TuM12, 15
Boutaud, B.: PS+AS+SS-WeA11, 33
Bouwstra, J.B.: TF+PS-ThA8, 48
Boyle, C.R.: PS+SE-MoM8, 5
Brandt, A.: EM+NS+PS-MoA9, 10
Brandt, St.: PS-ThA1, 43
Bredin, J.: PS-MoA10, 14
Brenning, N.: PS+2D+SE-WeM10, 27
Breton, M.: PS-MoM3, 7
Brichon, P.: PS+SS+TF-FrM11, **61**
Brink, M.: PS+EM-MoA4, 11
Brown, D.W.: SE+PS-TuA11, 26
Bruce, R.L.: PS+EM-MoA4, 11; PS1-TuA8, 21; PS1-TuA9, **22**; PS-MoM11, 8
Bruggeman, P.J.: PS+BI+SM-TuM10, 15; PS+BI+SM-TuM3, **15**
Bultman, J.: PS+2D+SE-WeM11, 27

— C —

Caldarella, G.: PS+EM-MoA9, 11
Camps, E.: PS-ThP29, 54
Canal, C.: SM+AS+BI+PS-ThA3, **47**
Carlström, C.F.: SE+PS-TuA7, 25
Caruso, A.N.: PS-ThP21, 53
Castaneda, H.: 2D+EM+NS+PS+SP+SS+TF-MoM3, 1
Cavallaro, A.: SE+PS+SM-TuM2, 18
Cavallo, F.: 2D+EM+IS+NS+PS+SP+SS-FrM10, 57
Chabal, Y.J.: SD+AS+EM+PS-ThA8, 45
Chabert, P.: PS2-TuA3, 23; PS-MoA5, 13
Chae, H.: PS-ThP14, 52
Chagarov, E.: EM+NS+PS-MoA9, 10
Chambettaz, F.: PS+SS+TF-WeM3, **28**
Chan, B.T.: PS-TuM11, 17
Chang, J.P.: PS1-TuA11, 22; PS1-TuA7, 21; TF+EM+NS+PS+SM-ThM5, **40**
Chang, M.: EM+NS+PS-MoM4, 3
Chang, S.H.: SM+AS+BI+PS-ThM4, 38
Chang, T.Y.: PS-ThP26, 54
Chao, R.: PS-MoM3, 7; PS-TuM6, 17
Chen, J.K.C.: PS1-TuA11, **22**; PS1-TuA7, 21
Chen, L.C.: PS+2D-ThM4, 37
Chen, M.C.: PS-ThP10, **51**
Chen, M.J.: SM+AS+BI+PS-ThM4, 38
Chen, Y.T.: PS+2D+SE-WeM13, 28
Cheng, G.: 2D+EM+NS+PS+SP+SS+TF-MoM8, 2
Chien, D.: TF+EM+NS+PS+SM-ThM5, 40
Choi, B.J.: SD+AS+EM+PS-ThA9, **45**
Chong, K.S.L.: SE+PS+SM-TuM11, 19
Chou, H.: SM+AS+BI+PS-ThM5, 38
Choudhury, F.: PS-ThP24, 54
Chu, J.P.: SM+AS+BI+PS-ThM4, 38
Chyntara, S.: SM+AS+BI+PS-ThM4, 38
Ciolan, M.A.: SM+AS+BI+PS-ThM5, 38
Clark, R.: EM+NS+PS-MoA3, **9**; SD+AS+EM+PS-ThA11, 46
Closser, R.G.: SD+AS+EM+PS-ThA6, **45**
Coad, B.R.: SM+AS+BI+PS-ThA6, **47**
Cogan, S.F.: TF+PS-ThA6, **48**
Coleman, D.: PS-ThP4, **50**
Collet, G.: SM+AS+BI+PS-ThM1, 38
Collins, K.S.: PS+SS+TF-FrM8, 60; PS+SS+TF-WeM11, 30; PS+SS+TF-WeM12, 30; PS2-TuA12, 24; PS2-TuA3, 23
Consiglio, S.: SD+AS+EM+PS-ThA11, 46
Cornelissen, L.E.: PS+TF-WeA7, 34
Couet, S.: PS1-TuA12, 22
Coumou, D.: PS-MoA8, 14
Creatore, M.: TF+EM+NS+PS+SM-ThM13, 41; TF+PS-ThA3, 48
Creyghton, Y.L.M.: PS+TF-WeA8, **35**
Crotti, D.: PS1-TuA12, 22
Cui, L.: SE+PS+SM-TuM4, **18**
Cullen, P.J.: PS+BI+SM-TuM12, 15
Cunge, G.: PS+2D-ThM1, 37; PS+SS+TF-FrM11, 61; PS+SS+TF-FrM6, 60
Curreli, D.: PS-ThP5, 50

— D —

Danek, M.: PS+SS+TF-FrM4, 60
Daniel, R.: SE+PS+SM-TuM3, 18
Darny, T.: SM+AS+BI+PS-ThM1, 38
Das, S.: 2D+EM+IS+NS+PS+SP+SS-FrM8, 57
Dauskardt, R.H.: PS+SE-FrM8, 58; PS+SE-FrM9, 58; SE+PS+SM-TuM4, 18
Davydov, A.V.: 2D+EM+NS+PS+SP+SS+TF-MoM4, 1
De Gendt, S.: PS-TuM11, 17
de la Barrera, S.: 2D+EM+NS+PS+SP+SS+TF-MoM9, **2**
De Lucia, F.C.: PS-MoA1, **12**
de Marneffe, J.-F.: PS-TuM12, 17
de Oliveira, N.: PS-MoA10, 14
De Temmerman, G.: PS+EM-MoA10, 12
de Vries, H.W.: TF+PS-ThA1, **48**; TF+PS-ThA8, 48
Debaille, V.: PS+EM-MoA9, 11
Dechene, J.M.: PS-TuM5, **17**; PS-TuM6, 17
Decoster, S.: PS-TuM11, 17
Dedrick, J.P.: PS-MoA10, 14
del Pozo, S.: PS-ThA2, **43**
Deshpande, V.: PS-ThP19, 53
Despiau-Pujo, E.: PS+SS+TF-FrM11, 61; PS+SS+TF-FrM6, 60
Desvoivres, L.: PS-MoM1, 6
Dev, P.: PS+2D-ThM10, 37
deVilliers, A.: PS-TuM3, 16
Dhayal, M.: PS+SE-FrM11, **59**
Dhungana, S.: PS-ThP21, 53
Dick, D.: SD+AS+EM+PS-ThA8, 45
Diyatmika, W.: SM+AS+BI+PS-ThM4, 38
Dogan, I.: PS+EM-MoA8, **11**
Donadio, G.: PS1-TuA12, 22
Dong, S.: PS+SE-FrM8, **58**
Donnelly, V.M.: PS+AS+SS-WeA3, **32**; PS-ThP20, 53
Dorf, L.: PS+SS+TF-FrM8, 60; PS+SS+TF-WeM11, **30**; PS+SS+TF-WeM12, 30
Dorf, S.R.: PS+SS+TF-WeM11, 30
Dozias, S.: SM+AS+BI+PS-ThM1, 38
Droopad, R.: EM+NS+PS-MoA7, 10; EM+NS+PS-MoM3, 3; EM+NS+PS-MoM4, 3
Dubois, G.: SE+PS+SM-TuM4, 18
Dubois, J.: PS+SS+TF-FrM6, 60; PS+SS+TF-WeM3, 28
Dulkin, A.: PS+SS+TF-FrM4, 60
DuMont, J.W.: PS+SS+TF-WeM10, 29; PS+SS+TF-WeM6, 29
Durand, W.: PS+EM-MoA4, 11
Dussart, R.: PS+AS+SS-WeA11, 33; PS1-TuA3, 20; PS-TuM12, 17
Dzarasova, A.: PS-ThP19, 53

— E —

Economou, J.: PS-ThP20, 53
Edmonds, M.: EM+NS+PS-MoA7, 10; EM+NS+PS-MoM4, **3**

Ehiasarian, A.P.: SE+PS-TuA7, 25
Ehrmann, O.: PS+TF-WeA4, 34
Eichfeld, S.M.: 2D+EM+NS+PS+SP+SS+TF-MoM9, 2
Eizenberg, M.: EM+NS+PS-MoM3, 3
El Hafni-Rahbi, B.: SM+AS+BI+PS-ThM1, 38
Elam, F.M.: TF+PS-ThA8, **48**
Ellison, C.: PS+EM-MoA4, 11
Emmelkamp, J.: PS+TF-WeA8, 35
Engelmann, S.U.: PS+EM-MoA4, 11; PS1-TuA8, 21; PS1-TuA9, 22; PS-MoM11, 8
Eom, T.: SD+AS+EM+PS-ThA9, 45
Ergun, C.: PS-ThP2, 50
Eriguchi, K.: PS+AS+SS-WeA10, **33**
Eriksson, M.A.: 2D+EM+IS+NS+PS+SP+SS-FrM10, 57

— F —

Farrell, R.: PS-TuM3, 16
Feenstra, R.: 2D+EM+NS+PS+SP+SS+TF-MoM9, 2
Feigelson, B.N.: 2D+EM+NS+PS+SP+SS+TF-MoM1, **1**; 2D+EM+NS+PS+SP+SS+TF-MoM3, 1
Feng, P.X.-L.: PS+SE-MoM11, 6
Fernando, N.: EM+NS+PS-MoA10, **10**
Fernsler, R.F.: PS-ThA6, 43; PS-ThA7, 44
Ferrah, D.: PS+2D-ThM1, 37
Finch, B.: PS+SS+TF-FrM1, 59
Fisher, E.R.: PS+BI+SM-TuM13, 16; PS-MoA3, 12; SM+AS+BI+PS-ThM13, 39
Foad, M.A.: EM+NS+PS-MoA2, 9
Foucher, M.: PS2-TuA3, 23; PS-MoA10, 14; PS-MoA5, 13
Fowlkes, J.D.: PS+SS+TF-WeM13, 30
Franek, J.: PS-ThA1, 43
Franke, E.: PS-TuM3, 16
Franz, R.: SE+PS-TuA10, **26**
Fredrickson, G.H.: PS+EM-MoA1, 11
Friddle, P.: PS-TuM6, 17
Fuerst, T.F.: PS+TF-WeA11, **35**
Fuhrer, M.: 2D+EM+NS+PS+SP+SS+TF-MoM3, 1
Fukasawa, M.: PS+AS+SS-WeA8, 32; PS2-TuA4, 23
Fullam, J.: PS-MoM3, 7
Furdyna, J.: 2D+EM+NS+PS+SP+SS+TF-MoM9, 2
Furnemont, A.: PS1-TuA12, 22
Furuta, R.: SM+AS+BI+PS-ThA11, 47

— G —

Gagnon, H.: PS+SE-MoM9, 6
Gang, Z.H.: PS-ThP15, 52
Gans, T.: PS-MoA10, 14
Garcia Espallargas, S.J.: TF+PS-ThA3, 48
Garcia-Barros, M.: PS+SS+TF-WeM4, 29; PS-MoM1, 6
Gaskill, D.K.: 2D+EM+NS+PS+SP+SS+TF-MoM3, 1
George, S.M.: PS+SS+TF-WeM10, 29; PS+SS+TF-WeM6, **29**
Ghosh, S.: PS+SE-MoM11, **6**
Gizzo, V.: PS-MoM6, 7
Go, D.B.: PS+SE-MoM8, 5
Gobina, E.: SE+PS+SM-TuM12, 19
Godyak, V.: PS-MoA7, 13
Goeckner, M.J.: PS-MoA8, 14; PS-ThP17, 52
Goldberger, J.: 2D+EM+NS+PS+SP+SS+TF-MoM10, **2**
Goossens, D.: PS1-TuA12, 22
Gordon, M.: PS+EM-MoA6, **11**
Goss, M.: PS-TuM6, 17
Gosset, N.: PS1-TuA3, 20
Goto, K.: SM+AS+BI+PS-ThM12, **39**
Granick, J.L.: PS+BI+SM-TuM10, **15**
Graves, D.B.: PS+BI+SM-TuM11, 15; PS+BI+SM-TuM5, **15**; PS+SE-FrM6, 58
Greczynski, G.: PS+AP+SE-ThA9, 42; SE+PS-TuA1, **24**
Greene, J.E.: SE+PS-TuA1, 24
Griesser, H.J.: SM+AS+BI+PS-ThA6, 47
Griesser, S.S.: SM+AS+BI+PS-ThA6, 47
Grosse, S.: PS-ThP18, 53
Grundmeier, G.: PS+TF-WeA9, 35
Gstrein, F.: SD+AS+EM+PS-ThA3, **44**
Gu, Y.: PS+TF-WeA12, 35
Gudmundsson, J.T.: PS+2D+SE-WeM10, **27**
Guenther, M.: PS-ThP18, 53
Guillorn, M.: PS+EM-MoA4, 11
Guo, Y.: EM+NS+PS-MoA5, 9
Gupta, A.: 2D+EM+IS+NS+PS+SP+SS-FrM8, **57**

— H —

Haidar, Y.: PS-ThP12, 51
Hamaguchi, S.: PS+AS+SS-WeA8, 32; PS2-TuA4, 23; SM+AS+BI+PS-ThM12, 39
Hamilton, J.R.: PS-ThA10, 44
Hanna, A.R.: PS-MoA3, 12
Hänninen, T.: SE+PS-TuA9, **25**
Hashemi, F.H.: SD+AS+EM+PS-ThA10, **46**
Hashizume, H.: SM+AS+BI+PS-ThA11, 47
Hassan, V.: EM+NS+PS-MoA2, 9
Haukka, S.: SD+AS+EM+PS-ThA1, **44**
Hausmann, D.M.: TF+EM+NS+PS+SM-ThM1, **39**
Hawker, M.J.: SM+AS+BI+PS-ThM13, **39**
Hawranek, G.: SE+PS-TuA10, 26
Hayashi, T.: PS-MoA4, 12
He, A.Y.: SE+PS+SM-TuM11, 19
Healy, K.E.: SM+AS+BI+PS-ThA8, **47**
Heinlein, E.: EM+NS+PS-MoA8, 10
Henry, P.: PS-ThP21, 53
Hernandez, K.: PS-ThP17, **52**
Hernandez, S.: PS+2D-ThM10, **37**
Hernández, S.C.: 2D+EM+IS+NS+PS+SP+SS-FrM1, 56; 2D+EM+NS+PS+SP+SS+TF-MoM1, 1; PS-ThA6, 43
Hickey, R.: EM+NS+PS-MoA10, 10
Hight Walker, A.: 2D+EM+NS+PS+SP+SS+TF-MoM8, 2
Higo, A.: PS+SS+TF-FrM10, 61
Hinkle, C.L.: PS+2D+SE-WeM12, 28
Hisamatsu, T.: PS-TuM4, **16**
Hite, J.K.: 2D+EM+NS+PS+SP+SS+TF-MoM1, 1; 2D+EM+NS+PS+SP+SS+TF-MoM3, 1
Hofmann, T.: PS+SE-FrM7, **58**
Högberg, H.: SE+PS-TuA9, 25
Holmes, R.: EM+NS+PS-MoA8, 10
Holsteyns, F.: PS-TuM11, 17
Holtmannspötter, J.: PS+SE-FrM7, 58
Honda, M.: PS+SS+TF-FrM3, 59; PS-TuM4, 16
Hori, M.: PS1-TuA1, 20; PS-MoA4, 12; SM+AS+BI+PS-ThA11, 47
Horvath, K.: PS1-TuA8, 21
Hovish, M.Q.: PS+SE-FrM9, **58**
Hsieh, C.Y.: SE+PS+SM-TuM10, **19**
Hsieh, J.H.: SM+AS+BI+PS-ThM3, 38
Hsu, C.C.: PS+SE-MoM6, **5**; PS-ThP10, 51; PS-ThP16, 52; PS-ThP9, 51
Hu, J.: PS+2D+SE-WeM11, 27
Hu, K.: EM+NS+PS-MoA1, **9**
Huang, S.: PS-ThA10, **44**
Huang, W.C.: SM+AS+BI+PS-ThM4, 38
Huang, Y.H.: PS+SE-MoM6, 5; PS-ThP16, **52**
Hubert, J.: SE+PS+SM-TuM1, 18
Hudson, E.A.: PS+SS+TF-FrM1, **59**; PS+SS+TF-FrM4, 60
Hultman, L.: PS+AP+SE-ThA9, 42; SE+PS-TuA1, 24; SE+PS-TuA9, 25
Hunold, O.: PS+2D+SE-WeM13, **28**
Hunter, R.C.: PS+BI+SM-TuM10, 15
Hwang, C.S.: SD+AS+EM+PS-ThA9, 45

— I —

Ikeda, N.: PS-MoM8, 7
Ikeda, Y.: SM+AS+BI+PS-ThA10, **47**
Im, Y.H.: PS2-TuA1, **23**
Ishiguro, M.: PS+AS+SS-WeA12, **33**
Ishii, Y.: PS-MoM10, **7**
Ishikawa, K.: PS1-TuA1, 20; PS-MoA4, 12; SM+AS+BI+PS-ThA11, **47**
Isobe, M.: PS2-TuA4, 23; SM+AS+BI+PS-ThM12, 39
Itagaki, N.: PS+SE-FrM5, 58; PS-ThP13, 52
Ito, A.: PS1-TuA8, 21
Ito, M.: SM+AS+BI+PS-ThA11, 47
Itou, A.: PS1-TuA9, 22; PS-MoM11, 8
Itsuki, D.: SM+AS+BI+PS-ThM12, 39
Izawa, M.: PS+SS+TF-WeM5, 29

— J —

Jacobberger, R.M.: 2D+EM+IS+NS+PS+SP+SS-FrM10, 57
Jäger, E.: SE+PS+SM-TuM3, 18
Jain, .: EM+NS+PS-MoM2, 3
Jang, H.: PS-ThP14, 52
Jantschner, O.: SE+PS+SM-TuM3, 18
Jasieniak, M.: SM+AS+BI+PS-ThA6, 47
Jena, D.: 2D+EM+NS+PS+SP+SS+TF-MoM9, 2
Jensen, J.: SE+PS-TuA9, 25
Jinno, M.: SM+AS+BI+PS-ThA10, 47
Job, N.: PS+EM-MoA9, 11
Johnson, E.V.: PS+2D-ThM1, 37
Johnson, K.: EM+NS+PS-MoA8, 10
Joseph, E.A.: PS+EM-MoA4, 11; PS1-TuA8, 21; PS1-TuA9, 22; PS-MoM11, 8
Joubert, O.: PS+SS+TF-FrM11, 61; PS+SS+TF-FrM6, **60**; PS+SS+TF-WeM3, 28
Joy, N.: PS-MoM6, 7
Joyeux, D.: PS-MoA10, 14
Junkermeier, C.: PS+2D-ThM10, 37
Jurczyk, B.: PS-ThP5, 50

— K —

Kachian, J.: EM+NS+PS-MoA1, 9; EM+NS+PS-MoM4, 3
Kalanyan, B.: 2D+EM+NS+PS+SP+SS+TF-MoM4, **1**
Kaler, S.: PS-ThP20, **53**
Kamei, M.: PS+AS+SS-WeA10, 33
Kanakasabapathy, S.: PS-MoM3, 7
Kanekiyo, T.: PS+SS+TF-WeM5, 29
Kao, P.K.: PS+SE-MoM6, 5
Kar, GS.: PS1-TuA12, 22
Karahashi, K.: PS+AS+SS-WeA8, 32
Karwal, S.: TF+EM+NS+PS+SM-ThM13, **41**
Kasashima, Y.: PS-ThP6, **51**
Katayama, R.: PS+SS+TF-FrM10, 61
Katsunuma, T.: PS+SS+TF-FrM3, 59
Kawakami, M.: PS+SS+TF-FrM5, **60**
Kawakami, S.: PS+AP+SE-ThA3, 42
Kawasaki, T.: PS-ThP13, 52
Kazior, T.: EM+MN+PS-TuA3, **20**
Keller, D.: PS-MoM4, 7
Kelly, M.W.: PS+2D+SE-WeM3, 27
Kenney, J.A.: PS+SS+TF-FrM8, 60; PS2-TuA12, **24**
Kent, T.: EM+NS+PS-MoA7, 10; EM+NS+PS-MoM3, 3; EM+NS+PS-MoM4, 3
Kessels, W.M.M.: PS+TF-WeA7, 34; TF+EM+NS+PS+SM-ThM10, 40; TF+EM+NS+PS+SM-ThM12, 41; TF+EM+NS+PS+SM-ThM13, 41; TF+EM+NS+PS+SM-ThM6, 40
Kesters, E.: PS-TuM11, 17
Khalili, P.: TF+EM+NS+PS+SM-ThM5, 40
Kiba, T.: PS+SS+TF-FrM10, 61
Kieda, C.: SM+AS+BI+PS-ThM1, 38
Kievit, O.: PS-TuM13, 18

Kihara, Y.: PS-TuM4, 16
Kikuchi, Y.: PS1-TuA10, 22
Kim, H.: EM+NS+PS-MoA9, 10
kim, H.J.: EM+NS+PS-MoM1, 3
Kim, H.S.: PS+EM-MoA3, 11; PS+SS+TF-FrM9, 61
Kim, M.J.: PS+2D+SE-WeM12, 28
Kim, N.: PS-ThP1, **50**
Kim, R.: PS-TuM3, 16
Kim, S.: PS-ThP22, 53
Kim, S.K.: EM+NS+PS-MoM1, **3**
Kim, T.: PS1-TuA11, 22
Kim, W.: PS1-TuA12, 22
Kimes, W.A.: 2D+EM+NS+PS+SP+SS+TF-MoM4, 1
King, S.W.: PS-ThP21, 53
Kitajima, T.: PS-ThP7, **51**
Knoll, A.J.: PS+BI+SM-TuM11, 15; PS+SE-MoM5, **5**
Knoops, H.C.M.: TF+EM+NS+PS+SM-ThM10, **40**
Ko, A.: PS-MoM3, 7; PS-TuM3, 16
Kobayashi, H.: PS+SS+TF-WeM5, 29
Kobayashi, Y.: PS+AP+SE-ThA3, 42
Koepke, M.: PS-ThA1, 43
Koga, K.: PS+SE-FrM5, **58**; PS-ThP13, 52
Koizumi, N.: PS1-TuA12, 22
Kolmakov, A.: 2D+EM+NS+PS+SP+SS+TF-MoM8, 2
Kolobov, V.I.: PS-ThP27, **54**
Kolodzey, J.: EM+NS+PS-MoA10, 10
Kondeti, V.S.S.K.: PS+BI+SM-TuM10, 15
Kondo, H.: PS1-TuA1, 20; PS-MoA4, 12; SM+AS+BI+PS-ThA11, 47
Kondo, T.: 2D+EM+IS+NS+PS+SP+SS-FrM7, 56
Kondo, Y.: PS-MoA4, **12**
Kosaka, Y.R.: 2D+EM+IS+NS+PS+SP+SS-FrM7, 56
Koshiishi, A.: PS+AS+SS-WeA9, 33
Koster, N.B.: PS-TuM13, 18
Kouzuma, Y.: PS+SS+TF-WeM5, 29
Kratzer, M.C.: PS+2D-ThM3, 37
Kröhnert, K.: PS+TF-WeA4, 34
Kubota, T.: PS1-TuA10, **22**
Kuboya, S.: PS+SS+TF-FrM10, 61
Kudo, Y.: PS+SS+TF-WeM5, 29
Kudriavtsev, V.: SE+PS-TuA11, **26**
Kummel, A.C.: EM+NS+PS-MoA1, 9; EM+NS+PS-MoA7, 10; EM+NS+PS-MoA9, 10; EM+NS+PS-MoM3, 3; EM+NS+PS-MoM4, 3
Kushner, M.J.: PS2-TuA11, 24; PS-ThA10, 44; SM+AS+BI+PS-ThA1, **46**
Kwon, Y.H.: PS-ThP15, **52**

— L —

Labelle, C.: PS-TuM3, 16; PS-TuM5, 17; PS-TuM6, 17
Labonte, A.P.: PS-TuM5, 17; PS-TuM6, **17**
Ladroue, J.: PS1-TuA3, 20
Lagally, M.G.: 2D+EM+IS+NS+PS+SP+SS-FrM10, 57
Lagrasta, S.: PS+SS+TF-WeM4, 29
Lai, C.S.: PS+SS+TF-FrM4, 60
Lai, Y.-C.: PS+SS+TF-FrM10, **61**
Lalor, J.: PS+BI+SM-TuM12, 15
Lane, B.: PS+AS+SS-WeA9, **33**
Lanford, W.A.: PS-ThP21, 53
Lang, K.D.: PS+TF-WeA4, 34
LaRoche, J.: EM+MN+PS-TuA3, 20
LaRose, J.D.: PS-MoM6, **7**
Lau, K.K.S.: SE+PS+SM-TuM10, 19
Laudrel, E.: PS+AS+SS-WeA11, **33**
Le, D.: 2D+EM+IS+NS+PS+SP+SS-FrM9, 57
Le, Q.T.: PS-TuM11, **17**
Lee, C.M.: SM+AS+BI+PS-ThM4, 38
Lee, C.S.: SE+PS+SM-TuM11, 19
Lee, C.Y.: PS+SS+TF-FrM10, 61
Lee, H.: PS-ThP14, 52
Lee, J.: PS1-TuA9, 22
Lee, J.U.: EM+NS+PS-MoM8, **4**
Lee, S.: PS-ThA10, 44
Lee, W.K.: PS+2D-ThM10, 37
Lee, Y.: PS+SS+TF-WeM10, **29**; PS+SS+TF-WeM6, 29
Lee, Y.T.: SM+AS+BI+PS-ThM3, **38**
Lefaucheux, P.: PS+AS+SS-WeA11, 33; PS1-TuA3, 20; PS-TuM12, 17
Lei, M.K.: SE+PS-TuA12, **26**
Leite, M.: 2D+EM+NS+PS+SP+SS+TF-MoM8, 2
Leou, K.C.: PS-ThP26, 54
Lerouge, S.: PS+SE-MoM9, 6
Leroy, F.: PS-TuM12, **17**
Leusink, G.: SD+AS+EM+PS-ThA11, 46
Leverd, F.: PS+SS+TF-WeM4, 29
Lewis, B.B.: PS+SS+TF-WeM13, 30
Li, C.: PS+SS+TF-FrM4, **60**; PS+SS+TF-FrM5, 60; SM+AS+BI+PS-ThM3, 38
Li, H.: PS+AS+SS-WeA8, **32**; PS+TF-WeA4, 34
Li, W.: PS-ThP22, **53**
Li, X.: SE+PS+SM-TuM11, **19**; TF+EM+NS+PS+SM-ThM5, 40
Liese, M.: PS-ThA1, 43
Lietz, A.M.: SM+AS+BI+PS-ThA1, 46
Likhanskii, A.: PS+AP+SE-ThA8, 42
Lin, C.C.: PS+AP+SE-ThA8, 42; PS-MoA6, 13
Lin, J.: SE+PS-TuA8, **25**
Lin, T.: PS1-TuA12, 22
Lin, Y.-C.: 2D+EM+NS+PS+SP+SS+TF-MoM9, 2
Lindsay, A.: PS+SE-FrM6, **58**
Liu, C.: PS+EM-MoA4, 11
Liu, H.: 2D+EM+IS+NS+PS+SP+SS-FrM5, **56**
Liu, X.: 2D+EM+NS+PS+SP+SS+TF-MoM9, 2
Liu, Z.: PS1-TuA1, 20
Lo, C.: EM+NS+PS-MoA2, 9
Löbel, T.: PS+SE-FrM7, 58
Loke, Y.C.: SE+PS+SM-TuM11, 19
Longo, V.: TF+EM+NS+PS+SM-ThM12, 41
Lopez, T.: PS+AS+SS-WeA2, **32**; PS-ThP4, 50
Lou, Q.: PS-ThP20, 53
Lu, N.: PS+2D+SE-WeM12, 28
Lu, S.: PS-ThA10, 44
Luan, P.: PS+BI+SM-TuM11, **15**; PS+SE-MoM5, 5
Lucas, J.: PS-TuM5, 17
Luere, O.: PS+SS+TF-FrM6, 60
Lundin, D.: PS+2D+SE-WeM10, 27
Luo, P.S.: PS-ThP26, **54**
Ly, N.: PS+AP+SE-ThA8, **42**

— M —

Ma, S.: PS-ThP23, **53**
Macco, B.: TF+EM+NS+PS+SM-ThM6, 40
Mackowiak, Piotr, P.: PS+TF-WeA4, 34
Madisetti, S.: EM+NS+PS-MoA1, 9
Maeda, K.: PS+SS+TF-WeM5, 29
Maekawa, K.: PS-TuM12, 17
Maes, J.W.: SD+AS+EM+PS-ThA1, 44
Maher, M.: PS+EM-MoA4, 11
Mancheno-Posso, L.: EM+NS+PS-MoM2, **3**
Mangolini, L.: PS+AS+SS-WeA2, 32; PS-ThP4, 50
Mankelevich, Y.A.: PS+2D+SE-WeM3, 27
Mann, M.N.: PS+BI+SM-TuM13, **16**
Manos, J.: PS-MoM10, 7
Marchack, N.P.: PS-MoM11, **8**
Mares, P.M.: SE+PS-TuA3, 25
Marinov, D.: PS+2D-ThM1, **37**; PS-MoA5, 13
Marot, L.: PS+EM-MoA10, 12
Marsh, R.: PS+AS+SS-WeA1, 32
Maslar, J.E.: 2D+EM+NS+PS+SP+SS+TF-MoM4, 1
Mathys, D.: PS+EM-MoA10, 12
Matsui, M.: PS+SS+TF-WeM5, 29; PS-MoM8, **7**
Matsukuma, M.: PS+AS+SS-WeA9, 33
Matsumoto, H.: PS1-TuA8, 21; PS-MoM11, 8; PS-TuM5, 17
Matsuoka, H.: PS-MoA9, 14
Matsuura, G.: PS1-TuA8, 21; PS1-TuA9, 22
Maury, P.: PS+SS+TF-WeM4, 29
McIntyre, P.: EM+NS+PS-MoM3, 3
McIntyre, P.C.: EM+NS+PS-MoA1, 9; EM+NS+PS-MoA2, 9
McLain, J.T.: PS-ThP3, **50**; SE+PS-TuA2, 25
Meer, T.: PS+SE-FrM7, 58
Mende, P.: 2D+EM+NS+PS+SP+SS+TF-MoM9, 2
Mendez Martin, F.: SE+PS-TuA10, 26
Merche, D.: PS+EM-MoA9, 11
Mertens, J.: SE+PS+SM-TuM1, 18
Mertens, S.: PS1-TuA12, 22
Meshkova, A.: TF+PS-ThA8, 48
Messer, B.: PS1-TuA8, 21; PS-TuM5, 17
Metz, A.: PS1-TuA8, 21; PS-TuM5, 17
Metzler, D.: PS+SS+TF-FrM4, 60; PS+SS+TF-FrM5, 60
Michels, J.J.: TF+PS-ThA3, 48
Michl, T.D.: SM+AS+BI+PS-ThA6, 47
Milosavljevic, V.: PS+BI+SM-TuM12, **15**
Minardi, L.: PS1-TuA7, 21
Minaye Hashemi, F.H.: SD+AS+EM+PS-ThA6, 45
Minea, T.: PS+2D+SE-WeM10, 27
Misra, V.: TF+EM+NS+PS+SM-ThM3, **40**
Mitschker, F.: PS+TF-WeA9, 35
Mitterer, C.: SE+PS+SM-TuM3, **18**
Miyake, K.: PS2-TuA4, 23
Miyake, M.: PS+SS+TF-WeM5, 29
Miyamoto, S.: SM+AS+BI+PS-ThM12, 39
Miyawaki, Y.: PS-MoA4, 12
Miyazoe, H.: PS+EM-MoA4, **11**; PS-MoM11, 8
Miyoshi, N.: PS+SS+TF-WeM5, **29**
Mohanty, N.: PS-TuM3, **16**
Mohr, S.: PS-ThP19, **53**
Mokrani, A.: PS-ThP12, 51
Molkenboer, F.T.: PS-TuM13, 18
Mon, H.H.: SM+AS+BI+PS-ThA6, 47
Monroy, T.G.: PS+SS+TF-WeM11, 30
Moreau, D.: PS-MoM3, 7
Morimoto, M.: PS-MoM8, 7
Moroz, D.J.: PS+TF-WeA3, 34
Moroz, P.: PS+TF-WeA3, **34**
Mourey, O.: PS+SS+TF-FrM11, 61
Mousa, M.B.: SD+AS+EM+PS-ThA7, 45
Mowll, T.R.: 2D+EM+NS+PS+SP+SS+TF-MoM2, **1**
Muhl, S.: PS-ThP29, 54
Muilwijk, P.M.: PS-TuM13, 18
Murakami, Y.: PS2-TuA4, **23**
Muratore, C.: PS+2D+SE-WeM11, 27
Murayama, A.: PS+SS+TF-FrM10, 61
Muscat, A.J.: EM+NS+PS-MoM2, 3
Music, D.: PS+2D+SE-WeM13, 28
Myoui, A.: SM+AS+BI+PS-ThM12, 39

— N —

Nad, S.: PS+TF-WeA12, **35**
Nagabhirava, B.: PS-TuM6, 17
Nagahata, K.: PS+AS+SS-WeA8, 32; PS2-TuA4, 23
Nagatsu, M.: SM+AS+BI+PS-ThM5, **38**
Nagorny, V.: PS-MoA7, **13**
Nahon, L.: PS-MoA10, 14
Nakakubo, Y.: PS+AS+SS-WeA10, 33
Nakamura, J.: 2D+EM+IS+NS+PS+SP+SS-FrM7, 56
Nakamura, K.: PS1-TuA4, 21; PS-MoA9, 14

Nakamura, M.: PS1-TuA8, 21; PS1-TuA9, 22; PS-MoM11, 8
Nakano, T.: PS-ThP7, 51
Nakano, Y.: PS1-TuA4, 21
Nakatsu, Y.: PS-ThP13, 52
Nath, A.: 2D+EM+NS+PS+SP+SS+TF-MoM3, 1
Nave, A.: PS+TF-WeA9, 35
Negara, M.: EM+NS+PS-MoM3, 3
Negishi, N.: PS-MoM10, 7
Nennie, F.A.: PS-TuM13, 18
Ngo, HD.: PS+TF-WeA4, 34
Nguyen, T.D.: PS-ThP21, 53
Niemi, K.: PS-MoA10, 14
Nishi, Y.: PS-ThP22, 53; PS-ThP24, 54
Nishimura, E.: PS1-TuA12, 22
Nisol, B.: PS+SE-MoM9, 6
Noh, J.H.: PS+SS+TF-WeM13, **30**
Nomura, T.: SM+AS+BI+PS-ThA11, 47
Norberg, S.A.: SM+AS+BI+PS-ThA1, 46
Nordell, B.J.: PS-ThP21, **53**
Nozawa, T.: PS+AP+SE-ThA3, 42
Nunley, T.N.: EM+NS+PS-MoA10, 10
Nwogu, N.C.: SE+PS+SM-TuM12, **19**
Nyakiti, L.O.: 2D+EM+NS+PS+SP+SS+TF-MoM3, 1

— O —

O'Connell, D.: PS-MoA10, 14
Oehrlein, G.S.: PS+BI+SM-TuM11, 15; PS+SE-MoM5, 5; PS+SS+TF-FrM4, 60; PS+SS+TF-FrM5, 60
Ogawa, D.: PS1-TuA4, **21**
Ogawa, S.: PS-TuM4, 16
Ohta, T.: SM+AS+BI+PS-ThA11, 47
Oishi, T.: PS-TuM4, 16
Oka, M.: PS+AP+SE-ThA3, 42
Okada, M.: SM+AS+BI+PS-ThM5, 38
Oktyabrsky, S.: EM+NS+PS-MoA1, 9
Okuma, K.: PS-MoM10, 7
Olsen, C.: EM+NS+PS-MoA2, 9
O'Meara, D.: SD+AS+EM+PS-ThA11, 46
Ong, E.W.: 2D+EM+NS+PS+SP+SS+TF-MoM2, 1
Oniszczuk, A.W.: SE+PS-TuA7, **25**
Ono, K.: PS+AS+SS-WeA10, 33; PS2-TuA7, **23**
Ono, T.: PS-MoM8, 7
Ooki, W.: 2D+EM+IS+NS+PS+SP+SS-FrM7, 56
Orzali, T.: 2D+EM+NS+PS+SP+SS+TF-MoM4, 1
Oulmane, M.: PS-ThP19, 53
Overzet, L.J.: PS+AS+SS-WeA7, **32**; PS-MoA8, 14; PS-ThP17, 52

— P —

Pan, J.: PS1-TuA1, 20
Pandey, A.: PS-MoA9, **14**
Panici, G.A.: PS-MoM5, 7
Papa, F.: PS+TF-WeA4, 34
Paquette, M.M.: PS-ThP21, 53
Paradiso, S.: PS+EM-MoA1, **11**
Paraschiv, V.: PS1-TuA12, 22
Park, J.W.: PS+EM-MoA3, 11; PS+SS+TF-FrM9, **61**
Park, S.P.: EM+NS+PS-MoA9, **10**
Parlakyigit, A.S.: PS-ThP2, **50**
Parsons, G.N.: SD+AS+EM+PS-ThA7, 45
Pateau, A.: PS-ThP12, 51
Paterson, A.: PS+AS+SS-WeA1, 32; PS2-TuA11, 24
Peck, A.: PS-MoM5, **7**
Peeters, F.J.J.: PS+SE-MoM10, **6**
Pegalajar-Jurado, A.: PS+BI+SM-TuM13, 16; SM+AS+BI+PS-ThM13, 39
Perrotta, A.: TF+PS-ThA3, **48**
Persing, H.: PS+AP+SE-ThA8, 42
Persson, P.O.A.: PS+2D+SE-WeM13, 28
Petrov, G.M.: PS-ThA6, 43; PS-ThA7, 44
Petrov, I.: SE+PS-TuA1, 24
Petrova, Tz.B.: PS-ThA6, 43; PS-ThA7, 44
Pfeifer, B.: PS-MoM6, 7
Pfuch, A.: SE+PS+SM-TuM3, 18
Phan-Vu, H-A.: PS-ThP23, 53
Pimenta-Barros, P.: PS-MoM1, 6
Piotrowicz, P.: PS+2D+SE-WeM2, 27; PS-ThP5, **50**
Pitchford, L.C.: PS+SE-MoM3, **5**
Piumi, D.: PS1-TuA12, 22
Poespawati, N.R.: SM+AS+BI+PS-ThM5, 38
Polcik, P.: SE+PS-TuA10, 26
Pollet, O.: PS+SS+TF-WeM4, 29; PS-MoM1, 6
Posseme, N.: PS+SS+TF-WeM4, **29**; PS-MoM1, 6
Poulose, J.: PS-MoA8, **14**
Pouvesle, J.-M.: PS+SE-FrM10, 59; SM+AS+BI+PS-ThM1, **38**
Press, A.: PS-ThP17, 52
Prosa, T.J.: PS+AP+SE-ThA6, **42**
Provo, J.L.: TF+PS-ThA9, **49**
Purnamaningsih, R.W.: SM+AS+BI+PS-ThM5, 38
Pyzyna, A.: PS+EM-MoA4, 11

— Q —

Qin, X.: PS+2D+SE-WeM12, 28

— R —

Rack, P.D.: PS+SS+TF-WeM13, 30
Radisic, D.: PS1-TuA12, **22**
Radovanov, S.: PS+AP+SE-ThA8, 42
Raes, M.: PS+EM-MoA9, 11
Rahman, T.S.: 2D+EM+IS+NS+PS+SP+SS-FrM9, 57
Raley, A.: PS-MoM3, 7; PS-TuM3, 16
Raman, P.: PS-ThP3, 50; SE+PS-TuA2, **25**
Ramaswamy, K.: PS+SS+TF-WeM11, 30
Ramiasa, M.: SE+PS+SM-TuM2, 18
Ramos, C.: EM+NS+PS-MoA8, 10
Randall, J.: SD+AS+EM+PS-ThA8, 45
Ranjan, A.: PS+SS+TF-WeM1, **28**; PS-TuM3, 16
Rassoul, N.: PS-TuM6, 17
Rastgar, N.: PS+AS+SS-WeA1, **32**
Ratner, B.D.: PS+BI+SM-TuM1, **15**
Rauf, S.: PS+SS+TF-FrM8, 60; PS+SS+TF-WeM12, **30**; PS2-TuA12, 24; PS2-TuA3, 23; PS-MoA5, 13
Rawal, T.B.: 2D+EM+IS+NS+PS+SP+SS-FrM9, **57**
Reed, E.J.: 2D+EM+IS+NS+PS+SP+SS-FrM2, 56
Rehbein, J.: PS+SE-FrM7, 58
Reinecke, T.L.: 2D+EM+IS+NS+PS+SP+SS-FrM1, 56; PS+2D-ThM10, 37
Renau, A.: PS+AP+SE-ThA1, **42**
Reniers, F.A.B.: PS+EM-MoA9, 11; SE+PS+SM-TuM1, **18**
Restrepo, J.S.: PS-ThP29, **54**
Rezek, J.R.: SE+PS-TuA3, 25
Rhallabi, A.: PS-ThP12, **51**
Ribton, C.N.: PS-ThA2, 43
Richard, C.: PS+SS+TF-WeM4, 29
Ridou, L.: SM+AS+BI+PS-ThM1, 38
Riposan, A.: SE+PS-TuA11, 26
Robert, E.: PS+SE-FrM10, 59; SM+AS+BI+PS-ThM1, 38
Robertson, J.: EM+NS+PS-MoA5, **9**
Robinson, J.A.: 2D+EM+NS+PS+SP+SS+TF-MoM9, 2; EM+NS+PS-MoM5, **4**
Robinson, J.T.: 2D+EM+IS+NS+PS+SP+SS-FrM1, 56; PS+2D-ThM10, 37
Robinson, Z.R.: 2D+EM+NS+PS+SP+SS+TF-MoM1, 1; 2D+EM+NS+PS+SP+SS+TF-MoM2, 1
Rojas Delgado, R.: 2D+EM+IS+NS+PS+SP+SS-FrM10, **57**
Roozeboom, F.: PS+TF-WeA8, 35
Röpcke, J.: PS+TF-WeA9, 35
Rui, Y.: PS-MoM4, 7
Rumphorst, R.F.: PS+SE-MoM10, 6
Russell, N.M.: PS-MoM6, 7
Ruzic, D.N.: PS+2D+SE-WeM2, 27; PS-MoM5, 7; PS-ThP3, 50; PS-ThP5, 50; SE+PS-TuA2, 25

— S —

Sabat, G.: PS-ThP24, 54
Safriet, A.: PS+2D+SE-WeM11, 27
Sahu, B.: EM+NS+PS-MoA1, 9; EM+NS+PS-MoA9, 10
Saifullah, M.S.M.: SE+PS+SM-TuM11, 19
Sakakibara, W.: PS-MoA9, 14
Sakudo, A.: SM+AS+BI+PS-ThM5, 38
Samukawa, S.: PS+SS+TF-FrM10, 61; PS1-TuA10, 22
Sanchez Perez, J.R.: 2D+EM+IS+NS+PS+SP+SS-FrM10, 57
Sanders, D.: PS+EM-MoA4, 11
Sankaran, R.M.: PS+SE-MoM11, 6; PS+SE-MoM8, 5
Sankarapandian, M.: PS-MoM3, 7
Sardashti, K.: EM+NS+PS-MoA1, 9
Sarinont, T.: PS+SE-FrM5, 58; PS-ThP13, **52**
Sarrazin, A.: PS-MoM1, 6
Satpathy, S.: 2D+EM+NS+PS+SP+SS+TF-MoM9, 2
Schäfer, J.: PS+SE-FrM7, 58
Schelkanov, I.: PS-ThP5, 50
Schmidt, J.: SE+PS+SM-TuM3, 18
Schmidt, S.: PS+AP+SE-ThA9, 42; SE+PS-TuA9, 25
Schneider, J.M.: PS+2D+SE-WeM13, 28
Schrinsky, A.: PS-MoM4, 7
Schroeder, D.: 2D+EM+IS+NS+PS+SP+SS-FrM10, 57
Schröter, S.: PS-MoA10, **14**
Schuengel, E.: PS-ThA1, 43
Schulze, J.: PS-ThA1, 43
Seal, S.: 2D+EM+IS+NS+PS+SP+SS-FrM8, 57
Sekine, M.: PS1-TuA1, **20**; PS-MoA4, 12; SM+AS+BI+PS-ThA11, 47
Selvan, T.: 2D+EM+IS+NS+PS+SP+SS-FrM8, 57
Seo, H.: PS+SE-FrM5, 58; PS-ThP13, 52
Seog, J.: PS+BI+SM-TuM11, 15
Shannon, S.: PS+SE-FrM3, **57**; PS+SE-FrM6, 58; PS-MoA8, 14
Sharma, A.: TF+EM+NS+PS+SM-ThM12, **41**
Shchelkanov, I.A.: PS-MoM5, 7; PS-ThP3, 50; SE+PS-TuA2, 25
Shearer, J.C.: PS1-TuA8, **21**; PS-TuM5, 17
Sheehan, P.E.: 2D+EM+IS+NS+PS+SP+SS-FrM1, **56**; PS+2D-ThM10, 37
Shehelkanov, I.A.: PS+2D+SE-WeM2, 27
Sherpa, S.: PS+SS+TF-WeM1, 28
Shin, K.S.: PS-ThP15, 52
Shinoda, K.: PS+SS+TF-WeM5, 29
Shiratani, M.: PS+SE-FrM5, 58; PS-ThP13, 52
Shohet, J.L.: PS-ThP22, 53; PS-ThP24, **54**
Shojiki, K.: PS+SS+TF-FrM10, 61
Shown, I.: PS+2D-ThM4, **37**
Siddiqui, S.: EM+NS+PS-MoA1, 9; EM+NS+PS-MoA9, 10
Siepa, S.: PS-ThP18, **53**
Sikorski, E.M.: PS1-TuA8, 21; PS1-TuA9, 22; PS-MoM11, 8
Singh, H.: PS+SS+TF-FrM1, 59

Smith, C.: SE+PS-TuA11, 26
Smith, D.R.: PS-ThA2, 43
Smith, J.: PS-TuM3, 16
Song, I.-C.: PS-ThA10, 44
Song, S.: PS-TuM3, 16
Soukiassian, G.: 2D+EM+IS+NS+PS+SP+SS-FrM3, **56**
Souriau, L.: PS1-TuA12, 22
Spange, S.: SE+PS+SM-TuM3, 18
Sperling, B.A.: 2D+EM+NS+PS+SP+SS+TF-MoM4, 1
Spiegelman, J.: EM+NS+PS-MoA8, 10
Sporre, J.R.: PS-MoM3, **7**
Sproul, W.D.: PS+TF-WeA4, **34**; SE+PS-TuA8, 25
Sridhara, K.: 2D+EM+NS+PS+SP+SS+TF-MoM1, 1
Sridhara, KS.: 2D+EM+NS+PS+SP+SS+TF-MoM3, **1**
Sripadarao, P.K.C.: PS-MoM3, 7
Sriraman, S.: PS+AS+SS-WeA1, 32; PS2-TuA11, 24
Stafford, L.: PS+2D-ThM11, **38**
Stanford, M.G.: PS+SS+TF-WeM13, 30
Starostin, S.A.: TF+PS-ThA8, 48
Stergiopoulos, V.: PS+EM-MoA9, 11
Stevens, E.: SD+AS+EM+PS-ThA7, **45**
Stine, R.: 2D+EM+IS+NS+PS+SP+SS-FrM1, 56
Stolbov, S.: 2D+EM+IS+NS+PS+SP+SS-FrM6, **56**
Stout, P.J.: PS2-TuA9, **24**
Stowell, M.: PS-ThP5, 50
Stranick, S.J.: 2D+EM+NS+PS+SP+SS+TF-MoM4, 1
Sugai, H.: PS-MoA9, 14
Sugimoto, S.: SM+AS+BI+PS-ThM12, 39
Sugimoto, Y.: PS+AP+SE-ThA3, 42
Sumiya, M.: PS+AS+SS-WeA12, 33
Sun, L.: PS-TuM3, 16
Sussman, M.: PS-ThP24, 54
Suzuki, A.: PS+AS+SS-WeA9, 33
Suzuki, T.: PS1-TuA8, 21; PS1-TuA9, 22; PS-MoM11, 8
Swerts, J.: PS1-TuA12, 22

— T —

Tabata, M.: PS+SS+TF-FrM3, 59
Tahara, S.: PS1-TuA12, 22
Taher, F.: PS-ThP12, 51
Takeda, K.: PS1-TuA1, 20; PS-MoA4, 12; SM+AS+BI+PS-ThA11, 47
Tanaka, A.: PS-ThP13, 52
Tanatsugu, Y.: SM+AS+BI+PS-ThM4, 38
Tang, K.: EM+NS+PS-MoA1, 9; EM+NS+PS-MoM3, **3**
Tanikawa, T.: PS+SS+TF-FrM10, 61
Tanyeli, I.: PS+EM-MoA10, **12**
Tapily, K.: SD+AS+EM+PS-ThA11, **46**
Tatsumi, T.: PS+AS+SS-WeA8, 32; PS2-TuA4, 23
Tavernier, A.: PS+SS+TF-FrM6, 60
Teichert, C.K.: PS+2D-ThM3, **37**
Tennyson, J.: PS-ThA10, 44; PS-ThP19, 53
Terryn, H.: PS+EM-MoA9, 11
Thissen, N.F.W.: TF+EM+NS+PS+SM-ThM6, 40
Thomas, C.: PS+SS+TF-FrM10, 61
Tian, W.: SM+AS+BI+PS-ThA1, 46
Tieckelmann, R.: 2D+EM+NS+PS+SP+SS+TF-MoM4, 1
Tillocher, T.: PS+AS+SS-WeA11, 33; PS1-TuA3, **20**; PS-TuM12, 17
Timilsina, R.: PS+SS+TF-WeM13, 30
Truong, A.: PS+BI+SM-TuM10, 15
Truscott, B.S.: PS+2D+SE-WeM3, 27
Tsai, H.: PS+EM-MoA4, 11
Tsamados, D.: PS-ThP19, 53
Tsoi, S.: 2D+EM+IS+NS+PS+SP+SS-FrM1, 56; PS+2D-ThM10, 37
Tsuji, A.: PS+SS+TF-FrM3, **59**
Tutuc, E.: EM+NS+PS-MoM10, **4**
Tyagi, P.: 2D+EM+NS+PS+SP+SS+TF-MoM2, 1

— U —

Uchida, G.: PS-ThP13, 52
Ueda, H.: PS+AP+SE-ThA3, **42**
Urrabazo, D.: PS+AS+SS-WeA7, 32; PS-ThP17, 52

— V —

Vallier, L.: PS+SS+TF-FrM6, 60; PS+SS+TF-WeM3, 28
van de Sanden, M.C.M.: PS+EM-MoA10, 12; PS+EM-MoA8, 11; PS+SE-MoM10, 6; PS+TF-WeA1, **34**; TF+PS-ThA8, 48
van der Zande, A.M.: 2D+EM+NS+PS+SP+SS+TF-MoM5, **2**
Vandencasteele, N.: SE+PS+SM-TuM1, 18
Vasilev, K.: SE+PS+SM-TuM2, 18
Ventrice, Jr., C.A.: 2D+EM+NS+PS+SP+SS+TF-MoM2, 1
Ventzek, P.: PS+AP+SE-ThA3, 42; PS+AS+SS-WeA9, 33; PS+SS+TF-WeM1, 28
Vishwanath, S.: 2D+EM+NS+PS+SP+SS+TF-MoM9, 2
Viswan, A.: SM+AS+BI+PS-ThM5, 38
Vivien, C.: PS+SE-FrM10, **59**
Vizioz, C.: PS-MoM1, 6
Vlcek, J.V.: SE+PS-TuA3, **25**
Voevodin, A.A.: PS+2D+SE-WeM11, **27**
Volynets, V.: PS-ThA10, 44
von Keudell, A.: PS-ThP18, 53
Vora, A.: PS+EM-MoA4, 11
Vos, M.F.J.: TF+EM+NS+PS+SM-ThM6, **40**

— W —

Wagenaars, E.: PS-MoA10, 14
Waite, A.R.: PS+2D+SE-WeM11, 27
Wajda, C.: SD+AS+EM+PS-ThA11, 46
Wallace, R.M.: PS+2D+SE-WeM12, 28
Walton, S.G.: 2D+EM+IS+NS+PS+SP+SS-FrM1, 56; PS+2D-ThM10, 37; PS+SS+TF-WeM12, 30; PS-ThA6, **43**; PS-ThA7, 44
Wang, C.M.: PS-ThP16, 52
Wang, J.: PS+SS+TF-FrM8, **60**
Wang, K.: TF+EM+NS+PS+SM-ThM5, 40
Wang, M.: PS+SS+TF-WeM1, 28
Wang, P.: PS-TuM6, 17
Wang, Q.: PS+2D+SE-WeM12, 28
Wang, S.: PS-MoA6, **13**
Wang, W.: PS-TuM3, 16
Watanabe, H.: PS+SS+TF-FrM3, 59
Webb, S.: EM+NS+PS-MoA8, 10
Weeks, S.L.: PS+EM-MoA8, 11
Wendt, A.E.: PS+AP+SE-ThA8, 42; PS-MoA6, 13
Wertheimer, M.R.: PS+SE-MoM9, **6**
Wheeler, V.D.: 2D+EM+NS+PS+SP+SS+TF-MoM1, 1
Whitener, K.E.: 2D+EM+IS+NS+PS+SP+SS-FrM1, 56; PS+2D-ThM10, 37
Williams, B.L.: TF+EM+NS+PS+SM-ThM13, 41
Willson, G.: PS+EM-MoA4, 11
Winter, R.: EM+NS+PS-MoM3, 3
Wolden, C.A.: PS+TF-WeA11, 35
Wolf, S.: EM+NS+PS-MoA7, **10**; EM+NS+PS-MoM4, 3
Wong, K.: TF+EM+NS+PS+SM-ThM5, 40
Wu, S.: 2D+EM+NS+PS+SP+SS+TF-MoM9, 2
Wu, Y.L.: PS+2D+SE-WeM2, **27**

— X —

Xing, H.: 2D+EM+NS+PS+SP+SS+TF-MoM9, 2
Xu, X.D.: 2D+EM+NS+PS+SP+SS+TF-MoM9, 2

— Y —

Yamashita, F.: PS1-TuA12, 22
Yamashita, I.: PS+SS+TF-FrM10, 61
Yang, GJ.: PS-MoM4, **7**
Yang, R.: PS+SE-MoM11, 6
Yang, R.B.: SE+PS+SM-TuM11, 19
Yang, Y.: PS+2D+SE-WeM5, **27**
Yang, Y.J.: PS+SE-MoM6, 5
Yasar-Inceolgu, O.: PS-ThP4, 50
Yatsuda, K.: PS-TuM12, 17
Ye, P.W.: PS-ThP9, **51**
Yeom, G.Y.: PS+EM-MoA3, 11; PS+SS+TF-FrM9, 61; PS-ThP1, 50; PS-ThP15, 52
Yoshida, N.: EM+NS+PS-MoA1, 9; EM+NS+PS-MoA9, 10; EM+NS+PS-MoM4, 3
Yoshikwa, H.: SM+AS+BI+PS-ThM12, 39
Yu, C.: SM+AS+BI+PS-ThM4, **38**
Yu, K.-H.: SD+AS+EM+PS-ThA11, 46
Yu, P.Yu.: PS+SS+TF-FrM10, 61
Yulaev, A.: 2D+EM+NS+PS+SP+SS+TF-MoM8, **2**
Yun, D.H.: PS+EM-MoA3, **11**; PS+SS+TF-FrM9, 61

— Z —

Zhang, D.: EM+NS+PS-MoA10, 10
Zhang, L.: EM+NS+PS-MoA2, **9**; PS-TuM12, 17
Zhang, X.R.: 2D+EM+IS+NS+PS+SP+SS-FrM7, **56**
Zhang, Y.: PS+SS+TF-FrM6, 60; PS+SS+TF-WeM11, 30; PS2-TuA11, **24**
Zhao, Z.: PS+SE-FrM8, 58
Zhou, X.: PS+2D+SE-WeM5, 27
Zhou, Y.: 2D+EM+IS+NS+PS+SP+SS-FrM2, **56**
Zollner, S.: EM+NS+PS-MoA10, 10
Zorman, C.A.: PS+SE-MoM11, 6