Electronic Materials and Photonics Division
Room 101A - Session EM+MP+PS-MoM

IoT Session: CMOS, Beyond the Roadmap and Over the Cliff

Moderators: Sean King, Intel Corporation, Wilman Tsai, TSMC

8:20am **EM+MP+PS-MoM-1 Aluminum Gettering Gate for Improving Defect Density in SiGe MOSCAP Devices***, **Emily Thomson**, M Kavrik, A Kummel,* University of California at San Diego

The use of SiGe alloys in place of silicon in semiconductor devices has been anticipated for many years due to its high carrier mobility and tunability of the band gap by varying Ge content. However, widespread use of SiGe in industry has been prevented by the presence of interface defects between the SiGe and oxide layer in MOSCAP devices. It has been shown that Ge-Ox bonds at the interface are the main source of these defects so by encouraging SiOx bonds or discouraging GeOx bonds, interface defects can be minimized. The higher heat of formation of SiOx compared with GeOx allows for the selective destruction of GeOx bonds using an oxygen scavenging metal as the gate metal, causing oxygen from GeOx bonds to diffuse through the oxide layer. Here, aluminum was used as an oxygen scavenging gate in order to achieve a low defect density of 3E11 $eV^{-1}cm^{-2}$. The high-k dielectric HfO_2 was deposited using atomic layer deposition with precursors TDMAH (tetrakis (dimethylamido) hafnium) and H2O and the aluminum gates were deposited using thermal evaporation. MOSCAP devices with nickel gates were fabricated and measured in parallel to show contrast with a non-scavenging gate metal. C-V measurements were used to characterize interface defect density. TEM images confirmed oxygen scavenging by showing a silicon rich SiGe-oxide interface and an Al2O3 layer at the HfO2-Al gate interface.

8:40am **EM+MP+PS-MoM-2 Direct Growth of Single Crystal Compound Semiconductor Materials on Diverse Substrates for Beyond the Roadmap Multifunctional Integrated Circuits***, **Debarghya Sarkar**, R Kapadia,* University of Southern California

Technological advancement in semiconductor devices for the past several decades has been mainly driven by scaling device dimensions to achieve high computational density and thus operational bandwidth. The next generation of technological advancement is likely to come from vertical fine-grain integration of multiple materials for 3D multifunctional integrated circuits. Epitaxial lift-off and transfer processes are currently employed towards realizing such structures, which though successful, have several shortcomings. On the other hand, direct growth of technologically relevant materials on amorphous dielectrics using state-of-the-art vapor-phase crystal growth techniques results in polycrystalline films with uncontrolled morphology unsuitable for high performance devices. As a potential solution addressing these issues, here we report the recent advances made in the templated liquid phase (TLP) growth technique that enables growth of large-area single crystals of compound semiconductors directly on diverse non-epitaxial substrates. We demonstrate growth of optoelectronic materials such as binary III-V InP and InAs, and optical bandgap tuning with ternary III-V materials like InGaP. We also show phase-controlled growth of binary IV-V materials such as Sn_4P_3 and SnP for high capacity anode materials in Li and Na ion batteries. Further, as the first step towards directly integrating multiple materials on the same substrate, we demonstrate atomically-sharp lateral heterojunctions of cubic InP and rhombohedral Sn_4P_3 crystals. We grow these materials in selective area with deterministic template geometry and conformal to underlying device nanostructures on any thermally stable crystalline (Gd_2O_3), amorphous (SiO_2, $Si_3N\text{-}_4$, TiO_2, and $Al\text{-}_2O_3$), or 2D (graphene) substrate. Despite grown on non-epitaxial substrates, the materials have been characterized to have high quality crystallinity, with high optoelectronic quantum yield irrespective of the substrate, and high carrier mobility. These demonstrations potentially mark the beginning of a new genre of material growth technique with increased opportunity for electronic, photonic, optoelectronic and energy devices, and system design with novel functionalities.

9:00am **EM+MP+PS-MoM-3 Going Beyond Traditional CMOS***, **Inge Asselberghs**, I Radu,* IMEC, Belgium **INVITED**

Continuous connectivity, we take it for granted in our daily life, but it did not exist a decade ago. Consequently, the information infrastructure keeps growing and the traditional scaling approach of the transistors could meet with these high demands. Transistor scaling was achieved by increasing performance with a comparable energy consumption while keeping the cost low. However, the traditional scaling approach may run into fundamental physical limits of device switching. Common materials such as Si and SiGe are reaching their materials scaling limit. Therefore, there is a strong drive to explore alternative materials for device scaling. Looking beyond the common charge based devices, there is a full field in exploratory device concepts that rely on spin, exciton or plasmonic states.

From this perspective, we cover several approaches in the search for higher performance and/or lower energy consumption. We firstly review activities on 2D semiconductors for MOSFET application. A large variety of reports on layered materials were published in literature in the last decade, starting with graphene, moving to transition dichalcogenides (MX2) and diving into the properties of materials such as black phosphorus. We will summarize some of this work, and focus on the more stable MX2 variants as an experimental study format. Here we will also describe some device considerations with respect to channel scaling and the role of double gate (2D equivalent of gate-all-around) aspects. Devices with steep-slope concepts are considered potential alternatives to power scaling as it is expected that the supply voltage could be reduced. In this context, we will describe work on tunnel FETs and summarize briefly the so-called negative capacitance devices.

Rather than looking at device scaling only, we will also describe how functional scaling can create an advantage by improving circuits. From this perspective, spintronic majority gates are ideal candidates as it expected a fewer number of devices is required for complex arithmetic circuits. Some majority gates hold the promise of ultra- low energy operation.

9:40am **EM+MP+PS-MoM-5 Suppression of Electronic Defects at HfO_2-SiGe Interface with Selective Surface Oxidation Using Ozone***, **Mahmut Sami Kavrik**,* University of California at San Diego*; V Hou,* TSMC, Taiwan, Republic of China*; E Thomson,* University of California at San Diego*; K Tang,* Stanford University*; Y Taur,* University of California at San Diego*; P McIntyre,* Stanford University*; A Kummel,* University of California at San Diego

Silicon germanium (SiGe) with high-k dielectric is appealing for low power electronics due to high intrinsic carrier mobility of SiGe. However, the SiGe channel in CMOS transistors can be implemented commercially only if low defect SiGe/high-k interface can be fabricated. Studies have shown that electronic defects are mainly generated by interfacial germanium oxide (GeO_x) which can be removed by selective oxygen gettering from GeO_x or selectively forming interfacial silicon oxide (SiO_x).

In this work, selective interface oxidation with ozone is studied. It is shown that ozone pulsing during the oxide ALD process can significantly lower the interface defect density (D_{it}) when the ozone is pulsed after deposition of at least a few monolayers of gate oxide. When ozone pulses are dispersed across the HfO_2 during ALD growth, the electronic defect density is reduced more than 60% compared to control HfO_2 samples. After careful optimization of ozone pulse and forming gas annealing, low interface defect density of $D_{it}=5x10^{11}$ $eV^{-1}cm^2$ with 1.75uF/cm^2 accumulation capacitance was demonstrated for the $HfO_2/Si_{0.7}Ge_{0.3}$ interface. Gate oxide and the interface composition was investigated with STEM-EELS and Si riched composition was observed consistent with DFT models. Suppression of electronic defects at the HfO_2- $Si_{0.7}Ge_{0.3}$(001) interface with SiO_x selective interface oxidation using ozone was demonstrated.

10:00am **EM+MP+PS-MoM-6 Surface Free Energy and Interfacial Strain in HfO2 and HZO Ferroelectric Formation***, **Andrew Kummel**, E Chagarov, M Kavrik,* University of California at San Diego*; M Katz, N Sanford, A Davydov,* National Institute of Standards and Technology (NIST)*; M Lee,* National Taiwan University

The mechanism of stability of the phases of HfO_2, ZrO_2, and HZO ($Hf_xZr_{1-x}O_2$) were systematically investigated with density functional theory molecular dynamics (DFT-MD). For the bulk states, the monoclinic phase ("m") is about 80 mV per formula unit more stable than either the orthorhombic ferroelectric ("f") phase or tetragonal (t-phase) for all three oxides. The surface free energies of the (001), (110), and (111) surfaces of all three oxides were calculated using an identical DFT technique. For all three oxides, the (111) face has the lowest surface free energies consistent with experimental data on columnar HZO grains showing [111] is the preferred growth direction. However, the surface free energy for all direction are nearly degenerate between HfO_2, ZrO_2, and HZO; therefore, even for nanocrystal formation the surface free energy does not favor f-phase formation. The effect of stress/strain was calculated by determining the free energy of formation as a function of the volume of the unit cell. When the oxides are grown in the low density amorphous phase but a post deposition anneal is perform for crystallization. The crystalline forms are more dense than the amorphous forms and the DFT calculation show that a higher surface area per unit cells will greatly favor f-phase formation. However, the effect is nearly identical for HfO_2, ZrO_2, and HZO; this is consistent with experiments showing the molar volumes of HfO_2 and ZrO_2 being within 2%. Instead, formation of nanocrystalites is hypothesized to be the source of the enhanced processing window for HZO. Experimental data is consistent with partial phase separation in HZO. Atom probe tomography imaging of the chemical composition of TiN/5 nm HZO/Si(001) ferroelectric films show an asymmetric distribution of the Hf and Zr within the HZO layer with the Zr being concentrated near the TiN/HZO interface; this is consistent with ZrO_2 having a 100C lower crystallization temperature than HfO_2 and therefore initiate the crystallization starting on the TiN(111) surface. It is hypothesized that the nanocrystals which template on TiN(111) can produce the interfacial stress/strain needed to stabilize f-phase formation; high resolution TEM shows regions of epitaxial alignment between HZO and TiN consistent with this mechanism. In addition atom probe tomography (APT) was performed on TiN/HZO/Si structures to determine the film composition of the interfaces for indication of possible phase separation of HZO since phase separation could promote nanocrystal formation.

Funding by LAM Research is gratefully acknowledged

10:40am **EM+MP+PS-MoM-8 The Role of Selective Processes in the Atomic Scale Era***, **Robert Clark**, J Smith, K Yu, K Tapily, G Pattanaik, S Consiglio, T Hakamata, C Wajda, A Raley, G Leusink,* TEL Technology Center, America, LLC **INVITED**

The semiconductor industry has reached the point where devices are approaching atomic scales. But continued scaling presents a number of new challenges to our industry. First, there is no longer plenty of room at the bottom, which has forced device makers to scale upward by adopting three dimensional device structures and architectures. This has resulted in a drastic increase in the aspect ratios encountered during chip manufacturing. In addition, even with the advent of EUV lithography it will be necessary to employ multi-patterning technologies in order to fabricate the sub-lithographic features necessary to scale further. Multi-patterning requires multiple masks per layer which presents a challenge in terms of aligning masks to each other within a layer, and from layer to layer as the chip is fabricated. Self-aligned process flows such as self-aligned blocks, fully self-aligned vias, and self-aligned contacts are being employed to increase the margin of allowable edge placement error (EPE) for aligning feature and layers to each other at the cost of additional process complexity as well as exacerbating the problem of ever-increasing aspect ratios. Finally, functional films at useful thicknesses need to be accommodated within the volume of the device without voids or seams that can impact chip yields through degraded electrical performance or by providing a source of particles or foreign material.

To overcome these difficulties it is necessary to begin transitioning from the current top down manufacturing paradigm to a bottom up or additive manufacturing style. Selective depositions and etches represent a path to make this transition for devices makers. Self-aligned process flows already make use of etch selectivity between materials in order to achieve feature self-alignment, but isotropic and anisotropic selective depositions can provide additional advantages. Because area selective depositions are inherently self-aligned to the target material, they can enable new process flows for self-alignment. In addition, anisotropic feature filling can be used to fill high aspect ratio, or reentrant features on the chip without deleterious voids and seems as well as reducing the overburden needed for chemical mechanical polishing (CMP). And selective depositions can also be used to avoid or relieve the crowding of functional films within devices or other structures. In this presentation we seek to illustrate, with examples of new processes currently under investigation, how selective depositions and etches can enable future manufacturing nodes by introducing additive processing into the manufacturing flow.

11:20am **EM+MP+PS-MoM-10 Selective Patterning of Silicon/Germanium Surfaces and Nanostructures via Surface Initiated Polymerization***, **Amar Mohabir**, T Weiss, G Tutuncuoglu, E Vogel, M Filler,* Georgia Institute of Technology

Functional devices (e.g., transistors) require controlled compositional heterogeneity and hierarchy at the nanoscale. When such devices are to be produced at very large throughputs (e.g., large-area integrated circuitry), an alternative to top-down patterning is necessary to define key features. Here, we show how surfaces exhibiting Si and Ge domains can be selectively masked using the surface-initiated growth of polymer films. Our approach is particularly useful for the patterning of, and subsequent deposition on, 3-D nanostructures, such as Si/Ge nanowire heterostructures. Such structures exhibit a variety of exposed facets that complicates direct (i.e., without a mask) area selective deposition approaches. Surface masking of Si, but not Ge, domains is accomplished by attaching an initiator to the surface followed by the atom transfer radical polymerization of polymethylmethacrylate (PMMA). Due to differences in initiator density on the Si and Ge regions, the resulting PMMA is approximately 2x thicker on the Si surface. A subsequent hydrogen peroxide etching step removes PMMA on the Ge surface, thus providing nearly 100% selectivity, but leaves the Si regions unaffected. We hypothesize the mechanism of PMMA removal is hydrogen peroxide diffusion through the polymer layer and etching of the underlying Ge atoms. In this study, we use a suite of spectroscopy and microscopy techniques to investigate the effect of initial Si/Ge surface treatment, PMMA polymerization conditions, and hydrogen peroxide etching conditions on the resulting polymer film properties and surface. The ability to selectively mask nanoscale objects in a bottom-up fashion opens up the possibility for nanoscale patterning in a simultaneously high-throughput and cost-effective manner.

11:40am **EM+MP+PS-MoM-11 Chemically Selective Imaging of Sequential Infiltration Synthesis with nm-scale Spatial Resolution***, D Nowak, **Tom Albrecht**,* Molecular Vista

Area selective deposition (ASD) is an active area of research for advanced nanofabrication. Closely related to ASD is sequential infiltration synthesis (SIS) where inorganic material is infused into select polymer material to render an organic/inorganic hybrid material based on a polymer-template. The organic component can be burned or etched away to leave only the inorganic component, which can be used as etch mask or for other purposes. For lithography applications, the length scale (in nanometers range) and the nature of material (organic and inorganic molecules) are such that traditional techniques such as FTIR, electron microscopy, and X-ray scattering are not able to yield real space, chemically selective imaging of SIS processes. Photo-induced Force Microscopy (PiFM) [1] combines infrared (IR) absorption spectroscopy and atomic force microscopy (AFM) via illumination of the tip-sample junction with tunable IR laser light and mechanical detection of forces acting on the tip in response to absorption of light by the sample. By mapping the IR absorption of the sample as a function of IR wavelength and position, nm-scale resolution is achieved in displaying the locations of heterogeneous materials on the surface of a sample. This imaging capability is useful for investigating chemical pre-patterns as well as selectively deposited materials in area-selective processes like block copolymer directed self-assembly, SIS [2], and a variety of area-selective deposition techniques. In this talk, we will present the PiFM results on a model system: Al_2O_3 SIS using trimethyl aluminum and H_2O with poly(styrene-block-methyl methacrylate) (PS-*b*-PMMA) block copolymer with 41 nm full pitch lamellae, demonstrating sub-10 nm spatial resolution of chemically selective imaging.

[1] D. Nowak et al., Sci. Adv. **2**, e150157 (2016).

[2] Y. Tseng et al., J. Mater. Chem. **21**, 11722(2011).

Plasma Science and Technology Division
Room 104A - Session PS+AS+EM+SS-MoM
Plasma-Surface Interactions

Moderators: Yohei Ishii, Hitachi High Technologies America Inc., Erik V. Johnson, LPICM, Ecole Polytechnique, France

8:20am **PS+AS+EM+SS-MoM-1 Atomic-scale Numerical Simulation of a Nanometer-Scale Hole Etching of SiO2 with a Carbon Mask***, **Charisse Marie Cagomoc**, M Isobe, S Hamaguchi,* Osaka University, Japan

The current generation of mass-produced semiconductor devices uses nanometer-scale technologies to fit millions of transistors in a single chip. However, the demand for higher integration density is still increasing. For example, sub-10 nanometer transistors have been already established for experimental devices, and fabrication technologies of such devices for mass production are now being developed. For nanometer-scale fabrication processes, the granularity of the structure reflecting the finiteness of atomic sizes and the stochasticity of atomic motion may play important roles in determining the final structure. In this study, to understand such atomic-scale effects in nano-scale fabrication processes, we performed molecular dynamics (MD) simulations of etching processes for silicon dioxide (SiO_2) with a carbon mask having a 4-nm diameter hole by energetic fluorocarbon ions. The incident ion energy was typically in the range from 200eV to 1000eV. For example, in the case of CF_3+ ion injections, we observed that the depth of the etched out SiO_2 increased with increasing incident ion energy while the channel width became narrower as the etching of SiO_2 went deeper. Tapering of the carbon mask was also observed when the incident ions hit and deform the mask instead of going straight towards the SiO2. Furthermore, if the incident energy was too high (e.g., 1000 eV in this case), closing of the carbon mask hole occurred due to the formation of long carbon chains that moved across the hole and were bonded to the opposite side. Deposition of carbon atoms from the mask onto the sidewalls of the etched SiO_2 was also observed, which caused the formation of silicon carbide and may have impeded horizontal etching of SiO_2.

8:40am **PS+AS+EM+SS-MoM-2 SF_6/O_2 Plasma Nanotexturing of Silicon: Decoupling How Ion Flux and Ion Energy Matter***, **Guillaume Fischer**[1],* Institut Photovoltaïque d'Ile-de-France (IPVF), France*; E DRAHI, S FILONOVICH,* Total SA Renewables, France*; E Johnson,* LPICM, CNRS, Ecole polytechnique, Université Paris-Saclay, France

Crystalline silicon (c-Si) solar cell performance can be improved by reducing front surface reflectance. A drastic decrease may be obtained by texturing the surface at the nanoscale ("nanotexturing"), leading to a graded refractive index from air to c-Si. SF_6/O_2 plasma etching of c-Si in a capacitively coupled radiofrequency (CCP-RF) discharge is known to induce spontaneous nanotexturing. This phenomenon – typically resulting in the formation of conical nanostructures (NS) with typical sizes ranging from 30 to 500 nm – occurs through *in-situ* formation of non-volatile inhibitors on the surface. The latter compete with simultaneous physical and chemical etching, and all these mechanisms may be influenced by ion bombardment.

In the present study, the ion energy distribution at the substrate electrode is tuned using Tailored Voltage Waveforms (TVWs) excitation in a reactive ion etching system. TVWs are obtained by adding harmonic frequencies with controlled amplitudes and phase-shifts to the basis driving signal at 13.56 MHz. This technique may give rise to amplitude and slope asymmetries in electronegative plasmas such as the SF_6/O_2 mixture.

Taking advantage of the edge-high total ion flux radial profile on the electrode but with a uniform energy distribution profile, we investigate the influence of both ion energy and ion flux on the nanotexturing process. Process conditions (etching time and driving voltage, i.e. sinusoidal signal or TVWs) are varied, and four samples are simultaneously textured for each set of conditions. The variations in etch rate suggest an ion energy-dependent etching yield. A phenomenological model (etching yield varying with the square root of the ion energy above a threshold at 13 eV) is proposed, and leads to the determination of a clear dependence between the energy weighted ion fluence and the final total hemispherical reflectance of the samples.

This trend is of great relevance for photovoltaic applications, and is explained by the constant increase in NS height during the process, which gradually smoothens the transition of refractive index from air to c-Si. However, the instantaneous ion flux is still observed to influence the aspect ratio (ratio between average height and width of the NS): the higher the ion flux, the higher the aspect ratio. This effect may stem from reduced lateral expansion of inhibitor species on the NS flanks due to the higher ion flux, and will affect the subsequent surface passivation required for photovoltaic applications. Finally, design rules for silicon nanotexturing using SF_6/O_2 plasma are drawn from the observed trends.

9:00am **PS+AS+EM+SS-MoM-3 Corrosion Resistance to F and Cl plasma of Yttrium Oxyfluoride (YOF) formed by Sintering***, **Akinobu Teramoto**, Y Shiba, T Goto,* Tohoku University, Japan*; Y Kishi,* Nippon Yttrium Co., Ltd, Japan*; S Sugawa,* Tohoku University, Japan

Corrosion resistance to the reactive species in some kinds of plasma is very important to construct the reliable semiconductor process equipment. Especially the Fluorine and/or Chlorine plasma have the strong corrosiveness, and then it is strongly required that the inner wall material of the plasma chamber and the components in the plasma chamber have corrosion resistance to them. We have reported the Yttrium oxyfluoride (YOF, Y:O:F=1:1:1) film has the higher resistance to some plasma conditions (N_2/Ar, H_2/Ar, NH_3/Ar, NF_3/Ar, O_2/Ar) than the Y_2O_3 and YF_3 films [1, 2]. In this presentation, we report the corrosion resistance to NF_3/Ar, Cl_2/Ar and O_2/Ar plasma of YOF formed by sintering. The Y, O and F composition was controlled by mixing ratio of the YOF, YF_3, and $Y_5O_4F_7$ before the sintering, as the results, the O concentration was varied from 3 to 12 %. All YOF formed by the sintering are more stable to NF_3/Ar and O_2/Ar plasma than the YOF film and both Y_2O_3 film and formed by sintering. Cl_2/Ar plasma shows the stronger corrosion effect to the Y_2O_3 and YOF's, however the corrosion resistance to Cl plasma of YOF's is higher than the Y_2O_3.

These results indicate that the YOF is much stable against the corrosion by the plasma, and YOF formed by sintering is the promising material to construct the components in the plasma chamber.

Acknowledgement

The plasma irradiation and inspection were carried out in Fluctuation-Free-Facility in Tohoku University.

References

1. Y. Shiba, A. Teramoto, T. Goto, Y. Kishi, Y. Shirai and S. Sugawa, J. Vac. Sci. Technol. A, **35** (2), 021405 (2017).

2. Y. Shiba, A. Teramoto, T. Goto and Y. Kishi, p. 111, AVS 64th International Symp., Tampa, 2017.

9:20am **PS+AS+EM+SS-MoM-4 Decay of Hydrogen in NF_3/Ar and O_2/Ar Cleaning Process by Optical Emission Spectroscopy***, **Hanyang Li**, Y Zhou, V Donnelly,* University of Houston*; J Chiu, X Chen,* MKS

Fluorine atom-generating plasmas are commonly used in many cleaning processes after chambers have been exposed to a variety of etching and deposition reactants and products. The most common feed gas used in these applications is NF_3, due mainly to its ease of dissociation. Repeated processing and chamber cleaning cycles can cause changes in the plasma source, thought to be due mainly to an altering of the nature of the chamber wall protective coatings. In the present study, high power density (5 – 50 W/cm^3), low frequency (400 kHz) toroidal inductive plasmas were operated with H_2/Ar (4/96) and N_2/H_2/Ar (3/9/88) feed gases for various periods, alternating with exposure to NF_3/Ar, O_2/Ar, or pure Ar "chamber cleaning" plasmas. H Balmer-alpha optical emission intensity, ratioed to emission from Ar at 750.4 nm, was measured during H_2/Ar exposure and the following cleaning plasma. Hydrogen was detected evolving from the anodized Al plasma source wall coating. The decay of intensity ratio of H/Ar increased with increasing H_2/Ar plasma exposure. NF_3/Ar plasmas enhanced evolution of H, tentatively ascribed to diffusion of F into anodized Al (most likely as F^-), which reacts with H that would otherwise remain trapped in the layer. The HF product then out-diffuses, leading to plasma dissociation and H emission. Conversely, O_2/Ar plasmas suppressed the evolution of H, presumably because O bonds to Al in anodized Al and ties up hydrogen as bound OH.

9:40am **PS+AS+EM+SS-MoM-5 Plasma-surface Interactions in the Strongly Coupled Regime***, **Thomas Morgan**,* DIFFER, Netherlands **INVITED**

At high fluxes and densities the interaction of a plasma with the walls of its confinement enter the strongly coupled regime [1], where the mean free paths for collisional processes become much smaller than those of the plasma scale size. The surface morphology in such cases may be pushed far out of equilibrium and in turn the recycling and erosion strongly perturbs the near-surface plasma. Such conditions are reached in high flux plasma processing as well as the exhaust region of future large-scale fusion reactors such as ITER and DEMO. The linear plasma generator Magnum-PSI [2] is uniquely capable of achieving high density low temperature plasmas with high similarity to fusion reactor exhaust fluxes. Using this device the power handling, long term erosion and evolution of plasma facing materials for ITER and DEMO can be studied, as well as the self-organisation effects and novel structures which occur under such conditions. At plasma-liquid metal interfaces considered as advanced wall components this strong coupling can give rise to vapour shielding of the surface, indicating a novel method to limit heat loading damage to wall surfaces in the reactor exhaust [3]. An overview of results will be given showing how this device is addressing urgent questions for ITER, helping to develop advanced walls for DEMO and beyond, and exploiting non-equilibrium for plasma processing.

[1] A.W. Kleyn et al. Phys. Chem. Chem. Phys. 8 (2006) 1761–1774

[2] G. De Temmerman et al. Fusion Eng. Des. 88 (2013) 483-487

[3] G.G. van Eden et al. Phys. Rev. Lett. 116 (2016) 135002

10:40am **PS+AS+EM+SS-MoM-8 Tailoring the Surface Properties of Porous Zeolite Constructs using Plasma Processing***, **Angela Hanna**[2], E Fisher,* Colorado State University

Zeolites have been widely used for adsorption, catalysis, and gas separation processes. Despite their extensive use, the ability to control the surface

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[1] **Coburn & Winters Student Award Finalist**

[2] **National Student Award Finalist**

properties of zeolites remains unoptimized. Plasma modification presents an ideal modification methodology with a wide parameter range and the potential to create tailored surface properties and functionalities. Thus, we sought to improve material performance through plasma surface modification, as well as through fabrication of various zeolite constructs (i.e., native zeolites, pellets and electrospun fibers). Moreover, our approach to understand the fundamental plasma chemistry allows us to provide significant insight into mechanisms that will ultimately provide a more thorough evaluation of plasma processing for zeolite surface modification. We employed a range of characterization tools to assess materials before and after plasma treatment and optical spectroscopies to examine the gas-phase of the plasma, both with and without zeolites to evaluate the impact of the material on the gas-phase. X-ray photoelectron spectroscopy (XPS), scanning electron microscopy, and powder X-ray diffraction were utilized to assess surface chemistry, substrate morphology, and bulk characteristics of the material, respectively, before and after plasma exposure. Water contact goniometry was employed to evaluate the surface wettability, where untreated zeolites were nominally hydrophilic. Here, we explored two fluorocarbon (FC) precursors (i.e., C_2F_6 and C_3F_8) to create more hydrophobic surfaces than the untreated materials. XPS analysis reveals surface fluorination and/or formation of a FC coating on the material. $H_2O_{(v)}$ plasmas were also employed to create a more hydrophilic zeolite surface, while maintaining a porous, interconnected network. By also studying the gas-phase, we can glean how the material changes the plasma environment. Species interactions and plasma energetics are intertwined; thus, temporally-resolved data are necessary to accurately probe the intricate dynamics within plasmas. We have investigated formation and destruction mechanisms of key excited state species (i.e., CF, CF_2, OH) to provide mechanistic insight that could be correlated with system energetics data and material properties. Emission spectroscopy was also used to measure the relative gas phase densities of the aforementioned key species as a function of plasma operating parameters (i.e., power, gas mixture, substrate architecture). Our studies have revealed correlations between gas-phase spectroscopic analyses, the gas-surface interface, and the resulting plasma modified surface properties, ultimately leading to improved plasma processes.

11:00am **PS+AS+EM+SS-MoM-9 Generation Kinetics of Plasma-induced Electronic Defects in Semiconductor Materials*, Shota Nunomura*,** *I Sakata, K Matsubara,* National Institute of Advanced Industrial Science and Technology (AIST), Japan

In state-of-the art semiconductor devices, electronic defects strongly influence the device performance. The electronic defects are often generated during the device fabrication, where a variety of plasma processing technology is used for film deposition, gate etching, dopant implantation and so on. Most defects are recovered by post-annealing, however some defects remain in the devices. Because these defects usually deteriorate the device performance, reduction of these defects is required. However, the kinetics of generation and annihilation of the defects are not fully understood yet.

We studied the kinetics of electronic defects in hydrogenated amorphous silicon (a-Si:H) during H_2 and Ar plasma treatments. The generation and annihilation of defects are monitored via in-situ photocurrent measurement during the treatment [1-2]. A decrease in the photocurrent indicates the generation of defects whereas an increase in the photocurrent indicates the annihilation of defects. This photocurrent-based monitoring is highly sensitive in the detection of small amount of defect density (~10^{16}cm^{-3}).

The photocurrents in a-Si:H films under various conditions of H_2 and Ar plasma were measured. From the measurements, we find the following [3]. (i) Each plasma treatment immediately causes the generation of defects, indicated by a strong reduction in the photocurrent. (ii) The defects are generated dominantly by the radicals such as hydrogen atoms (H) and argon metastable atoms (Ar^*). (iii) The residual defects are created by the bombardment of Ar^+ ions rather than H_3^+ ions, radicals and photons. However, the residual defects are recovered mostly by an additional H_2 plasma and post-annealing treatment. (iv) The radicals and photons also generates defects, however these defects are annihilated by the simple post-annealing. The details of the experimental setup, results and discussion are given in the presentation.

This work was supported by JSPS KAKENHI (Grant Number 18K03603 and 15K04717) and NEDO.

[1] S. Nunomura, I. Sakata, and M. Kondo,*Appl. Phys. Express* **6**, 126201 (2013). [2] S. Nunomura and I. Sakata, *AIP Advances* **4**, 097110 (2014). [3] S. Nunomura et al., submitted.

11:20am **PS+AS+EM+SS-MoM-10 Evolution of Photoresist Layer Structure and Surface Morphology under Fluorocarbon-Based Plasma Exposure*, Adam Pranda,*** *S Gutierrez Razo, J Fourkas, G Oehrlein,* University of Maryland, College Park

Fluorocarbon-based plasma chemistry is an integral component in enabling the pattern transfer step in the semiconductor manufacturing process. Although significant work has gone towards understand the overall etching behavior, surface roughness, and chemistry development for continuous-wave (CW) plasmas with Ar/fluorocarbon admixtures,[1] a complete understanding of the photoresist layer structure evolution and surface roughness distribution has not been well established. Specifically, under high-energy ion bombardment, a dense amorphous carbon (DAC) layer forms at the surface, impacting the etch resistance and surface roughness. For discrete evaluation of the DAC layer/fluorocarbon interaction, we employed a pulsed plasma setup in which a biased, steady-state Ar plasma was used to develop DAC layers of various thicknesses at the photoresist surface, after which fluorocarbon (C_4F_8) pulses of various lengths were introduced. We sought to answer three key questions: 1. How does the fluorocarbon interaction with the DAC layer impact the layer structure? 2. How is the surface roughness affected by the fluorocarbon interaction? 3. How does the pulsed process compare to a CW Ar/C_4F_8 admixture process?

For sample characterization, we utilized a combination of real-time, *in situ* ellipsometry and X-ray photoelectron spectroscopy at various points during the plasma exposure on an industry-standard 193 nm photoresist, several model polymers, and a 3-color-lithography-compatible photoresist that we are developing. Atomic force microscopy (AFM) was used to monitor the surface roughness evolution and the distribution was calculated using a power spectral density (PSD) analysis.

From the combined analyses, we find that the fluorocarbon depletes the DAC layer by a partial conversion of the surface of the DAC layer into an F-rich mixed layer. Furthermore, the mixing of the fluorocarbon into the DAC layer results in an overall smoothening of the sample surface. By comparing the pulsed process to the CW process, we evaluate the significance of the layer structure in determining the surface behavior in response to variations in fundamental plasma parameters such as the ion energy or exposure time.

The authors gratefully acknowledge the financial support of this work by the National Science Foundation (NSF CMMI-1449309) and the US Department of Energy Office of Fusion Energy Sciences (DE-SC0001939).

[1] S. Engelmann et al., J. Vac. Sci. Technol. B Microelectron. Nanom. Struct. **27**, 1165 (2009).

11:40am **PS+AS+EM+SS-MoM-11 Fundamental Studies of Plasma Species with Organic Materials of Varying Hydrogen and Oxygen Composition by Computational and Experimental Approaches*, Yusuke Fukunaga,*** Nagoya University, Japan*; P Ventzek, B Lane,* Tokyo Electron America, Inc.*; A Ranjan,* TEL Technology Center America, LLC*; M Sekine, T Tsutsumi, H Kondo, K Ishikawa,* Plasma Nanotechnology Research Center, Japan*; R Upadhyay,* Esgee Technologies*; L L. Raja,* The University of Texas at Austin*; G Hartmann,* McKetta Department of Chemical Engineering, The University of Texas at Austin*; G S. Hwang,* The University of Texas at Austin*; M Hori,* Institute of innovation for future society, Japan

Organic film etching is important for semiconductor device fabrication especially as it relates to self-aligned-multiple-patterning in which sub-nanometer scale pattern replication is critical. Even though the etching of organic materials has been studied for decades (e.g., O_2 plasma ashing), new process applications (e.g. ALE) and new chemistry regimes render older models of organic etching such as those employing the Ohnishi parameter of limited use.[1] Existing kinetic models rely on untested assumptions such as the role of dangling bonds as reaction initiating sites.[2] A need exists to revisit the fundamentals of plasma surface interactions as they pertain to the etching of organic films. Moreover, a need exists to incorporate fundamental kinetic models with macroscale models which could be used for process development.

Progress has been slow because of the computational weight of modeling the chemical kinetics and difficulty defining a tractable problem. In this presentation, we describe the use of an integrated modeling framework involving fundamentals-based ab-initio and plasma chemistry simulations with high performance computing to describe chemical kinetics on model polymer systems. In O_2 and Ar plasmas, we use finite carbon size strands with varying degrees of O, OH or H termination as model structures. For simplicity, the structures are polyethylene-like. We use density functional theory (DFT) to model the interactions between plasma species and representative structures. To estimate the relative importance of plasma species and their energy, we derive species and energy flux from a macroscale plasma chemistry model. Both DFT and ab-initio molecular dynamics (AIMD) simulations are used to probe the chemical stability of representative structures to different plasma species (e.g., Ar, O) and energy fluxes. We found that O addition to H terminated structures results in OH group formation on polyethylene by exothermic reaction. Ar ion bombardment formed carbon strands may also be oxidized. The resultant structures (oxo-carbon) are also stable up to large oxygen to carbon ratios. The stability to Ar ion bombardment will be presented. An essential test of any new mechanism is experimental validation. In addition to the computational results, we will present experimental results ranging from basic etch rate measurements to measurements of plasma processed material chemical composition (e.g., XPS).[3]

References:

[1] H. Gokan, *et al.*, J. Electrochem. Soc.: Solid-state Sci. Technol. **130**, No. 1, 143 (1983).

[2] F. D. Egitto, Pure & Appl. Chem. **62**, No. 9, 1699 (1990).

[3] D. U. B. Aussems, *et al.*, Chem. Sci. **8**, 7160 (2017).

Plasma Science and Technology Division
Room 104C - Session PS+TF-MoM
Plasma Deposition and Plasma-Enhanced ALD

Moderators: Kazunori Koga, Kyushu University, Japan, Erwine Pargon, CNRS-LTM, Université Grenoble Alpes, France

8:20am **PS+TF-MoM-1 ZrO_2 Deposition using a 2.45 GHz Atmospheric Pressure Plasma Torch***, **Dhruval Patel**, L Bonova, C Ahn, D Krogstad, D Ruzic,* University of Illinois at Urbana-Champaign*; S Chaudhuri,* University of Illinois at Chicago

Partially stabilized zirconia is widely used in thermal barrier coatings that requires a thermodynamically stable and highly durable interface with a natively grown aluminum oxide (Al_2O_3) scale. The potential of ZrO-$_2$ to serve as an effective Thermal barrier coating (TBC) has already been demonstrated along with modest corrosion resistance. The ECAP experiment (Evaporative Coatings at Atmosphere Pressure) was developed at CPMI (Center for Plasma Materials Interaction at UIUC) as a device for surface treatment at atmosphere pressure utilizing a 2.45 GHz microwave plasma torch. Recent modifications to this system allows for delivery of precursors and target materials through the torch that gives it the capability to deposit thin films. The goal of this study is to compare the quality of the ZrO-$_2$ films grown using each of these methods. Various methods will be used to characterize the quality of films grown including Nanoindentation, XPS, XRD and Profilometry.

8:40am **PS+TF-MoM-2 Ion Energy Characteristics during Plasma-Enhanced Atomic Layer Deposition and their Role in Tailoring Material Properties***, **Tahsin Faraz**[1],* Eindhoven University of Technology, The Netherlands, Netherlands*; K Arts,* Eindhoven University of Technology, The Netherlands*; S Karwal, M Creatore,* Eindhoven University of Technology, The Netherlands, Netherlands*; H Knoops,* Oxford Instruments, The Netherlands*; E Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands

As we enter an era of atomic scale device dimensions, there is a significant demand for synthesizing ultrathin films with precise growth control. Plasma-enhanced atomic layer deposition (PEALD) has obtained a prominent position in obtaining films with atomic scale precision. Although the effects of ion-surface interactions have been investigated for conventional plasma-enhanced chemical and physical vapor deposition in great detail, very little is known about the role of ions during PEALD. In this work, we demonstrate how the properties of materials (oxides and nitrides of Ti, Hf and Si) grown using PEALD (on planar and 3D substrates) can be tailored by controlling the kinetic energy of ions, **E_i**, impinging on a growing film surface with RF substrate biasing.[1] This technique harnesses the well-known synergism of ion-radical processes under energetic ion bombardment during reactive plasma exposure. It was demonstrated to significantly enhance the versatility of PEALD processes by providing two knobs (magnitude and duration of bias) enabling control over materials with dielectric or conductive properties, relevant for a wide variety of applications.

We measured **E_i** characteristics of reactive plasmas typically used for PEALD (O_2, H_2, N_2) to investigate their role in tailoring material properties. Performing such measurements is essential towards understanding how a given PEALD process at different operating conditions can be influenced by energetic ions. Ion energy distributions (IEDs) were measured in a commercial 200-mm remote inductively-coupled-plasma (ICP) ALD system equipped with RF substrate biasing. IEDs were obtained using a gridded retarding field energy analyzer (RFEA) for the aforementioned plasmas without and with RF biasing. The properties of materials grown using these plasmas in this ALD system were analyzed as a function of the parameters derived from IEDs. These results have provided more insight on the relation between ion characteristics and the ensuing properties, e.g., identifying **E_i** thresholds between property improvement and degradation. They demonstrate how the measurement and control of **E_i** characteristics during PEALD provides a platform for synthesizing ultrathin films with desired properties.

Furthermore, we analyzed the effects of controlling **E_i** during PEALD on 3D substrates frequently employed in state-of-the-art devices. It yielded an intriguing effect of inducing differing material properties at different surfaces of 3D trench nanostructures. This demonstrated the potential of this technique in enabling new routes for achieving topographically selective deposition.

[1] Faraz *et al. ACS Appl. Mater. Interfaces* **10**, 13158 (2018)

9:00am **PS+TF-MoM-3 Plasma Deposition of Functional, Nanostructured Coatings on Materials and Nanomaterials Derived from the Wood Biomass***, **Luc Stafford**,* Université de Montréal, Canada **INVITED**

Wood components have been used as a building material for centuries. In light of the growing concern over the environmental impact of human industrial activity, wood has taken on a new importance worldwide. The main advantages of this widely-distributed and renewable resource lie in its versatility, strength-to-weight characteristics, ease of processing, aesthetics, and its sustainability as a green-material. Its bio-polymeric structure, however, renders it susceptible to degradation due to moisture, microorganisms, insects, fire, and ultraviolet radiation. In this context, important research efforts have been devoted to the further development of existing wood protection systems either through the application of paints, varnishes, stains, and water repellents or through direct modification by thermal, chemical, and impregnation methods. In recent years, we have shown that non-thermal plasmas represent a very promising approach for tailoring the surface properties of wood-based materials for both improvement of existing protection systems or as standalone treatment for the growth of functional coatings. In this presentation, the scientific and technological accomplishments associated with the use of plane-to-plane dielectric barrier discharges at atmospheric pressure for plasma-enhanced chemical vapor deposition (PECVD) of various barrier coatings on wood surfaces are reviewed. These aspects cover the effects of wood conditions and properties, such as wood inhomogeneities and wood outgassing, on both the plasma characteristics and the plasma deposition dynamics of SiOCH barrier layers using organosilicon precursors. This description is extended to more complex systems such as the plasma-assisted growth of nanocomposite coatings (for example TiO2 or ZnO nanoparticles embedded into a SiOCH matrix) using colloidal solutions as the growth precursor for PECVD. For such applications, a combined low-frequency-high-frequency voltage waveform is used to achieve significant and spatially uniform deposition of nanoparticles across the whole substrate surface. Finally, very recent studies on the plasma-assisted functionalization of highly porous microfibrillated cellulose materials derived from the wood biomass are presented.

9:40am **PS+TF-MoM-5 Mechanisms of Halogenated Silane Decomposition on an N-rich Surface during Atomic Layer Deposition of Silicon Nitride***, **Gregory Hartmann**,* University of Texas at Austin*; P Ventzek,* Tokyo Electron America, Inc.*; K Ishibashi, T Iwao,* Tokyo Electron Technology Solutions Ltd., Japan*; G Hwang,* University of Texas at Austin

Atomic layer deposition (ALD) has recently received increasing attention for the growth of high-conformity silicon nitride (SiN) thin films for use in microelectronics, particularly as charge storage layers in vertical-NAND. Plasma enhanced ALD (PEALD) allows SiN deposition at substantially lower temperatures (< 400 °C) with better film properties, compared to thermal ALD. The challenge of PEALD is that Si deposition must occur via a thermal

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[1] **Coburn & Winters Student Award Finalist**

mechanism due to the low temperatures. The PEALD of SiN films involves a two-step cycle: (1) adsorption and decomposition of silicon-containing precursors and ii) nitridation of the Si-rich surface by active N species emanating from the plasma. Halogenated silanes such as hexachlorodisilane, bis(tertiary-butyl-amino)- silane, and dicholorosilane (DCS, SiH_2Cl_2) have been utilized as Si precursors. Despite efforts directed towards process development, the underlying reaction mechanisms of Si deposition remain uncertain. Methods to improve growth rate and uniformity have been demonstrated experimentally, but without knowledge of the reaction mechanisms, direct contributions of specific process conditions cannot be explained. Using first-principles density functional theory (DFT) calculations, we have examined and identified a novel mechanism for the adsorption and decomposition of DCS on a N-rich SiN surface. Our study predicts that the DCS adsorption and dissociation can occur by overcoming a moderate barrier (» 0.3 eV), lower than the prohibitively large barriers predicted for previously proposed mechanisms. Through a detailed electronic structure analysis of the reaction intermediates, we have also elucidated the principles underlying the reaction mechanism, notably the hypercoordination of Si which permits the facile reaction of molecularly adsorbed DCS with primary and secondary amines on the surface, followed by dissociation releasing protons and Cl anions with subsequent HCl formation. We have examined the same mechanism utilizing alternative precursors and the predicted trends are found to be corroborated with the important properties of the system. Understanding these principles allows us to develop guidelines for processing conditions, such as the importance of maintaining the proper surface composition to facilitate Si precursor adsorption and dissociation. Our study provides insight into the SiN ALD process via chlorosilanes and guidelines to control the deposition for high-quality SiN films and provides a framework for future theoretical studies of surface reactions during ALD.

10:00am **PS+TF-MoM-6 Characterization of Inductively Coupled Plasma Source for Plasma Enhanced Atomic Layer Deposition***, **Premkumar Panneerchelvam**, A Agarwal,* KLA-Tencor*; D Boris, S Walton,* Naval Research Laboratory

Plasma enhanced atomic layer deposition (PEALD) is a technique which provides an efficient alternative to thermal ALD systems by enabling low-temperature wafer processing using energetic and reactive plasma species. Utilization of plasma sources to drive atomic layer deposition stems from the ability to generate active radicals which are more reactive than molecular precursors used in thermal ALD processes. Aside from the fact that plasma processing systems are already utilized in semiconductor manufacturing, PEALD affords significant advantages over thermal ALD processing such as lower temperature processing coupled with active tuning of film properties, wafer level uniformity control, wider variety of film growth, and conformality. Remote inductively coupled plasma (ICP) sources are a common choice for PEALD as they enable high density discharges which efficiently generate reactive neutral species. Characterization of these plasma sources is important in understanding the properties of the species incident on the wafer to not only tailor the chamber architecture but also understand the role of different radicals in the plasma in the surface mechanism.

In this work, we will discuss characterization of a reactor that imitates an industrial PEALD tool using experimental and computational investigations. The system is flowing afterglow geometry, where a barrel-type ICP source is mounted on one side of the reactor and produces a plasma that expands into a chamber with access ports to diagnose the plasma properties using optical emission spectroscopy and charged particle flux probes. The computational model is based on a multi-species, two-temperature fluid description of plasma with finite rate chemistry. Results will be discussed in Ar and Ar/N_2 plasmas over varying pressure and inductive power with particular emphasis on the impact of N_2 addition on plasma properties and the chemical composition of radicals incident on the wafer.

*This work was partially supported by the Naval Research Laboratory base program.

10:40am **PS+TF-MoM-8 Structural, Optical, and Electrical Properties of Plasma-Enhanced Atomic Layer Deposited ZnO: Influence of Substrate Temperature***, **Julian Pilz**, A Perrotta, A Coclite,* Graz University of Technology, Austria

ZnO is a direct band gap semiconductor with attractive piezoelectrical, optical, and electrical properties, particularly appealing for a variety of functional devices (e.g., gas, bio, and UV sensors, piezoelectric nanogenerators and actuators). Being able to tailor these material properties to meet specific technological requirements is crucial for enhancing the device efficiency or sensitivity.

In a previous study [1], the effect of plasma power on plasma-enhanced atomic layer deposited (PE-ALD) ZnO had been investigated at room temperature. By tuning the power, properties such as the refractive index, bandgap, and crystallite size had been tailored. However, the power had shown little influence on the texture of the crystalline films.

In this study, we investigated the effect of substrate temperature in the range 25 °C – 250 °C on the ZnO material properties. The films were grown by direct PE-ALD adapting diethylzinc and O_2-plasma as reactants. By adjusting the substrate temperature, it was possible to switch the texture of the films from (100) at room temperature to (002) above 150 °C. The growth per cycle (obtained by spectroscopic ellipsometry, SE) ranged from 1.6 to 4.0 Å/cycle, suggesting a temperature dependent growth behavior. Further SE analysis showed a range of refractive index (at 633 nm) from 1.87 to 1.94 and a bandgap range of 3.255 to 3.270 eV. X-ray photoelectron spectroscopy survey scans pointed out a non-detectable carbon content and a O/Zn ratio of around 1.17 (constant over the whole temperature range), while high-resolution scans of the O1s-peak showed a decrease in OH-content from 21 % (at 25 °C) to 9 % (at 250 °C). Further analysis will focus on resistivity (and its relation to OH-content), transparency, and piezoresponse.

Correlating the results of these techniques, interesting insights can be gained into the quality of the PE-ALD ZnO and which substrate temperature should be chosen for specific applications. This paves the way for optical, electrical, or sensing devices on the basis of tailored ZnO thin films, which can be grown conformally and with Å-level thickness control due to the PE-ALD characteristics.

[1] Pilz et al. "Tuning of material properties of ZnO thin films grown by plasma-enhanced atomic layer deposition at room temperature." J. Vac. Sci. Technol. A 36.1 (2018): 01A109.

11:00am **PS+TF-MoM-9 Critical Effect of the Presence and Position of Double Bonds in the Atmospheric Plasma Synthesis of Organic Coatings***, **Jérémy Mertens**[1], J Baneton, A Ozkan, F Reniers,* Université Libre de Bruxelles, Belgium

Last decades, atmospheric plasma systems have become a powerful tool for the synthesis of organic/inorganic coatings. Even though the well-known Yasuda parameter[1] is a good indicator of the fragmentation process of the injected monomers during the low-pressure synthesis, it faces severe limitations at ambient conditions. This can essentially be related to the wider range of collisions and the lower mean free path of the plasma species at atmospheric pressure. Also, the key role of the chemical structure of the injected monomer such as the presence of double bonds on the synthesized coating properties has not been included in the Yasuda model but strongly influences the plasma polymerization/fragmentation mechanisms.[2]

It is well known, not only in plasma science, that the presence of double bonds increases the deposition rate which has been confirmed in this research. Yet, our group previously demonstrated that unsaturations could also play a protective role of an ester function during the atmospheric plasma polymerization process[3] but no explanationwas proposed so far. Using various saturated and unsaturated precursors, this study proposes a novel point of view of the essential role of the presence of sp^2 carbon atoms, their spacing with a function of interest and the planar geometry of the monomer in the polymerization mechanisms in dielectric barrier systems. Therefore, the plasma phase and physico-chemical properties of the synthesized coatings analysis are correlated. The influence of the addition of each molecule on the electrical behavior of the discharge is monitored by oscilloscope measurements. The fragmentation of the precursor in the plasma, evidenced by in situ mass spectrometry and optical emission spectroscopy, show that the polymerization mechanisms are different when the precursor contains double bonds. The suggested synthesis pathways for each precursor are correlated to the surface and bulk chemical structure of the synthesized films, determined by X-Ray photoelectron spectroscopy and infrared reflectance absorbance spectroscopy. It is evidenced that the distance separating the function of interest from the double bond is a major parameter to take in account for the conservation of the structure of the injected molecule. We suggest that it is possibly due to a planar geometry arrangement and to a resonance phenomenon for specific double bonds positions.

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[1] **Coburn & Winters Student Award Finalist**

The authors would like to thank the Walloon Region for their financial support through the FLYCOAT project (n°131847).

[1] H.K.Yasuda & al. , J. Polym. Sci., 16, 743

[2] J.Hubert & al., Plasma Process. Polym. **2015**, 12, 1174

[3] A.Batan & al., Plasma Process. Polym. **2013**, 10, 857

11:20am **PS+TF-MoM-10 Capacitively Coupled DC/RF Discharges for PEALD Process of Titanium Dioxide Films***, **Shinya Iwashita**, A Suzuki, T Shindo, T Kikuchi, T Matsudo, Y Morita, T Moriya,* Tokyo Electron Technology Solutions Ltd., Japan*; A Uedono,* University of Tsukuba, Japan

We are working on the development of a discharge source using tailored waveforms for plasma enhanced atomic layer deposition (PEALD) processes. The discharge sources employed in this study are 13.56 MHz RF, pulsed DC or their combination [1], and their applicability to PEALD process of titanium dioxide (TiO_2) thin films has been evaluated. A titanium precursor adsorbed on a silicon substrate having amorphous carbon (a-C) patterns is oxidized by applying these discharges in argon/oxygen mixtures. Thus PEALD process of TiO_2 films is achieved accordingly. The experimental results obtained from scanning transmission electron microscope show that TiO_2 films are deposited with excellent step coverage independent of the discharge sources. However, the film characteristics at each deposition position of a-C patterns (i.e. at the top, side and bottom) greatly vary depending on the discharge sources, which has been confirmed by the evaluation of the wet etching rate using a diluted hydrogen fluoride solution. The clear variation of the film characteristics is presumably attributed to the change in the number density of reactive species (electrons, ions, radicals), their ratio and the ion angle distributions, all of which are determined by the discharge sources.

[1] Denpoh K and Ventzek P, *J. Vac. Sci. Technol. A* **26** (2008) 1415, Kawamura E et al *J. Vac. Sci. Technol. A* **25** (2007) 1456.

11:40am **PS+TF-MoM-11 The effects of Varying Plasma Conditions on Plasma Enhanced Atomic Layer Epitaxy***, D Boris, V Wheeler,* U.S. Naval Research Laboratory*; V Anderson,* Kennesaw State University*; N Nepal,* U.S. Naval Research Laboratory*; S Rosenberg, A Kozen,* ASEE Postdoctoral Fellow*; S Walton, **Charles Eddy**,* U.S. Naval Research Laboratory

Plasma enhanced atomic layer epitaxy (PEALE) is a method for growing very thin crystalline films at low temperature in a conformal layer-by-layer manner that is based on a pair of self-terminating and self-limiting gas-surface half-reactions, in which at least one half-reaction involves species from a plasma. This approach generally offers the benefit of substantially reduced growth temperatures and greater flexibility in tailoring the gas phase chemistry to produce varying film characteristics. The flexibility and lower growth temperatures that plasmas provide come at the cost of a complex array of process variables that often require great care on the part of the user.In response to this challenge, this work focuses on the use of plasma diagnostics to inform the choice of process conditions for PEALE systems. In this work we employ VUV-NIR spectroscopy and charged particle collectors to characterize the inductively coupled plasma source of a Fiji 200 (Ultratech/CNT) ALD tool. In particular, we assess the total ion flux reaching the substrate surface and the relative fractions of atomic and molecular species generated in the plasma under a variety of pressures and gas input flow fractions in context of PEALE of AlN, InN, TiO_2 and Ga_2O_3 films. Changes in plasma parameters are then linked with changes in film characteristics.________________________________* This work supported by the Naval Research Laboratory Base Program

Electronic Materials and Photonics Division
Room 101A - Session EM+AM+NS+PS-MoA

Atomic Layer Processing: Selective-Area Patterning (Assembly/Deposition/Etching)

Moderators: Michael Filler, Georgia Institute of Technology, Jessica Hilton, RHK Technology

1:20pm **EM+AM+NS+PS-MoA-1 Area-Selective Deposition of Crystalline Perovskites***, E Lin, **Brennan Coffey**, Z Zhang, P Chen, B Edmondson, J Ekerdt,* University of Texas at Austin

Epitaxial growth of crystalline perovskites enables opportunities in integrating perovskite properties into electronic and photonic devices. Pattern definition is a necessary step in many device applications and definition through etching can be problematic with titanium-based perovskites. We report a process to grow the perovskite film into the final patterned-dimensions through area-selective atomic layer deposition (ALD) followed by epitaxial regrowth from a crystalline substrate to form a single crystal perovskite film. Epitaxial barium titanate (BTO) films can be grown by ALD on strontium titanate (STO(001)) and STO(001)/Si(001) substrates. The substrates are coated with 40 nm of polystyrene (PS) and 185- and 264-nm UV light projected through a shadow mask is used to crosslink the PS under a N_2 atmosphere. The unexposed PS is stripped using toluene to expose the STO surface. Amorphous BTO films are deposited by ALD at 225 °C on the PS-patterned STO(001) surfaces. The low temperature process prevents the degradation of the PS layer. The PS mask is subsequently removed with an oxygen plasma exposure step. Atomic force microscopy and scanning electron microscopy after BTO growth and crosslinked-PS removal demonstrate high fidelity pattern transfer in the BTO films. Reflective high-energy electron diffraction and x-ray diffraction show that the film crystallizes after annealing the sample in vacuum at ≥ 750 °C, with oxygen partial pressure of 1×10^{-6} Torr. Film orientation as a function of annealing temperature is established with transmission electron and piezoresponse force microscopy.

1:40pm **EM+AM+NS+PS-MoA-2 A Dry NF_3/NH_3 Plasma Clean for Removing Si Native Oxide and Leaving a Smooth Si Surface***, **Christopher Ahles**, J Choi,* University of California, San Diego*; A Kummel,* University of California at San Diego

As devices are scaled to sub 5nm, it is critical to prepare clean and atomically flat surfaces. The traditional aqueous HF clean for removal of native Si oxide suffers from an inevitable air exposure resulting in re-oxidation of the Si surface as well as carbon contamination. The Siconi™ process is a dry clean which utilizes a low temperature (<30C) NF_3/NH_3 based plasma to selectively etch the native oxide layer on Si without etching the underlying Si layer. However the Siconi™ process leaves behind a $(NH_4)_2SiF_6$ salt which must be removed in a subsequent anneal. In this work we present a dry clean which eliminates $(NH_4)_2SiF_6$ salt formation and provides a surface which is just as flat as with the traditional aqueous HF clean.

The silicon surface following removal of the native oxide with an NF_3/NH_3 plasma was studied using X-Ray Photoelectron Spectroscopy (XPS) for elemental analysis as well as Atomic Force Microscopy (AFM) for surface roughness measurements. It was found that when the silicon substrate is held at 65-70C during the etching no $(NH_4)_2SiF_6$ salt formation is observed. The $NF_3:NH_3$ ratio was found to be a critical parameter for controlling the surface roughness, with the surface roughness decreasing with decreasing $NF_3:NH_3$ ratios. A $NF_3:NH_3$ ratio of 1:5 gave a Si surface with an RMS roughness of 3.4nm while a $NF_3:NH_3$ ratio of 1:10 gave a Si surface with an RMS roughness of 1.9nm. Further decreasing the $NF_3:NH_3$ ratio is expected to provide an even smoother surface, and experiments towards this end are ongoing. The plasma time was also optimized, and it was found that exposure to the NF_3/NH_3 plasma for 10 seconds and 1 minute resulted in essentially no removal of the native oxide, while exposure for 2 minutes resulted in complete removal of the native oxide. For comparison, Si surfaces cleaned with aqueous HF in our laboratory typically have ~10% oxygen and ~10% carbon contamination, while after cleaning with a NF_3/NH_3 plasma with $NF_3:NH_3 = 1:10$ for 2 minutes at 70C there was 3% O, 0% C, 4% F and 4% N impurities. Additionally, all of the silicon was in an oxidation state of 0 which means that there was no $(NH_4)_2SiF_6$ salt formation since this salt has silicon in an oxidation state of +4. To validate the applicability of this process, a molybdenum silicide film was deposited via atomic layer deposition (ALD) on dry-cleaned Si as well as on HF cleaned Si. The RMS roughness of the ALD $MoSi_x$ film on the dry-cleaned Si was 2.26nm while on the HF cleaned Si the RMS roughness was 2.78nm. This shows that the dry clean developed in this study is capable of producing cleaner and smoother Si surfaces than the traditional aqueous HF clean.

2:00pm **EM+AM+NS+PS-MoA-3 Probing Strategies for Selective Deposition that Exploit Competitive Interactions***, **James Engstrom**,* Cornell University **INVITED**

Selective thin film processes, including atomic layer deposition, have the potential to enable next-generation manufacturing and patterning at the 5 nm node and beyond, with direct applications in the nanofabrication of functional layers such as gate dielectrics, metal contacts, and capping/barrier layers. Well-known for its ability to deposit atomically thin films with Å-scale precision along the growth direction and conformally over complex 3D substrates, atomic layer deposition (ALD) has emerged as a key nanomanufacturing process. In this regard, the range and scope of ALD-based applications and capabilities can be substantially extended by also controlling the in-plane growth—a timely and significant development that can be realized *via* area-selective deposition processes that depend on the chemical composition of the underlying surface. In this presentation we will review the approaches that have been taken to achieve area-selective ALD, and we shall highlight both the strengths and shortcomings of these approaches. We will also discuss our efforts to achieve selective deposition that exploit competitive interactions—these interactions can occur both on the surface(s) where the film is, or is not, being deposited, and in the gas phase. In our approach we couple well controlled experiments that involve *in situ* surface analysis using techniques such as X-ray photoelectron spectroscopy and high level quantum chemistry calculations of specific and non-specific binding of molecules to target surfaces. We find that this combination of techniques is capable of shedding considerable light on deposition processes that are both potentially fast and leave no trace of their use in guiding thin film deposition to those areas where growth is desired.

2:40pm **EM+AM+NS+PS-MoA-5 The Interconnect Resistivity Bottleneck***, **Daniel Gall**, T Zhou, E Milosevic,* Rensselaer Polytechnic Institute*; P Zheng,* Micron Technology

The effective resistivity of conventional Cu interconnect lines increases by more than two orders of magnitude as their width is decreased from 30 to 6 nm. The resulting increase in signal delay and energy consumption limits downscaling of integrated circuits. This presentation will discuss the search for the most conductive metal solutions for narrow interconnect lines, focusing on three key aspects. (i) Electron surface scattering: In situ transport measurements on epitaxial Cu(001) layers with various monolayer cap-layers demonstrate specular electron surface scattering when the local surface density of states at the Fermi level is negligible, resulting in a considerable copper resistivity reduction. (ii) Alternative metals: The resistivity scaling at reduced dimensions is measured using epitaxial metal layers (Cu, Ag, W, Ta, Ru, Mo, Ni) and directly compared to results from classical transport models using first-principles electronic structure calculations. Multiple elemental metals are expected to be more conductive than Cu for polycrystalline lines <10 nm. (iii) Confined transport model: First-principles non-equilibrium transport simulations in combination with measurements of the resistivity vs roughness and dimensionality are used to develop a new model that accurately accounts for electron surface scattering in quantum-confined 1-D and 2-D conductors. This model will replace semiclassical models that fail to predict the resistivity <10 nm.

3:00pm **EM+AM+NS+PS-MoA-6 Sub 0.3 micrometer Copper Patterns Etched with a Plasma-Based Process and Pattern Dependent Electromigration Failure Mechanism***, **Yue Kuo**,* Texas A&M University

Copper (Cu) is a popular interconnect material for high density ICs, large area TFT LCDs, and many advanced electronic and optical devices. Since Cu does not form volatile products under the conventional plasma etching condition, the only available method in preparing fine lines is the chemical mechanical polishing (CMP), i.e., the single or dual damascene, method. The author's group has invented a new plasm-based Cu etching method that has a high rate at room temperature (1). This method has been successfully demonstrated in defining submicron lines for IC chips as well as being used in the large area TFT LCDs (2). However, this are few papers on defining the sub 0.5 micrometer Cu line using this new etch method. The lifetime of the plasma-etch Cu line on the flat and stepped surfaces has been studied with the electromigration method (3,4). However, the pattern size effect is rarely discussed.

In this talk, the author will discuss the process that can be used to prepare sub 0.3 micron dimension Cu patterns. The success of this process is due to the simultaneous Cu conversion reaction and sidewall passivation. In addition, the failure mechanism of the plasma-etched Cu line over a large range of line widths, i.e., from 1.5 to 30 micrometers, will be examined based on the electromigration test result. In summary, Cu lines prepared from the plasma-based process can be reliably applied in the many nano electronic and photonic products.

1. Y. Kuo and S. Lee, *Jpn. J. Appl. Phys.***39**(3AB), L188-L190 (2000).

2. Y. Kuo, *Proc. 16th Intl. Workshop on Active-Matrix Flat Panel Displays and Devices*, 211-214 (2009).

3. G. Liu and Y. Kuo, J. Electrochem. Soc., 156(6) H579-H584 (2009).

4. C.-C. Lin and Y. Kuo, *J. Vac. Sci. Technol. B*, 30(2), 021204-1 (2012).

3:40pm **EM+AM+NS+PS-MoA-8 The Effect of Metal Diffusion on Contacts to Semiconducting Chalcogenides: Examples for 2D and 3D Materials***,* ***Suzanne E. Mohney****, K Cooley, M Abraham, A Domask, H Simchi, L Kerstetter, C Lawrence, T Walter,* The Pennsylvania State University**INVITED**

We review our recent studies of contacts to a variety of chalcogenide semiconductors, including few-layered molybdenum disulfide and tungsten diselenide, as well as the phase-change material germanium telluride. In some cases, diffusion of a transition metal into the semiconductor has been correlated with an especially low contact resistance. For example, annealing silver contacts on field effect transistors fabricated from few-layered molybdenum disulfide resulted in a reduction in contact resistance by a factor of 4–5 to 0.2–0.7 kOhm-µm, while the ON/OFF current of the device remained high. Diffusion of silver into molybdenum disulfide was confirmed by secondary ion mass spectrometry. On the other hand, nickel appears to be even more soluble in molybdenum disulfide (as observed by Auger electron spectroscopy), but annealing nickel contacts resulted in an increase in resistance. For the phase-change material germanium telluride, incorporation of iron seems to play a role in achieving a low contact resistance of 0.004 Ohm-mm in annealed Au/Fe/Sn/*p*-GeTe contacts. Diffusion of iron into germanium telluride at a low but detectable level was found beneath a narrow-gap tin telluride interfacial reaction product using energy dispersive spectroscopy in the scanning transmission electron microscope. Using only iron or tin without the other did not result in such a low contact resistance. The influence of iron on the electronic properties of germanium telluride is now under study. Besides diffusion of metals into the semiconductor, we also present cases of reactive contacts to germanium telluride, whereby the contact resistance is greatly increased by interfacial reactions that led to the formation of a new phase (especially nickel tellurides and platinum tellurides). Finally, we consider the influence of surface diffusion on quasi van der Waals epitaxy of metals on layered transition metal dichalcogenides.

4:20pm **EM+AM+NS+PS-MoA-10 TiN_x and TaN_x Films via Low-T Thermal ALD using Anhydrous N_2H_4***,* ***Steven Wolf****, M Breeden, M Kavrik,* University of California at San Diego*; D Alvarez, J Spiegelman,* RASIRC*; M Naik,* Applied Materials*; A Kummel,* University of California at San Diego

For device back end of line processing, there is a need to deposit conformal barrier layers on high aspect ratio 3D architectures via low-T ALD. Titanium nitride (TiN) and tantalum nitride (TaN) have been studied as diffusion barriers to WF_6 during W metal fill and to Cu, as Cu can readily diffuse, causing device reliability issues. Organometallic-grown films are required when Cu is present to prevent etching, however, metal halide precursors are preferred for gate stack applications as films typically contain lower levels of carbon and oxygen contamination; this has been correlated with improved film conductivity. This work aims to deposit thermal ALD titanium nitride and tantalum nitride utilizing anhydrous N_2H_4 at lower temperatures than previously reported with NH_3 while still maintaining good film properties.

In this study, low temperature thermal ALD TiN_x from anhydrous N_2H_4 vs. NH_3 and $TiCl_4$ was performed on degreased and UHV annealed SiO_2/Si substrates at temperatures of 300°C and 400°C. The deposited films were studied using x-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). TaN_x films were grown at 150°C utilizing N_2H_4 and tris(diethylamido) (*tert*butylimido)tantalum (TBTDET) and characterized similarly. In addition, the resistance of air-exposed ultra-thin films was measured using a 4-point probe technique. Resistivities were estimated from thicknesses obtained from cross-sectional scanning electron microscopy (SEM) images. First, saturation dosing was performed to determine optimal half-cycle pulses of $TiCl_4$ and N_2H_4. After TiN_x ALD cycles, AFM imaging showed uniform deposition with sub-nanometer RMS surface roughness. The corrected and normalized XPS showed near stoichiometric Ti_3N_4 with low O and C and ~10% Cl. There was approximately 2x more O and C and 50% more Cl in NH_3 grown films at 400ºC. N_2H_4 films exhibited lower resistivities (359 vs. 555 µohm-cm), attributed to this lower contamination and likely better nucleation density. For TaN_x films, XPS of 15 cycles ALD TaN_x films resulted in 9% O and 4% C and had a Ta/N ratio of 4/5. Analysis on the Ta 4d peaks confirmed nucleation after the initial exposure of TBTDET (Si-O-Ta formation) based on the Ta 4d 5/2 peak BE of ~231.5 eV. A chemical shift to 229 eV was observed upon forming Ta-N bonds. Resistance measurements indicated insulating films consistent with the formation of Ta_3N_5. In summary, N_2H_4 grown TiN_x films showed lower resistivities with fewer impurities. The anhydrous N_2H_4 chemistry was extended to an organometallic Ta precursor, in which nearly stoichiometric films were deposited with low contamination at a modest substrate temperature of 150ºC.

Plasma Science and Technology Division
Room 104A - Session PS+PB-MoA

Plasma and Polymers: 'The Legacy of Riccardo d'Agostino and Beyond'

Moderators: Ankur Agarwal, KLA-Tencor, Mohan Sankaran, Case Western Reserve University

1:20pm **PS+PB-MoA-1 Foreword/introduction to the session: "Reflections on the Legacy of Riccardo d'Agostino"***, P Favia,* University of Barii, Italy

In this contribution I will review the career of Prof. d'Agostino and reflect on his scientific achievements, his extensive network in the field of plasma chemistry, plasma processing of materials and applications, and his role as mentor for several generations of M.Sc. students as well as PhD and postdocs.

1:40pm **PS+PB-MoA-2 Atmospheric Pressure PE-CVD of Drug-containing Nanometric Capsules***,* ***Pietro Favia****, C Lo Porto, A Treglia,* University of Bari, Italy*; F Palumbo,* CNR Institute of Nanotechnology NANOTEC, Italy

Plasma Enhanced Chemical Vapor Deposition Processes have been investigated by Riccardo d'Agostino and co-workers, and by many of his colleagues, in the late 80s and early 90s, mainly at low pressure, resulting in a large number of publications on the deposition kinetics and on the applications of coatings of different composition and properties. Many other PE-CVD approaches have been developed since then, and the deposition processes have been or are going to be deeply investigated, following the legacy of Riccardo d'Agostino in this field.

In this talk we present a set of data on the direct PE-CVD of nanometric capsules in the plasma phase resulting from Aerosol Assisted (AA) Atmospheric Pressure (AP) PE-CVD processes fed with Helium (carrier), Ethylene (film precursor) and aerosol droplets of solutions of drugs (nancomicyn, gentamicyn, etc). This approach [1, 2, 3] can lead, in certain conditions, to the deposition of thin coatings directly on the droplets of the aerosol, thus leading to the synthesis of drug-containing nanometric capsules, of potential interest for biomedical applications, e.g., as anti-bacterial surfaces [4].

The influence of various plasma parameters on the AA-AP-PE-CVD processes is discussed, as well as some properties of the coatings.

acknowledgements

The mentorship of Prof. d'Agostino is acknowledged by the authors of this contribution, as well as the recognition of his legacy in the field of plasma processing of materials.

references

1. A. Heyse et al, Plasma Proc. Polym. 8, 965 (2011)

2. Palumbo et al, Plasma Proc. Polym. 12, 1302 (2015)

3. Lo Porto et al, Polym. Chem. 8, 1746 (2017)

4. Sardella et al, *Materials* 2017, 9, 515

2:00pm **PS+PB-MoA-3 Ultrathin Metal-Organic Covalent Networks by initiated Plasma Enhanced Chemical Vapor Deposition (iPECVD) for Gas Separation Membranes***,* ***Karen Gleason****, M Wang,* MIT*; N Boscher,* Luxembourg Institute of Science and Technology (LIST), Luxembourg*; M Creatore, A Perrotta,* Eindhoven University of Technology, The Netherlands, Netherlands*; K Heinze,* Johannes Gutenberg-Universität, Mainz, Germany

Metal-Organic Covalent Networks (MOCN) were synthesized as ultrathin (<100 nm), defect-free and mechanically flexible layers by initiated Plasma

Enhanced Chemical Vapor Deposition (iPECVD). The low substrate temperature used for iCVD allowed use of thermal sensitive porous poly[1-trimethylsilyl)-1-propene] (PTMSP) as a substrate. Uniform layers were grown over 150 nm diameter substrates and did not delaminate upon mechanical deformation. The resulting robust MOCN/PTMSP composite membranes exhibiting outstanding gas separation performance for multiple pairs of gases. Using zinc (II) meso-tetraphenyl porphphyrin (ZnTPP) as the monomer and tert-butyl peroxide as the initiator, film deposition was achieved at low plasma excitation powers. The nearly unchanged intensity of the Soret bands in the UV-vis spectra confirmed the retention of the 18 pi e- conjugation of the monomer units incorporated into the films. The gas selectivity for the separation of H_2/CH_4 or H_2/N_2 is small (<3) for either the PTMSP base membrane or for thin films of evaporated ZnTPP. However, the gas selectivity for both H_2/CH_4 or H_2/N_2 rises to >500 for the PTMSP/iPECVD ZnTPP composite membrane, exceeding the performance of commercial membranes. Ellipsometric Porosimetry and Density Functional Theory Calculations are consistent with a pore size of ~0.4 nm in the MOCN film. Additionally, iPECVD layers derived from a metal-free porphyrin and from porphyrins containing magnanese (III) and cobalt (III) will be described.

2:20pm **PS+PB-MoA-4 Influence of Energetic Conditions on the Plasma Polymerization of Cyclopropylamine in Capacitively Coupled Discharges***, **Lenka Zajickova**, M Michlicek,* Masaryk University, Czech Republic*; S Hamaguchi,* Osaka University, Japan

Thin films prepared by plasma polymerization of cyclopropylamine (CPA) in capacitively coupled discharges demonstrated their attractive functional properties as a matrix layer in immunosensors or surface modification of synthetic polymers used for a cell cultivation. These bioapplications required tuning the concentration of amine and other bio-active groups together with the film stability in aqueous media. Since the final plasma polymer composition is influenced by the discharge power and the polymer cross-linking can be modified by ion energy flux towards the growing film the investigation of bulk plasma and plasma-surface interactions with respect to the energetic conditions are necessary for fundamental understanding of the overall process. This work puts together the results on the plasma polymer properties with the plasma diagnostics by mass and ion spectrometry, optical emission spectroscopy and retarding field energy analyzer placed at the substrate position. The experiments are complemented by the molecular dynamic simulations of the film growth.

2:40pm **PS+PB-MoA-5 Electrochromic Investigation of PEDOT Film Deposited by Plasma Radicals Assisted Polymerization *via* CVD***, **Bianca Rita Pistillo**, G Lamblin, J Polesel-Maris, K Menguelti, D Arl, D Lenoble,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

Quite recently conducting polymer have been introduced into a broad range of organic electronic devices in place of analogous inorganic semiconductors, owing to their numerous merits as flexibility, low cost and lightweight over their forerunners. Similarly to inorganic material, also conducting polymer display electrochromism. The oxidation or reduction of these films is usually associated with reversible ion insertion and extraction across an electrochromic material/electrolyte interface with complementary electron transfer across the electrochromic material/electrode interface. In the last years, the study and implementation of organic electrochromic materials (OEM) into devices had a tremendous growth also because of their relatively narrow absorption band in displaying diverse and clear colour. [T.T. Steckler et al. J. Am. Chem. Soc. 2014, 136, 1190] There are many interesting applications of OEM such as smart windows, flexible displays, electrochromic fibres, etc. One of the most attractive ones is Poly(3,4-ethylenedioxythiophene) (PEDOT) with its derivatives. PEDOT changes its colour from dark blue/purple, in its reduced state, to light blue, in the oxidised state with very low applied switching potential. Plasma Radicals Assisted Polymerization via Chemical Vapour Deposition (PRAP-CVD) has been developed at Luxembourg Institute of Science and Technology as an efficient alternative to conventional vapour-based processes of conductive thin films as PEDOT. [D. Lenoble, Controlled radical assisited polymerization, Lux. 91934, 2013] This process is based on the concomitant but physically separated injection of low-energy oxidative radical initiators and vaporized monomer species into a reactor where temperature and pressure are finely controlled. [B.R.Pistillo et al. J. Mater. Chem. C 2016, 4, 5617] A few advantages of making the process completely dry include the possibility of processing solvent-sensitive substrates such as paper, overcoming the effects of rinsing on the underlying films in the case of multilayer structures. Moreover, PRAP-CVD allows the deposition of highly conformal coatings, which accurately follows the geometry of the underlying substrate independently from its nature, enlarging the application of PEDOT as OEM. In this work, we present the investigation of electrochromic properties of PRAP-CVD PEDOT films. The behaviour of films was compared with the data in the literature revealing a faster switching time compared to other vapour-based processes reported. The range of switching potential with limited electrochemical degradation of the thin electrochromic film was also investigated by the means of UV-visible spectroelectrochemistry.

3:00pm **PS+PB-MoA-6 Initial ZnO Crystallite Formation by Plasma Enhanced ALD***, **Alberto Perrotta**, J Pilz, A Coclite,* Graz University of Technology, Austria

ZnO is a wide direct bandgap semiconductor, extensively studied as thin film because of its unique optical, electrical, and piezoelectric properties. Its crystalline structure and degree of crystallinity have a crucial impact on the material characteristics and a particular crystallographic texture may be beneficial for gaining optimized piezoelectric properties or enhanced velocities in surface acoustic wave devices. Therefore, the possibility to control the preferred crystallographic orientation in ZnO thin films has been often investigated.

Atomic layer deposition (ALD) offers the possibility to study in detail the growth of ZnO, due to its layer-by-layer nature and sub-nm thickness control. The initial growth of ZnO adopting diethylzinc (DEZ) and water and its impact on the crystallographic texture of the resulting thin films shed light on the growth mechanisms and the influence of the substrate nature on the in-plane and out-of-plane crystal orientations.

However, thin films deposited with plasma enhanced ALD are known to show several differences when compared to thermal ALD. Therefore, for ZnO thin films the growth mechanism and initial crystallite formation may be greatly influenced by the use of plasma. In this contribution, the initial growth of direct plasma ALD ZnO grown on Si (100) is investigated. DEZ and pure oxygen plasma are adopted during the process. The first 20 cycles of growth are analysed using synchrotron light grazing incidence X-ray diffraction (GIXD), X-ray reflectivity (XRR), and spectroscopic ellipsometry (SE). The influence of substrate temperature ranging from 25 °C to 250 °C on the crystal growth and crystal orientation are studied. A closed layer was obtained within 7 cycles as measured by XRR for all the temperature explored, suggesting island growth of the ZnO. However, GIXD showed no crystalline texture forming at this stage. An amorphous intermixed interface between the native SiO_2 and the growing layer was found, with a density in between pure SiO_2 and ZnO. Irrespective of the deposition temperature, the first crystal structure was measured at around 3 nm, with a preferential out-of-plane orientation transiting from (100) at room temperature to (002) at 250 °C. The first crystallographic seeds were found to largely determine the final microstructure of thicker films.

3:40pm **PS+PB-MoA-8 On Fluorocarbons and Fish: Creating a Global Impact on Generations of Plasma Chemists***, **Ellen Fisher**,* Colorado State University

Plasma processing represents a powerful approach to modification of a range of substrates with an array of chemistries and morphologies. One of the most useful plasma processing tools is that of plasma polymerization for thin film formation. Arguably, the work of Riccardo d'Agostino and his coworkers over numerous decades, especially in the arena of fluorocarbon film deposition, has significantly enhanced our understanding of plasma polymerization and influenced countless additional studies around the globe. Here, we will detail how d'Agostino's work based in Bari, Italy inspired a range of studies of various fluorocarbon systems that have been performed over more than 2 decades in one laboratory nearly 6000 miles away. Despite the foundational data provided by d'Agostino's early examination of plasma polymerization processes, the remaining paucity of data regarding the fundamental, molecular-level mechanisms that drive fluorocarbon and hydrocarbon plasma polymerization begged further examination. Combining a range of spectroscopy techniques, materials characterization tools, and plasma-surface interface studies has yielded another generation (or two) of insight. This presentation will focus on film deposition studies utilizing multidimensional substrates (e.g. membranes, scaffolds, nanomaterials), and the connections between d'Agostino's pioneering plasma polymerization work and our more recent studies relevant to a range of value added products, including blood-contacting devices, sensors, tissue engineering, and separation technologies.

4:00pm **PS+PB-MoA-9 DIRECT and Remote Surface Functionalization using Atmospheric Pressure Dielectric Barrier Discharges***, **Francesco Fracassi,*** University of Bari, Institute of Nanotechnology (NANOTEC), NRC, Italy, Italia*; F Fanelli,* Institute of Nanotechnology (NANOTEC), NRC, Italy, Italia*; V Armenise, A Uricchio, R d'Agostino,* University of Bari, Italy, Italia

The utilization of atmospheric pressure dielectric barrier discharges (DBDs) for the surface modification of materials is a very interesting and actual topic. In recent years, efforts have been directed toward the development of a large variety of processes which exploit different DBD configurations and electrode geometries. This contribution describes DBD-based deposition and treatment processes which are potentially of interest also for environmental applications. The processes are performed on polyurethane (PU) foams, i.e., three-dimensional porous substrates which can be quite uniformly surface functionalized by DBDs, since, under suitable experimental conditions, the discharge ignites both outside the foam and throughout its entire porous structure. Three experimental strategies are utilized: i) direct treatment and deposition in parallel plate DBD; ii) direct aerosol-assisted deposition in parallel plate DBD; iii) remote deposition of thin films containing carboxylic acid groups with DBD jet.

The direct treatment is performed by feeding the DBD with He-O_2 mixtures in order to form carboxyl groups on the polyurethane surface. The treated foams are able to adsorb heavy metals from water solutions and can be regenerated (release of adsorbed heavy metals) through immersion in concentrated sodium chloride solution. However, the treated foams suffer ageing in water and, therefore, at the second reuse the amount of adsorbed metals decreases. A water-stable surface containing carboxyl groups is obtained with the DBD jet fed with helium-acrylic acid-ethylene mixtures (remote thin film deposition). No morphological and chemical modifications of the deposits are detected also after 72 h of immersion in water.

When the parallel plate DBD is fed with He-C_3F_6 mixtures, the deposition of fluoropolymer thin films occurs on both the exterior and interior of the foam. The treated foams are superhydrophobic and oleophilic, simultaneously, with potential application for the separation of oil from polluted water, since they selectively adsorb oil, while repelling water.

The direct aerosol-assisted deposition in parallel plate DBD is utilized to prepare hybrid organic-inorganic nanocomposite coatings composed of a hydrocarbon polymer and ZnO or TiO_2 nanoparticles. Under appropriate deposition conditions, it is possible to obtain multifunctional coating characterized by superhydrophobicity, superoleophilicity as well as by the peculiar photocatalytic properties of the utilized nanoparticles. The application of the treated foams for oil-water separation and for the photocatalytic degradation of organic pollutants in water is currently under investigation.

4:20pm **PS+PB-MoA-10 Quest for Durable Low-index Optical Coatings: From Plasma Polymerized Fluorocarbons to Hybrid Organic-inorganic and Nanostructured Films***, L Martinu, **Jolanta Klemberg-Sapieha,** O Zabeida,* Ecole Polytechnique de Montreal, Canada

Low (n less than about 1.55@550nm) and ultra-low refractive index materials (n less than 1.38@550nm) are of particular interest in the context of enhanced optical performance of interference filters (IF, including anti-reflective coatings). In addition, for many years now, there has been a lot of effort to develop such low and ultra-low index films with multifunctional characteristics making them suitable for the applications of IF on plastic and flexible substrates. This includes a necessity to better understand and optimize the thermo-mechanical properties (hardness, Young's modulus, adhesion, thermal expansion coefficient), surface energy (hydrophobicity), and possibly provide complementary functionalities (color, electrical conductivity, etc.). This presentation provides an overview of the progress in the field outlined above, starting with the work performed jointly with Professor Riccardo d'Agostino. In the first part, we describe the main optical, mechanical and dielectric characteristics of plasma polymerized fluorocarbons and related metal-doped plasma polymers. In the second part, we introduce hybrid organic-inorganic (SiOCH) materials that are shown to combine high mechanical resistance of ceramics with high elasticity of polymers. We demonstrate, that the refractive index of such films can vary from 1.50 to 1.53, while the extinction coefficient is kept below 10-4. At the same time, the hardness-to-Young's modulus ratio, H/E, is substantially increased (to 0.16) compared to 0.08 for pure SiO2), a result that is well correlated with the increased resistance to crack formation and propagation. Such layers, incorporated in multilayer structures on plastic substrates, provide significantly enhanced optical and mechanical stability in environments involving large temperature and humidity excursions. In the third part, we explore the characteristics of a new category of hybrid SiOCH thin films prepared by glancing angle deposition (GLAD) using electron beam evaporation of SiO2, in the presence of an organo-silicone precursor. The resulting layers are shown to exhibit n as low as 1.2, high elastic rebound and high hydrophobicity, and better mechanical properties than their inorganic counterparts. Their performance is discussed in terms of their anisotropy assessed by the nanostructure-based spectroscopic ellipsometry model. Finally, we demonstrate successful implementation of the ultra-low index material in a complete IF stack.

Thin Films Division
Room 102A - Session TF+EM+MI+PS-MoA
Thin Films for Advanced Memory Applications and Magnetics

Moderator: Robert Grubbs, Sandia National Laboratories

1:40pm **TF+EM+MI+PS-MoA-2 ---Multiferroic Integration of Undoped Ferroelectric HfO_2 and Ferrimagnetic $CoFe_2O_4$ Thin films by Radical-Enhanced Atomic Layer Deposition***, J Chang, **Adrian Acosta,** J Chang,* University of California at Los Angeles

Multiferroic materials that exhibit the coexistence and coupling between ferroelectricity and magnetism are of great interest due to their potential for enabling next-generation memories. To overcome the scarcity and weak response of intrinsic multiferroics, composite strategies were proposed to realize robust multiferroic behavior by coupling the properties from constituent ferroelectric and magnetic phases. However, additional challenges for an applicable multiferroic composite are present in the ferroelectric phase since conventional perovskite-based ferroelectrics lack the necessary electrical stability and silicon-compatibility for device integration.

Orthorhombic ferroelectric HfO_2 (FE-HfO_2) based thin films have emerged in the field of microelectronics research owing to its superior compatibility with CMOS technology as well as desirable electrical properties. In this work, multiferroic integration of undoped FE-HfO_2 thin films and ferrimagnetic $CoFe_2O_4$ (CFO) on Si substrates via radical-enhanced atomic layer deposition (RE-ALD) are first demonstrated. For the RE-ALD process, atomic oxygen was utilized in conjunction with TDMAHf and TMHD-based metalorganic precursors for the growth of HfO_2 and CFO respectively. In the composite design, CFO acts as a mechanical constraint to stabilize FE-HfO_2 as well as an active magnetic layer.

Composite ferroelectricity was studied as a function of FE-HfO_2 film thickness as well as post-deposition annealing temperatures. Film crystallinity was investigated through the use of a synchrotron beam source to understand the structural evolution. The induced ferroelectricity was observed to correlate with HfO_2 orthorhombic phase and was maximized when HfO_2 is ~6 nm and after annealing at ~700-800 °C. CFO/FE-HfO_2 composites showed ferroelectric behavior with remnant polarization ~5.5 $\mu C/cm^2$ and electrical coercivity ~340-2000 kV/cm, with the potential to be further enhanced via the inclusion of dopants. Comparable magnetism was observed with out-of-plane anisotropy, a saturation magnetization of ~155 emu/cm^3, and a magnetic coercivity ranging from ~1000-3400 Oe. Piezoresponse force microscopy (PFM) verified the strain interaction in the CFO/FE-HfO_2 design. Lastly, a magnetoelectric coupling coefficient of ~5.5×10^{-8} s/m (~55 Oe cm/kV) was obtained from the multiferroic structure with 6-nm thick HfO_2 layer via an *ex situ* poling SQUID magnetometer setup. This work not only highlights the potential of FE-HfO_2 based multiferroic composites in realizing magnetoelectric spintronic devices but also unveils the possibility of utilizing alternative capping layers for achieving multifunctional composite heterostructures.

2:00pm **TF+EM+MI+PS-MoA-3 Growth and Characterization of BeO Thin Films Grown by Atomic Layer Deposition using H_2O and O_3 as Oxygen Sources***, **Lee Woo Chul**, C Cheol Jin,* Center for Electronic Materials, Korea Institute of Science and Technology, Korea*; K Sangtae,* Center for Electronic Materials, Korea Institute of Science and Technology, Korea*; L Eric S., Y Jung Hwan,* Center for Multidimensional Carbon Materials (CMCM), Institute for Basic Science (IBS), South Korea*; H Cheol Seong,* Department of Materials Science and Engineering, and Inter-University Semiconductor Research Center, College of Engineering, Seoul National University, South Korea*; B Christopher W.,* Center for Multidimensional Carbon Materials (CMCM), Institute for Basic Science (IBS), South Korea*; K Seong Keun,* Center for Electronic Materials, Korea Institute of Science and Technology, Korea

BeO has a very large band gap (10.6 eV), which is even larger than that of representative large band gap materials; SiO_2 (~9 eV) and Al_2O_3 (~8 eV). BeO thin films reveal high quality of the interface with Si and semiconductors, showing a possibility as a gate dielectric. Furthermore, rocksalt BeO was recently predicted to have a very high dielectric constant (~ 275) and a very large band gap (10.6 eV). However, the fascinating dielectric properties have not been experimentally realized yet because of the instabilty of the rocksalt BeO. Nowdays, atomic layer deposition (ALD) is a common technique for film growth in a semiconductor industry. The ALD process of the BeO thin films is necessary to be developed to implement BeO in the semicoductor industry. Herein, the growth characteristics and properties of BeO thin films grown by ALD are investigated. We demonstrated that ALD chemistries between dimethylberyllium (DMB) and two different oxygen sources, H_2O and O_3, are governed by different reaction mechanisms, resulting in different film properties.

BeO thin films were grown in a traveling-wave type reactor by ALD with DMB and different oxygen sources, such as H_2O and O_3, in the temperature range of 150 to 300 ^oC. Although H_2O-ALD and O_3-ALD of BeO all showed self-saturation behavior, the growth behavior and film properties are strongly dependant on the oxygen sources. With increasing growth temperatures, the growth per cycle (GPC) of H_2O-ALD of BeO decreases, while that of O_3-ALD of BeO is almost constant. The properties of the BeO films grown in H_2O-ALD are nearly temperature-independent, whereas the BeO films grown in O_3-ALD at low temperatures (< 200 ^oC) reveal high impurity concentrations and a low film density. These cause lowering of the band gap and dielectric constant of the BeO films grown by O_3-ALD at low temperatures. These findings demonstrate that the O_3-ALD process requires relatively more thermal energy than H_2O-ALD does, to produce high-quality BeO thin films.

2:20pm **TF+EM+MI+PS-MoA-4 Atomic Layer Deposition of Magnetic Films and Patterned Features with Tunable Magnetic Properties***, Z Zhang, **John Ekerdt**,* University of Texas at Austin

We report a process to generate carbon-free Co metal films and patterns by first growing films of CoO via atomic layer deposition on various hydroxylated surfaces and then reducing the CoO at low temperatures to Co metal. The CoO ALD process employs (bis(N-tert butyl, N'ethylpropionamidnato) cobalt (II) and water at 180 °C. Similar processes work for Fe and Ni growth. The metal oxides have a lower density than the metal and will spread uniformly over oxide substrates whereas ultra-thin metal films tend to dewet from the oxide and generate discontinuous films. This dewetting is a strong function of temperature and can be mitigated by lowering the temperature of the reduction process or by lowering the energy of the free surface. Temperatures in excess of 420 °C are required to achieve full reduction of 4.5-nm CoO in H_2 (or D_2); films reduced at this temperature are discontinuous. We report the use of atomic deuterium that is generated over a heated tungsten filament and show that we can fully reduce 4.5-nm CoO to Co at 220 °C without the metal film dewetting oxides such as SiO_2, MgO, ZrO_2, and Al_2O_3. Thermal history of the film is critical to tuning the magnetic properties. As ultra-thin films roughen by extended annealing at 200 °C the film coercivity can be manipulated from 90 to 500 Oe. Since the CoO ALD process is initiated on hydroxylated surfaces and can blocked by organic films, we pattern polystyrene using UV crosslinking through a shadow mask or a diblock co-polymer to generate features ranging from microns to tens of nanometers and deposit CoO on the hydroxylated surfaces that are opened in the polystyrene. This presentation will address the interface issues in achieving selective growth and in manipulating the magnetic properties of continuous Co films and shaped features.

2:40pm **TF+EM+MI+PS-MoA-5 Tuning of the Magnetic and Electronic Properties of Epitaxial Heusler Compound Heterostructures***, **Christopher Palmstrøm**,* University of California, Santa Barbara **INVITED**

Heusler compounds have received a lot of attention because of their large range of properties. Their properties depend on the number of valence electrons per formula unit and have been predicted to be semiconductors, metals, ferromagnets, antiferromagnets, half metals, superconductors and topological insulators. Similar to compound semiconductors, the band structure and lattice parameters of Heusler alloys can also be tuned through alloying but over a much larger range of properties. Magnetic tunnel junctions using Heusler alloys that are predicted to be half metals have shown record tunneling magnetoresistance. Heusler half metals have been predicted to have very low Gilbert damping coefficients. They can also be lattice matched to most compound semiconductors and have been used for spin injecting contacts. Recent theoretical predictions suggest that atomic level Heusler superlattices can result in half metallicity and perpendicular magnetization. This presentation will emphasize the molecular beam epitaxial growth combined with in-situ and ex-situ structural, electronic and magnetic characterization of Heusler heterostructures on III-V semiconductors and MgO single crystal substrates. Tuning of their magnetic and electronic properties through elemental substitution to change the number of valence electrons per formula unit and atomic level superlattice growth will be discussed. Examples of Heusler heterostructures and controlling of their magnetic and electronic properties include tuning of the spin polarization in $Co_2Mn_{1-x}Fe_xSi$, Heusler contacts for spin injection into GaAs, spin polarization and magnetic anisotropy of Co_2MnAl/Fe_2MnAl atomic scale superlattices, substitution with Fe in CoTiSb with the aim to convert a semiconductor to half metal and interfacial reactions at Co_2MnSi/MgO interfaces. By careful tuning of the half metallic Heusler film composition, Gilbert damping coefficients <0.001 have been observed.

3:40pm **TF+EM+MI+PS-MoA-8 Stabilization of Ferroelectric Phase of $Hf_{0.5}Zr_{0.5}O_2$on NbN at 4 K***, **Michael David Henry**, S Smith, R Lewis,* Sandia National Laboratories*; J Ihlefeld,* University of Virginia

This work demonstrates cryogenic ferroelectric behavior of atomic layer deposited (ALD) hafnium zirconium oxide (HZO) using reactively sputtered niobium nitride electrodes. With the discovery of ferroelectricity in doped HfO_2, perturbations of the dopants expanded from silicon into mixtures utilizing yttrium and zirconium and with electrodes ranging from platinum to nitrides such as titanium nitride and tantalum nitride. This set of materials have demonstrated stabilizing a crystalline phase permitting both ferroelectric and anti-ferroelectric behaviors to have been observed. With the atomic similarities between Ta and Nb, a natural extension the electrode materials' set to include NbN was explored in this work.

Devices tested at both room temperature (RT) and under cryogenic conditions demonstrated ferroelectric behavior as determined by polarization vs. electric field (P-E) loops. The polarization results show comparable ferroelectric behavior at room temperature and 4 K, however the effect of the dielectric polarization is combined with the remnant polarization (P_r) in this measurement. To separate the two effects, remnant polarization sweeps were performed and plotted only displaying the P_r. A typical measurement on a 170 mm diameter device, was performed starting at 4 K and ending at 150 K. By adding the positive and negative $P_r$with the electric field at 0 MV/cm ($2P_r$), polarization was observed to decrease as the stage was warmed up. A second known behavior of ferroelectrics is the so-called wake-up effect where the ferroelectric phase is understood to be stabilized by oxygen movement as a positive and negative voltage is applied. Here, a 3 V square wave at 1Hz was utilized in 60 second intervals with $P_r$loops performed before and after each wake-up cycling at room temperature. The $2P_r$was seen to come to steady state after approximately 100 seconds. Remnant polarization at the conclusion of 360 seconds is seen to have polarization approximately 10 mC/cm^2, a value comparable to other findings. Polarization values of approximately 10 mC/cm^{2}suggest that these ferroelectric films could be utilized with superconductors at liquid He temperatures for a new class of superconductor-ferroelectric based devices.

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4:00pm **TF+EM+MI+PS-MoA-9 Atomic Layer Deposition of Co/Pt Multilayer films for Perpendicular Magnetic Anisotropy***, **Devika Choudhury**, A Mane, C Phatak, A Petford Long, J Elam,* Argonne National Laboratory

"Smaller, Faster and Efficient" are the key words describing the ever increasing need of data-storage industry.[1] This demand has brought about a shift from longitudinal recording in magnetic media to perpendicular recording, where magnetic bits are perpendicular to the plane of the recording media instead of being in the same plane. Significantly higher storage density is obtained as a result of using the perpendicular magnetic recordings utilizing materials demonstrating perpendicular magnetic anisotropy (PMA). Strong PMA is usually observed in ultrathin films of ferromagnetic metals like Co and Fe forming alloys with heavy metals like Pt, Pd, Au and Ta.[2] Of them Co/Pt alloys and multilayer structures are probably the most widely investigated system for understanding the PMA origin and behavior.

The effective anisotropy energy of the multilayer films in the PMA regime depends on various factors like thickness of the individual Co/Pt layers, quality of interfaces and crystallinity of the films.[3] Till date, the commonly used techniques for growth of Co/Pt multilayers have been electron beam evaporation and sputtering. However, for development of higher areal density using three-dimensional media, conformal, uniform and controlled deposition of the thin films is certainly required.

In this work, we utilize atomic layer deposition (ALD) of Co/Pt multilayers to overcome limitations of the other growth processes. ALD provides precise control over the film thickness along with uniform and conformal films thus resulting in distinct sharp interfaces between the individual metal films. Bis(N-t-butyl-N'-ethylpropanimidamidato)cobalt(II) and hydrogen precursors are used for Co ALD while Trimethyl(methylcyclopentadienyl)platinum(IV) and water are used as precursors for Pt deposition. QCM studies confirm self-limiting ALD growth nature of the individual metal films at 300°C. Pt(10nm)/[(Co/Pt)x8](16nm)/Pt(2nm) stacks are grown using alternate cycles of Co and Pt. QCM measurements reveal a short nucleation regime of Pt over Co films. HRTEM imaging and XPS analysis of the multilayer stacks are utilized to study the interfaces of the multilayer films closely. Preliminary SQUID measurements show a change in anisotropy between pure Co and Co/Pt multilayer films. Effects of variation in individual layer thicknesses, deposition temperature, post-deposition annealing temperature etc. remains to be seen.

References:

[1] B. Tudu and A. Tiwari, *Vacuum*, 146, 329 (2017).

[2] V. M. Parakkat, K. R. Ganesh, and P. S. A. Kumara, *AIP Advances*, 6, 056118 (2016).

[3] B. F. Vermeulen, J. Wu, J. Swerts, and S. Couet et al. *Journal of Applied Physics*, 120, 1639031 (2016).

Plasma Science and Technology Division
Room 104A - Session PS+EM+SE-TuM
Plasma Processing of Challenging Materials - I

Moderators: Necmi Biyikli, University of Connecticut, Jun-Chieh Wang, Applied Materials

8:00am **PS+EM+SE-TuM-1 Development and Understanding of Isotropic Etching Process of Si Selectively to $Si_{0.7}Ge_{0.3}$,** ***Sana Rachidi**, A Campo, V Loup,* CEA-LETI, France*; N Posseme,* CEA, LETI, France, France*; J Hartmann, S Barnola,* CEA-LETI, France

The vertically stacked wires MOSFET architecture pushes further the scaling limits of the CMOS technology. Now deemed as a possible extension to FinFET, it offers multiple benefits. A low IOFF current is indeed expected, thanks to multi-gate electrostatic control, with a high current drivability due to 3D vertically stacked channels.

The fabrication starts with the epitaxial growth of ($Si_{0.7}Ge_{0.3}$/Si) multilayers (8-12 nm for Si and SiGe layers) on blanket SOI substrates. Then, individual and dense arrays of fins were patterned to fabricate stacked-NWs FETs with 40 nm-pitch fins which are 36 nm high and roughly 20 nm wide. After that, dummy gates and spacers are defined prior to the anisotropic etching of the (Si/SiGe) multilayers. Today one of the most critical step in such device realization is the isotropic silicon removal selectively to silicon germanium.

In this study an understanding of selectivity evolution between Si and SiGe as a function of CF4/O2/N2 remote plasma parameters is presented. The experiments performed on 300mm blanket wafers (Si and $Si_{0.7}Ge_{0.3}$) have been carried out on CDE-Allegro.

The impact of etching parameters (CF_4, O_2, N_2, microwave-power, pressure and temperature of the electrostatic chuck) and different pre-treatments on etching rates and selectivity is first investigated. X-ray photoelectron spectroscopy (XPS) analyses will show that for Silicon, a SiO_xF_y thick reactive layer is formed on the etched surface and controls its etching regime. As for $Si_{0.7}Ge_{0.3}$, a passivation layer of 2 nm is observed. And it contains a mixture of GeO_x and SiO_xF_y species.

Based on these results, application to patterned wafers will be shown. Scanning Electron Microscopy (SEM), Transmission electron microscopy (TEM) and Energy Dispersive X-ray Spectroscopy (EDX or EDS) are here used for the pattern characterisation.

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8:20am **PS+EM+SE-TuM-2 III-V/Ge Heterostructure Etching for Through Cell Via Contact Multijunction Solar Cell***,* ***Mathieu de Lafontaine**, G Gay, C Petit-Etienne, E Pargon,* LTM, Univ. Grenoble Alpes, CEA-LETI, France*; M Darnon, A Jaouad, M Volatier, S Fafard, V Aimez,* 3IT, Univ. de Sherbrooke, Canada

Through cell via contact architecture aims to increase the multijunction solar cell efficiency by 3% and the power yield per wafer by 20% by transferring the front side contact to the backside using insulated and metallized vias. Via hole plasma etching through the III-V/Ge heterostructure is a key step to fabricate this new architecture. It is challenging, as dozens of layers must be anisotropically etched with low roughness and free damage to ensure optimal cell performance. Moreover, etched patterns must have a depth of >30 µm and present >3 aspect ratio. In this abstract, several patterning strategies are presented to address these challenges.

The epiwafers consist of a 8µm-thick III-V heterostructure (InGaP, InGaAs, GaAs, AlInP, AlGaAs, AlGaInP layers and quantum dots) epitaxially grown on Ge substrate. A 5µm thick SiO_2 hard mask (HM) is first deposited by PECVD and patterned by contact photolithography and plasma etching. The optimization of both the lithography and HM opening steps is crucial for an optimal transfer into the III-V/Ge layers. It is observed that sloped and rough hard mask sidewalls after the HM opening step are detrimental to the via hole etching and lead to severe damage on the heterostructure sidewalls. Combining a thick photoresist mask with vertical sidewalls and an optimized $Ar/C_4F_8/O_2$ plasma process developed in a capacitive coupled plasma reactor allows to pattern the 5µm-thick HM with vertical and quite smooth sidewalls.

A room temperature $SiCl_4/Cl_2/H_2$ plasma process was developed in an inductively coupled plasma reactor to etch vias in the III-V/Ge heterostructures. The cell performance loss associated to via etching was almost absent, indicating that such chemistry is suitable for photovoltaic applications. However, some layers present isotropic etching, which is problematic for the via insulation and metallization. Indeed, III-V compounds with low indium concentration are more sensitive to lateral etching, thus creating preferential isotropic etching in several III-V layers. This represents a challenge considering the aspect ratio and the depth targets. Indeed, lateral etching will be even greater for a longer process time. To obtain anisotropic etching, a high temperature (200°C) $SiCl_4/Cl_2/H_2$ process is proposed. The enhanced volatility of the indium by-products combined with the Si-based passivation could improve the anisotropy while maintaining optimal cell performance. FIB-TEM and EDX are performed to characterize both the etch morphology and the passivation layer. Moreover, optoelectrical measurements will assess the cell performance after via etching.

8:40am **PS+EM+SE-TuM-3 Feature Scale Modeling of Etching of High Aspect Ratio Silicon Structures in Pulsed Plasmas***,* ***Wei Tian**, J Wang, S Sadighi, J Kenny, S Rauf,* Applied Materials

As critical dimensions shrink below 7 nm, etching of high aspect ratio (HAR) Si structures, such as those used for shallow trench isolation (STI), is becoming challenging. Some strategies to deal with these challenges include multi-step cyclic processes and pulsed plasmas. In this paper, we consider a cyclic pulsed plasma process for Si etch. Etching is done by cycling three steps: oxidation (OX), Si main etch (ME) and clean. The OX step passivates the Si sidewalls and protects them during Si ME. Si is mainly etched during the ME step, where the ion energy and angular distribution (IEAD) and ion / neutral flux ratio are controlled through power pulsing. The clean step removes the Cl/Br-containing passivation from the Si surface prior to re-oxidation. Pulsed plasmas have demonstrated several advantages compared to continuous wave (CW) plasmas and have become indispensable in etching of the next generation of microelectronic devices [1-2]. When source power and/or bias power are pulsed, a variety of pulsing modes are possible. Pulsing duty cycles and phase shift provide additional knobs for controlling the etching characteristics. In order to understand the effects of pulsing modes on etching properties, a feature scale model coupled to a plasma model is desired.

In this work, we investigate several pulsing modes during the Si ME step including separate pulsing of the plasma source or bias powers, and their synchronized pulsing. Plasma models for the 3 steps including the pulsed plasma step [3] are coupled to a 3D Monte Carlo feature scale model. Process performance has been quantitatively evaluated by examining etch rates for Si and the SiO_2-like mask, Si/mask etch selectivity, and critical dimensions within the HAR features. When only the radio-frequency (RF) bias power is pulsed, Si and mask etch rates scale with pulse duty cycle. As a result, if Si is etched to the same depth, the HAR trenches are wider at higher duty cycles due to less total oxidation time and less protection of the sidewalls. Source power pulsing provides higher Si etch rate because of RF bias power being on continuously, but suffers from poor mask selectivity. Synchronized pulsing of both the source and RF bias powers in conjunction with phase control provides additional flexibility in modulating the IEAD and the ion/neutral flux ratio. RF bias pulsing and in-phase synchronized pulsing yield the best selectivity for the conditions explored.

[1] S. Banna, *et al*., J. Vacuum Sci. Technol. A **30**, 040801(2012).

[2] K. Tokashiki *et al*., Jpn. J. Appl. Phys. **48**, 08HD01(2009).

[3] A. Agarwal, S. Rauf and K. Collins, Plasma Sources Sci. Technol. **21**, 055012 (2012).

9:00am **PS+EM+SE-TuM-4 Plasma Etching of High Aspect Ratio Oxide-Nitride-Oxide Stacks***, S Huang, C Hurard,* University of Michigan*; S Nam, S Shim, W Ko,* Samsung Electronics Co., Ltd., Republic of Korea*;* ***Mark Kushner**,* University of Michigan

Increasing demand for large memory capacity is now being met by 3-dimensional vertical structures. Fabricating these structures requires plasma etching through hundreds of stacked layers resulting in extremely high aspect ratio (up to 100) vias. The stack typically consists of alternately deposited silicon nitride and silicon oxide layers which serve as the sacrificial material and gate dielectric respectively. When combining the high aspect ratio (HAR) and hybrid materials, the etching of oxide-nitride-oxide (ONO) stacks faces both traditional (e.g., aspect ratio dependent etching, bowing and charging) and new challenges (e.g., mixing layers, line edge striation and tapered etch front through several layers).

In this paper, we report on results from a computational investigation of the etching of ONO stacks using tri-frequency capacitively coupled plasmas sustained in fluorocarbon gases. The reactor scale modeling was performed using the Hybrid Plasma Equipment Model (HPEM), from which the neutral and ion fluxes and ion energy and angular distributions (IEADs) to the wafer surface were obtained. The feature scale modeling was performed using the 3-dimensional Monte Carlo Feature Profile Model (MCFPM) with a newly developed polymer mediated fluorocarbon etching mechanism for oxide and nitride.

During the etching of ONO stacks, the etch front quickly evolves to a tapered profile at low aspect ratio (~5) and persists into deeper features, mainly due to re-deposition of sputtered fluorocarbon radicals within the feature. The etch rate generally decreases with increasing aspect ratio due to limited transport of radicals and ions. Conductance, ion reflection from sidewalls and charging all play of role in the flux of reactive species to the etch front. When the etching proceeds through the ONO stack, the etch rate fluctuates, becoming higher for the nitride and lower for the oxide. The formation of scalloping due to different lateral etch rates for each material is observed for some conditions while not for others. The mechanism behind this scalloping, and methods to minimize its effect will be discussed.

* Work supported by Samsung Electronics Co. Ltd, National Science Foundation and the Department of Energy Office of Fusion Energy Sciences.

9:20am **PS+EM+SE-TuM-5 Etch Profile Evolution in Poly-silicon using Halogen Containing Plasmas for Next Generation Device Fabrication*, Shyam Sridhar*, *S Voronin, P Biolsi, A Ranjan,* TEL Technology Center, America, LLC

The shrinking and introduction of complex three-dimensional device structures poses a great challenge for plasma etching. With ever-decreasing feature pitches, it is extremely important to achieve a near ideal etch profile, i.e. vertical sidewalls and flat etch fronts. The challenges are manifold in etching three-dimensional structures. For example, in etching high aspect ratio square shaped holes, it is difficult to remove the targeted material from the corners, especially at the bottom of the feature.

In this work, we report the impact of process parameters such as ion energy, neutral and ion fluxes on the profile evolution of closely spaced poly Si lines using F, Cl, and Br containing plasmas. Etching in Cl and Br plasmas resulted in anisotropic profiles with bowed and tapered sidewalls. Addition of gases such as oxygen or fluorocarbons to minimize bowing resulted in enhanced tapering of sidewalls. The etch fronts were found to be relatively flat or curved depending on the ion energy. Micro trenching was also found to influence the shape of the etch front. We attempt to extend the learning from etching two-dimensional lines to three-dimensional features, in order to define a better processing space for new and emerging applications.

9:40am **PS+EM+SE-TuM-6 Flux and Energy of Reactive Species Arriving at the Etch Front in High Aspect Ratio Features During Plasma Etching of SiO_2 in $Ar/CF_4/CHF_3$ Mixtures*, Soheila Mohades*,** University of Michigan*; M Wang, A Mosden,* TEL Technology Center America, LLC*; M Kushner,* University of Michigan

Multi-frequency, capacitively coupled plasmas (CCPs) provide additional control in semiconductor processing by separating production of ion fluxes from acceleration of ions into the wafer. In dual-frequency capacitively coupled plasmas (DF-CCPs), the higher frequency (HF, tens to hundreds of MHz) sustains the plasma and the lower frequency (LF, a few to 10 MHz) controls acceleration of ions into the wafer. Although the goal is to have completely separate control, changing the frequency and power of the LF does affect the magnitude of reactive fluxes to the wafer in addition to the ion energy and angular distributions (IEADs). As the aspect ratio (AR) of features approaches 100 in high aspect ratio (HAR) etching of dielectrics, the parameter of interest is the flux of reactants that reaches the etch front, which is not necessarily the same as the fluxes that enter the feature. Issues such as side-wall scattering and neutral conductance in the feature modify those fluxes as the AR increases.

In this paper, the IEADs and reactive fluxes reaching the etch front during fluorocarbon plasma etching of SiO_2 were computationally investigated as a function of AR. The feature scale modeling was performed using a 3-dimensional implementation of the Monte Carlo Feature Profile Model (MCFPM). The IEADs and reactive fluxes incident onto the feature were obtained using the 2-dimensional Hybrid Plasma Equipment Model (HPEM). The parameter space for the DF-CCP has LF of a few to 10 MHz, HF of 40 MHz, with powers of 100-1000 W applied to the bottom electrode with and without a dc-augmented top electrode in a gas mixture of $Ar/CF_4/CHF_3$ at 10s of mTorr. The reactive fluxes and energies onto the etch front for AR of up to 100 are discussed for ions, hot-neutrals and thermal neutrals.

* Work supported by TEL Technology Center, America, LLC, National Science Foundation and the Department of Energy Office of Fusion Energy Sciences.

11:00am **PS+EM+SE-TuM-10 Wafer-scale Fabrication of Suspended Graphene Nanoribbon Arrays -from Growth Dynamics to Optoelectrical Applications-*, Toshiaki Kato*,** *T Kaneko,* Tohoku University, Japan **INVITED**

Graphene nanoribbons (GNRs) combine the unique electronic and spin properties of graphene with a transport gap that arises from quantum confinement and edge effects. This makes them an attractive candidate material for the channels of next-generation transistors. However, the reliable site and alignment control of nanoribbons with high on/off current ratios remains a challenge. We have developed a new, simple, scalable method based on novel plasma catalytic reaction [1-5] for directly fabricating narrow GNRs devices with a clear transport gap [6]. Since the establishment of our novel GNR fabrication method, direct conversion of a Ni nanobar to a suspended GNR is now possible. Indeed, GNRs can be grown at any desired position on an insulating substrate without any post-growth treatment, and the wafer-scale synthesis of suspended GNR arrays with a very high yield (over 98%) is realized [7]. The growth dynamics of suspended GNR is also investigated through the systematic experimental study combined with molecular dynamics simulation and theoretical calculations for phase diagram analysis. The improvement of thermal stability of Ni nanobar can be a key to realize the GNR nucleation in our method, which can be given by supplying higher density of carbon from plasma to liquid-phase Ni nanobar. The wettability of liquid-phase Ni nanobar against to the SiO_2 substrate is also found to be an important factor forming the suspended structure of GNR. It is also revealed that the minimum length of GNR can be decided by the wavelength of Plateau-Rayleigh instability known as a traditional instability of fluid flow. We believe that our results can contribute to pushing the study of atomically thin layered materials from basic science into a new stage related to the optoelectrical applications [8-10] in industrial scale.

References

[1] T. Kato and R. Hatakeyama, J. Am. Chem. Soc. 130 (2008) 8101.

[2] T. Kato and R. Hatakeyama, ACS Nano 4 (2010) 7395.

[3] T. Kato and R. Hatakeyama, ACS Nano 6 (2012) 8508.

[4] T. Kato and R. Hatakeyama, ACS Nano 4 (2010) 7395.

[5] B. Xu, T. Kaneko, Y. Shibuta, T. Kato, Scientific Reports 7 (2017) 11149.

[6] T. Kato and R. Hatakeyama, Nature Nanotechnology 7 (2012) 651.

[7] H. Suzuki, T. Kaneko, Y. Shibuta, M. Ohno, Y. Maekawa, and T. Kato, Nature Communications 7 (2016) 11797.

[8] T. Kato and T. Kaneko, ACS Nano 8 (2014) 12777.

[9] T. Akama, W. Okita, R. Nagai, C. Li, T. Kaneko, T. Kato, Scientific Reports 7 (2017) 11967.

[10] T. Kato and T. Kaneko, ACS Nano 10 (2016) 9687.

11:40am **PS+EM+SE-TuM-12 Investigation of Surface Reactions for GeSbTe-based Phase Change Material: From Etching to Final Sealing Process*, Yann Canvel*,** *S Lagrasta,* STMicroelectronics, France*; C Boixaderas, S Barnola,* CEA-LETI, France*; E Martinez,* CEA/LETI-University Grenoble Alpes, France

Chalcogenide phase-change materials (PCMs), such as Ge-Sb-Te (GST) alloys, have shown outstanding properties, which have led to their successful use for a long time in optical memories (DVDs) and, recently, in non-volatile resistive memories. The latter, known as PCM memories, are among the most promising candidates to be integrated into next generation smart-power and automotive applications [1].

Chalcogenide PCMs exhibit fast and reversible phase transformations between crystalline and amorphous structures with very different resistivity states. This distinctive ability to store the information gives a unique set of features for PCMs, such as fast programming, flexible scalability, high data retention and performing endurance [2][3].

In the perspective of large-scale integration, which means incorporation of the PCM into more and more confined structures, the device performances are getting increasingly more sensitive to surface effects of the GST layer. Thus, it is crucial to maintain a homogeneous stoichiometric composition in the GST surface/volume all along the manufacturing process, particularly during the patterning of PCM cells.

In this study, we examine the main surface reactions that GST material must face and we illustrate how these reactions are likely to modify its composition.

In particular, we will focus on the surface damages generated by different halogen-based plasma etching processes [4][5]. An innovative etching method, compatible with extreme confined structures, will be highlighted.

Then, we will study the oxidation of GST, responsible of the critical surface degradation after the etching process [6]. According to the exposure conditions, the GST surface undergoes some specific chemical modifications that will be pointed out.

Finally, the stability of GST composition will be evaluated at each point of a standard GST patterning process: from etching to final sealing of PCM cells. It will allow us to understand how the chalcogenide material is degraded during the whole process. Some improvements will be exhibited in order to reduce this degradation.

Plasma etching were carried out in a 12 inch planar ICP reactor. And all the surface analyses were performed by using different techniques of material characterization, such as XPS, PP-TOFMS and EDS.

References

1. Pasotti, M. et al. IEEE European Solid State Circuits (2017).

2. Sousa, V. et al. VLSI Technology Digest (2015).

3. Noé P. et al. Semicond. Sci.Technol. 33, 013-002 (2018).

4. Kang, S. et al. Jpn. J. Appl. Phys. 50, 086-501 (2011).

5. Li, J. et al. Appl. Surf. Sci. 378, 163-166 (2016).

6. Golovchak, R. et al. Appl. Surf. Sci. 332, 533-541 (2015).

12:00pm **PS+EM+SE-TuM-13 Behaviors of Charged Species in Afterglow of Dual Frequency Pulsed Capacitively Coupled Plasma with a Synchronous Negative DC-bias***, **Takayoshi Tsutsumi**, T Ueyama, K Ishikawa, H Kondo, M Sekine,* Nagoya University, Japan*; Y Ohya,* Tokyo Electron Miyagi Limited*; M Hori,* Nagoya University, Japan

Dual frequency pulsed capacitively coupled plasma with a synchronous negative DC-bias to a top electrode is developed for the improvement of high-aspect-ratio contact hole (HARC) fabrications. It enables to suppress the distorted etched profiles such as twisting. These distortions are due to the distortions of ion trajectories inside the deep contact holes, which are charged up positively. It is expected that charged species presented in early afterglow were neutralized on the surfaces in the holes. we focus on the behavior of charged species in the afterglow period of the synchronous negative DC-bias imposition to the top electrode in the pulsed dual frequency CCP.

For temporal change of electron density in the afterglow, the synchronous negative DC-bias resulted in lower decay rate of electron density in afterglow[1]. The result indicate that higher DC-bias imposition causes more electron generation. Moreover, the decay rate near the bottom electrode is lower than that of near the top electrode. The possible explanation is electron generation or sustaining mechanism in the afterglow of DC synchronized pulsed plasma. We measured OES to confirm the electron generation or plasma sustainment in the afterglow. The intensities of Ar emission (at a wavelength of 750.38 nm) in afterglow decreased at the beginning of RF off period and increased after several µs. This phenomenon was not observed in the constant DC-bias condition.

The synchronous DC-bias voltage seems to accelerate the positive ions to the top electrode. And ion bombardment to the top electrode surface enhance the generation of the secondary electron in the afterglow. We consider that this influence the generation of negative ions and the neutralization of the charged surface of the hole in afterglow.

[1] T. Ueyema, Y. Fukuanga, T. Tsutsumi, K. Takeda, H. Kondo, K. Ishikawa, M. Sekine, M. Iwata, Y. Ohya, H. Sugai, and Hori, Jpn. J. Appl. Phys. **56**, 06HC03 (2017).

Plasma Science and Technology Division
Room 104C - Session PS+PB-TuM

Plasma Medicine

Moderator: Deborah O'Connell, University of York, UK

8:00am **PS+PB-TuM-1 Lessons from Tesla for Plasma Medicine***, **David Graves**,* University of California at Berkeley

It can be argued that plasma medicine originated with Nikolai Tesla in the late 19th century when he showed that one could pass large quantities of high frequency currents through a human body with no apparent damage. [1, 2] Tesla interpreted the significant sensations he experienced following exposure to these currents as being potentially valuable therapeutically. Tesla's work inspired much more extensive investigations over a period of several decades by numerous other researchers, on both the physics and biomedical effects of these currents. Researchers such as Arsene d'Arsonval and Paul Oudin in France and Frederick Strong in the United States, among others, were important pioneers. These early pioneers had a surprisingly modern view of some aspects of the therapeutic mechanisms of high frequency currents that clearly overlap with recent results. The perspective of this community was that the most important physiological effects are associated with the high frequency currents rather than the gas phase plasma. Some early work, such as the analgesic effects of dielectric barrier air plasma on tissue, is not well known today. [3] The range of afflictions that early practitioners treated successfully is remarkable. This body of work, in some cases almost 130 years old, has important lessons for current investigations into plasma medicine. Observations from Tesla and other early practitioners suggests that high frequency currents are potentially important and plasma medicine researchers should probably pay more attention to them.

[1] F.F. Strong, High Frequency Currents, Herman Company, New York, 1908.

[2] S.H. Monell, High Frequency Electric Currents in Medicine and Dentistry, WR Jenkins, New York, 1910.

[3] P. Oudin, Application therapeutique locale des courants de haute frequence en gynecologie, Archives d'électricité médicale, 287, 10 juin, 1910.

8:20am **PS+PB-TuM-2 Characterization of a Helium Atmospheric Pressure Plasma Jet by Measuring the Total Yield of Reactive Species in Real Time***, **Ek Adhikari**, V Samara, S Ptasinska,* University of Notre Dame

Recently, we performed in-situ measurements of reactive oxygen species of a helium atmospheric pressure plasma jet (APPJ) using an acidified ferrous sulfate solution (Fricke) as a sample. The total yield of reactive species reached to or originated in the solution corresponds to the amount of the yield of Fe^{3+} from reactions that transform Fe^{2+} into Fe^{3+} during plasma irradiation. The measurements indicated that the number of reactive species formed in the plasma jet is proportional to the applied pulse voltage and repetition frequency. However, there is a decrease in the yield of Fe^{3+} per pulse for an increase in the frequency. For higher frequencies, there is not enough time to complete all reactions before the next pulse arrives to the sample. Whereas, for lower frequencies, this yield is higher due to the relatively longer time period necessary for reactions to complete. Further, the flow rate of feed gas and treatment distance, which is the distance between the sample and glass capillary, have a minor effect on the formation of reactive species, but the yield of Fe^{3+} gradually decreases for a treatment distance longer than 20 mm. Moreover, we calculated the yield of Fe^{3+} in a very short time (equivalent to time period used in the experiment), and compared with the experimental results. The yield of Fe^{3+} formed within 15 s of plasma irradiation was also compared with the fractions of plasma induced DNA damage level under similar experimental conditions.

8:40am **PS+PB-TuM-3 Dry Etching of Patterned Medical Grade Titanium Alloys***, **Eitan Barlaz**, J Mettler, D Ruzic,* University of Illinois at Urbana-Champaign

We report on the development of a plasma etch process for Ti-6Al-7Nb, an alloy of titanium common for performance biomedical implants due to its excellent mechanical properties and corrosion resistance. The process uses the same chlorine and oxygen chemistry common to etches of pure titanium, with added ion bombardment to remove reaction products with low volatility and to ensure minimal texturing of the surface. The process is capable of etch rates in excess of 50 nm/min in 50 mTorr of Argon and 20 mTorr of CCl_4 using 50 W of RF power and a negative sample bias of > 500 Volts. Due to the need to produce irregularly shaped geometries, relative etch rates are reported for a variety of features including through holes and posts on representative parts. Plasma diagnostics including Langmuir and radical were applied to the process to compare the efficacy of both inductively coupled and surface wave plasma sources over large part sizes.

9:00am **PS+PB-TuM-4 Electron Temperature And Plasma Density Of Ar Plasma In Atmospheric Pressure Micro-DBD***, **Pradoong Suanpoot**, J Sornsakdanuphap,* Maejo University Phrae Campus, Thailand*; B Ghimire, Y Hong,* Plasma Bioscience Research Center, Republic of Korea*; G Cho,* Charged Particle Beam and Plasma Laboratory, Republic of Korea*; E Choi,* Plasma Bioscience Research Center, Republic of Korea

A model based on plasma propagation velocity has been recently developed to estimate the electron temperature (T_e) of atmospheric pressure μ-DBD plasma. In this work, we have extended this model to calculate T_e for plasma generated with Ar gas. Plasma has been generated by input discharge voltage of 2.7 kV at driving frequency of ≈ 45 kHz. A high-speed single-frame intensified charged coupled device (ICCD) has been used to observe the space and time-resolved discharge images and estimate the value of plasma propagation velocity (u_g). The value of u_g for Ar plasma has been obtained in the range of 6.2´10^3 m/s. The electron temperature has been calculated for this plasma. The average electron temperature has been found to be about 1.18 eV and the average plasma density has been found to be about 3.62×10^{14} cm^{-3} for Ar plasma. Our results obtained with modified convective-wave packet model can be a new contribution to plasma medicine.

Keywords: Atmospheric-pressure μ-DBD plasma, Ar plasma, plasma propagation speed, electron temperature, plasma density

9:20am **PS+PB-TuM-5 Plasma Immunotherapy of Cancers***, **Vandana Miller**, A Lin, P Ranieri,* Drexel University*; A Snook,* Thomas Jefferson University*; A Fridman,* Drexel University **INVITED**

Non-thermal plasmas are currently being developed as an alternative therapy for cancer. Local application of plasma to tumors *in vivo* has led to reduced tumor size and increased life expectancy of treated animals.[1] The body's immune system plays a vital role in the control of cancer.[3] In fact, cancer immunotherapy, the control of cancer by employing components of the patient's own immune system, is emerging as an appealing strategy.[3] New approaches being explored include increasing the immunogenicity of tumor cells by inducing immunogenic cancer cell death (ICD).[4] ICD of cancerous cells has been demonstrated with certain chemotherapeutic drugs and through physical methods such as X-ray therapy and UVC.[5, 6] Cells undergoing ICD express damage associated molecular patterns (DAMPs) which assist immune responses that may mediate systemic elimination of cancer.[4] We have demonstrated that non-thermal plasma is a good candidate for cancer therapy via immunomodulation by:

direct effects on immune cells[7, 8] and

indirect effects of cancer cell ICD.[8]

The role of plasma augmentation on the immune system, based on our *in vitro* and *in vivo* studies, will be discussed as a potential modality for clinical application in cancers. *In vivo* studies using Balb/c mice inoculated with subcutaneous CT26 colorectal cancer cells, treated with nspDBD plasma showed DAMP signal expression and recruitment of immune cells in the local tumor environment. Furthermore, there was development of a systemic, tumor-specific immune response. This demonstrates that plasma elicits ICD locally, in the treatment area, which leads to beneficial host immune responses both locally and systemically. The clinical potential of plasma cancer immunotherapy will be discussed and the challenges to address will be identified for further development of this technology. Results from a small clinical trial will also be presented.

References

[1] Keidar, M., et al., *Br J Cancer*, **105**, 2011.

[2] Schlegel, J., J. Köritzer, and V. Boxhammer, *Clinical Plasma Medicine*, **1**, 2013.

[3] Mellman, I., G. Coukos, and G. Dranoff, *Nature*, **408**, 2011.

[4] Krysko, D.V., et al., *Nature Reviews Cancer*, **12**, 2012.

[5] Kalbasi, A., et al., *The Journal of clinical investigation*, **123**, 2013.

[6]Zitvogel, L., et al., *Nature Reviews Immunology*, **8**, 2008.

[7] Kaushik, N.K., et al., *Journal of Physics D: Applied Physics*, **49**, 2016.

[8] Lin, A., et al., *Plasma Processes and Polymers*, **12**, 2015.

11:00am **PS+PB-TuM-10 Hydroxyl Radical Footprinting with Plasma-Induced Modification of Biomolecules (PLIMB): A Novel Tool for Protein Structural Analysis***, **Faraz Choudhury**, D Benjamin, B Minkoff, J Blatz, M Sussman, J Shohet,* University of Wisconsin-Madison

The protein-therapeutic industry, typified by anti-cancer proteins like Herceptin, has accelerated the need to be able to analyze the 3-dimensional structure of proteins in solution. Mass spectrometry is widely used for this. This has generated a need for new types of probes that covalently label protein solvent-accessible sites. Two common ones rely upon the creation of and covalent modification with highly reactive hydroxyl (OH) radicals. The first, fast photochemical oxidation of proteins (FPOP), generates hydroxyls from H_2O_2 via laser photolysis, and the second, synchrotron X-ray beam exposure, produces OH radicals via direct radiolysis of water. These techniques suffer from issues such as: a reaction times that are potentially too long to correctly measure protein structure or the necessity to add chemicals. Furthermore, both are cumbersome & expensive, either by accessing a synchrotron or building an instrument to perform FPOP. As a result of a collaboration at the interface of plasma physics and biochemistry, we developed a technique that generates µsecond bursts of OH radicals, using a surface-barrier discharge, for labeling proteins at solvent-accessible amino acid side chains. We call this Plasma-Induced Modification of Biomolecules (PLIMB). PLIMB does not require chemical additives, circumvents the issues associated with reaction timescale, and ultimately costs far less. Using a model protein in solution, cytochrome C, the protein was modified in a dose-dependent fashion in only a lightly buffered water-based solution, demonstrating that the system can generate OH radicals capable of labeling proteins without additional reagents. In addition, only discrete peptides within the protein are modified. Perturbing protein structure via digestion prior to plasma exposure significantly increases the observed covalent modification, suggesting that conformational structure is maintained during exposure. Experiments with myoglobin, a second protein, also revealed distinct regions of modification despite examining in depth the entirety of the protein's sequence. Mapping the oxidized peptides to myoglobin's crystal structure reveals that all of these peptides fall within the same face of the protein, suggesting the preservation of a higher-order structure under the solution conditions described. These experiments suggest that PLIMB provides a means of efficaciously generating microsecond bursts of OH radicals while providing a low cost and readily accessible means of probing the conformation of proteins in solution using mass spectrometry. We envision PLIMB being useful in a wide range of biological, medical and pharmaceutical fields.

11:20am **PS+PB-TuM-11 Biological Effects of Plasma-Irradiated Organic Molecules in Plasma- Treated Liquids***, **Kenji Ishikawa**, Y Hosoi, D Kanno, Y Kurokawa, H Tanaka, M Mizuno, F Kikkawa, M Hori,* Nagoya University, Japan

Selective killing of cancer cells incubated in non-equilibrium atmospheric pressure plasma (NEAPP)-activated medium (PAM) has been reported.[1] This antitumor effect revealed by involvement of reactive oxygen and nitrogen species (RONS) in PAM.[2] The effect was also found in plasma-activated lactate in Ringer's solution (Lactec), so called as PAL.[3] We found that the cancer cells incubated in the PAL received lesser oxidative stress than that of the PAM.[3] A cause of intracellular oxidation with respect to the RONS reactions has been studied by nuclear magnetic resonance (NMR) analysis of organic substances in the Lactec solution.

From the NMR measurements, reactive organic acids, that is, plasma activated lactate (LA) involved pyruvic acid (PA) and acetic acid (AA)-like components in the PAL were detected. The plasma activated organic acids act potentially as antitumor agents other than RONS.

Furthermore, NEAPPs irradiated to fullerenol. The plasma irradiated fullerenol demonstrated a cytotoxic effect on cells. The PF was modified by the plasma irradiation, arising carbonyl groups, ether bonds, and intercalated nitrate anion. Endocytosis of the PF induced to apoptotic cell death and generated intracellular RONS on cells cultured in the PF-added cell culture medium.

1 mL of fullerenol-added water (1.6 mM) was irradiated by the NEAPP (Ar 2 slm) for 3 min. Precipitates of the PF were collected by drying water at 70°C for 1 hr. The collected PF dissolved again into 50 µM of cell culture media (DMEM). 5 × 10^3 of HeLa cells were cultured for 24 hr in the PF-added DMEM and the same amount (50 µM) of fullerenol-added DMEM, respectively. Cell viability was evaluated by the MTS assay. Caspase

activation and fullerenol permeation of the cell membrane were observed by fluorescent microscopy.

Although the viability of the fullerenol-added DMEM remained at a constant of 110 %, the HeLa cell viability decreased to 70 %, when the cells were incubated in the PF-added DMEM. The cells showed caspase 3/7 activation. The PF activate the caspase cascade pathway to induce apoptosis and permeation of the fullerenol into the cells. Therefore, the fullerenol properties were modified by the plasma-irradiation to enhance the cytotoxicity of PF.

Acknowledgments This study was supported by KAKENHI 24108002.

[1] S. Iseki et al., Appl. Phys. Lett. **100**, 113702 (2012).

[2] N. Kurake et al., Arch. Biochem. Biophys. **605**, 102 (2016).

[3] H. Tanaka et al., Sci. Rep. **6**, 36282 (2016).

11:40am **PS+PB-TuM-12 OH-Radical Generation in an Atmospheric-Pressure Plasma Discharge for use in Three-Dimensional Protein Structural Analysis***, **Joshua Blatz**, B Minkoff, F Choudhury, D Benjamin, J Shohet, M Sussman,* University of Wisconsin-Madison

Atmospheric-pressure plasma discharges are well-known to generate OH radicals when interacting with water. However, the use of radicals created in this way for protein footprinting is virtually non-existent. Here, we describe a novel technique which utilizes a dielectric-barrier plasma discharge to oxidize proteins in solution. These oxidation events are quantified using mass spectrometry and allows us to determine the exterior domain and solvent accessibility of a protein.

To generate the plasma a high-voltage A.C. signal is applied to a needle electrode in close proximity to the surface of the liquid sample. This causes the gas to breakdown and form the plasma. These plasma discharges have been measured to be on the order of microseconds which prevents the protein from cleaving. During plasma exposure the sample is cooled to maintain temperature and prevent denaturation.

Protein bovine serum albumin was exposed to plasma. Labeling of the exterior domain was found in a manner consistent with other protein structural analysis techniques. Additionally, initial measurements have been collected which indicate that by changing various electrical, physical, and chemical parameters the technique may still be optimized. This could lead to greater OH-radical generation, reduced sample heating, and reduced pH change.

In addition to the consistent initial results and optimization potential there are many advantages it holds over competing techniques. It can be built inexpensively and on a space-limited benchtop. There are no necessary chemical additives which may interfere with the results and there seems to be no limit to the size of the protein which can be treated. All the samples are treated in liquid solution so they are free to move as they would *in vivo*.

12:00pm **PS+PB-TuM-13 Plasma-Surface Interaction at Atmospheric Pressure: From Mechanisms with Model Polymers to Applications for Sterilization***, **Pingshan Luan**[1], G Oehrlein,* University of Maryland, College Park

Cold atmospheric plasma (CAP) produces many types of chemically reactive species and is capable of modifying materials at atmospheric pressure. Studying plasma-surface interaction (PSI) at such pressure has been challenging due to the small mean-free-path (< 100 nm) which prohibits the method of using independently controlled beams of ions/neutrals. In the past few years, we developed an alternative approach of studying PSI at atmospheric pressure using well-controlled source-ambient-sample systems and comprehensive characterization techniques. First, we characterized and compared a few types of CAP sources such as atmospheric pressure plasma jet (APPJ) and surface micro-discharge (SMD). We found that the dominant reactive species generated by different CAP sources can be dramatically different. By tuning source operating parameters, we were able to manipulate the dominant reactants generated by these sources. Second, by controlling the gaseous environment wherein PSI took place, we could suppress certain unwanted interactions of plasma species with the ambient and regulate the delivery of reactive species to material surfaces. Lastly, we used polymers with representative functional groups to study the effect of reactive species on certain surface moieties. Due to the multi-phase nature of PSI, we integrated many characterization techniques in our study, including that of plasma/gas phases such as optical emission spectroscopy (OES), Fourier transform infrared spectroscopy (FTIR) and UV absorption, and that of material surfaces such as X-ray photoelectron spectroscopy (XPS), attenuated total reflection (ATR) FTIR and Ellipsometry. To our knowledge, the perpendicular electric field enhanced ATR-FTIR was used for the first time to study plasma processed polymer films less than 10 nm-thick. Combined with XPS, these techniques provide rich chemical information of both surface and subsurface modifications. By correlating plasma/gas phase with surface/subsurface measurements, we showed the dominant effect of a few types of reactive species such as O, OH and N_2O_5 on materials. We also provided evidence showing the competition between etching and surface modification during plasma treatment. Besides, we extended our investigation to studying the CAP-induced bacterial membrane damage, which might help understand the sterilization mechanism of CAP. We gratefully acknowledge funding from National Science Foundation (PHY-1415353) and US Department of Energy (DE-SC0001939). We thank Andrew J. Knoll, Elliot A. J. Bartis, V. S. S. K. Kondeti, Peter J. Bruggeman, Andrea Gilbert, Rohan Tikekar and David B. Graves for collaborations.

Advanced Surface Engineering Division
Room 202C - Session SE+PS-TuM

Plasma-assisted Surface Modification and Deposition Processes

Moderators: Jolanta Klemberg-Sapieha, Ecole Polytechnique de Montreal, Canada, Matjaz Panjan, Jozef Stefan Institute, Slovenia

8:00am **SE+PS-TuM-1 Surface Modification of 304 Stainless Steel by Neutral Nitriding***, **Petros Abraha**,* Meijo University, Japan

Austenitic stainless steel is the choice of material in the manufacturing industries for its corrosion resistance but lacks surface hardness leading to poor wear resistance and ultimately short lifetime. Stainless steel possesses the same microstructure at all temperatures and therefore, cannot be hardened by heat treatment. Attempts to increase the hardness of austenitic stainless steels by plasma nitriding has been successfully demonstrated in using different processes and methods. Here, we have introduced a nitriding method that improves the hardness and corrosion resistance of stainless steel while maintaining the initial surface conditions of the untreated surface.

In this research, neutral nitriding, a plasma nitriding method performed on a sample inside a cathodic grid in using an electron beam excited plasma device is presented. In this method, nitrogen ion incidence onto the sample surface is prevented by a positive bias to the sample ultimately controlling the formation of the compound layer. Further, the incidence of electrons causing an excessive rise in sample temperature is prevented by applying a negative bias to the cathodic grid. The setup creates a favorable condition that enables the neutral nitrogen species to be the primary species within the plasma to diffuse into the sub-surface of the sample and form a hardened layer.

The results obtained are as follows: (1) The S-phase without any compound layer on the surface was confirmed and the surface roughness of the untreated surface (Ra 10 nm) was maintained (Ra 15 nm). (2) The surface hardness was increased to more than two times, 550 Hv. (3) Pitting potential tests confirm Improved critical pitting potential on samples nitrided at 350 °C and 375 °C.

8:20am **SE+PS-TuM-2 Plasma Cratering and Hardening for Friction Reduction and Wear Resistance of Cast Iron***, **Wei Zha**,* Univesity of Windsor, Canada*; C Zhao, X Nie,* University of Windsor, Canada

Cathodic plasma electrolysis (CPE) is used to reduce the friction and increase the wear resistance of cast iron. During the process, cast iron sample serves as a cathode where the plasma discharging occurs, increasing the surface hardness and leaving an irregular array of craters on the surface. As the applied voltage increases, the number and size of craters become larger. The areal density of craters (as reservoir) and oil retention are determined from SEM image analysis and surface profiler. Reciprocating tribotests are conducted on blank sample, CPE-treated samples and sample with crosshatched surface. The results show that the CPE-treated samples can have a lower coefficient of friction and higher wear resistance than other two kinds of samples. As for the CPE-treated samples, the friction behaviors are also discussed by considering effects from their areal density of craters, surface roughness and oil retention.

Keywords: Cathodic plasma electrolysis, Cratering, Hardening, Friction, Wear

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[1] **Coburn & Winters Student Award Finalist**

8:40am **SE+PS-TuM-3 Area-selective Deposition by Surface Engineering for Applications in Nanoelectronics. From Blanket to Confined Dimensions***, **Silvia Armini,*** IMEC, Belgium

At advanced nodes targeting 10nm feature size and below, lithography starts to dominate costs (EUV, multiple mask passes per layer, pattern placement error). Complementary techniques and materials are needed to continue 2D scaling and extend the Moore's law. Area-selective atomic layer deposition (AS-ALD) is rapidly gaining interest because of its potential application in self-aligned fabrication schemes for next-generation nanoelectronics. The strong sensitivity of ALD to the chemistry of the surface and its self-limiting nature are particularly appealing. In this talk we report two examples of AS deposition triggered by i) area activation, i.e. a H2-based plasma triggered selective placement of ALD Ru catalyst on SiCN liner with respect to amorphous carbon materials (Fig. 1) followed by AS electroless metal bottom-up deposition and ii) area deactivation by a combination of surface functionalization by molecular self-assembled organic films and ALD of metal oxides and metal nitrides. In the latter case the idea is to chemically and locally bond a molecule directly to the metal surface in order to inhibit reactive sites and then prevent further reactions between the precursor molecules and the surface. A selectivity driven benchmarking of organic passivation films deposited on copper surface from the vapor and liquid phase will be presented, both on blanket surfaces, micron-scale and nanometer-scale patterned features. Two major challanges will be investigated: i) defectivity induced by a reactive ALD process which also nucleates on the part of the surface covered with the organics and metrology; ii) understanding and control of AS ALD material shape at the boundaries between Cu and dielectrics. In Fig.2 the top-down SEM images after AS ALD Hf nitride on 240nm Si oxide/50nm Cu lines are shown. A target thickness of 10nm Hf nitride is deposited by ALD at 120˚C.

9:00am **SE+PS-TuM-4 Experimental and Numerical Evaluation of Cohesive and Adhesive Failure Modes during Indentation of TiAlN Coatings on Si(100) Deposited by MPPMS***, **Z.T. Jiang**, M Lei,* Dalian University of Technology, China

The mechanical behavior of TiAlN coatings was studied by Indentation test and FEM modeling. The TiAlN coatings were deposited by modulated pulse power (MPP) magnetron sputtering. The peak power was used from 21 kW to 50 kW with the gas flow ratio of Ar/N_2=4:1. The microstructure of the indented regions was observed by focused ion beam (FIB), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). XRD with grazing angle of incidence reveals that the coatings consisted with c-TiAlN. The achieved hardness and modulus for the coatings show significant increase from 23.6 GPa to 46.7 GPa and 396 GPa to 461 GPa. The eXtended Finite Element Method (XFEM) was applied to study the cohesive cracks through the coatings, while the Cohesive Zone Model (CZM) was to evaluate the coating/substrate interfacial crack. The stress transfer from the coating to the substrate was dependent on the elastic and elastic/plastic properties of the coating and substrate. The energy release rate of the coating and the cohesive zone parameters were investigated by the fracture toughness of the coatings. Compared with the experimental results, the simulation results were able to accurately observe the deformation as well as the fracture behavior of the coatings. Under indentation loading, the crack initiation tended to begin at the outer surface and to propagate along the coating in thickness direction until the cracks reached the substrate.

9:20am **SE+PS-TuM-5 Growth of TiB_x Thin Films by DC Magnetron Sputtering and High-Power Impulse Magnetron Sputtering: Effect of Pressure and Substrate Temperature***, **Niklas Hellgren,*** Messiah College*; J Thörnberg, I Zhirkov,* Linköping University, Sweden*; G Greczynski,* Linköping University, Sweden*; J Palisaitis,* Linköping University, Sweden*; M Sortica,* Uppsala University, Sweden*; P Persson,* Linköping University, Sweden*; I Petrov, J Greene,* University of Illinois at Urbana-Champaign*; L Hultman, J Rosen,* Linköping University, Sweden

We report on titanium boride, TiB_x, thin films grown by both direct current magnetron sputtering (DCMS) and high power impulse magnetron sputtering (HiPIMS) from a compound TiB_2 target, in an attempt to grow high-quality stoichiometric TiB_2 films. The composition, microstructure, and texture was analyzed as a function of deposition temperature (room temperature – 900 °C) and pressure (5 – 20 mTorr). Films deposited by DCMS at low pressure, regardless of temperature, result in over-stoichiometric films (B/Ti ≈ 3), while high pressure gives close to stoichiometric films. This can be explained by differences in angular distribution of sputtered B and Ti atoms, as well as differences in gas scattering [1]. These high-pressure films, however, are under-dense and have a mixed 100/101 preferred crystal orientation.

The composition of the HiPIMS-deposited films show a more complex dependence on pressure and temperature: At low temperatures, the trend vs pressure is opposite to DCMS, with the higher pressure resulting in higher B/Ti ratio. At higher temperatures, the effect of pressure is smaller, and even reverses slightly, with higher pressure giving lower B/Ti ratio.

We attribute these trends to a combination of several factors: (1) The much higher degree of ionization in HiPIMS, and the different transport of the ionized sputtered particles in the presence of a magnetic field, (2) gas density decrease at higher temperature resulting in less scattering, and (3) more sublimation, primarily of boron, at higher substrate temperatures. The highest quality stoichiometric TiB_2 films, with 001-textured nano-columnar structure, form by HiPIMS at 5 mTorr and 500-700 °C.

[1] J. Neidhardt et al., Appl. Phys. 104, 063304 (2008).

9:40am **SE+PS-TuM-6 Time-resolved Analysis of the Cathodic Arc Plasma from Nb-Al Cathodes***, S Zöhrer,* Montanuniversität Leoben, Austria*; A Anders,* Lawrence Berkeley National Laboratory, Leibniz Institute of Surface Engineering (IOM), Leipzig, Germany*; D Holec, **Robert Franz,*** Montanuniversität Leoben, Austria

Cathodic arc deposition has been established as one of the standard techniques for the physical vapour deposition of thin films and coatings as it allows the synthesis of a wide variety of materials including metallic films, but also nitrides, carbides and oxides if a reactive background gas is used. In addition, the highly ionised plasma and the achievable high deposition rates allow a variety of control mechanisms to influence the film growth while the manufacturing costs remain rather low due to the short deposition times. With the advent of multifunctional thin films and coatings, the use of multi-element cathodes providing the non-gaseous elements during the synthesis has become an industrial standard. However, a detailed understanding of the discharge properties is vital for the further optimisation of the deposition processes to enable synthesising thin films or coatings with improved properties.

By using a time-resolved method in combination with pulsed arcs and a comprehensive Nb-Al cathode model system in this work, we investigate the influence of cathode composition on the plasma, while making the influence of neutrals visible for the observed time frame. This model system consists out of three different Nb-Al compositions with the atomic ratios 75/25, 67/33 and 25/75, as well as pure Nb and Al cathodes. The results visualize ion detections of 600 µs plasma pulses, extracted 0.27 m from the cathode, resolved in mass-per-charge, energy-per-charge and time. In addition to high vacuum at a base pressure of 10^{-4} Pa, the measurements were carried out at three elevated Ar gas pressures: 0.04 Pa, 0.20 Pa and 0.40 Pa. Ion properties were generally found to be strongly dependent on the cathode material in a way that cannot be deduced by simple linear extrapolation. For high vacuum, current hypotheses in cathodic vacuum arc physics applying to multielement cathodes, like the so called "velocity rule" or the "cohesive energy rule", are tested for early and late stages of the pulse. In addition, the influence of an inert background gas is analysed by comparing the results with those at increased pressure, which show reduced ion charge states, up to a state where mostly Nb^{2+} and Al^{1+} ions are detected. Beside Nb and Al ions, time-resolved energy and charge distributions of Ar ions are taken into account, providing further insights on the processes involved.

11:00am **SE+PS-TuM-10 Dedicated Experiments to Challenge a Model for Reactive Magnetron Sputtering***, **Diederik Depla,*** Ghent University, Belgium **INVITED**

Reactive magnetron sputter deposition is conceptual easy technique which can be explained in a few lines. Behind this apparent simplicity there is a complex interplay between different plasma and surface related processes. To get a better understanding of the impact of the different process parameters, modelling is inevitable. Therefore, the paper will first focus on the RSD (Reactive Sputter Deposition) model. As this code is freely downloadable and it has a GUI, it permits not only the research team to investigate this fascinating deposition technique, but also you. Important target processes such as sputtering, chemisorption, direct and knock-on reactive ion implantation will be discussed. With the model as a guide, some important fundamental questions will be tackled. Experiments related to the transition from metallic to poisoned mode, the deposition rate during reactive sputtering, the presence of parameter hysteresis will be presented. The confrontation between model and experiment will highlight not only the success of the RSD model, but also the further challenges to improve this model, and our understanding of reactive magnetron sputtering.

11:40am **SE+PS-TuM-12 Current-voltage-time Characteristics of HiPIMS Discharges Revisited***, **André Anders**,* Leibniz Institute of Surface Engineering (IOM), Germany

Continuous discharges can be characterized by their current-voltage (*I-V*) characteristics, which expresses the quasi-steady-state plasma impedance for slowly varying parameters of the driving circuit. For fast and strongly changing conditions, the plasma impedance may become a strong function of time and therefore one needs to explicitly add time as a parameter, leading to current-voltage-time (*I-V-t*) characteristics .

This general approach is applicable to magnetron sputtering, where the magnetron's *I-V* characteristic is a power law, $I = K\ V^n$, with *K* being a device-specific constant and the power exponent *n* typically in the range from 6 to 10. For HiPIMS, the current is a strong function of time, and one needs to consider *I-V-t* characteristics [1]. In the special case when HiPIMS pulses have similar pulse shapes *I(t)* at various voltages, one may reduce the description to *peak* current - voltage characteristics and arrive again at a power law $I_p = K\ V^n$, this time with *n* in the range between 1 and 2. Most interesting, however, is the case when the *I(t)* curves are more complicated because they contain additional information. Since the appearance of publication [1] more than a decade ago we have learned a lot about HiPIMS, such as the relative importance of self-sputtering and gas recycling [2], leading to a more unified model [3]. In this contribution, *I-V-t* characteristics are revisited in light of today's knowledge.

Acknowledgments: The experimental data for this work were primarily generated during the tenure of the author at Lawrence Berkeley National Laboratory, Berkeley, California.

[1] A. Anders, J. Andersson, A. Ehiasarian, J. Appl. Phys. 102 (2007) 113303.

[2] A. Anders, J. Čapek, M. Hála, L. Martinu, J. Phys. D: Appl. Phys. 45 (2012) 012003.

[3] N. Brenning, J.T. Gudmundsson, M.A. Raadu, T.J. Petty, T. Minea, D. Lundin, Plasma Sources Sci. Technol. 26 (2017) 125003.

12:00pm **SE+PS-TuM-13 Advantages Associated with Applying a Positive Pulse Option to a HIPIMS Power Supply***, **Jason Hrebik**,* Kurt J. Lesker Company

HIPIMS is an ionized PVC technique that produces a high density, high performance films. The extreme power densities in HIPIMS create a higher ionized plasma that creates a very high energy of material being deposited onto the substrate.

Many advanced techniques have been found to further enhance the quality of HIPIMS films, creating more ideal process and applications for utilizing this technique.

We will show advantages of integrating a positive "kick" pulse into a HIPIMS application. The "kick" pulse is an ideal feature for reactive sputtering applications due to its ability to carry out the HIPIMS plasma for extended period of time, minimizing the disapperating anode effect and repelling metal ions from the plasma toward the substrate resulting in higher sputtering rates.

Surface Science Division
Room 203C - Session SS+HC+NS+PS-TuM

Controlling Mechanisms of Surface Chemical Reactions

Moderators: Bruce D. Kay, Pacific Northwest National Laboratory, Arthur Utz, Tufts University

8:00am **SS+HC+NS+PS-TuM-1 Bond Making and Bond Breaking at Wet and Dry Surfaces***, **Angelos Michaelides**,* University College London, UK **INVITED**

The making and breaking of chemical bonds at the surfaces of crystalline materials is key to an almost endless list of physical phenomena and technological processes. Increasingly computer simulation techniques are playing an important role in helping to understand such processes, acting as a complement and guide to experiments. In this talk I will discuss recent simulation work in which we are working at: (i) obtaining fundamental physical insight of chemical reactions at the surfaces of transition metal alloys; and (ii) understanding and improving the accuracy of electronic structure simulations of surface chemical processes.

8:40am **SS+HC+NS+PS-TuM-3 Stability and Reactivity of Isolated Rh_1 Atoms on Fe_3O_4(001)***, **Gareth Parkinson**,* TU Wien, Austria

In this talk I will address the thermal and chemical stability of Rh adatoms adsorbed on Fe_3O_4(001), and discuss the reactivity of these species with a view to single-atom catalysis. Using a combination of atomic-scale imaging, spectroscopies and DFT-based calculations, I will show that Rh adatoms adsorb in a bulk-continuation cation site at room temperature on Fe_3O_4(001), where they remain stable upon CO adsorption and can catalyze CO oxidation via a reaction with the support at 500 K. However, at this temperature Rh begins to incorporate within the support lattice, and the higher coordination environment significantly modifies the reactivity. In addition, I will show that Rh1 species efficiently dissociate water, leading to H spillover of H onto the support, and that Rh1 diffusion is induced upon adsorption of O_2 and NO.

9:00am **SS+HC+NS+PS-TuM-4 The Mechanism of Glaser Coupling Reactions on Ag(111) and Cu(111) Surfaces: a Case for Halogen Substituted Terminal Alkyne***, T Wang, H Lv,* University of Science and Technology of China, China*; L Feng,* University of Science and Technology of China*; J Huang, X Wu,* University of Science and Technology of China, China*; **Junfa Zhu**,* National Synchrotron Radiation Laboratory and Department of Chemical Physics, University of Science and Technology of China, China

Ullman and Glaser homo-couplings are the two most well-developed on-surface coupling reactions, which have been successfully employed to fabricate one-dimensional and two-dimensional nanostructures on metal surfaces. The mechanism towards surface-confined Ullman coupling has been well-established. However, the mechanism of surface-confined Glaser coupling has been poorly understood. In this presentation, we report our recent studies on the surface-confined Glaser coupling reactions on Ag(111) and Cu(111) using 1,1'-biphenyl,4-bromo-4'-ethynyl (BPBE) as the precursor molecule. By direct observations of alkynyl-Ag-alkynyl and alkynyl-Cu-alkynyl type organometallic intermediates on Ag(111) and Cu(111), respectively, we have proposed a reaction pathway initiated by single-molecule dehydrogenation, similar as the mechanism of on-surface Ullman coupling. The reaction processes were further explored by density functional theory based transition state calculations. Interestingly, the dehydrogenation of terminal alkyne is revealed as a H adatom-related process on Ag(111) while a Cu adatom-related process on Cu(111). After the release of interstitial metal adatoms in the organometallic intermediates, the final C-C coupling occurs easily on Ag(111), but shows extremely low efficiency on Cu(111) due to the too strong interaction between ethynylene and the Cu(111) substrate. In addition, we have demonstrated that Glaser reaction of the molecule is prior to Ullman reaction on Ag(111), which provides a promising approach of stepwise fabrication of sp-hybrid nanostructures. *This work is supported by the National Natural Science Foundation of China (21773222, 21473178) and the National Key R&D Program of China (2017YFA0403402).*

9:20am **SS+HC+NS+PS-TuM-5 Sulfur-driven Switching of the Ullmann Coupling on Au(111)***, **Jonathan Rodríguez-Fernández**, S Schmidt, J Lauritsen,* Aarhus University, Denmark

Ullmann coupling reaction has been attracted great interest in the last decades due to the advantage to build 1D-2D nanostructures from bottom-up fabrication like graphene nanoribbons, polymer, etc[1]. This reaction, it is used to generated covalent molecular linked coupling, C-C, by different halogen molecule precursors. The reaction is activated by the substrate, where the precursors will be dehalogenated. Thus, the substrate plays an important role in the success of the reactions. There are several challenges, one of them is the scaling-up production of high quality nanostructures, where defects or co-adsorbates can reduced the success of this process. It has been reported two cases, where the Ullmann coupling reaction are partially inhibited[2,3]. Here, we reported for the first time the reactivation of the reaction after inhibited on Au(111) by molecular gases[4].

In this work we describe a variable temperature Scanning tunneling microscopy (VT-STM) study that allows us to identify the switch on and off of the Ullmann coupling reaction of this molecule (2,8-Dibromodibenzothiophene) on Au(111). After low temperature deposition on pristine Au(111), the results show that surprisingly Ullmann coupling mechanism happen even at 100 K. We speculate that the modification of the herringbone reconstruction due to the strong interaction between S and Au atoms can facilitate the lifting of the Au adatoms inducing the reaction even at low temperature. On the other hand, when we firstly dose sulfur atoms on the pristine gold crystal by H_2S vapor and subsequently depositing DBDBT molecules, the Ullmann coupling reaction has been completely inhibited due to the formation of S-Au complexes, which is blocking the activation of the reaction due to the gold adatoms on the terrace and step-edges are not available. Dysprosium and Iodine atoms have reported similar partial inhibition on silver and copper, respectively. However, we are able to reactivate the reaction by removing the sulfur atoms from the substrate by exposing the sample to H_2 (gas). STM images show again the Ullmann coupling reaction has been switched on. This result shows the important of co-adsorbates on the substrate and also emphasizes the strong interaction between substrate adatoms (terraces and step edges) and the molecule precursors during the dehalogenation reaction.

[1]M. Lackinger, Chem. Commun. 53 (2017) 7872-7885.

[2]A. R. Lahrood, et. al. Chem. Commun. 51 (2015) 13301-13304.

[3]B. Cirera, J. Björk, R. Otero, J.M. Gallego, R. Miranda, D. Ecija, J. Phys. Chem. C. 121 (2017) 8033-8041.

[4]J. Rodriguez-Fernandez, S.B. Schmidt, J.V. Lauritsen, Chem. Commun. 54 (2018) 3621-3624.

9:40am **SS+HC+NS+PS-TuM-6 The Step Sites of Ultrathin ZnO Promote Methanol Oxidation to Formaldehyde***, **Xingyi Deng**, D Sorescu, J Lee,* National Energy Technology Laboratory

We investigated the adsorption and oxidation of methanol on ultrathin ZnO layers supported on Au(111) using temperature programmed reaction spectroscopy (TPRS) and density functional theory (DFT) calculations. In the TPRS experiments, we found that only molecular methanol-^{18}O desorbed from the planar ZnO bilayer surface at T = 220 K and 260 K following adsorption of methanol-^{18}O at T = 100 K, whereas a partial oxidation product, formaldehyde-^{18}O (~95% selectivity), and a small amount of carbon dioxide ($C^{16}O^{18}O$) were produced at T = 580 K at the bilayer-trilayer step sites. Computational modeling based on the DFT calculations identified the adsorption configurations of methanol on the planar ZnO surface and at the step sites, as well as the reaction pathways to gaseous formaldehyde. The most stable adsorption configuration was found to be a methanol molecule adsorbed at the bilayer-trilayer step sites with its C-O axis parallel to the upper terrace edge, forming a bond between its O atom and a Zn site on the lower terrace, and also a hydrogen bond between its H atom in the OH group and a lattice O anion at the upper terrace edge. Starting from the most stable adsorption configuration at the step sites, formation of gaseous formaldehyde was shown to take place preferentially via a methoxy (CH_3O(ad)) intermediate, following the pathways CH_3OH(ad) → CH_3O(ad) + H(ad) → CH_2O(g) + 2H(ad) with an overall barrier of 19.0 kcal/mol. Formation of CO_2 was kinetically hindered due to a much larger barrier of ~ 38 kcal/mol to produce a lattice O-bonded formaldehyde ($H_2COO_{lattice}$(ad)), the proposed precursor leading to CO_2. These computational results suggesting the preference to produce gaseous formaldehyde from methanol oxidation at the step sites agreed well with the high selectivity toward formaldehyde observed in the TPRS experiments.

11:00am **SS+HC+NS+PS-TuM-10 Investigation of Configuration Change in Water Clusters on a Bilayer ZnO Surface***, **Junseok Lee**, D Sorescu, X Deng,* National Energy Technology Laboratory

Adsorption of water on the nanostructured metal oxide surfaces has implications in catalysis and serves as a prototypical system in studying water-oxide interfaces. In many cases, the water molecules form hydrogen bonded clusters or extended networks on surfaces. On a bilayer ZnO/Au(111) surface, two types of cyclic triangular water clusters are found to be formed at a specific Moire domain. By using scanning tunneling microscopy (STM) and density functional theory (DFT) calculations, the behavior of the water clusters on the bilayer ZnO surface have been further interrogated. The configurations of the two types of cyclic water clusters can be converted to each other by the excitation from the STM tip at a threshold energy. In addition, another pathway for the cluster configuration change was identified at a higher electron energy where the cyclic water clusters could be turned into non-cyclic clusters reversibly. The physical origin of the configuration changes will be discussed.

11:20am **SS+HC+NS+PS-TuM-11 Oxygen Reduction Reaction on Fullerene***, **Yosuke Kikuchi**, J Nakamura,* The University of Electro-Communications (UEC-Tokyo), Japan

It has been reported that nitrogen-doped graphene exhibits high oxygen reduction reaction (ORR) activity, while pristine graphene does not [1]. This is because that doped-nitrogen atoms provide extra electrons to graphene, leading to the stabilization of the reaction intermediates on graphene surface. On the other hand, if curvature can be given to graphene, the chemical bond nature between carbon atoms varies from pure sp^2 to sp^3-like sp^2, and then the reactivity of graphene surface is expected to increase. In this study, we evaluated the ORR activity of fullerene as an example of carbon materials with a curvature.

We investigated the ORR activity of fullerene (C_{60}) using first-principles calculations based on the density functional theory. Electrocatalytic activities were evaluated on the basis of the computational hydrogen electrode model proposed by Nørskov *et al*. [3] We evaluated the energetics of reaction intermediates in terms of free energy of adsorption. In general, the ORR mainly proceeds in two pathways: For the two-electron pathway ($2e^-$), oxygen molecule (O_2) is reduced to hydrogen peroxide (H_2O_2), and for the direct four-electron pathway ($4e^-$), the final product is water (H_2O). H_2O_2 for the $2e^-$ pathway might corrode a carbon-based electrocatalyst material itself, causing to low durability. Therefore, we also played up the selectivity for the $4e^-$ pathway.

It was found that the fullerene molecule has ORR activity with extremely high selectivity for the four-electron pathway, even if the nitrogen atom is not doped. On the other hand, nitrogen-doped fullerene hardly shows the ORR activity, because the reaction intermediates are overstabilized by nitrogen-doping to fullerene; the maximum electrode potentials show negative values for both the direct four-electron and two-electron pathways.

[1] K. R. Lee, K. U. Lee, J. W. Lee, B. T. Ahn, S. I. Woo, Electrochem. Commun. 12, 1052 (2010)

[2] S. Ni, Z. Li, J. Yang, Nanoscale, 4, 1184 (2012)

[3] J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. Phys. Chem. B 108, 17886 (2004)

11:40am **SS+HC+NS+PS-TuM-12 Surface Structure and Reactivity of Ni-Cu Single-Atom Alloys***, **Dipna Patel**, C Sykes,* Tufts University

Ni is one of the most extensively used industrial catalytic metals. Utilized for steam reforming of hydrocarbons, Ni atom ensembles detrimentally catalyze the formation of graphitic carbon which leads to coking and deactivation of the catalyst. By alloying Ni into Cu, a catalytically less active host metal, our single-atom alloy approach has the potential to greatly enhance catalytic selectivity and reduce poisoning, analogous to other systems such as Pt-Cu and Pd-Cu. First, we report characterization of the atomic-scale surface structure and local geometry of low coverages of Ni deposited on a Cu(111) single crystal, using scanning tunneling microscopy. Near room temperature, Ni preferentially alloys into the Cu host by forming Ni rich brims along ascending step edges. Next, temperature programmed desorption studies reveal that CO binds more weakly to single Ni atoms in Cu compared to larger Ni ensembles in Ni(111) which is promising for catalytic applications in which CO poisoning is an issue. This characterization of Ni-Cu surface alloys the catalytic activity and selectivity of the surface to be correlated with the atomic-scale structure of the alloy. Using this approach, the catalytic selectivity and resilience to poisoning can be tuned via both ligand and ensemble effects.

12:00pm **SS+HC+NS+PS-TuM-13 Effective Local Structure for Bottom-up Designed ORR Catalyst Using Pyridinic Nitrogen Containing Molecules***, **Kotarou Takeyasu**, Y Shimoyama, M Furukawa, S Singh, J Nakamura,* University of Tsukuba, Japan

Nitrogen containing carbon materials have been reported to be low-cost and durable catalysts for reactions such as an oxygen reduction reaction ($O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$, ORR) in fuel cells. Among several types of nitrogen species in carbon materials, pyridinic nitrogen (nitrogen atom bound to two C atoms) was found to create ORR active sites in our previous work [1]. Recently, we also have shown that the active site is superseded by pyridinic nitrogen-containing aromatic molecules covering a carbon substrate with high density [2]. That is, bottom-up catalysts composed of pyridinic nitrogen-containing molecules and carbon supports. In the present study, we aim to investigate which local structure for pyridinic nitrogen in a molecule strongly contributes to the ORR activities and to clarify the mechanism.

For this purpose, various nitrogen-containing molecules were prepared, which were 1,10-phenanthroline, 4,7-phenanthroline, 1,7-phenanthroline, benzo[h]quinoline, phenanthridine, acridine, phenazine, quinoxaline, and dipyridophenazine. The bottom-up catalysts were prepared by simply immersing carbon black (CB) as a support material into a catalyst solution with solvent of nafion. The catalytic performances for oxygen reduction reactions (ORR) of the prepared catalysts were measured by rotating disc method in acidic electrolyte (0.1 M H_2SO_4) at a room temperature. The prepared catalysts were also evaluated by X-ray photoemission spectroscopy (XPS) and density functional calculations.

Among the molecules, 1,10-phenanthroline, quinoxaline, and dipyridophenazine on CB showed highest activities, whose onset potentials (potentials versus RHE at a current density of 10 mA cm^{-2}) were 0.29 V, 0.28

V, and 0.21 V, respectively. This tendency suggested that an 1,10-phenanthroline type local structure showed high ORR activities because quinoxaline and dipyridophenazine also contains the same local structure. XPS spectra after the superimposed voltage of 0.2 eV in an ORR condition for 1,10-phenanthroline showed two peaks corresponding to pyridinium N and pyridinic N. This also suggested that N-H…N structure promoted the following ORR reaction. The detail of the effect of the local electronic structure in the adsorbed molecules will be discussed.

References

[1] D. Guo, R. Shibuya, C. Akiba, S. Saji, T. Kondo, J. Nakamura, Science, 2016, 351, 361-365.

[2] R. Shibuya, T. Kondo, J. Nakamura, ChemCatChem, 2018

Thin Films Division

Room 104B - Session TF+AM+EM+PS-TuM

Atomic Layer Processing: Area Selective Deposition

Moderators: Christophe Vallee, LTM - MINATEC - CEA/LETI, France, Steven George, University of Colorado at Boulder

8:00am **TF+AM+EM+PS-TuM-1 New Approaches for Area-Selective Atomic Layer Deposition: Inspiration from Etching**, ***Adrie Mackus,*** Eindhoven University of Technology, The Netherlands, Nederland **INVITED**

While selectivity has always been one of the most important features of an etching process, only in recent years there has been significant interest in selectivity for deposition, motivated by the application of area-selective deposition in self-aligned fabrication. With selective etching being a more mature technology, previous work in etching can serve as inspiration for how to make deposition processes selective. For example, inhibition layers have been employed in etching to obtain selectivity. Similarly, the use of small molecule inhibitors is currently being explored for achieving area-selective atomic layer deposition (ALD).[1]

Moreover, with the recent advancements in atomic layer etching (ALE), new opportunities emerge for selective processing of material based on novel combinations of ALD and ALE. In recent work, ALE cycles have been implemented in area-selective ALD processes to improve the selectivity.[2]

In this presentation, the similarities between etching and area-selective ALD will be described, in order to discuss what the area-selective ALD community can learn from previous work in etching. Recent developments in area-selective ALD will be illustrated by discussing new area-selective ALD approaches based on the use of inhibitors in ABC-type (i.e. three-step) ALD cycles, and on supercycles combining ALD and ALE cycles.

1. A. Mameli, M.J.M. Merkx, B. Karasulu, F. Roozeboom, W.M.M. Kessels, and A.J.M. Mackus, *ACS Nano* **11**, 9303 (2017)

2. R. Vallat, R. Gassiloud, B. Eychenne, and C. Vallée, *J. Vac. Sci. Technol. A.***35**, O1B104 (2017)

8:40am **TF+AM+EM+PS-TuM-3 Nucleation of HfO_2 on Si, SiO_2 and TiN Substrates in PE-ALD Processes Investigated by In situ Ellipsometry and Optical Emission Specroscopy (OES)**, ***Marceline Bonvalot,*** *S belahcen, V Pesce, A Chaker, P Gonon, C Vallée, A Bsiesy,* LTM, Univ. Grenoble Alpes, CEA-LETI, France

It is generally admitted that the physical properties of ultrathin layers elaborated by ALD processes are strongly dependent upon the very initial stages of layer growth, defined as the nucleation step. This nucleation step may for instance affect the cristallinity and the texturation of the material when growing in a crystalline state, it can also significantly contribute to the sharpness of the interface between the substrate and the growing material and/or determine the layer density and surface rugosity. Moreover, this nucleation step also plays a major role in the advancement of Selective Area Deposition Processes (SALD), which are considered, as of today, as a very promising approach for the development of bottom-up routes alternative to increasingly expenseive thin layer patterning processes. In these regards, a good knowledge of the phenomena affecting the nucleation mechanisms in ALD is required.

In this work, the initial stages of layer growth has been investigated during the deposition of HfO_2 by Plasma-Enhanced ALD in a FlexAL set-up equipped with an ALE (Atomic Layer Etching) bias system developed by Oxford. Four types of substrates have been put on trial for this purpose, namely, HF last treated Si(100), SiO_2 (45 nm dry oxide)/Si, SiO_2 (500 nm wet oxide)/Si, and TiN (15 nm ALD)/Si. Several in situ surface treatments have been applied on these substrates, prior to HfO_2 ALD cycles with TEMAH as hafnium precursor. They include exposure to a plasma treatment composed of either Ar, CF_4 and O_2 or any mixture of these gases. A very low power (1-10 W) can be applied on the substrate to allow low DC self-bias voltage, which determines energies of ions extracted from the plasma in the vicinity of the substrate. This bias in turn allows an estimation of the contribution of both chemical and physical plasma-surface interactions to the growth mechanism. The nucleation process is followed in situ by spectroscopic ellipsometry assisted by Optical Emission Spectroscopy for the identification of plasma active species and desorbed by-products.

This presentation will describe how the nucleation time on different substrates can be successfully tuned, either delayed or accelerated, thanks to appropriate in situ surface treatment parameters, without inducing any significant perturbation in the subsequent steady state layer growth. These results will be discussed in view of literature data and potential applications to the development of selective ALD.

9:00am **TF+AM+EM+PS-TuM-4 Topographical Selectivity with BN Electron-Enhanced ALD**, ***Jaclyn Sprenger,*** *A Cavanagh, H Sun,* University of Colorado at Boulder*; A Roshko, P Blanchard,* National Institute of Standards and Technology*; S George,* University of Colorado at Boulder

Electron-enhanced atomic layer deposition (EE-ALD) is a new growth technique using sequential self-limiting exposures of electrons and precursor. The electrons produce dangling bonds at the surface through the process of electron stimulated desorption (ESD). The dangling bonds then facilitate the adsorption of precursor resulting in film growth. Because the electron flux is directional, EE-ALD can be used for selective area deposition. For portions of the sample that are masked from the e^--beam, no dangling bonds are produced and no film growth occurs. Additionally, any portion of the surface that is parallel to the e^--beam, e.g. the walls of a trench, may be considered topographically masked because the e^--beam is not incident on the surface.

The topographically selective area deposition by EE-ALD was investigated by depositing boron nitride (BN) EE-ALD films on a trench structure. EE-ALD of BN has been demonstrated using sequential exposures of borazine ($B_3N_3H_6$) and electrons (50-450 eV) at room temperature [1]. GaN [2] and Si [3] have also been deposited earlier using EE-ALD. The topographical selectivity was investigated by growing an EE-ALD BN film on a trench structure. On the vertical walls of a trench structure, aligned parallel to the e^--beam, there should be no electron flux and no film. In contrast, the top and bottom of the trench will receive the full flux of the e^--beam. To test these ideas, high resolution TEM images were recorded after 1000 cycles of BN EE-ALD on a trench structure.

BN films were observed on the top and bottom of the trench. For the trenches used in this study, the side walls were not vertical. Some BN film deposition did occur on these sidewalls, but at a lower growth rate than the horizontal surfaces at the top and bottom of the trench. The electron flux on the side walls was reduced by a factor of cos θ where θ is the angle between the surface normal of trench wall and the e^--beam. Incorporating the reduced electron flux into the model for EE-ALD film growth showed excellent agreement with film thicknesses observed on the trench walls. The topographic selectivity of EE-ALD, demonstrated with BN, coupled with a metal chemistry, would offer a promising solution to challenges such as the bottom-up-fill of conductors in trenches or vias.

[1] J. K. Sprenger, H. Sun, A. S. Cavanagh, A. Roshko, P. T. Blanchard and S. M. George, J. Phys. Chem. C. DOI: 10.1021/acs.jpcc.8b00796 (2018).

[2] J.K. Sprenger, A.S. Cavanagh, H. Sun, K.J. Wahl, A. Roshko and S.M. George, Chem. Mater. 28, 5282 (2016).

[3] J.K. Sprenger, A.S. Cavanagh, H. Sun, and S.M. George, J. Vac. Sci. Technol. A. 36, 01A118 (2018).

9:20am **TF+AM+EM+PS-TuM-5 Optimization by In situ Ellipsometry of ALD and ALE Successive Steps for the Selective Atomic Layer Deposition of Ta_2O_5 on TiN and Si.**, ***Vincent Pesce,*** *C Vallée,* LTM, Univ. Grenoble Alpes, CEA-LETI, France*; R Gassilloud,* Cea Leti, France*; A Chaker, M Bonvalot, B Pelissier,* LTM, Univ. Grenoble Alpes, CEA-LETI, France*; P Nicolas,* Cea, France*; A Bsiesy,* LTM, Univ. Grenoble Alpes, CEA-LETI, France

The drastic reduction of microelectronic device dimensions, traditionally achieved through a photolithography process, requires more and more stringent process conditions in this top-down approach. Recent developments in atomic layer deposition processes (ALD) have shown that a new bottom-up approach is possible by the combination of ALD and Atomic Layer Etching (ALE) steps for the selective growth on patterned surfaces [1]. Indeed, it has been shown that the nucleation kinetics in the initial stages of a deposition process is strongly dependent on the chemical state of substrate surfaces. Thus, different nucleation delays can be achieved on patterned substrates, leading to significant variation of thickness in spite of a similar growth rate after nucleation (in the steady state). Prior to precursor deposition, a first step is carried out, which activates or inhibits nucleation sites on patterned substrates. For instance, an O_2/CF_4 plasma treatment leads to the formation of a fluorocarbon polymer, whose thickness depends on the chemistry of the surface: its thickness may be less on Si as compared to TiN, because SiF_4 molecules are more volatile than their TiF_4 counterparts. In turn, this CF_x rich layer can serve as a passivation layer to alter the nucleation sites during the subsequent deposition process. Similarly, an oxidation plasma treatment serves to activate nucleation sites through the formation of metal-oxygen bonds on the patterned substrate, which in turn favors an immediate growth during deposition process.

In this work, we have investigated the impact of both chemical and physical surface interactions during the deposition of Ta_2O_5 in a PE-ALD process. These investigations have been carried out in a FlexAL PEALD tool equipped with an ALE bias system developed by Oxford. A selective deposition super cycle has been defined, which consists in alternating a CF_4 plasma treatment with a Ta_2O_5 ALD deposition cycle with an O_2 plasma as oxidation step. In situ ellipsometry measurements have been used to investigate the impact of ion bombardement and the CF_x layer growth during the optimization of the ALE parameters.

These measurements have been correlated to ex situ XRR and XPS to confirm the thickness on both Si and TiN substrates and analyze the chemistry of the different layers or interfaces.

[1] R. Vallat et al. "Selective deposition of Ta_2O_5 by adding plasma etching super-cycles in plasma enhanced atomic layer deposition steps." *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* 35.1 (2017): 01B104. (DOI: 10.1116/1.4965966)

9:40am **TF+AM+EM+PS-TuM-6 ALD and PEALD of ZnO on MoS_2 and WSe_2**, ***Timothy N. Walter***[1], *S Lee,* The Pennsylvania State Univeristy*; M Chubarov,* The Pennsylvania State University*; X Zhang,* The Pennsylvania State Univeristy*; T Choudhury, J Redwing,* The Pennsylvania State University*; T Jackson, S Mohney,* The Pennsylvania State Univeristy

Inducing nucleation on the inherently passivated surfaces of 2D materials such as transition metal dichalcogenides (TMDs) can be challenging for atomic layer deposition (ALD); however, this situation also presents an opportunity for selective growth by ALD. Additionally, ZnO/TMD heterojunctions have favorable band alignments for catalysis and offer possibilities for nanoscale electronic devices including transparent electronics, photodiodes, and piezo-phototronics. This work explores the growth of ZnO on the TMDs MoS_2 and WSe_2 using thermal ALD, thermal ALD with UV-O_3 surface pre-treatment, and plasma enhanced ALD (PEALD). Depositions were performed on both few-layer exfoliated flakes and coalesced single-layer films (with scattered 2- or 3-layer islands) that were already grown by gas source chemical vapor deposition (CVD). Samples were characterized by atomic force microscopy (AFM), Raman spectroscopy, photoluminescence (PL), and X-ray photoelectron spectroscopy (XPS) before and after deposition of ZnO. For both MoS_2 and WSe_2, thermal ALD of ZnO using diethyl zinc (DEZ) and water at 125 °C resulted in a long nucleation delay on the TMD surfaces, showing selectivity against ZnO growth on TMDs compared to the surrounding SiO_2/Si substrate. Even after hundreds of cycles, very little change was detected by XPS, Raman spectroscopy, or AFM; however, nucleation did occur at defects and caused surface roughness to increase. UV-O_3 pre-treatment before thermal ALD yielded different results on MoS_2 compared to WSe_2. UV-O_3 functionalizes MoS_2 for nucleation and subsequent growth of ZnO without destroying the underlying MoS_2; however, UV-O_3 fully oxidized regions of the WSe_2 surface and promoted nucleation. PEALD using DEZ and N_2O on both TMDs resulted in a conformal and smooth film, but it oxidized the top layer of the TMDs according to XPS. In conclusion, UV-O_3 pre-treatment and plasma-enhanced deposition allow for nucleation and growth of ZnO on TMD substrates, sometimes to the detriment of the top layer of material; however, the planar surfaces of 2D materials resist nucleation for hundreds of cycles of thermal ALD.

11:00am **TF+AM+EM+PS-TuM-10 From Fundamental Insights into Growth and Nucleation Mechanisms to Area-selective Deposition***, **Annelies Delabie**,* IMEC & KU Leuven, Belgium*; J Soethoudt,* KU Leuven, Belgium*; G Pourtois, S Van Elshocht, K Barla,* Imec, Belgium*; F Grillo, E Marques, R van Ommen,* TU Delft, Netherlands **INVITED**

Area-selective deposition holds the potential to build structures from the bottom up, only where needed, with atomic precision. It is gaining importance for manufacturing of nano-electronic devices as it enables self-aligned deposition for accurate pattern placement and bottom-up deposition in trenches or holes. It can simplify complex integration flows and implies significant cost reduction. The key to area-selective deposition is surface chemistry, as it is based on the surface dependence of deposition techniques like chemical vapor deposition (CVD) and atomic layer deposition (ALD). Today, however, only few industrial processes make use of area-selective deposition, mainly because only few materials can be deposited with sufficient selectivity. In addition, defectivity is a great challenge, as substrate inhibition is often associated with island growth. Detailed insights into the surface chemistry and nucleation mechanisms is essential, as this insight can be used to expand the material combinations accessible by area-selective deposition, as well as to design defect removal strategies. Finally, area-selective deposition is affected by patterning due to changes in surface composition and/or due to diffusion. This illustrates the need for understanding and optimization of the processes in patterns with relevant dimensions. In this work, we review our current understanding of the inherent surface dependence of ALD processes. We show how insight into the growth and nucleation mechanisms of ALD can be applied to enable area-selective deposition with defect removal solutions.

11:40am **TF+AM+EM+PS-TuM-12 DETA SAMs as ALD Ru Inhibitor for Area-selective Bottom-up Interconnects***, **Ivan Zyulkov**,* IMEC & KU Leuven*; S Armini,* IMEC, Belgium*; S De Gendt,* IMEC, KU Leuven, Belgium

Replacement of Cu interconnects by an alternative metal will be required beyond 32 nm metal pitch in order to decrease the metal line resistance and prevent IC failure due to the Cu electromigration. Based on recent studies, Ru has several advantages when compared to Cu, which make it an attractive candidate for the Cu replacement: i) lower thickness dependence of the resistivity due to a short electron mean free path (6.6/4.9 nm for Ru vs 39.9 nm for Cu), ii) higher melting temperature (2334 ºC for Ru vs 1032 ºC for Cu) which represents better Ru resistance to electromighration and iii) possibility of integration without a diffusion barrier, resulting in a larger effective metal area. However, conventional electrochemical and electroless deposition methods used in IC manufacturing are not available for the Ru metallization. Additionally, downscaling of the metal structures down to 10 nm causes metal lines filling issues even using conformal ALD, since seams are likely to be formed due to trench pinch-off. As a solution, area selective deposition (ASD) can be exploited, allowing bottom-up and void-free filling of high aspect ratio structures. In addition, ASD of Ru can find application in advanced patterning schemes.

This work is focused on ASD of Ru in a via area of the interconnect structure. In this case ALD selectivity to metallic via bottom (underlying metal line) should be achieved with respect to organosilicate glass (OSG) via sidewalls. In this work, thermal ALD Ru using an ethylbenzene-ethyleyelohexadiene (EBECHRu) precursor with O_2 co-reactant was used. The precursor molecule has ethyl-cyclohexadienyl ligands, which are expected to show a preferential interaction/ inhibition with specific surface groups. In order to passivate the hydroxy-terminated OSG sidewalls against the Ru deposition different siloxane derived self-assembled monolayers (SAMs) were used. According to RBS and SEM analysis, (3-trimethoxysilylpropyl)diethylenetriamine (DETA) SAMs provide more than 300 cycles inhibition of the ALD Ru growth on Si oxide and OSG. XPS, FTIR and spectroscopic ellipsometry on the SAM film before and after ALD are compared in order to identify relevant selectivity mechanisms. In order to prevent DETA passivation of the Cu interface where ALD Ru is expected to grow for the bottom-up via fill, undecanethiol (UDT) SAMs were used as a selective sacrificial Cu protection before the DETA deposition. The thiol SAMs can be removed from the Cu surface at 250 ºC while silane (DETA) is stable on the dielectric surface at temperatures above 350 ºC and higher. The double SAM and area selective bottom-up ALD Ru tested in 45 nm half-pitch lines will be presented.

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[1] **TFD James Harper Award Finalist**

Plasma Science and Technology Division
Room 104A - Session PS+EM+NS+SS-TuA

Plasma Processing of Challenging Materials - II

Moderators: Michael Gordon, University of California at Santa Barbara, Wei Tian, Applied Materials Inc.

2:20pm **PS+EM+NS+SS-TuA-1 Self-limiting Growth of III-nitride Materials via Hollow-cathode Plasma-ALD: Structural and Chemical Analysis*, Necmi Biyikli,* *A Mohammad, D Shukla,* University of Connecticut **INVITED**

Plasma-assisted/enhanced atomic layer deposition (PALD) provides an alternative route for the low-temperature synthesis of III-nitride thin films with sub-monolayer precision thickness control, ultimate three-dimensional conformality, and large-area uniformity. On the other hand, PALD synthesis of AlN, GaN, and InN films required relatively long plasma co-reactant exposure durations (40 - 120 sec) to achieve self-limiting surface saturation with minimal carbon impurities which directly correlates the effectiveness of the ligand-removal process. During such extensive plasma half-cycles, the plasma source itself is exposed to elevated temperatures and along with energetic hydrogen radicals, which resulted in etching of conventional quartz-based inductively coupled plasma (ICP) sources. We have mitigated this problem by using a stainless-steel based capacitively-coupled hollow-cathode plasma (HCP) source, which reduced the oxygen impurity levels at least two orders of magnitude in GaN films while increasing the average film grain/crystallite size of AlN films by one order of magnitude.

Using HCP-assisted ALD (HCP-ALD), we have grown the entire III-nitride wide bandgap semiconductor family (AlN, GaN, InN) at ≤200°C substrate temperatures with single-phase hexagonal poly-crystalline material quality. However, there is still plenty of room and need for improvement in material properties before we can use these layers as active device layers. A careful systematic study needs to be carried out to achieve device quality III-nitride films via HCP-ALD. In this talk, we will present an overview of our HCP-ALD efforts including our recent materials characterization results obtained with a custom-design HCP-ALD reactor. A particular focus will be devoted to the structural and chemical properties of the III-nitride films and how they correlate with reactor parameters and plasma conditions.

3:00pm **PS+EM+NS+SS-TuA-3 Electrostatic Charge of Solution-droplet in Plasma-coupled Micro Reactor*, Tae Hwan Kim,*** *S Lee,* National Fusion Research Institute, Republic of Korea

Plasma-liquid interaction research has increased because of emerging technological applications such as material synthesis, plasma bio-applications, environmental applications, and agriculture/food applications. Recently, an important scientific breakthrough in the understanding of the liquid reaction at the plasma-liquid interface that an electron transfer reaction at the plasma-liquid interface that leads to electrochemical reactions, which is referred to as the plasma electrochemical reaction [1]. Further evidence of plasma electron reaction (PER) was observed that the electrons in plasma can be solvated in a plasma electrochemical system [2].

In this talk, we present a new reaction pathway in which plasma-liquid interaction can cause an electrostatic charge in a liquid and the electrostatically charged solution can produce an electrochemical reaction. The experiments were performed with our newly designed plasma-coupled-microreactor (PCM), which can control the ambient gas and initiate a rapid plasma electrochemical reaction. Helium(He)-droplets and liquid-droplets were formed, and microplasma-droplets were ignited by dielectric barrier discharge (DBD). The generated microplasma-droplet can induce not only PER but also an electrostatic charge in a solution. The charge of the solution by microplasma-droplet and liquid-droplet interaction can be affected by the type and amount of stabilizer, the acidity of the solution, and the length of the electrodes used to form microplasma-droplets.

[1] C. Richmonds, M. Witzke, B. Bartling, S. W. Lee, J. Wainright, C. Liu, R. Mohan Sankaran, Electron-Transfer Reactions at the Plasma-Liquid Interface. J. Am. Chem. Soc. 133, 17582-17585 (2011)

[2] P. Rumbach, David M. Bartels, R. Mohan Sankaran, David B. Go, The solvation of electrons by an atmospheric-pressure plasma. Nat. Commun. 6, 7248 (2015).

3:20pm **PS+EM+NS+SS-TuA-4 Surfactant-free and Stable Colloidal Metal Oxide Ultra-small Quantum Dots via Plasma-liquid Electrochemistry*, Dillibabu Padmanaban,*** *D Carolan, R McGlynn, T Velusamy, P Maguire, D Mariotti,* Nanotechnology & Integrated Bio-Engineering Centre, Ulster University, UK

Metal oxides are materials of great importance and interest with exceptional chemical stability, tunable optical and electrical properties and, importantly, meeting cost and environmental requirements for a sustainable future. For these reasons metal oxides nanoparticles are being investigated for a very wide range of applications that include energy harvesting and solar conversion and for exploiting nanoscale effects. However, due to synthesis challenges, the properties of ultra-small and quantum confined metal oxide nanoparticles, or quantum dots (QDs), are still very little understood while expected to offer exciting opportunities. Here we demonstrate that the synthesis of metal oxide QDs can be achieved by plasma-liquid electrochemistry with exceptional control of the size distribution even for particles well below 2 nm in diameter. Plasma-induced chemistry initiated at the plasma-liquid interface allows for rapid and simple production of highly stable colloidal suspension in ethanol of surfactant free metal oxide QDs, where a solid metal foil acts as the metal precursor. We provide an overview of these capabilities for a range of metal oxides that include Cu, Ni, Co, Mo and Zn oxides. We then study in detail the synthesis mechanisms leading to cupric oxide (CuO) QDs providing a range of experimental evidence that clarifies chemical reaction pathways due to the plasma interacting with ethanol. For a better understanding of the plasma chemistry, the process was also studied with different electrodes so to assess the impact of QDs formation in the overall plasma-ethanol chemistry. We have carried out extensive material characterization for the QDs and we have also analysed liquid products at different conditions by Fourier transform infrared spectroscopy, ultraviolet-visible spectroscopy, nuclear magnetic resonance, mass-spectroscopy etc. Our work points at the role of different species in the synthesis of QDs. We believe that some of these chemical pathways may be general and applicable to the formation of other metal oxide QDs, however in some cases (e.g. for Mo-oxide) we expect some deviations. Overall our work discloses important general aspects of plasma-liquid interactions, in particular when ethanol is used. The study of the properties of our metal-oxide QDs uncovers quantum confinement effects that can become particularly useful in many application and suggest exciting opportunities in the control of defects and achieving phases that are difficult to produce with other methods.

4:20pm **PS+EM+NS+SS-TuA-7 From Organometallic Precursors to Bimetallic Nanocatalysts using Atmospheric-pressure Plasma Processes*, Joffrey Baneton,*** *J Mertens, M Smiljanic, S Cauchies, T Segato,* Université Libre de Bruxelles, Belgium*; Y Busby,* Université de Namur, Belgium*; G Caldarella,* Université de Liège, Belgium*; V Debaille, S Godet,* Université Libre de Bruxelles, Belgium*; J Pireaux,* Université de Namur, Belgium*; N Job,* Université de Liège, Belgium*; M Gordon,* University of California at Santa Barbara*; M Sankaran,* Case Western Reserve University*; F Reniers,* Université Libre de Bruxelles, Belgium

Developing new technologies to produce energy while respecting the environment is one of the important challenges in materials science. One of the possible routes is the use of hydrogen fuel cells. Unfortunately, some limitations remain such as the electrocatalysis of the reduction of dioxygen which requires a rare and expensive metal: platinum [1]. Therefore, minimizing its amount at the cathode while maximizing its accessibility, electroactivity and stability constitutes one of the main goal of current research. An interesting way consists in the synthesis of platinum-based alloys. Indeed, it is well known in the literature that combining two metals leads to the production of durable materials with higher activity [2].

Different routes can lead to the formation of bimetallic nanostructures including wet-chemistry, ultrasound processes or thermal evaporation. In this catalogue of methods, atmospheric-pressure plasma techniques are very attractive due to their versatility, rapidity and ease of use. In the present research, two different kinds of reactors, a microplasma device [3] and radio-frequency plasma torch [4], have been used to study the synthesis of bimetallic nanoparticles from acetylacetonate precursors. A complete chemical and morphological characterization is provided thanks to the combined use of X-ray photoelectron spectroscopy, transmission electron microscopy, UV-visible spectroscopy and X-ray crystallography.

Different experimental parameters can play a crucial role is the reduction process of the organometallic precursors. For example, concerning the microplasma system, the initial concentrations have a direct influence on the size distribution and agglomeration while, concerning the RF plasma torch treatment, the nature of the plasma gas mixture can limit the production of nanoparticles or favor their anchoring at the surface of a carbon support [5]. After optimization of the processes, electrochemical measurements were conducted to evaluate their activity, stability and performances as catalysts for hydrogen fuel cells.

The authors would like to thank the Walloon Region (HYLIFE project n°1410135, Energinsere program) for the financial support.

[1] F. Maillard et al. In: Carbon materials for catalysis (**2009**), 429-480.

[2] Z. Li et al. Int. J. of Hydrogen Energy (**2012**), 37, 14152–14160.

[3] C. De Vos et al. J. Phys. D: Appl. Phys. (**2017**), 50, 105206.

[4] D. Merche et al. Plasma Process. Polym. (**2016**), 13, 91–104.

[5] A. Felten et al. J. Phys. D: Appl. Phys. (**2007**), 40, 7379.

4:40pm **PS+EM+NS+SS-TuA-8 Synthesis of Hydrogenated Amorphous Carbon Nanoparticles using High-Pressure CH_4+Ar Plasmas and Their Deposition**, ***Kazunori Koga***, *S Hwang, K Kamataki, N Itagaki,* Kyushu University, Japan*; T Nakatani,* Okayama University of Science, Japan*; M Shiratani,* Kyushu University, Japan

Nanostructure fabrication such as nanoparticles through bottom-up processes is important in nanotechnologies due to their size-related properties [1]. Plasma is a powerful tool to produce nanoparticles. To control their size, pulsed discharge plasmas are commonly employed, but the plasmas have the limitation of the throughput. To realize continuous production, we have developed a multi-hollow discharge plasma chemical vapor deposition (MHDPCVD) method. We have succeeded in producing crystalline Si nanoparticles of 2 nm in size using hydrogen diluted silane plasmas [2, 3]. Here we applied the method to synthesis carbon nanoparticles. The experiments are carried out by CH_4+Ar MHDPCVD. CH_4 and Ar were injected into the reactor, flowed through hollows of 5 mm in diameter in the electrode. The gas flow rate ratio of CH_4 and Ar was 1:6. The total gas flow rate was 10 to 200 sccm . The pressure was kept at 2 Torr. Discharges were generated in hollows by applying rf power of 40 W at 13.56 MHz. Nanoparticles are nucleated and grow in the discharges. They are transported outside of the discharges by the fast gas flow and the growth of the nanoparticles are stopped. They deposited on TEM mesh grids set on the substrate holder 50 mm far from the electrode. From TEM measurements, spherical nanoparticles were deposited on the grid. The mean size decreases from 270 nm for 10 sccm to 20 nm for 120 sccm . The gas residence time for 120 sccm is 1/12 of that for 10 sccm . The size for 120 sccm is 1/13.5 of that for 10 sccm . The results indicate that the size of carbon nanoparticles are controlled by gas residence time of nanoparticles in plasmas. Above 125 sccm, No nanoparticle is observed on the TEM mesh. It suggests that deposition of nanoparticles depends on gas flow velocity and direction on the substrate.

[1] M. Shiratani, et al., J. Phys. D 44 (2011) 174038.

[2] T. Kakeya, et al., Thin Solid Films 506 (2006) 288.

[3] K. Koga et al., ECS Transactions 77 (2017) 17.

5:00pm **PS+EM+NS+SS-TuA-9 Antimony-doped Tin Oxide Nanocrystals Synthesized by Low Temperature Plasma**, ***Qinyi Chen***, *E Thimsen,* Washington University in St. Louis

For electrochemical applications, metal-oxide materials are attractive as electrodes for reactions occurring at positive potentials in the presence of water. Often, these metal-oxide materials function as an electrically-conductive support for a noble metal catalyst, and therefore must have very high specific surface area. Among conductive metal-oxide materials, antimony-doped tin oxide (ATO) stands out with its combination of: 1) high chemical stability over a wide range of pH values and reduction potentials, 2) high electrical conductivity, and 3) abundant constituent elements. Synthesis of ATO nanocrystals has been developed in liquid phase using sol-gel and colloidal methods. However, post-synthesis heat treatments are required to activate the electron donors and increase the conductivity of ATO nanocrystal assemblies prepared using liquid-phase techniques, which may adversely affect the surface area and pore structure of the material. In this work, we report on our efforts to synthesize monodispersed, conductive ATO nanocrystals through a single-step low temperature plasma growth method without any post treatments. Precursor vapors of tin and antimony were fed into a radiofrequency, flow-through low temperature plasma reactor. The precursor vapors reacted to nucleate ATO nanocrystals. Thin films comprised of ATO nanocrystals were then immediately deposited by supersonic impact deposition of the aerosol resulting from plasma synthesis. The resulting materials were characterized by a variety of methods to determine film thickness, porosity, nanocrystal size, and elemental composition. Local electron concentration and mobility within the nanocrystals were assessed by Fourier-transform infrared absorption spectroscopy. Hall effect was used to characterize longitudinal electrical transport in the film. The nanocrystal growth mechanism in the plasma will be discussed with a focus on antimony dopant incorporation. The effects of nanocrystal size on the transport properties of ATO thin films will be presented.

5:20pm **PS+EM+NS+SS-TuA-10 Femtosecond Laser Texturing of Plasma-immersed Ti to Create TiN**, ***Chisung Ahn***, *E Barlaz, D Ruzic,* University of Illinois at Urbana-Champaign

Pulsed femtosecond lasers have been used as a functionalization method for metal surfaces due to their ability to produce nanostructures uniformly with easily controlled user inputs such as spot size and exposure repetition. Laser assisted nitriding of Ti in ambient nitrogen has previously been demonstrated in our group to significantly reduce native oxides. A major challenge to the current process is the limited ability of the laser to produce nitrogen radicals.

In this study, we investigate the effects of increased nitrogen radical concentration on surface topography and chemical composition for textured Ti metal. A secondary DC plasma is generated along the path length of the laser close to the sample surface in ambient nitrogen and under vacuum. The surface topography and chemical compositions of the resultant Ti coupons are analyzed by SEM and XPS respectively. Changes to hydrophilicity are quantified using contact angle measurements.

5:40pm **PS+EM+NS+SS-TuA-11 Modeling Chemical Reactions in Contact Glow Discharge Electrolysis**, ***Bocong Zheng***, *M Shrestha, K Wang, T Schuelke, Q Fan,* Michigan State University

Contact glow discharge electrolysis is becoming attractive for nanomaterials manufacturing and surface engineering. In this discharge electrolysis, an electrode is submerged in a liquid electrolyte and a plasma is formed in a vapor layer around the electrode. The process combines the characteristics of electrolysis and plasma discharges, creating high-energy-density plasmas that lead to intensive physical processes and chemical reactions on the working electrode. The authors have found that the physical processes and the chemical reactions could be decoupled under certain conditions. In that case, a textured electrode surface could be created through a chemical-reaction-dominated process instead of an irregular porous surface produced by the physical-reaction-dominated interactions. The mechanisms are not clearly understood yet. This study aims to elucidate the plasma characteristics and the chemical reactions in contact glow plasma electrolysis. A plasma fluid model is established to predict the discharge process with constraint conditions obtained from the experiments. The modeling reveals that the plasma is highly electronegative, and the dominant neutral species are H_2 and O_2 dissociated from water vapor. The formation of textured surface is attributed to the anisotropic chemical etching by the reactive species generated in the plasmas.

6:00pm **PS+EM+NS+SS-TuA-12 Effects of Light Ion Beam Irradiation in Plasma Etching Processes**, ***Kazuhiro Karahashi***, *T Ito, H Li, M Isobe, K Mizotani, S Shigeno,* Osaka University, Japan*; M Fukasawa, A Hirata, T Tatsumi,* Sony Semiconductor Solutions Corporation, Japan*; S Hamaguch,* Osaka University, Japan

Gases containing hydrogen are widely used in microfabrication processes of electronic devices using plasma etching. For example, HBr gas is used for silicon etching, hydrofluorocarbon gases are used for silicon oxide etching, and Hydrocarbon-based non-corrosive gases are used for transparent conducing oxides etching. Unlike other atoms, hydrogen is lighter in weight, smaller in atomic radius, and chemically reactive, so it has various effects in the etching process. In order to precisely control the etching reaction and realize nanometer order microfabrication processes, it is necessary to clarify the effect of hydrogen. In this study, by comparing various effects on etching processes between hydrogen and helium incident ions using molecular dynamics (MD) simulation and ion beam experiments, physical and chemical effects by such light ion injection on etching processes were evaluated.

We have shown in this study based on MD simulation and ion beam experiments that, when a Si surface exposed to an O radical flux is simultaneously irradiated by an H^+ or He^+ ion beam, diffusion of oxygen atoms into the Si film is promoted. Since the enhanced diffusion occurs in a similar manner in both cases of H^+ and He^+ ion injections, it is clear that the enhanced diffusion is essentially caused by knock-on effects by incident light ions. On the other hand, in the case of etching of ZnO, which is an ionic crystal, our beam experiments have shown that its crystal size decreases by light ion irradiation using in-plane X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM) measurements. The reduction of grain sizes seems correlated with the reduction of the physical sputtering yield of the ZnO film.

The results above show the following two physical effects by irradiation of a substrate with light ions such as H^+ and He^+ ;1) enhancement of diffusion of heavy atoms deposited on the substrate surface into it's the bulk of the film and 2) decrease of grain sized of ionic crystalline substrate due to amorphization and recrystallization. The decrease of grain sizes, which induce the increase in grain boundary areas may contribute to an increase in sputtering yield of the substrate.

Plasma Science and Technology Division
Room 104C - Session PS+PB+SE-TuA

Atmospheric Pressure Plasmas

Moderators: Francois Reniers, Université libre de Bruxelles, Steven Vitale, MIT Lincoln Laboratory

2:20pm **PS+PB+SE-TuA-1 Compact, Low Cost Atmospheric Pressure Plasma Jets Driven by Piezoelectric Transformers***, **Michael Johnson**,* National Research Council*; D Boris, L Petrova, S Walton,* Naval Research Laboratory

In order for non-thermal atmospheric pressure plasma technology to be used for applications outside of the laboratory, there is a need to develop low-cost, portable devices that can be used for applications in the field. Constructing portable power supplies that can produce stable, non-thermal plasmas in full density air can be challenging as large electric fields are required to generate breakdown. Piezoelectric transformers are solid state transformers that can produce large gains in voltage, which makes them attractive candidates for plasma production. In this work, a piezoelectric transformer is used to amplify a low voltage AC signal in order to produce an atmospheric pressure plasma jet. Using this approach, plasma jets were generated with input voltages as low as 10 V when the piezoelectric transformer was operated at its resonance frequency (≈ 88 kHz). The electrical and optical characteristics of the piezoelectric driven plasma jet was compared to a plasma jet produced using a conventional high voltage sinewave of comparable operating frequency. Both jets were examined in helium and argon for a variety of different flow rates and operating voltages. The length of the jets were measured to determine if the piezoelectric transformer limited the potential size of the plasma jet. The current carried by the plasma jets were measured along with optical emission spectroscopy to examine the relative characteristics of the jets. Together, the results suggest the piezoelectric material may have influence beyond simple voltage amplification.

This work was supported by the Naval Research Laboratory Base Program. This research was performed while Michael Johnson held an NRC Research Associateship award at the U.S. Naval Research Laboratory.

2:40pm **PS+PB+SE-TuA-2 Process Regimes of Atmospheric Pressure Plasma-enhanced Chemical Vapor Deposition with Source Materials Highly Diluted in Inert Gases***, **SeungJae Baik**, J Jang,* Hankyong National University, Republic of Korea*; H Oh,* Yonsei University, Republic of Korea

Plasma-enhanced chemical vapor deposition (CVD) is appropriate for fast deposition with moderate film quality, but to form high quality materials such as epitaxial thin films, thermal processes at higher temperature are more favorable. High energy particles that are statistically produced in plasma processes are sources of film quality degradation. It has been previously reported that the plasma process at high working pressure, e.g., atmospheric pressure is feasible for epitaxial Si growth; where source gas species are highly diluted in inert gas. Employing a large dilution of source materials opens a new process regime in plasma-enhanced CVD: (1) low damage plasma processing (2) high deposition rate process with controlled powder generation (3) efficient usage of source materials.

We have performed Si thin film deposition processes with silane and hydrogen as source materials highly diluted in He or Ar gases under working pressure close to the atmospheric pressure (up to 700 torr). The new process regimes showing low damage plasma processing, high deposition rate with controlled powder generation, and efficient usage of source materials are experimentally demonstrated in various process conditions. In addition, the impurity incorporation into the film during deposition processes degrades the crytalline quality of the deposited Si thin films, which can be improved by employing plasma electrode pre-coating or pre-deposition cleaning process. Furthermore, the trade-off relation of plasma power and gas flow velocity revealed the process window of polycrystalline thin film deposition, and even epitaxial growth.

Atmospheric plasma-enhanced CVD tool is promising for fast deposition and low damage processing, and moreover, cheaper setup may also be viable via pre-deposition cleaning processes instead of utilizing expensive vacuum facilities.

3:00pm **PS+PB+SE-TuA-3 Plasma-enhanced Chemical Film Conversion (PECFC): Direct, Low-temperature Growth of Solution-processible and Printable Layered Thin Films***, T Liu, **R. Mohan Sankaran**,* Case Western Reserve University

In plasma-enhanced chemical vapor deposition (PECVD) and plasma-enhanced atomic layer deposition (PEALD), the addition of a plasma to dissociate or excite the gas molecules and create active chemical and energetic species can lower the thermal energy required at the substrate to drive thin film nucleation and growth. Here, we show that a similar approach can be used to lower the temperature required to convert molecular precursors deposited from solution onto a substrate to a functional, crystalline thin film which we term plasma-enhanced chemical film conversion (PECFC). We apply this method to layered materials such as hexagonal boron nitride (h-BN) and molybdenum disulfide (MoS_2) whose applications are currently limited by the lack of large-area, low-temperature, direct (substrate independent) growth processes.

Our experimental setup consists of an atmospheric-pressure, planar, dielectric barrier discharge and a cold wall substrate heater. Single molecular precursors for h-BN, ammonia borane, or MoS_2, ammonia tetrathiomolybdate were dissolved in solution and deposited by a variety of methods including dropcasting, airbrush spraying, spin coating, and inkjet printing on different substrates such as silicon (Si), silicon dioxide (SiO_2), and copper. The area of the film was only limited by the current size of our plasma source which is ~2 in^2. After conversion, the films were characterized by X-ray diffraction, micro Raman spectroscopy, atomic force microscopy, scanning electron microscopy, and transmission electron microscopy. We systematically compared thermal and plasma-assisted conversion at the same temperatures, background gas environments, and substrates. For h-BN, our results show that thermal conversion requires a minimum of 800 ^oC to nucleate on SiO_2, but only 650 ^oC with the addition of a plasma. Adding 20% H_2 enables a further 150 ^oC reduction for plasma conversion. For MoS_2, our results show that nucleation is enhanced in the presence of a plasma at the same growth temperature of 500 ^oC and a subsequent annealing step leads to a smooth (<0.2 nm RMS surface roughness) and highly crystalline film. We suggest that plasma species, especially atomic hydrogen (H), are involved in several important surface reaction mechanisms including abstraction of hydrogen, insertion in strained bonds, and radical formation, to enhance grain growth that overall enhance nucleation and growth of crystalline domains. We will also discuss the performance of the PECFC materials in electronic and energy devices.

3:20pm **PS+PB+SE-TuA-4 Plasma-based Remediation of Nanoscale Particulate Matter in Charbroiler Smoke Emissions***, **Sisi Yang**, S Subramanian,* University of Southern California, Los Angeles*; D Singleton,* Transient Plasma Systems*; C Schroeder, W Schroeder, M Gundersen, S Cronin,* University of Southern California, Los Angeles

Recent studies have shown ultrafine particulate matter (UFPM) produced in commercial charbroiling processes represents a serious health hazard and has been linked to various forms of cancer. In this study, we demonstrate a highly effective method for treating restaurant smoke emissions using a transient pulsed plasma reactor based on a nanosecond high voltage pulse generator. We measure the size and relative mass distribution of particulate matter produced in commercial charbroiling processes (e.g., cooking of hamburger meat) both with and without the plasma treatment. Here, the plasma discharge is produced in a 3" diameter cylindrical reactor with a 5-10 nanosecond high voltage (17 kV) pulse generator. The distribution of untreated nanoparticle sizes peaked around 125-150 nm in diameter, as measured using a scanning mobility particle sizer (SMPS) spectrometer. With plasma treatment, we observe up to a 55-fold reduction in total particle mass and a significant reduction in the nanoparticle size distribution using this method. The effectiveness of the UFPM remediation increases with both the pulse repetition rate and pulse voltage, demonstrating the scalability of this approach for treating higher flow rates and larger systems.

4:20pm **PS+PB+SE-TuA-7 The Interactions of Atmospheric Pressure Plasma Jets with Surfaces: *In situ* Measurements of Electron Heating in Materials***, **Scott Walton**,* U.S. Naval Research Laboratory*; J Tomko, B Foley,* University of Virginia*; D Boris,* U.S. Naval Research Laboratory*; M Johnson,* National Research Council*; T Petrova,* U.S. Naval Research Laboratory*; A Giri, P Hopkins,* University of Virginia

The energy flux to a surface during plasma exposure and the associated surface heating are of long standing interest since both contribute to the physicochemical changes during plasma-based materials processing. A unique feature of plasmas compared to other methods of materials synthesis and processing is that the energy flux is delivered and absorbed at or very near the surface over short time scales, and thus requires fast, surface-sensitive techniques to fully appreciate the dynamics of the plasma-surface interface. To achieve this, we employ pump-probe Time-Domain Thermoreflectance (TDTR) to measure electron and phonon excitation and energy transport dynamics in thin metal films during exposure to an atmospheric pressure plasma jet. The results show the energy delivered by the plasma jet causes a localized thermal spike that is dissipated radially from the point of contact. More specifically, energy delivered via the flux of particles and photons causes the kinetic energy of the electrons within the material to increase over an area commensurate with the plasma jet radius. That energy is then dissipated through electron-electron collisions and electron-phonon interactions as the electrons propagate radially from the point of contact. These results, in conjunction with voltage and current measurements, will be discussed in an effort to develop a first order understanding of energy transfer and relevant kinetics during plasma jet–surface interactions. This work is partially supported by the Naval Research Laboratory base program.

4:40pm **PS+PB+SE-TuA-8 Surface Activation by Atmospheric Plasma: the Right Technology for the Right Application***, A Ozkan, D Merche, **Francois Reniers**,* Université Libre de Bruxelles, Belgium

Cold atmospheric plasma are widely used for surface activation in many applications. Today, many technologies are available, such as coronas, dielectric barrier discharges (DBDs), remote (or post-discharge) DBDs, torches, operating in the radiofrequency mode, gliding arcs, ……. A wide variety of operating conditions can be found in the literature or on the websites of the manufacturers : AC, DC, kHz range, noble gas or air, high or low power, ….. For the scientist, the lab manager, or the CTO of a company looking for a new, clean, activation technique, the vast list of possibilities, although representing opportunities, may represent a challenge. In this paper, we try to set up a product driven roadmap to help the scientist making the best choice for the plasma technology to implement for his application. Through a few selected examples, all tested in our laboratory equipped with 7 different plasma technologies and 15 reactors, we show which is the best technology for the application of interest. Advantages and drawbacks of each of the tested technologies with respect of the material, the energy consumption, and the time and cost of operation are presented, and discussed in terms of plasma and surface characterization.

The applications chosen addresses a wide range of questions such as:

- which plasma to chose to clean and activate glass substrates (a comparison between torches and in-situ DBDs is proposed)

- atmospheric plasma to grow an oxide layer on aluminium : a comparison between an air operated torch and plasma electrolytic oxidation

- how to activate a macroscopic 3D pre-painted metal piece for further painting using an atmospheric plasma torch. A comparison between 4 torches is presented

- how to activate the surface of selected polymers using DBD, RF torches with different gases

- how to activate surfaces (silicon, polymers, nanotubes) for further grafting of metal nanoparticles

- how to modify PTFE using a torch, what are the side effects, and why.

These examples will be starting points for a more general discussion about methodology, based on the final expectations and the chemistry and physics of each technology.

5:00pm **PS+PB+SE-TuA-9 Aluminum Alloy Surface Cleaning by Atmospheric Pressure Microwave Discharge***, **Lucia Bonova**, W Zhu, A Farrokhpanah, D Krogstad, Z Jeckell, S Chaudhuri, D Ruzic,* University of Illinois at Urbana-Champaign

Aluminum and its alloys are commonly used as lightweight materials in many industrial sectors including aerospace. During the manufacturing process of aluminum, a series of lubricants and additives are used to avoid sticking of layers and prevent degradation or corrosion. The residual hydrocarbon film is typically removed by a chemical chromate process prior to the deposition of an anticorrosive layer. We present an alternate method to remove the hydrocarbons deposited on the aluminum surface by an atmospheric pressure microwave discharge.

The Center for Plasma Material Interaction (CPMI) at University of Illinois has developed novel patented technologies of Evaporative Coatings at Atmosphere Pressure (ECAP) using a 2.45 GHz microwave power to treat the aluminum surface with an air plasma at atmospheric pressure. The cleaning effect of this microwave plasma was analyzed by contact angle measurements, XPS and ATR-FTIR.

5:20pm **PS+PB+SE-TuA-10 Temporal and Spatial Study of a Parallel pin-plate Plasma Reactor***, **Vladimir Milosavljević**, M Gulan, L Scally, P Cullen,* BioPlasma Research Group, Dublin Institute of Technology, Dublin, Ireland

Electrical discharges in gases have demonstrated a wide range of effects for material science and energy applications. Under both laboratory and industrial setups, such electrical discharges can produce a stable plasma. From both fundamental and applied purposes, such gaseous plasmas are well studied, the technology has found many applications. Recent interest has turned to operating such plasma under atmospheric conditions. The main advantage of the plasma discharge at atmospheric pressure over low-pressure plasma or high-pressure plasma, is that no reaction vessel is needed. However, with increasing gas pressures, the stability and reproducibility of the plasma discharge are significantly impacted. For atmospheric pressure, in order to obtain a stable plasma discharge in addition to the electrodes a dielectric barrier is required. The function of this dielectric is to spread the electrical charge throughout the entire electrode in order to create multiple conducting paths for the discharges to occur. This is the foundation of the Dielectric-barrier discharge (DBD). One or both electrodes in DBD could be covered by a dielectric material which serves as an electric polarizer, and helps maintain a low gas temperature. Over the course of its life, for any DBD system, the biggest disadvantage is the dielectric contamination. In most cases, this dielectric is a polymer, and polymers are generally fragile materials. Therefore, developing a plasma system that does not require a dielectric, and has a reproducible and stable electrical discharge at atmospheric pressure would offer new system designs and applications.

This work presents a pulsing plasma system (PPS) which can run at atmospheric pressure under various external parameters. The system has a planar configuration with a bottom (grounded) flat electrode and a top multiple pin electrode (high voltage). The design of this PPS allows several parameters to be modified, such as: discharge frequency (30-125 kHz), duty cycle (1-100%), duty cycle frequency (100-3000 Hz), peak-to-peak voltage (up 60 kV), power (up to 700 W), distance between electrodes (up to 55mm), and treatment time (unlimited). The new plasma system allows an increase in the surface-plasma interaction selectivity and to reduce plasma induced damages to surfaces. The electron properties and gas radical density generated for the system under such control parameters are reported.

This work was funded by the Dublin Institute of Technology and PlasmaLeap Technologies, Ireland.

5:40pm **PS+PB+SE-TuA-11 Plasma-modulated Metamaterials and Photonic Crystals***, **Jeffrey Hopwood**, H Kim,* Tufts University

Metamaterials are periodic assemblies of man-made structures that can mimic naturally occurring materials. By clever design, electromagnetic transmission through metamaterials may have extraordinary properties such as negative refractive index. In this paper we describe the formation of atmospheric pressure argon microplasmas within metamaterials as well as photonic crystals. Microplasma ignition within these materials is initiated by first creating an implicit microwave or millimeter wave resonance within the structure. For example, a vacancy in the artificial crystalline structure can act as a millimeter wave cavity. Incident EM waves excite this resonance and the strong resonant electric field causes gas breakdown.

In general, metamaterials are pre-configured during the design process and exhibit fixed transmission characteristics. The self-initiated plasma, however, dynamically changes the metamaterial. We show that depending on the gas pressure and electron density, microplasma inclusions may act as dielectrics or conductors. Experimentally one observes that the appearance of microplasma causes a change in the material from transparent to reflective, or vice versa. A metamaterial consisting of an array of copper split-ring resonators (3x3x9) is described in terms of the plasma density and its microwave transmission from 1-3 GHz. The appearance of microplasmas quenches the resonance and decouples the resonators from one another; the transmission spectra are radically changed upon de-coupling. In the millimeter wave band, a photonic crystal consisting of alumina rods is shown to support argon plasma at 43 GHz. The transient response of the photonic crystal during pulsed EM radiation and plasma formation is measured and found to act as a power limiting device.

6:00pm **PS+PB+SE-TuA-12 Generation of Large-Volume Transient Glow Discharge Plasma by an External Fast Ionization Wave (FIW) from a Plasma Jet***, **Hamid Razavi**, M Laroussi,* Old Dominion University

A non-thermal transient glow discharge can be generated remotely in a nonconductive low–pressure chamber by an external guided fast ionization wave (FIW). We used an atmospheric-pressure LTP jet (APLTPJ) as an external source of FIW to transfer the enhanced electric field at the wavefront to a reduced–pressure Pyrex glass chamber with no electrical connection to the chamber [1]. Here, we study on the interaction of FIW with a dielectric surface which forms the wall of the low-pressure system.

In this study, key characteristics of the transient diffuse plasma are discussed. Plasma parameters were measured by Langmuir probe and APLTPJ electrical measurements were done to elucidate the operational mechanisms of the FIW as an igniter of a reduced pressure glow discharge plasma. It is shown that the transient discharge in the low-pressure chamber generates a bulk plasma with negative potential due to the nonconductive boundary. We also used Optical emission spectroscopy (OES) to show the physical and chemical characteristics of the APLTPJ plasma and the transient glow discharge plasma. It is shown that the glow discharge plasma is capable of producing second and third ionized nitrogen and oxygen atoms (OII, NII, and NIII). Fast images were taken by an intensified CCD to study the launching and propagation phases of both APLTPJ plasma and the transient reduced pressure glow discharge plasma as well as the incidence of the guided FIW on a dielectric surface.

[1] M. Laroussi and H. Razavi, "Indirect Generation of a Large Volume Diffuse Plasma By an Ionization Wave from a Plasma Jet", *IEEE Trans. Plasma Sci*., Vol. 43, No. 7, pp. 2226-2229, (2015).

Thin Films Division
Room 104B - Session TF+PS-TuA

Atomic Layer Processing: Chemistry & Surface Reactions for Atomic Layer Processing

Moderators: Jessica Kachian, Intel Corporation, Keren Kanarik, Lam Research Corporation

2:20pm **TF+PS-TuA-1 N-heterocyclic Carbenes on Au and Cu Surfaces***, **Cathleen Crudden**,* Queen's University, Canada **INVITED**

N-Heterocyclic carbenes (NHCs) are an exciting new class of ligand for metal surfaces, with potentially interesting applications in patterning and surface functionalization. In this talk, we will address the use of NHCs as ligands for various metal surfaces including coinage and other metals. The functionalization of flat and structured surfaces will be presented and potential applications in etching.

3:00pm **TF+PS-TuA-3 Enhancing Nucleation in Platinum Atomic Layer Deposition by Surface Pre-Treatment with Small Organometallic Molecules***, **Camila de Paula**, L Zeng, S Bent,* Stanford University

Pt thin films have a wide variety of applications in microelectronics, catalysis, and energy technologies. Since most of these applications require a conformal and pinhole-free thin film, achieving good nucleation is an important requirement. It is believed that a low abundance of dissociated oxygen atoms in the initial stages of the Pt ALD process leads to a nucleation delay and island growth. The nucleation and growth mechanisms have a big impact on the properties of the resulting thin film. If nucleation is inhibited, isolated particles rather than a continuous film may be deposited at low cycle numbers (island-growth), whereas if nucleation is facile, a continuous film may be formed at much lower thicknesses.

While there have been studies focused on the surface reactions that occur during Pt ALD, there is still a lack of understanding of how the substrate surface properties affect nucleation in the initial stages of ALD. There have been reports of methods aimed at enhancing nucleation for specific substrates, such as using a wet piranha etch on silicon substrates. Other studies have used high surface energy adhesion layers, such as W, in order to overcome the nucleation delay.

The goal of this study is to develop a surface pre-treatment technique that enhances Pt ALD nucleation independent of substrate choice, while inducing minimum surface modification of the substrate. In this work, the influence of a sub-monolayer surface coverage of small organometallic molecules on the nucleation and growth of Pt by ALD was studied. It was observed that introducing a short pulse of dimethylaluminum chloride (DMACl) prior to Pt deposition leads to the formation of a continuous film after fewer than 100 cycles on thermally grown silicon oxide vs. over 200 cycles on a non-treated sample. Scanning electron microscopy (SEM), synchrotron based grazing incidence small angle X-ray scattering (GISAXS) and X-ray photoelectron spectroscopy (XPS) were used to analyze the ALD growth mechanism on various treated and untreated substrates. The formation of densely-packed large Pt nanoparticles was observed on the treated surface. GISAXS analysis of the Yoneda-Peak position and pattern showed that the surface treatment leads to nanoparticle coalescence in the very early stages of ALD. Interestingly, a comparison of DMACl to other small organometallic molecules showed that some molecules induced the opposite behavior, instead leading to inhibited Pt ALD. The detailed growth mechanism and possible reaction pathways leading to these results will be discussed.

3:20pm **TF+PS-TuA-4 Mass Spectrometer Studies of Volatile Etch Products Produced by Ligand-Exchange Reactions During Thermal Atomic Layer Etching***, **Joel Clancey**, A Cavanagh, S George,* University of Colorado Boulder

Atomic layer etching (ALE) using sequential, self-limiting surface reactions is an important technique for removing material with atomic layer control. In addition, selective ALE is required for the maskless fabrication of advanced devices as feature sizes become smaller than available lithography. This study reports the study of volatile etch products produced by ligand-exchange reactions during thermal ALE and develops our understanding of selective thermal ALE.

Previous studies have revealed selective thermal ALE in the etching of Al_2O_3, ZrO_2 and HfO_2 using fluorination and ligand-exchange reactions [1]. In this work, we used metal fluoride powders to study volatile etch products produced by fluorination and ligand-exchange reactions during thermal ALE. An *in situ* quadrupole mass spectrometer (QMS) was employed to characterize the etch products produced during the thermal etching of AlF_3, ZrF_4 and HfF_4 powders between 200°C and 300°C using TMA, DMAC, $SiCl_4$ and $TiCl_4$ as the metal precursors.

Thermal Al_2O_3 ALE occurs using HF and TMA as the precursors [2]. For the reaction of TMA with AlF_3 powders, the observed etch products are dimers such as $[AlF(CH_3)_2]_2$ and $[AlF(CH_3)_2\text{-}Al(CH_3)_3]_2$. These products are equivalent to the dimer etch products observed earlier for the reaction of TMA with fluorinated Al_2O_3 during thermal Al_2O_3 ALE. In contrast, Al_2O_3 ALE does not occur with either $SiCl_4$ or $TiCl_4$ as the metal precursors [1]. For the reaction of $SiCl_4$ and $TiCl_4$ with AlF_3 powders, the observed reaction products are $SiFCl_3$ and $TiFCl_3$, respectively. There is halide-exchange between the $SiCl_4$ and $TiCl_4$ metal precursors and the AlF_3 surface. However, there is no observation of volatile Al-containing products that would be consistent with Al_2O_3 etching.

We are developing a matrix that correlates volatile etch or ligand-exchange products with the previous etching results. We are also using density functional theory (DFT) to predict the etch products during thermal ALE. These DFT calculations correctly predict the dimer etch products during Al_2O_3 ALE. This approach is advancing our understanding of selective thermal ALE.

[1] Younghee Lee, Craig Huffman, and Steven M. George, "Selectivity in Thermal Atomic Layer Etching Using Sequential, Self-Limiting Fluorination and Ligand-Exchange Reactions", *Chem Mater*. **28**, 7657 (2016).

[2] Younghee Lee, Jaime W. DuMont and Steven M. George, "Trimethylaluminum as the Metal Precursor for the Atomic Layer Etching of Al_2O_3 Using Sequential, Self-Limiting Thermal Reactions", *Chem. Mater.* **28**, 2994 (2016).

4:20pm **TF+PS-TuA-7 Beyond Conventional Lithography – Using Self-assembly to Create Patterns for New Device Fabrication Techniques***, **Michael Morris**,* Trinity College Dublin, Ireland **INVITED**

The microelectronics industry is being challenged to maintain progress at a similar rate to that which has been seen for nearly 50 years. With the dissolution of the International Technology Road Map for Semiconductors (ITRS) has come the realization that scaling is not the only solution that can drive improvements in the silicon chip industry. Indeed several competing technologies may emerge in the near future including device and interconnect structures fabricated from 2D materials. At device level, feature size will probably continue to decrease as solutions for sub-10 nm nodes become available. Note that whist feature size has shrunk, gate length has not significantly decreased for several years. New device materials with higher mobilities such as 2D materials will be seen as promising but their implementation into conventional device fabrication methods remains problematical. The interconnect issue may be the most critical area for development since delay times limiting clock speed. For these reasons the integration of non-traditional active circuitry in back end of line (BEOL) processes is highly attractive to control chip processes or add function such as memory. It also allows promising materials such as 2D to be intergated at less challenging length scales.

All of these approaches and others will require innovative fabrication techniques suitable for integrating new materials, patterning them and developing function. We will centre on the use of self-assembled block copolymer films and related methods that may be able to develop device structures without expensive high resolution lithography and at low thermal budgets needed for integration of multiple device layers.

5:00pm **TF+PS-TuA-9 Calculations of Etch Products from Thermal Atomic Layer Etching Using Fluorination and Ligand-Exchange Reactions***, **Andrew Cavanagh**, J Clancey, S Sharma, S George,* University of Colorado at Boulder

Thermal atomic layer etching (ALE) of Al_2O_3 can be accomplished using sequential, self-limiting fluorination and ligand-exchange surface reactions with hydrofluoric acid (HF) and trimethyl aluminum (TMA, $Al(CH_3)_3$) as the precursors. Fluorination by HF converts the surface of Al_2O_3 to AlF_3. Ligand-exchange reactions then occur between TMA and the AlF_3 surface. The first ligand-exchange reaction is believed to be: $AlF_3(s) + Al(CH_3)_3(g) \rightarrow AlCH_3F_2(s) + Al(CH_3)_2F(g)$ where "s" indicates a surface species and "g" indicates a gas phase species. Additional ligand-exchange reactions can then react $AlF_2CH_3(s)$ to $AlF(CH_3)_2(g)$. Recent quadrupole mass spectrometry (QMS) studies have observed that the main etch products during Al_2O_3 ALE are the dimers $AlF(CH_3)_2$-$AlF(CH_3)_2$ and $AlF(CH_3)_2$-$Al(CH_3)_3$. These dimers may be formed from the monomer $AlF(CH_3)_2$ etch product pairing with itself or with the $Al(CH_3)_3$ metal precursor.

To understand these dimer etch products, density functional theory (DFT) calculations were performed on all possible dimers that could be produced from the four possible monomer species ($Al(CH_3)_3$, $Al(CH_3)_2F$, $AlCH_3F$, AlF_3). Each dimer consisted of a pair of bridging ligands between the two Al metal centers and four terminal ligands. The bridging ligands could be (F, F), (F, CH_3) or (CH_3, CH_3). The (F, F) bridges resulted in the most stable dimers while the (CH_3, CH_3) bridges resulted in the least stable dimers. In agreement with the QMS results, these DFT calculations predict that the $AlF(CH_3)_2$-$AlF(CH_3)_2$ dimer with a (F,F) bridge and four terminal methyl groups is the most viable etch product.

Additional DFT computational studies have also been performed for ligand-exchange reactions on fluorinated surfaces of Al_2O_3, ZrO_2 and Ga_2O_3 with various metal precursors including $Al(CH_3)_3$, $Al(CH_3)_2Cl$, $SiCl_4$, $GeCl_4$, $SnCl_4$, and $TiCl_4$. These calculations model the ligand-exchange surface reactions during Al_2O_3, ZrO_2 and Ga_2O_3 ALE. For all systems studied to date, the calculations indicate that dimer species are the preferred etch products. Future QMS experiments will observe etch products and compare with the DFT computational studies for a more complete understanding of thermal ALE.

5:20pm **TF+PS-TuA-10 Formation of Monolayers and Multilayers During the Vapor-Phase Deposition of Dodecanethiols on Copper Oxide***, **David Bergsman**, T Liu, R Closser, S Bent,* Stanford University

The deposition of alkanethiols onto copper and copper oxide has been widely studied for use in the passivation of surfaces and as ultrathin blocking layers. The formation of alkanethiol self-assembled monolayers (SAMs) on copper oxide is particularly interesting in that thiols are known to etch and reduce copper oxide surfaces before ultimately forming a SAM. This has sometimes resulted in films much thicker than expected for a monolayer, leading to the hypothesis that this etching process can create multilayers, though the structure of those multilayers and the mechanism behind their formation were not explored. In recent years, the use of SAMs to enable area-selective atomic layer deposition (ALD) for back-end semiconductor processing has created renewed interest in the study of thiol deposition onto copper, particularly through vapor-phase approaches that can be more easily incorporated into industrial semiconductor fabrication processes. However, no studies have reported the formation of Cu-thiolate multilayers through the vapor-phase.

In this work, we examine the vapor deposition of dodecanethiols (DDTs) onto copper and copper oxide surfaces. We show using atomic force microscopy, X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy/electron energy loss spectroscopy that this deposition onto copper oxide surfaces results in the formation of up to 8 nm thick Cu-thiolate multilayer films, rather than SAMs. In contrast, pre-removal of the copper oxide and subsequent DDT exposure creates 2 nm thick SAMs, suggesting that the etching of the copper oxide films by thiol molecules is a key step in the multilayer formation. Synchrotron-based grazing-incidence X-ray diffraction shows these thick films to be highly crystalline, with bilayer thiol structures sandwiched between layers of copper atoms. Crystallites are shown to be oriented both perpendicular and parallel to the surface. We further explore the degradation of these multilayers, demonstrating with scanning electron microscopy and XPS that the films appear to dewet into micron-sized particles after exposure to air. Continued air exposure results in the oxidation of the sulfur and copper in the films on a time scale consistent with DDT monolayers. Finally, the implications of this multilayer formation on area-selective ALD will be discussed.

5:40pm **TF+PS-TuA-11 Exchange Reactions During Atomic Layer Deposition: ZnO Conversion to Al_2O_3 by Trimethylaluminum***, **Tyler Myers**, A Cano, J Clancey, D Lancaster, S George,* University of Colorado at Boulder

Atomic layer deposition (ALD) is typically described by the self-limiting reaction of precursors with surface species that leads to controlled thin film growth. Missing from this picture is the possibility that the precursors can also undergo exchange reactions and convert the surface of the initial substrate to a new material. These exchange reactions are expected if the conversion produces a more thermodynamically favorable reaction product. These exchange reactions may be common during ALD nucleation.

In this study, the exchange between Zn and Al is explored during the initial reaction of trimethylaluminum (TMA) on ZnO films during Al_2O_3 ALD at temperatures from 150-250°C. The exchange is evident from a variety of experimental measurements. Fourier transform infrared (FTIR) investigations detect absorbance changes consistent with ZnO loss and Al_2O_3 gain after the TMA reaction on ZnO ALD films. Quadrupole mass spectrometry (QMS) measurements also observe $Zn(CH_3)_2$ reaction products as expected from the conversion reaction: $3ZnO + 2Al(CH_3)_3 \rightarrow Al_2O_3 + 3Zn(CH_3)_2$. In addition, studies of the effect of TMA exposures on ZnO nanoparticles with a diameter of ~10 nm measured the conversion of ZnO to Al_2O_3. The conversion produces a large mass loss that is consistent with the formation of an Al_2O_3 surface layer. The ZnO to Al_2O_3 conversion is also self-limiting as a function of TMA exposure.

X-ray photoelectron spectroscopy (XPS) and X-ray reflectivity (XRR) investigations are also consistent with the conversion of the surface of ZnO ALD films to Al_2O_3 after the initial TMA exposure. The XPS and XRR measurements both yield an Al_2O_3 surface layer with a thickness of ~1.0 nm on the ZnO ALD film. In addition, quartz crystal microbalance (QCM) measurements detect a substantial conversion of ZnO to Al_2O_3 after the initial TMA exposure during Al_2O_3 ALD. The QCM studies reveal that the mass losses are much more pronounced for thin ZnO films compared with thick ZnO films. In addition, the mass losses are more for ZnO surfaces terminated with Zn-CH_3CH_3 species compared with Zn-OH species.

These studies of the exchange between Zn and Al during the initial reaction of TMA on ZnO illustrate that ALD precursors can convert the surface of the initial substrate to a new material. These exchange reactions must be considered when analyzing ALD nucleation.

6:00pm **TF+PS-TuA-12 3D Feature Profile Simulation Coupled with Realistic Plasma Surface Reaction Model for ALE Process***, Y Im, **YeongGeun Yook**, H You, J Park,* Chonbuk National University, Republic of Korea*; D You,* KW Tech, Republic of Korea*; K Choi,* Chonbuk National University, Republic of Korea*; W Chang,* National Fusion Research Institute, Republic of Korea

Recently, atomic layer etching (ALE) processes have attracted much interest for sub-10nm semiconductor fabrication process. Notably, a cyclic plasma-enhanced fluorocarbon ALE process using the conventional plasma etch tools has investigated for its selective etching and atomic-level control. In spite of its superior merits, the detailed studies remain to apply sub-10nm 3D nanoscale feature patterns due to its complexity. To address this issue, we developed a 3D feature profile simulator which was composed of a Zero-D bulk plasma simulator, a multiple-level set moving algorithm based on a hash map, a GPU based ballistic transport algorithm, and a surface reaction model. In this work, we focus on the development of a transient surface reaction model of ALE process to capture the realistic surface reaction. Finally, 3D feature profile simulations coupled with the surface reaction model were verified with experimental data. We believe that this approach enables us to understand unveiled phenomena of ALE process.

Plasma Science and Technology Division
Room Hall B - Session PS-TuP

Plasma Science and Technology Division Poster Session

PS-TuP-1 Surface Modification for the Enhancement of the Patterning Margin by Using Plasma Treatment*, **Wanjae Park**, L Huli, S Chae, A Ko, P Biolsi,* TEL Technology Center, America, LLC

Extreme ultraviolet (EUV) lithography has been investigated to extend lithographic technology beyond its optical limits and replace current photolithography methods to pattern tiny critical dimension (CD) features. As the feature size is reduced, the adhesion between photo resist (PR) and its under layer such as silicon containing anti-reflective coating layer (Si-ARC) is getting worse. Recently, one of issuses of EUV process is pattern collapse or flop-over phenomena that may ultimately render the substrate useless. This pattern collapse may be more observed, as the feature size is smaller due to smaller contact surface topographically. In this study, we carried out plasma treatments by using various gases on the under layer of PR which is Si-ARC, before PR coating. The CH$_4$ plasma treatment remarkably improves the pattern collapse phenomena. This surface modification effect as following as plasma chemistries was characterized by Fourier Transform Infrared Spectroscopy (FTIR), X-ray Photoelectron Spectroscopy (XPS) and Contact Angle measurement. From the FTIR analysis, we can detect additional Si-CH$_3$ peak (around 1261cm^{-1}) after CH$_4$ plasma treatment on Si-ARC. The chemically bond Si-(CH$_3$) groups might be thought as forming a hydrophobic surface while the surface oxidation was suppressed, which was proved by XPS results and Contact Angle results. Finally, the CH$_4$ plasma modifies hydrophilic property of the under layer of PR to hydrophobic surface thus enhancing the adhesion to PR. The benefit of increased adhesion results substantial improvements on production yield and enlarges the margin of Litho process window. This study will be helpful in enhancing the margin of EUV lithography process window and improvement on production yield for the manufacturing of Nano metric devices.

Keywords: Line Pattern Collapse, Surface Modification, Plasma Treatment, CH$_4$ Plasma, Contact Angle

PS-TuP-2 N$_2$/H$_2$, O$_2$ and NF$_3$ Dissociation Percentages in a Remote, Low Frequency, High Density Plasma Source*, **Yingliang Zhou**, H Li, V Donnelly,* University of Houston*; J Chiu, X Chen,* MKS Instruments, Inc., Pressure and Vacuum Measurement Group

Remote plasmas are drawing increasing attention for applications including chamber cleaning, chemical vapor deposition (CVD), surface modification and isotropic etching. The process is purely chemical in nature, with no surface damage from ion bombardment. The dissociation and recombination rates in the plasma source determine the reactive species fluxes delivered to the downstream chamber. The presentation will focus on measurements of percent dissociation of source gases commonly used in chamber cleaning and flowable CVD processes. Mixtures of N$_2$/H$_2$, O$_2$, and NF$_3$ feed gases with Ar were delivered to the plasma at 400 sccm total flow rate and pressures of 0.4-4.0 Torr. The purely inductive, low frequency (400 kHz), toroidal plasma source (MKS Instruments) operates at a power density of 5 – 50 W/cm^3. Radical densities and feed gas dissociation percentages in the plasma were measured by UV-visible optical emission spectroscopy (OES), combined with Ar actinometry. Effluents from the plasma source flowed into a downstream chamber that was equipped with a Deuterium lamp and a VUV spectrometer, for absorption spectroscopy measurements. The dissociation of O$_2$, NF$_3$ and N$_2$/H$_2$ gases in the plasma source will be compared to those measured downstream as a function of added Ar, total flow rate, discharge current, relative electron density and other plasma parameters.

PS-TuP-3 Thermal Atomic Layer Etching of Silicon and Silicon Nitride Using an Oxidation and "Conversion-Etch" Mechanism*, **Aziz Abdulagatov**, S George,* University of Colorado at Boulder

The thermal atomic layer etching (ALE) of silicon (Si) and silicon nitride (SiN) was performed using an oxidation and "conversion-etch" mechanism. In this process, the Si or SiN surface is oxidized to a silicon oxide layer using O$_2$ or ozone. The silicon oxide layer is converted to an Al$_2$O$_3$ layer using trimethylaluminum (TMA). The Al$_2$O$_3$ layer is fluorinated by HF to an AlF$_3$ layer prior to the removal of the AlF$_3$ layer by ligand-exchange using TMA. Si ALE was studied using silicon-on-insulator (SOI) wafers and SiN was examined using LPCVD SiN films. These investigations were performed in a warm wall reactor with a hot sample stage. *In situ* spectroscopic ellipsometry was employed to monitor the thickness of both the Si or SiN film and the silicon oxide layer during ALE.

These studies observed that the Si and SiN film thickness decreased linearly with number of reaction cycles while the silicon oxide thickness remained constant. Using an O$_2$-HF-TMA reaction sequence, the Si ALE etch rate was 0.4 Å/cycle respectively at 290°C. This etch rate was obtained using static reactant pressures of 250, 1.0 and 1.0 Torr, and exposure times of 10, 5 and 5 s, for O$_2$, HF and TMA, respectively. The order of the reactant sequence affected the Si etch rate. Changing the reactant sequence from O$_2$-HF-TMA to O$_2$-TMA-HF reduced the etch rate from 0.4 to 0.2 Å/cycle at 290°C. Comparable etching rates were observed using ozone instead of O$_2$ as the oxidant. Comparable etching rates were observed for SiN ALE under similar reaction conditions. The Si and SiN ALE etch rates decreased with process temperature. An oxide thickness of $\sim$10 Å remained after ALE at 290°C. However, this oxide thickness could be removed by sequential TMA and HF exposures without influencing the underlying silicon film.

These new thermal Si and SiN ALE processes are expected to yield isotropic etching. Thermal Si and SiN ALE should be useful in advanced semiconductor fabrication. Thermal Si ALE could also be utilized for atomic-scale polishing and cleaning of silicon surfaces. In addition, there may be applications in other areas such as silicon-based optoelectronics, photonics and MEMS fabrication. Thermal SiN ALE could be utilized in a broad spectrum of IC applications where SiN commonly used as an etch stop and diffusion barrier.

PS-TuP-4 Annihilation Kinetics of Plasma-induced Electronic Defects in Semiconductor Materials*, S Nunomura, **Isao Sakata**, K Matsubara,* National Institute of Advanced Industrial Science and Technology (AIST), Japan

In semiconductor devices such as transistors, memory, solar cells, and light emitting devices, the electronic defects strongly impact on the device performance and reliability. These defects are often generated during the device fabrication, in which plasma processing technology is widely used for deposition, etching and implantation. To remove the defects in the devices, a annealing treatment is usually performed. However, some defects remain in the devices, and they deteriorate the device performance. The reduction of these residual defects is required, and thus it is important to understand the annihilation kinetics during the annealing period.

We studied the annihilation kinetics of electronic defects in hydrogenated amorphous silicon (a-Si:H). The electronic defects were generated by photon irradiation and plasma treatment. The annihilation of defects during the annealing is observed by in-situ photocurrent measurement [1-2]. An increase in the photocurrent reflects the annihilation of the defects. From the time evolution of the increasing photocurrent, we obtained the characteristic time, τ, and an Arrhenius plot is prepared to determine the activation energy.

From the experiments, we find the following [3]. (i) The time evolution of the photocurrent exhibits the stretched exponential behavior, indicating the dispersive nature of a-Si:H. (ii) An Arrhenius plot shows an exponential decay of $1/\tau$ vs $1/T$, verifying defect annihilation due to the thermal activation. Here, T is the annealing temperature. (iii) The activation energy is different, depending on the origin of defect generation. It is smaller for the defects generated by plasma treatments, compared with that of the defects induced by the photon irradiation. (iv) The exponential prefactor is different between the UV and VUV photon-induced defects. The details of the experimental setup, results and discussion will be given in the presentation.

This work was supported by JSPS KAKENHI (Grant Number 18K03603 and 15K04717) and NEDO.

[1] S. Nunomura, I. Sakata, and M. Kondo, *Appl. Phys. Express* **6**, 126201 (2013). [2] S. Nunomura and I. Sakata, *AIP Advances* **4**, 097110 (2014). [3] S. Nunomura et al., submitted.

PS-TuP-5 High efficiency Magnetic Induction Plasma Source for Remote Plasma Removal Process*, **TaeSeung Cho**, S Park, D Lubomirsky,* Applied Materials

Selective material removal by using remote plasma becomes an indispensable process for 3D structures of semiconductor. In selective material removal process by remote plasma, the wafer process regime is completely isolated from the plasma source by perforated metal plates such as showhead. The radicals generated by electrical discharge pass through the perforated metal plate, while the charged particles cannot pass through. Thus, in the wafer process regime, the specific radicals from the remote plasma react with the target material to be removed from the wafer. Since the charged particles are screened by the plate, the damages by energetic charged particles can be drastically reduced. Therefore, the plasma source for remote plasma removal process should have features of (1) efficient radical generation with higher dissociation rate and (2) less charged particle leakage to wafer process regime.

Magnetic induction plasma concept is being used for lighting bulbs as well as Tokamak fusion reactor for several decades. Especially, the magnetic induction lighting and its driving electronics is being optimized for many years. Since the magnetic induction lighting doesn't have any electrode inside the bulb there's no particles from the electrode sputtered by energetic ions. In addition, magnetic induction plasma source as an inductively coupled plasma has higher dissociation rate compared to typical capacitively coupled plasma. Thus, introducing the magnetic induction lighting and its driving technologies to remote plasma removal process would make removal process more efficient and reliable with reduced cost of ownership.

Prototype chamber for magnetic induction plasma source for remote plasma removal process was assembled with standard KF flanges that could be brought off the shelf. To generate stable plasma, we modified the commercial electronic ballast. We introduced initial plasma generation concept to avoid the ignition failure which was one of the most common issue of magnetic induction plasma source. For preliminary study with the electrical and optical diagnostics, Ar+N_2 plasma was successfully generated/modulated in the chamber by using the ballast with wide operating pressures from 50mTorr to 200Torr.

PS-TuP-6 Aspect-ratio and Line-edge Fluctuation Controlled Nanolithography using Poly(styrene-*b*-Dimethylsiloxane) and Amorphous Carbon Layer*, JiSoo Oh, G Yeom,* Sungkyunkwan University, Republic of Korea

Of the various alternative lithography technologies, direct self-assembly (DSA) patterning technology using block copolymer (BCP) has received great attention due to excellent pattern resolution, process simplicity, low cost, and long-range ordering (good scalability).

Polystyrene-block-polydimethylsiloxane (PS-*b*-PDMS) with high Flory-Huggins interaction parameter (χ) have been extensively studied because they provide ultra-fine patterning and improved pattern quality. However, due to the preferential segregating property of PDMS in air and PS interface, it is disadvantageous to vertical orientation and it is difficult to fabricate BCP patterns with high aspect ratio (HAR)

Here, we will introduce the process of effectively pattern transfer by inserting an amorphous carbon layer (ACL) between the PS-*b*-PDMS BCP patterns and the underlying silicon substrate. In this study, we have overcome limitations of PS-*b*-PDMS BCP patterns with low aspect ratios by developing an etch selectivity close to infinity using plasma etch process. The PDMS patterns of various shapes could be fabricated into lamellar, rod, hole pattern with HAR by pattern transfer to ACL due to high etch selectivity plasma process. Also, line edge roughness (LER) and line width roughness (LWR) was improved due to the plasma trimming effect.

PS-TuP-7 Development of A Low-Cost ZnO Nanorods-Based Gas Sensor with an Integerated Microplasma Generation Unit for Ethanol Sensing*, Sz-Yun Lin, F Huang, C Hsu,* National Taiwan University, Taiwan, Republic of China

ZnO-based materials have been widely used as the gas sensing elements. The major limitations for this type of materials are the need to operate in high temperature or the requirement of the annealing step for fabrication or re-condition.

In this work, we developed a ZnO nanorods–based gas sensor integrated with a microplasma generation unit (MGU) that allows for detection of ethanol vapors at room tempertaire. This device consists of a specially-designed electrode set was fabricated using toner transfer method. This allows for the operation of microplasma generation mode(MGM) and gas sensing mode(GSM). After the fabrication of the 3-electrode set, ZnO nanorods was grown by hydrothermal method for 24 hours between two electrodes. ZnO-nanorods was first treated using the plasma for 10 minutes by sensing test. By proper connection of the electrodes, the device can be operated in GSM, which allows for ethanol vapor sensing test by measuring the resistance across the ZnO nanorods. The sensor is capable to detect a wide range of ethanol vapor, from 25 to 20000 ppm. In addition, the sensor shows excellent recyclibility after repetitatively testing for over 30 cycles. We will also show that the plasma treatment of the ZnO nanorods serves as the regeneration of the sensing materials after the nanorods expose to humid air and loses their functionality for ethanol sensing.

This newly-developed integrated device offers a novel route for the dvelopment of sensing devices that allows for plasma treatment of sensing materials in-situ and on-site.

PS-TuP-8 Development of a Plasma Generation Device Integrated with a Piezoelectric Spray to Detect Metal Ions in Solution*, Ting-Ting Pan, S Lin, C Hsu,* National Taiwan University, Taiwan, Republic of China

In this work, we develop a system that contains a plasma generation device, a piezoelectric spray, and a spectrometer to detect metallic ions in solution. The plasma consists of a needle and a copper sheet as the anode and the cathode respectively. This plasma is driven by a homemade high voltage module that delivers 3 kV DC and is powered by a 5 V commercial portable power bank. The plasma is ignited in ambient air without the need of any purging gases. The mist of metal-ion-containing solution is sprayed to the plasma. The optical emission of the plasma is analyzed using a spectrometer for metallic element analysis. Such an arrangement allows for analysis of solutions with a wide range of electrical conductivities.

It is shown that the addition of a ballast resistor in series of the high voltage module effectively limits the current and plays an important role for metal detection. Without the ballast resistor, no metallic emission line is observed, despite of the fact that the plasma shows very bright emission. With the use of a ballast resistor of proper resistance, plasma appears to be more stable and clear Na and Pb emission lines are observed when a solution containing 1000 and 10000 ppm of Na and Pb, respectively, is spray to the plasma. We also observe that the gap between the electrodes is very critical for plasma characteristics. With a gap smaller than 0.5 mm, the plasma exhibits stable (DC) IV waveforms, while it shows self-pulsing characteristics with a gap greater than 0.5 mm.

We will show the progress toward the ultimate goal of this work: development of a system to detect metal ions in solution by integrating the plasma and spray devices with a home-made low cost spectrometer, and control the system using a Raspberry pi, a portable computer. Such an integrated system is fully functionalized and standalone and allows for simultaneous detection of multiple metal ions using plasma spectroscopy.

PS-TuP-9 Development of a Light-weight System for Detection of Metal Ions in Solutions Using Plasma Spectroscopy*, Ching-Yu Su, S Lin, C Hsu,* National Taiwan University, Taiwan, Republic of China

This work presents the development of a light-weight system that allows for simultaneous detection of multiple metallic elements in solution using plasma spectroscopy. This system consists of a pin-to-surface-type plasma, driven by a home-made high voltage module, and an atomizer to spray test solution into plasma. The optical emission of the plasma is analyzed using a spectrometer. Such an arrangement allows for detection metallic elements in solution with wide range of electrical conductivity of the solution by analyzing the optical emission of the plasma. A stainless steel pin and a copper sheet serve as the anode and the cathode, respectively, of the plasma. This plasma operates under atmospheric pressure in ambient air. The high voltage module delivers 3 kV DC to ignite the plasma and is powered by a 5-V commercial portable power bank. The atomizer is a piezoelectric spray. The power source of this spray is connected in series with a bipolar junction transistor (BJT), which is driven by a function generator to modulate the on and off of the spray. When the metallic element-containing solution is sprayed to the plasma, metallic emission can therefore be acquired.

We have observed that the spray frequency and duty greatly influence the plasma behavior and therefore its optical emission. Proper modulation of the spray is the key to generate stable plasmas with clear metallic emission. When the spray is set at 1 Hz with 50% duty using solution with 1000 and 10000 ppm of Na and Pb, respectively, clear metallic Na and Pb emissions are observed. We will further analyze the temporal-resolved optical emission to better understand the interaction between the mist and the plasma.

Finally, we will also demonstrate the use of a Raspberry Pi, a low-cost and credit-card-sized computer, to synchronize the spray and the plasma, and its integration with a homemade low cost spectrometer to develop a standalone and fully-functional device for detection of metallic elements in solution.

PS-TuP-10 Inductively Coupled Plasma Reactive Ion Etching of Nanometer-scale Patterned Copper Thin Films using Alcohol-based Gases, *Jinsu Ryu, E Lim, D Park, C Chung,* INHA University, Republic of Korea

Copper has been known as the next-generation interconnect materials in the metallization layer beyond the ultra large scale integration. Recently, the conventional aluminum interconnect materials needs to be replaced by copper which has many advantages compared to aluminum: high conductivity, less susceptible to electromigration, and lack of hillocks formations.

Copper thin films could not be patterned by the previous patterning techniques of photoresist masking and plasma etching that had been used with great success with aluminum. The inability to plasma etch the copper films called for the development on new etching technique. At last, it lead to a unique patterning process referred to as an additive patterning, also known as a 'Damascene' or 'dual-Damascene' process by analogy to a traditional technique of metal inlaying. However, as the critical device dimensions keep shrinking, the thickness of copper interconnect also should be decreased. This shrinkage in the copper thickness cause several issues in the copper patterning, which contain the increase in the resistivity of copper interconnect due to the increase in the resistivity of barrier layer and the change in grain size. There were many etching studies on the copper thin films using halogen-containing gases (Cl_2, HBr), hydrogen, and some organic materials, and all of their results were not satisfactory to apply to the copper patterning.

In this study, we will introduce an etching process of copper thin films using high density plasma etching in alcohol-based gases. The etch characteristics such as etch rate and etch profile will be presented as a function of gas concentration. Then the systematic parameter variation will be performed to improve the etch profiles. Finally, the etch mechanism will be investigated using X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDS). In addition, the plasmas properties will be analyzed using optical emission spectroscopy (OES) and Langmuir probe.

Acknowledgements This research was supported by Basic Science Research Program through the National Research Foundation of Korea(NRF) funded by the Ministry of Education (NRF-2017R1D1A1B03033143).

PS-TuP-11 Etch Characteristics of Nanometer-scale Patterned Cu Thin Film Using Pulse- modulated RF Source Plasma, *Euntaek Lim, J Ryu, C Chung,* INHA University, Republic of Korea

The critical dimensions of the semiconductor devices have been shrunk for better performance and functionality. As the minimum feature length keeps decreasing, the aluminum metal electrodes and wiring can not be used anymore and the need to use copper wiring instead of aluminum is increasing. Copper has very low resistance and high electromigration resistance, so the copper thin films is known as an excellent interconnect material compared to aluminum although the copper is more expensive than aluminum. In order to apply copper films into the interconnect, the pattering and etching process of copper films should be developed. Up to date, the studies on etch characteristics of copper thin films were performed using Cl_2, HBr, and H_2 gases but the satisfactory results were not obtained.

In this study, the pulse-modulated RF plasma etching of copper thin films has been introduced to achieve good etch results such as proper etch rate and good etch profile compared to those by the conventional continuous wave (CW) plasma etching which can produce low etch selectivity, etch residues, and poor etch profiles. This modulated plasma can provide the specific plasma conditions modified by special matching system that can change on-off duty ratio of 13.56 MHz RF power and frequency on the specific duty ratio. Currently, no good etch gases have been known to etch copper thin films. In this research, etching characteristics of copper thin film masked with nanometer-scale patterns was investigated in carboxylic acid using pulse-modulated inductively coupled plasma reactive ion etching (ICP RIE). The effects of on-off duty ratio and frequency of pulsed plasma on the etch characteristics of copper were examined.

Acknowldgments This research was supported by the MOTIE(Ministry of Trade, Industry & Energy (10080450) and KSRC(Korea Semiconductor Research Consortium) support program for the development of the future semiconductor device.

PS-TuP-12 Etch Characteristics of Magnetic Tunneling Junction Materials by Using Noble Gas and Hydrogen, *SooGang Kim, K Yang, Y Shin, D Sung, G Yeom,* Sungkyunkwan University, Republic of Korea

As next generation non-volatile memory device, spin transfer torque magnetic random access memory (STT-MRAM) is one of the prospective memory devices. But anisotropic etching of magnetic tunneling junction material (MTJ) is vey difficult especially in nano-scale. Ar ion beam etch (IBE) not only has low etch selectivity but also induces sidewall re-deposition. Even though tilted ion beam can remove deposited materials at sidewall, a shadow effect restricts the effective removal of deposited materials in nano-scale pitch size. Some chemical reactive ion etching (RIE) can improve problems of Ar IBE, but they show other problem such as low selectivity, corrosion and chemical damage to magnetic materials.

In this study, MTJ materials were etched by using H_2, Ne, Ar and Xe inductively coupled plasma (ICP) and observed their etch characteristics. The nano-scale patterned MTJ material sample which is composed of CoPt(10nm), MgO(1nm), CoFeB(10nm) with W hardmask was used for comparing etch profiles with re-deposition. The results show that H_2 and Ne etch showed better etch profile and higher etch selectivity of MTJ materials over W than those with Ar. With Xe, etch selectivity was lower than the other gas, even though Xe showed an anistropic profile. Also using the vibrating sample magnetrometer (VSM), we compared saturated magnetic moments (Ms) to identify magnetic degradation. The patterned sample etched with Ne and Ar showed similar Ms, which means no significant magnetic degradation when using Ne.

PS-TuP-13 Particle Temperature Histories in a Tubular Low Temperature Plasma Reactor: Relevance to the Synthesis of Amorphous Metal Alloys, *N Uner, Elijah Thimsen,* Washington University in St. Louis

The nonequilibrium environment of low temperature plasma (LTP) allows it to incorporate a significant amount of specific free energy to materials with which it is in contact. It has been shown recently that LTP is capable of synthesizing materials that are far away from equilibrium, as in the case of hyperdoped silicon nanocrystals [1]. Furthermore, LTP can also process pre-synthesized materials in such a way that the material is pushed far away from equilibrium, as demonstrated with in-flight size focusing of polydisperse aerosols [2]. However, examples on the transformation of materials with equilibrium atomic structure to materials with non-equilibrium structure are scarce. In this work, we propose that the distinct nanoparticle (NP) temperature histories in tubular LTP reactors can be utilized to transform crystalline metals into amorphous metals. Spatial characterization of an Ar plasma in a capacitively coupled tubular reactor revealed the existence of a zone with sharply elevated ion density and gas temperature in the vicinity of the powered electrode. Theory suggests that such an intense zone would heat NPs to temperatures above 1000 K, and rapid cooling would follow as NPs leave the zone. In the characterized reactor, an aerosol processing scenario was simulated, where pre-synthesized crystalline NPs were sent into the LTP. Copper-zirconium (CuZr), which is a well-established glass former and is of interest for low temperature electro-catalysis applications, was taken to be the particle material. Calculations showed that the temperature history of a NP is strictly dependent on diameter, and on the intensity of the zone. CuZr melted in the intense zone, and subsequent cooling of the melt in the low intensity plasma downstream lead to quenching rates on the order of 10^5 K/s, all while particles maintaining a unipolar negative charge. Quenching rates of this magnitude are known to be sufficient to arrest an amorphous atomic structure [3].

[1] Zhou Shu *et al.*, “Boron- and Phosphorus-Hyperdoped Silicon Nanocrystals,” *Part. Part. Syst. Charact.*, vol. 32, no. 2, pp. 213–221, Aug. 2014.

[2] N. B. Uner and E. Thimsen, “In-Flight Size Focusing of Aerosols by a Low Temperature Plasma,” *J. Phys. Chem. C*, vol. 121, no. 23, pp. 12936–12944, Jun. 2017.

[3] F. Gillessen and D. M. Herlach, “Crystal nucleation and glass-forming ability of Cu-Zr in a containerless state,” *Mater. Sci. Eng.*, vol. 97, pp. 147–151, Jan. 1988.

PS-TuP-14 Building Tailored Chemistry Sets for Plasma Modelling using a Statistical Approach Embedded in an Online Engine, *Sebastian Mohr, G Evans, A Dzarasova,* Quantemol Ltd., UK*; M Virdee,* University College London, UK

The Quantemol Plasma Chemistry Generator has been developed within the PowerBase project to explore the vast number of potential chemical species and reactions present in a variety of plasma systems. Advances in computational and experimental plasma science as well as the increasing demand for precise and complex etching/depostion patterns have resulted in the use of increasingly complex plasmas for both research and industrial applications. Critical to the understanding and development of such methods in the semiconductor industry, is the identification of important chemical species and reactions present in the plasma, often a resource and time intensive endeavour. The Plasma Chemistry Generator tool suggests chemical species, important reactions and cross-section data for a given mixture of feed gases (e.g SF_6/C_4F_8), helping researchers to curate self-consistent sets of chemical reactions that are specific to the system of interest. Firstly, constituent plasma species are obtained from the Quantemol Database of Plasma Chemistries (QDB) [1] based on the chemical composition of the feed gases. Potential reactants and products for a hypothetical reaction are combined iteratively from these species, obeying mass and charge conservation rules, to form sets of allowed chemical reactions. Classification of these reactions into different process types, using models of reactions already available in QDB, facilitates the selection of important reactions based upon process parameters, such as the pressure of the plasma or the input power required for the users' application. In the final step, rate coefficients and/or cross sections are obtained from QDB where available. In case of unknown coefficients/cross sections, a suggestion by analogy to similar reactions will be made. By significantly reducing the time necessary to assemble a chemistry set, the Quantemol Plasma Chemistry Generator provides quick fundamental insights into plasma chemistries, accelerating the development and optimisation of new plasma systems and their applications. Examples of generated chemistry sets will be presented.

Funded by the PowerBase project under grant agreement No 662133 from the Electronic Component Systems for European Leadership Joint Undertaking

1] J. Tennyson et al, QDB: a new database of plasma chemistries and reactions, Plasma Sources Sci. Technol. **26** (2017) 055014

PS-TuP-15 Easy Synthesis of Hybrid Laterally or Vertically Patterned Hydrophobic/Hydrophilic Surfaces using a Dielectric Barrier Discharge

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The quest for obtaining smart materials with combined surface properties is driven by their many potential applications. Whereas the surface science community can now easily synthesize (super)hydrophilic or (super)hydrophobic surfaces, there is nowadays a specific interest for having stable surfaces where some spots are hydrophobic and some are hydrophilic, leading for instance to controlled chemistry at the hydrophilic part, leaving the hydrophobic part unchanged (this is particularly useful for biomedical applications where controlled adsorption of biological molecules can be requested)[1]. Similarly, for antibiofouling applications in marine environment, having layers alternating in depth an hydrophilic/hydrophobic behavior may lead to lower shell adsorption[2]. This type of multilayers coating can also find applications in the manufacturing of water filtration membranes[3].

In this research, we present a simple approach for synthesizing such patterns using a combination of two precursors, namely propargyl methacrylate (precursor for hydrophobicity) and acrylic acid (precursor for hydrophilicity) injected in a dielectric barrier discharge (DBD) operating at atmospheric pressure. A thin PVC mask is used for the surface patterning of the coating. Various amounts of the two precursors are injected in the DBD, which runs with argon as the main operating gas. These two precursors can indeed lead to coatings exhibiting contact angles varying from 140° to 15°[4]

The samples are characterized by secondary ion mass spectrometry (SIMS), both in static and dynamic mode, X-ray photoelectron spectroscopy and water contact angle. Despite the strong similarities between the two precursors, SIMS unambiguously show alternating in-depth composition of specific fragments. Similarly, water contact angle (with a reduced water drop size) shows that surface patterning is easily obtained by DBD, with contact angles of ~130° in hydrophobic areas and ~25° in hydrophilic areas. An alternate approach, consisting in exposing selected areas of the hydrophobic coating to an oxygen containing plasma, leads to angle of ~130° and ~17°, respectively. Such patterns are stable with time, opening the route for potential applications.

References:

(1) Ueda, E.; Levkin, P. A. *Adv. Mater.***2013**, *25* (9), 1234–1247.

(2) Xu, G.; Liu, P.; Pranantyo, D.; Neoh, K.-G.; Kang, E.-T. *ACS Sustain. Chem. Eng.***2018**.

(3) Kong, Y.; Lin, X.; Wu, Y.; Chen, J.; Xu, J. *J. Appl. Polym. Sci.***1992**, *46* (2), 191–199.

(4) Nisol, B.; Ghesquière, J.; Reniers, F. *Plasma Chem. Plasma Process.***2016**, *36* (5), 1239–1252.

Acknowledgements :

This work is funded by the Walloon region programs “complements FEDER”, Flycoat and Hylife.

PS-TuP-16 Plasma-based Approach to Driving an Amorphous-To-Crystalline Phase Change in MoS_2 Grown on Polymers

S Walton, D Boris, U.S. Naval Research Laboratory*; A Kozen,* American Society for Engineering Education*; **Gary Kushto**,* U.S. Naval Research Laboratory*; M Johnson,* National Research Council*; R Rai,* University of Dayton*; N Glavin,* Air Force Research Laboratory*; C Muratore,* University of Dayton

The ability to grow high-quality, continuous 2D transition metal dichalcogenides (TMDs) on polymer substrates is a prerequisite for commercial flexible devices based on these materials. Molybdenum disulfide (MoS_2) is a promising 2D semiconductor due to its relatively high charge mobility and a direct band gap of 1.8 eV coupled with optical transparency and high mechanical flexibility. Recently, magnetron sputtering from pure TMD targets, such as MoS_2 and WS_2, was used for growth of amorphous precursor films at room temperature on polydimethylsiloxane substrates. *Ex situ* laser annealing after film growth was then used to drive an amorphous-to-crystalline phase change. While successful, the phase change was limited to the area defined by the beam diameter. Rapid, large scale, *in situ* methods would be an attractive alternative to meet the demands for commercial scale manufacturing.

In this work, we discuss the development of a plasma-based approach to driving the crystallization of few-layer, amorphous MoS_2 on polymers. The amorphous MoS_2 was deposited, via magnetron sputtering of MoS_2 targets, on polydimethyl siloxane (PDMS) substrate**s**. The films were then exposed to electron beam generated plasmas produced in pure and dilute argon backgrounds to drive crystallization. The use of electron beam generated plasmas are attractive since they are both scalable to large areas and deliver a large ion fluence with kinetic energies as low as a few eV. The ion energies can be raised using DC or RF biasing, allowing the system to be tuned to deliver the energy required to drive the phase transition but limit etching and damage to monolayer films. The treated films are characterized using Raman, XPS, and Kelvin probes and those results will be discussed in terms of operating conditions such as treatment times, operating gas mixture, and ion energy. This work was partially supported by the Naval Research Laboratory base program.

PS-TuP-17 Atmospheric Plasma Deposition of Vanadium Oxide Thin Coatings on Cold and Heated Substrates

Antoine Remy, Université Libre de Bruxelles, Belgium*; M Gordon,* University of California at Santa Barbara*; F Reniers,* Université Libre de Bruxelles, Belgium

Atmospheric plasma deposition of vanadium oxide thin coatings on cold and heated substrates

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Vanadium oxides present interesting applications in thermochromic devices, electronic components, optoelectronics sensors, battery electrodes and catalysis. They can be synthesized by chemical vapor deposition (CVD) [1], or by magnetron sputtering [2]. In this research, we report, to the best of our knowledge, the first synthesis of vanadium oxide with a reactive atmospheric dielectric barrier discharge. This approach allows the direct synthesis of oxide layers on a wide variety of substrates, starting from an organometallic precursor in the vapor phase. Vanadium(V) oxytriisopropoxide vapours were injected in a DBD operating with argon as the main plasma gas. Variable quantities of the precursor and of oxygen (from 50 mL/min to 100 mL/min), operating as secondary reactive gas, were introduced in the discharge, and the plasma power was varied from 40 W to 60 W.

The coatings were deposited at room temperature, or, thanks to a new home made internal heating device, at higher substrate temperatures (ranging from 373 K to 573 K). Some coatings were post-annealed in air at 573 K.

The samples were characterized by X-ray diffraction, X-ray photoelectron spectroscopy and Infrared Spectrometry, in the IRRAS mode, and the electrical characteristics of the plasmas were studied by a high voltage probe. It is shown that the plasma power decreases with the introduction of oxygen, but remains virtually unchanged when the precursor is injected. Although, according to XPS, a significant amount of carbon still remains embedded in the final coating in the normal conditions of operation, typical IR bands for V_2O_5 at 1020 cm^{-1} and 850 cm^{-1} were observed for samples prepared with 50 mL/min of oxygen flow and at 300°C of sample temperature. This is confirmed by the oxidation state of vanadium (V5+), as observed by the XPS peak at 517.2 eV. The oxidation state seems to change with the conditions of the synthesis, starting from +5 for the original precursor, going down to +4, and then reaching +5 again for V_2O_5.

References

[1] S. Wanga, K.A. Owusu, L. Mai, *Applied Energy 211 ,* p. 200–217, 2018.

[2] M. S.B. de Castro, C.L. Ferreira, R.R. de Avillez, *Infrared Physics & Technology 60,* pp. 103-107, 2013.

Acknowledgements : this work is supported by the Belgium EOS Nitroplasm project, and by the Walloon region projects Cleanair and Amorpho.

PS-TuP-18 The Increased Efficiency Of The Amorphous/Silicon Heterojunction Solar Cells With Silicon Micro-Channels In Back Side Substrate*, **Hugo Alvarez**, G Bertão, A Silva, F Ciodin, J Diniz,* University of Campinas, Brazil

In this work, silicon based heterojunction (SHJ) solar cells were fabricated without a intrinsic layer using a 200 nm a-Si:H p$^+$ layer deposited by Electron Cyclotron Resonance-Chemical Vapor Deposition (ECR-CVD) system on to p$^+$-c-Si substrate. The electrical parameters of the obtained solar cells, such as efficiency, are related to the effects of: i) radio-frequency (RF) chuck power, used during the deposition of amorphous silicon (a-Si:H) Electron Cyclotron ECR-CVD, in the incorporation of H into the a-Si:H films for different RF powers; ii) Silicon micro-channels, which were fabricated in the back-side substrate with the solar cells.

The films were deposited using a ECR power of 500W, pressure of 4mTorr, substrate temperature of 20 °C, gas flows of SiH_4 and Ar, 200 and 20 sccm and 20 minutes and RF power of 1, 3 and 5W. To create the p$^+$ layer, the samples were boron implanted and annealed in a RTA process. Back and front aluminum contacts of 500 nm were deposited by sputtering and a thin layer of silicon oxide for passivation and an antireflective coating of silicon nitrite was deposited in the ECR for PV Cells efficiency measurements. The back-side contacts were corroded in circular dots (200 µm of diameter) and used as mask to define the silicon micro-channels using ICP (Inductively Coupled Plasma) plasma etching based on SF_6/Ar gas mixture. This SHJ solar cells were fabricated and the current density versus voltage curves in illuminated (AM 1.5) condition were measured. Before the microchannel etching, all solar cells, presented lowest efficiencies of about 0.001%. After the formation of the Micro-Channels (depths of about 7.5 µm and 8.2µm, for 10 and 40 minutes, respectively) using ICP plasma etching increased these values at least one order of magnitude. The maximum of 0.4% of efficiency was obtained for the SHJ cell, which was fabricated with the a-Si:H film of 3W RF power and with micro-channel in back-side, using 10 minutes of ICP etching. In the future, we intend to fabricate a microfluidic system to introduce the fluid into the Micro-Channels to cool and to increase the efficiency values of solar cells.

PS-TuP-19 Effect of RF Plasma on H Radical Generation on DCMS Produced a-Si:H*, **Jan Uhlig**, E Barlaz, D Ruzic,* University of Illinois at Urbana-Champaign

We report on the correlation between hydrogen radical concentrations and the densities of amorphous silicon produced by DCMS in Ar. Previously, the addition of molecular hydrogen during growth at pressures sufficient to produce viable inclusion rates frequently led to blister formation and potential delamination in the final film. An alternative approach demonstrated here is to improve the concentration of hydrogen radicals relative to molecular hydrogen th rough the use of a secondary plasma from an RF coil in the deposition chamber. At 300 W RF power and 1 mTorr of Ar, the addition of a fraction of a mTorr of hydrogen gas leads to a 20% reduction on film density. The relationship between hydrogen radical concentration production and secondary plasma power will be characterized by radical probe measurements.

PS-TuP-20 Hardmasks of TiN and Al for Silicon Micro-Channel Definition via ICP Plasma Etching Process*, **Camila Ruiz,*** Plasma Nanotechnology Research Center, UNICAMP, Brazil*; J Diniz, A Rosa,* Plasma Nanotechnology Research Center, University of Campinas, Brazil

TiN and Al films were used as hard mask (HM) materials in Si etching using a high-density inductively coupled plasma (ICP) reactor for silicon micro-channel (SiMC) (with depth > 1 µm) fabrication. The main proposal on this research is define a best hard mask (HM) for silicon micro-channel (SiMC) fabrication using ICP (Inductively Coupled Plasma) etching process. In addition, there are some important properties for hard mask should achieve, such as high mechanical performance and etch resistance to support the high process conditions. The TiN and Al films were deposited on silicon substrate by sputtering. Table 1 presents the obtained samples, with the thickness values and whether the annealing was performed or not.

Table 1. The obtained samples and the Hard Mask (HM) conditions

Samples	HM	Thickness	Annealing
A	TiN	100nm	YES
B	TiN	100nm	NO
C	Al	100nm	YES
D	Al	100nm	NO
E	Al	500nm	YES
F	Al	500nm	NO

Table 2 The used ICP parameters(fixed conditions: P=30mTorr, 450WICP, 100WRIE)

Process	ICP Parameters(sccm)	Time(min)
#1	48SF6+87Ar	10
#2	48SF6+87Ar	20
#3	48SF6+87Ar	30
#4	48SF6+87N2	10
#5	48SF6+87N2	20
#6	48SF6+87N2	30
#7	First sequence:20seconds, 48SF6+87ArSecond sequence:20seconds,48C3F8+87Ar	20
#8	First sequence:20seconds, 48SF6+87N2Second sequence:20seconds,48C3F8+87N2	20

The ICP processes to fabricate the silicon micro-channels (SiMC) and to characterize the mask resistance under the plasma etching were carried out using these fixed parameters as table 2. Two different gas mixtures were used for etching steps without the environment changing: SF_6+Ar, and SF_6+N_2 for 10, 20 and 30 minutes were employed. Two sequences of gas mixtures were used for etching steps in cycles with the gas environment changing: the first cycle was: 20 seconds SF_6+Ar, and in the sequence, 20 seconds, with C_3F_8+Ar; the second cycle was: 20 seconds with SF_6+N_2, and in the sequence, 20 seconds, with 48sccm of C_3F_8+N_2 for 20 minutes. The steps in cycles with different gas environments were based on Bosch process [1,2]. Usually, the Bosch process is performed using the cycles based on one sequence with SF_6/Ar gas mixture, with C_4F_8/Ar. In this work, we have used C_3F_8 gas, instead of traditional C_4F_8. Table 2 shows the conditions of ICP etching processes. The TiN hard masks have presented high resistance to etching process. However, the 100 nm Al films did not present high resistance, because the sputtering mechanism can occur. The 500 nm thick layers (samples E and F, Table 1), have presented the high resistance to etching process.

PS-TuP-21 Time- and space-resolved Diagnostics of a Self-Neutralized Ion Beam Extracted from a Pulsed Plasma*, **Ryan Sawadichai**, Y Chen,* University of Houston*; S Tian,* Lam Research Corporation*; V Donnelly, P Ruchhoeft, D Economou,* University of Houston

Ion beams are extensively used in a variety of thin film deposition and etching technologies. To neutralize the space charge of a positive ion beam extracted from a plasma, hot filaments, emitting electrons thermionically, are strategically placed on the downstream side of the extraction grid. Charge neutralization prevents spreading of the ion beam by Coulomb collisions among the ions. This work reports our observation that a self-neutralized ion beam can be obtained when the beam is extracted in the afterglow of a pulsed plasma, in the absence of any hot filaments. Specifically, a nearly monoenergetic ion beam was realized by applying a synchronous DC bias on an electrode in contact with the plasma during a specified time window in the afterglow of a pulsed plasma. Interestingly, the ion beam flux in the pulsed plasma case was much higher than that in a continuous wave plasma, under comparable operating conditions. Time resolved measurements of the ion and electron energy distributions were performed along the beam axis to characterize the spatiotemporal evolution of the beam and arrive at a plausible explanation for self-neutralization. Near the grid, positive ions reach a peak current during the active glow, and again soon after the application of bias in the afterglow, while electron current peaks only at the beginning of the afterglow. At distances greater than 10 cm away from the extraction grid, ions are only detected after the application of bias at a peak current with a delay corresponding to the flight time, while the electron peak did not shift. The time- and spaced-resolved measurements support a mechanism in which electrons from a low-density plasma near the ion extraction grid neutralize the space charge in the transiting beam.

Work supported by the National Science Foundation.

PS-TuP-22 Vacuum-ultraviolet-radiation Damage of Low-k Dielectrics*, **J. Leon Shohet**, S Kim, H Nguyen, P Xue, J Blatz, H Cheng,* University of Wisconsin-Madison*; Y Lin,* NSRRC, Taiwan*; J de Marneffe, M Redzheb, S Armini,* IMEC, Belgium*; C Chen,* NSRRC, Taiwan*; Y Wu,* University of Wisconsin-Madison

VUV exposure of dielectrics during processing can cause damage and can also be beneficial.. The goal of this work is to optimize the "beneficial" spectrum of photon radiation during plasma processing. To fully separate the effects of charged-particle bombardment a synchrotron can be used to provide a continuous spectrum of radiation over the range that most processing plasmas generate. In this work, four low-k samples were provided by IMEC. Their properties before exposure are as follows:

Precursor	Template	UV cure	k value at 100 kHz	
Sample 1	PMO	CTAC (C)	No	2.35
Sample 2	MSQ	BrijL4 (L4)	No	2.36
Sample 3	MSQ	BrijS10 (S10)	No	2.26
Sample 4	MSQ	BrijS10 (S10)	Yes	2.13

To determine the spectral effects of irradiation a five-step procedure was followed. The steps are (1) a rapid photon energy scan to measure the substrate current caused by photoemission as a function of photon energy. (2) Determine which photon energies generate the highest and lowest substrate currents. (3) Irradiate samples separately at the photon energy for the (a) the highest and (b) the lowest substrate current. (4) Measure the substrate current as a function of time for each of the monochromatic irradiations. (5) Following the monochromatic irradiation, a rapid photon energy scan was made again to determine whether changes could be observed in the dielectrics.

For each case, the substrate current begins at a high value and then decays as a function of time until it reaches a steady state. This is typically found after photoemission occurs because the dielectric acquires a net positive charge and thus photoemitted electrons tend to be attracted back to the dielectric. It should be emphasized that the substrate current does not decay to zero but reaches a constant value which is caused by photoinjection of electrons from the silicon substrate.

The damage effects were measured by examining the changes in dielectric constant, dielectric thickness, mechanical properties using nanoindentation, and chemical bond structures using FTIR. It was determined that VUV irradiation with photon energies > 7 eV increased the concentration of silicon dangling bonds in low-k SiCOH. Photons of lower energy were not able to bread the Si-O bonds that have a dissociation energy of 6.3 eV. TDDB degradation and negative mobile-charge generation were observed when the photon energy was greater than 9 eV. The k value increased when the dielectrics were exposed to photon energies > 8 eV. VUV photon irradiation increased the film hardness at photon energies of 10.2 and 11.8 eV. The dielectric constant increased slightly after exposure for all samples.

PS-TuP-23 Porous Alumina as a Vacuum Ultraviolet Transmission Window*, **Yuting Wu**, H Cheng,* University of Wisconsin-Madison*; Y Lin, C Chen, H Fung,* NSRRC, Taiwan*; J Shohet,* University of Wisconsin-Madison

Porous alumina is examined as a coupling window between an electron-cyclotron-resonance plasma used as a vacuum ultraviolet vuv source and a separate processing chamber. The porous alumina sample coupon used in this work has the following properties. The sample is 2 x 2 cm. Its thickness is 38 microns. It is composed of pores that are 20 nm in diameter resulting in a porosity of 50%.

To eliminate the effects of particles, a synchrotron was utilized to obtain the transmission properties as a function of photon energy. The transmission of VUV through porous alumina was measured as a function of wavelength is measured and was found to be nearly 50%. A silicon wafer with a dielectric surface is then placed in the processing chamber and exposed to VUV, both with and without the porous alumina window. A Kelvin probe is used to measure the surface charge induced on the wafer by photoemission in both cases, which will determine whether porous alumina can efficiently couple the VUV irradiation to a sample in a processing plasma.without significant modification to its spectrum and its resulting effects on the material. The advantage of porous alumina over a glass capillary-array window is that the hole diameters are in the nanometer range and this minimizes any particle flux compared with the glass capillary array.

PS-TuP-24 Frequency Response of Microwave Excited Argon Microplasmas using Continuum Simulations*, **Ayyaswamy Venkattraman**, A Verma,* University of California Merced

Scientific computing has emerged as an essential tool for the investigation and prediction of microwave sustained microplasmas for applications in metamaterials research. In this work, we intend to perform an in-depth numerical analysis of microwave microplasmas and present a broader scope of physical mechanism characteristics to microplasmas with an emphasis on frequency response of plasma dynamics. We will report two-dimensional fluid simulations of low-temperature microwave excited argon microplasmas in split ring resonators operating at or near atmospheric pressure. An in-house plasma solver is used to simulate these geometries in practical engineering conditions. Some salient features of these parallel simulations include the use of an unstructured mesh with both plasma and dielectric regions solved in a strongly-coupled manner. The simulations also utilized full-momentum equation for all species thereby doing away with possible approximations involved in the drift-diffusion approximation. We also present direct comparisons with experiments and drift-diffusion simulations performed by the Hopwood group in comparable geometries. The two-dimensional simulations will also be compared with previously published results using one-dimensional continuum and kinetic (particle-in-cell with Monte Carlo collision) simulations thereby quantifying the error associated with a one-dimensional approximation. Specifically, the frequency response predicted by one-dimensional simulations point to the existence of several interesting operating regimes depending on the excitation frequency in comparison to the collision frequency and the plasma frequency which will need to be compared with the predictions of the two-dimensional simulations (because of the ability of the plasma to expand). The feasibility of performing realistic two-dimensional/three-dimensional simulations of microwave microplasmas opens several possibilities in terms of optimizing the operating characteristics of these devices in various applications including plasma-based metamaterials.

PS-TuP-25 Development of an In-situ Plasma Enhanced Atomic Layer Etching System for III-group Nitride Device Process*, **C.P. Lin**, Y Lin, C Chen, M Wang,* National Applied Research Laboratories, Taiwan, Republic of Korea*; C Hsiao,* National applied research Laboratories,Taiwan, Republic of Korea, Taiwan, Republic of Korea*; F Chen,* National Applied Research Laboratories, Taiwan, Republic of Korea

An in-situ plasma enhanced atomic layer etching system has been design and fabricated. NO_2, BCl_3 and Ar plasma were used as the precursor for AlGaN epitaxy layer at various temperature. The optical detector was used to in-situ monitor the plasma spectrum during the step by step etching process. It is found that the layer by layer etching feature shows the process is a controlled self-limited reaction. In addition, the saturation curve of etching rate and precursor pulsed time has been established. Furthermore, This system could be used for the III-group nitride semiconductor device process.

PS-TuP-26 Advances in the Spectroscopic Characterization of Ceramic Films and Coatings*, **Fuhe Li**, A Tavakoli, J Brim,* Air Liquide Electronics - Balazs NanoAnalysis

A variety of radio frequency (RF) plasma source atomic optical emission spectroscopy and atomic mass spectrometry have been developed and implemented in our laboratory to characterize various solid ceramic materials, thick coatings and metal-oxide thin films. The techniques that we have developed include but are not limited to glow discharge OES, ICP-OES, laser ablation ICP-MS. Utilizing advanced RF plasma or a high energy laser beam for material sputtering, excitation or ionization, many intrinsic limitations associated with Auger, EDS, GD-MS, RBS, and SIMS techniques such as surface charging are eliminated. The signal intensities produced by these advanced techniques all have a simple and well-defined mathematical (linear) relationship with elemental concentrations in the material. A wide linear dynamic range (over seven orders of magnitude) in these techniques coupled with traceable NIST material standards developed in our laboratory have made accurate surface, interfacial and bulk analyses possible. The advances have also led to a much higher sensitivity in impurity analysis and a much higher accuracy in compositional verification. In addition, deep depth profiling a > 50 µm hard and thick ceramic coating (e.g. Type III anodized coatings) throughout its entire thickness in a real-time fashion can now be accomplished.

PS-TuP-27 Effect of Plasma Configuration on Defect-free Functional Doping on Graphene Surface*, Goo-Hwan Jeong*, *S Jo,* Kangwon National University, Republic of Korea

In this presentation, I will present the effect of plasma configuration on defect-free functional doping on graphene surface. The system is a vertical-type direct-current plasma with parallel electrodes. We change the electrode configuration and adjust the plasma input power and treatment time to utilize various ion-bombardment energies and plasma doses. The up-cathode system with a powered upper electrode and ground lower anode is more suitable than the traditional down-cathode system for efficient plasma doping. This configuration yields a low-energy ion process and thus suppresses high-energy ion-induced damages.

The graphene was prepared by mechanical exfoliation and the doping was performed using ammonia gas. The degree of a structural damage on graphene after the doping was mainly evaluated using Raman spectroscopy. Finally, the structural evolution of graphene and the doping components with respect to the plasma conditions are extensively characterized with Raman spectroscopy, atomic force microscopy, and X-ray photoelectron spectroscopy. In addition, we provide the results of *in-situ* OES analysis during plasma-doping process. The results provide an effective doping condition for doping nanomaterials without plasma-induced damage.

PS-TuP-28 Fluid Model Numerical Simulation Analysis of Microwave Plasma Discharges*, Wan-Ting Chiu,* National Tsing-Hua University, Taiwan, Taiwan, Republic of China*; I Yeh, K Leou,* National Tsing-Hua University, Taiwan, Republic of China

Microwave plasma discharges have been widely employed for diamond synthesis. In this work, fluid model numerical simulation analysis, using a commercial available code, COMSOL-Multi-physics, has been conducted for microwave hydrogen plasma discharges operated at 2.45 GHz. The simulation model consists of all basic physical mechanisms, including electromagnetics, plasma discharge, gas flow and heat transfer, along with gas phase and surface reactions of gaseous species and charged particles. For our first study, we investigated a plasma reactor based on the TM_{02} mode microwave applicator and a quartz dome. The simulation analysis was first employed to fine tune the structure dimension maximize the coupling of the 2.45 GHz microwave to the desired waveguide mode, TM_{02}, while minimizing its coupling to the major competing mode TM_{01}. The simulation analysis with plasma discharge shows that a plasma ball is formed above the substrate stage for certain operating conditions, while a separate plasma discharge appears if operated outside those operating “window”, a common characteristics of microwave plasma discharge operated under microwave cavity resonator mode. Parametric analysis of plasma discharge characteristics for different gas pressure and microwave power have been carried out. Detailed simulation results will be presented.

Acknowledgement :

Work supported by the Ministry of Science and Technology (MOST) of ROC/Taiwan

PS-TuP-29 Evaluation of Simulation Tool for a Plasma Generation based on the Dual Property of Electrons*, Shinichiro Kitamoto,* *P Abraha,* Meijo University, Japan

This research presents the development of a simulation tool that characterizes and optimizes the plasma characteristics of a new plasma device based on the dual property of electrons. The plasma device consists of three areas, namely the expansion area, the diffraction area, and the processing area. Successive electrodes generate, expand, and diffract the electrons that dissociate and ionize the nitrogen gas into a plasma. The device is specifically tailored to produce a uniform and large-volume plasma that can harden the surface of large mechanical parts or a large number of mechanical parts. Evaluation of the performance of the plasma device in attaining a uniform and large-volume treated materials requires extensive experimental work, modeling and numerical simulation in addition to plasma diagnostics. In this research, the principle of the plasma generation and the operating conditions of the plasma device are considered in constructing the simulation tool that illustrates the qualitative relations of the plasma parameters against the magnitude and uniformity of the plasma. Numerical simulation of three sequential regions namely particle, wave, and particle regions corresponding to the expansion, diffraction, and processing areas are modeled to give the total framework. The two particle regions, Particle-In-Cell and Monte-Carlo-Collusion methods, are carried out to determine the particle energy and position within the plasma chamber. While in the wave region, the Fresnel theory is used to determine the diffracted electron intensity distribution. In combining the results of the particle and wave regions, the plasma characteristics of the device are holistically determined. Comparison of the results of the simulation and experimental data obtained show good agreement, thus verifying the validity of the simulation tool.

PS-TuP-30 Plasma Nitriding of Highly Polished Metallic Surfaces*, Yoshiki Handa,* *P Abraha,* Meijo University, Japan

This research presents an appropriate plasma nitriding method for highly polished precision metallic components that need to maintain the as-finished surface conditions after the plasma treatment. Conventionally, a nitrided layer consists of a hard but brittle nitrogen compound layer and a layer made of diffused interstitial nitrogen atoms. The compound layers, $Fe_{3-2}N$ (gamma-prime) and Fe_4N (epsilon) form when the phase field has a solubility range of about 6-8 percent weight nitrogen. A high concentration of the nitrogen atoms on the surface, or concentration gradient, drives the atoms along the grain boundaries of the sample to form the diffusion layer. In this research, the incidence of the electrically charged electrons and ions is controlled to suppress the formation of the gamma-prime and epsilon phase fields and maintain a steady flow of interstitial nitrogen atoms along the subsurface. In this configuration, the sample is set inside a shielding grid that is located in the electron beam excited plasma chamber. The shielding grid is a 40-mesh screen biased negatively, while the sample is biased positively. The negatively biased grid repels the electrons that cause overheating in addition to attracting the ions for possible charge exchange with the meshed wire, thus increasing the atom density. On the other hand, the sample is positively biased to avoid any incoming ions from approaching the sample. In this experiment, the driving parameters of the built-in bias configuration were optimized to guarantee a diffusion-based nitriding that suppresses the formation of the compound layer. A comparison is then made based on measurements of the plasma species that interact with the samples and the characteristics of the treated samples in using both the diffusion-based method, neutral nitriding, and the conventional ion nitriding method. The results show neutral nitriding is a successful nitriding method that can strengthen the surface while keeping the surface free of the compound layer.

MEMS and NEMS Group
Room 202B - Session MN+NS+PS-WeM
IoT Session: Multiscale Manufacturing: Enabling Materials and Processes

Moderators: Susan Burkett, The University of Alabama, Roya Maboudian, University of California at Berkeley

8:00am **MN+NS+PS-WeM-1 Miniaturizing 3D Printed Microfluidics: State-of-the-Art and Outlook***, **Greg Nordin**,* Brigham Young University **INVITED**

While there is great interest in 3D printing for microfluidic device fabrication, the challenge has been to achieve feature sizes that are in the truly microfluidic regime (<100 µm). The fundamental problem is that commercial tools and materials, which excel in many other application areas, have not been developed to address the unique needs of microfluidic device fabrication. Consequently, we have created our own stereolithographic 3D printer and materials that are specifically tailored to meet these needs. We show that flow channels as small as 18 µm x 20 µm can be reliably fabricated, as well as compact active elements such as valves and pumps. With these capabilities, we demonstrate highly integrated 3D printed microfluidic devices that measure only a few millimeters on a side, and that integrate separate chip-to-world interfaces through high density interconnects (up to 88 interconnects per square mm) that are directly 3D printed as part of a device chip. These advances open the door to 3D printing as a replacement for expensive cleanroom fabrication processes, with the additional advantage of fast (30 minute), parallel fabrication of many devices in a single print run due to their small size.

8:40am **MN+NS+PS-WeM-3 A Novel Inkjet Printing Technology Based on Plasma Conversion of Metal-Salt Based Inks for the Fabrication of Microfabricated Sensors***, Y Sui, M Sankaran, **Christian Zorman**,* Case Western Reserve University

Inkjet printing is a leading additive manufacturing method to produce patterned metal thin films on flexible substrates. The most commonly-used inks consist of colloidal nanoparticle suspensions that employ organic molecules to stabilize the nanoparticles from agglomeration and precipitation. High temperature (>200°C) treatment is used after printing to remove the insulating organics and sinter the nanoparticles. The thermal step can limit printing on polymers such as PDMS, paper, and other temperature-sensitive substrates. Moreover the selection of metals is limited by those available in nanoparticle suspensions, with the most popular being Ag.

In this paper, we present the development of an ink-jet printing process that uses a particle-free, stabilizer-free ink and low-temperature plasma to produce electrically conductive metallic patterns on temperature-sensitive substrates. The inks are comprised of a metal salt, a solvent, and a viscosity modifier tailored to enable printing using a Dimatix DMP3000 series printer. The as-printed structures are treated with a low-pressure argon plasma which serves to convert the metal salt-based structures to metal structures with conductivities that approach bulk values. To date, we have demonstrated the process for Sn, Pb, Bi, Cu, Pt, Ag, Pd, and Au-based inks. The plasma-treated structures exhibit a high degree of porosity that can be as high as 70%, making them particularly well suited for use as active elements in microfabricated sensors. The extended paper will present details pertaining to the printing process, material characterization and testing of mechanical, chemical and biological sensors fabricated by this printing process.

9:00am **MN+NS+PS-WeM-4 Full Wafer Thickness Through Silicon Vias for MEMS Devices***, **Andrew Hollowell**, E Baca, D Dagel, M Jordan, L Menk, K Musick, T Pluym, J McClain,* Sandia National Laboratories

A significant amount of development has been achieved integrating TSVs with standard silicon (Si) substrates; however, there are unique challenges associated with integrating TSVs with MEMS substrates. Industry has achieved TSV integration through a dependence on substrate thinning, a TSV reveal approach. However, often these MEMS devices depend on the thickness of the substrate for controlling the radius of curvature of the substrate, such as throughout Sandia's ultra-planar multilevel MEMS technology (SUMMiT^{TM}). TSV filling relies on tight control of the fluid kinetics during the electroplating process and the ability to balance the diffusion of Cu^{2+} and organic suppressor molecules throughout the depth of the via in order to realize a void-free fill of the TSV. In this work we have extended the filling model for 60 µm deep TSVs, developed by Tom Moffat and Dan Josell, up to 675 µm deep TSVs.

In addition to the thickness constraints for MEMS integration, often MEMS devices are realized through unique release processes and are dependent on high temperature anneals. The most common release process is a hydrofluoric acid (HF) based release to selectively remove supporting oxide films and preserve the Si features that make up the MEMS components. The necessity to release structure in selective etchants presents additional challenges for integrating TSVs with MEMS components. We have overcome this challenge through the integration of additional capping layers which are selectively removed after the MEMS release. In order to accommodate the need for high temperature anneals we have removed the use of metal in the MEMS device and instead used doped silicon. The Cu TSVs are then integrated with the device after all the high temperature anneals are complete, making direct electrical contact to the doped Si. In this work, we present our integration approach for mating Cu TSVs with doped Si MEMS contacts and our plating approach for superfilling 675 µm deep, 100 µm wide TSVs.

This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. SAND2018-5012 A.

9:20am **MN+NS+PS-WeM-5 Scaling from Die Level to Full 150 mm Wafer TSV Filling through Fluid Dynamics Modeling and Current Controlled Deposition***, **Ehren Baca**, M Jordan, L Menk, K Musick, P Yeh, A Hollowell,* Sandia National Laboratories

In this work we have developed a novel methanesulfonic acid (MSA) based electrolyte with a single suppressor additive for filling 100 µm diameter 675 µm deep through silicon vias (TSVs). Contrary to conventional three-additive systems we have achieved bottom up super filling of these large TSVs with a single suppressor additive. This bottom up super filling mechanism is dependent on a strict balance between applied potential and diffusion of both suppressor molecules and Cu^{2+} ions. The bottom up deposition was developed through die level plating experiments on sample sizes approximately 1 in^2. We control the solution replenishment by connecting the sample, both electrically and mechanically, to an aluminum rod and rotating the sample in solution. The rotation rate is directly correlated to the velocity of solution moving across the opening of the vias and therefore related to the solution replenishment inside the TSVs. At first a potentiostatic approach was used to supply a sufficient potential to break down the suppressor with a reference electrode in our plating cell. Mapping the current, during deposition allowed us to develop a galvanostatic plating process.

Experiments were performed to scale this plating process to be compatible with production level electroplating tools. The fluid dynamics and applied current are significantly different on production plating tools. The tools do not come equipped with reference electrodes and in some cases, they have multiple anodes for current partitioning to control the uniformity of the electric field. Further, the wafer rotates about the center of the wafer and baffles are integrated into the tool to control the uniformity of a fountain type fluid replenishment system. With the wafer rotated about its center, there is a large variance in the velocity of fluid at different radii along the wafer. In this work, we present a set of scaling experiments performed on die with incremental increases in sample size to clearly map the die level plating parameters to a full wafer plating tool and achieve uniform TSV filling across a 150 mm wafer.

This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. SAND2018-5013 A.

9:40am **MN+NS+PS-WeM-6 Batch Level Electroless Under Bump Metallization for Singulated Semiconductor Die**, ***Matthew Jordan**, E Baca, J Pillars, C Michael, A Hollowell,* Sandia National Laboratories

Multi project-wafers (MPWs) allow multiple customers to share the cost of a manufacturing run from an advanced semiconductor foundry. This offers a cost-effective solution for low volume the fabrication or prototyping of application specific integrated circuits (ASICs). This practice is especially appealing for those in academia or government that often only require small quantities of devices for research or niche applications. With many products on a wafer, all the products must adhere to the same strict design rules. In practice this means that the final metallization is made using AlCu. This presents challenges for advanced packaging of MPW die as AlCu is not compatible with conventional flip chip solder because of oxidation of the AlCu metal. Further complicating the integration of MPW die is the fact that they are singulated prior to delivery, preventing the use of lithography, and thus ruling out the deposition and patterning of solder-compatible metals over the AlCu. This leaves the use of electroless plating schemes to prepare MPW die for 2.5D/3D die stacking.

We propose a batch process to facilitate MPW die processing through the electroless under bump metallization (UBM) process. This process includes passivation of the Si die sidewalls post dicing, MPW die mounting, batch Zn or Sn immersion followed by electroless Ni, electroless Pa, immersion Au (ENEPIG) or electroless Ni, immersion Au (ENIG) UBM deposition for reliable, UBM deposition. We have demonstrated 2.5D integration of batch processed, AlCu finished die that have UBM deposited using this process to an interposer using electroplated Cu pillars bumps and Au bumps.

Supported by the Laboratory Directed Research and Development program at Sandia National Laboratories, a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

11:00am **MN+NS+PS-WeM-10 MEMS-based Atomic Force Microscopy Probes: From Electromechanical to Optomechanical Vibrating Sensors**, ***Bernard Legrand**,* LAAS-CNRS, France*; L Schwab,* LAAS-CNRS, Univ Tououse, France*; P Allain, I Favero,* MPQ, CNRS, Univ Paris Diderot, France*; M Faucher, D Théron,* IEMN, CNRS, Univ Lille, France*; B Walter,* Vmicro SAS, France*; J Salvetat,* CRPP, CNRS, Univ Bordeaux, France*; S Hentz, G Jourdan,* CEA-LETI, France **INVITED**

Scanning probe microscopy has been one of the most important instrumental discoveries during the last quarter of the last century. In particular, atomic force microscopy (AFM) is a cross-disciplinary technique able to provide sample morphology down to the atomic scale. It offers invaluable tools to support the development of nano-sciences, information technologies, micro-nanotechnologies and nano-biology. For more than 20 years, boosting the scan rate of AFM has been an increasingly important challenge of the community. However still today, performing routine and user-friendly AFM experiments at video rate remains unreachable in most cases. The conventional AFM probe based on a micro-sized vibrating cantilever is the major obstacle in terms of bandwidth and resonance frequency.

Following a brief description of the context of the work, the talk will first describe the development of AFM probes based on MEMS devices that make use of ring-shaped microresonators vibrating above 10 MHz. A focus will be dedicated to the electrical detection scheme. Based on capacitive transduction and microwave reflectometry, it achieves a displacement resolution of 10^{-15}m/√Hz, allowing the measurement of the thermomechanical vibration of the MEMS AFM probes in air. Imaging capability obtained on DNA origamis samples at a frame rate greater than 1 image/s will be shown as well as investigation of block copolymer surfaces to elucidate the tip-surface interaction when vibration amplitudes are lower than 100 pm.

In the following, our recent research direction at the convergence of the fields of micro/nanosystems and VLSI optomechanics on silicon chips will be presented. Optomechanical resonators allow indeed overcoming the resolution limitation imposed by usual electromechanical transduction schemes. Here, we will introduce fully optically driven and sensed optomechanical AFM probes which resonance frequency is above 100 MHz and Brownian motion below 10^{-16}m/√Hz, paving the way for high-Speed AFM operation with exquisite resolutions at sub-angstrom vibration amplitudes.

11:40am **MN+NS+PS-WeM-12 Suppressing Secondary Grain Growth in $Sc_{0.125}Al_{0.875}N$ Using a CMOS Compatible Electrode**, ***Giovanni Esteves**, M Berg, M Henry, B Griffin, E Douglas,* Sandia National Laboratories

The electromechanical response of AlN can be enhanced by doping Sc into AlN up to ~43%. Challenges arise in processing high Sc doped AlN films due to the presence of secondary grain growth. Templating $Sc_xAl_{1-x}N$ (ScAlN) from a platinum bottom electrode has shown immense success in yielding highly textured *c*-axis ScAlN without the presence of secondary grain growth. However, platinum is not complementary metal-oxide-semiconductor (CMOS) compatible which makes it unattractive to those in industry. There is a need for a new bottom electrode that suppresses secondary grain growth while maintaining CMOS compatibility. In this work, $Sc_{0.125}Al_{0.875}N$ and AlN films were grown on various underlying CMOS compatible metal stacks. Optimal film microstructure and texture was obtained for films deposited on highly textured {111} $AlCu_{0.05}$ bottom metal. AlN and ScAlN thicknesses were 750 nm and 850 nm and showed rocking curves of 0.81° and 1.09°, respectively. Atomic force microscopy was used to determine the presence of secondary grain growth and film roughness. The success of this bottom metal stack is attributed to lattice matching and low surface roughness which allows for highly oriented *c*-axis textured AlN and ScAlN. This work presents a metal stack that allows for the creation of higher Sc-doped AlN films while maintaining a high-quality microstructure and texture. Therefore, allowing for commercialization of Sc-doped AlN technologies which are capable of higher electromechanical coupling coefficients than AlN devices.

This work was supported by the Laboratory Directed Research and Development program at Sandia National Laboratories. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

12:00pm **MN+NS+PS-WeM-13 A Low Voltage NEMS Relay. Design, Fabrication and Challenges**, *A Solot, A Dinescu,* National Institute for R&D in Microtechnologies (IMT), Bucharest, Romania*; M Fernandez-Bolaños, A Ionescu,* École Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland*; **Gina Adam**,* National Institute for R&D in Microtechnologies (IMT Bucharest), Romania

Microelectromechanical switches (MEMS) have a wide variety of applications, such as in radio frequency switching, sensing, etc. thanks to their high non-linearity, sensitivity and integrability. Unfortunately, traditional MEMS typically need tens of volts for actuation, which prevents their use in applications that require low voltage CMOS circuitry. The typical size for MEMS switches is ~100µm, but recent work [1] has shown a scalable two-terminal nanoelectromechanical (NEMS) switch with low actuation voltage (<1V). The pipe clip structure is based on side edge actuation and is prone to reliability issues due to stiction since the electrode width is quite large (~300nm). We propose a structure based on a protrusion (dimple) small contact area and tunable dimensions during the fabrication process.

This paper presents a nanoelectromechanical switch with <3V actuation voltage. The proposed design is based on a fixed bottom electrode line (Pt) and two pillars that support a metallic nanowire (~100nm wide) beam line. Since stiction is a significant issue for this device, the design includes protrusions (dimples) positioned in the center of the beam line with the scope of creating a small contact point with the bottom electrode. The structure is electrostatically actuated through a voltage applied on the beam while the fixed electrode is grounded. A small air gap between the beam and the bottom electrode line is crucial for reducing the actuation voltage, but can cause problems during the release. Finite element simulations in Comsol Multiphysics 5.2 were used to investigate the constraint space needed for the design of a NEMS relay with such a low actuation voltage, as needed for compatibility with a typical 3.3V CMOS technology. These simulations informed the geometries explored in the fabrication of a low power NEMS device with a double-clamped metallic beam. The surface micromachining process was developed to have a low-thermal budget (< 200 ^{o}C) and be multilayer CMOS compatible. The fabrication flow was based on SiO_2 as an inorganic sacrificial layer for obtaining a clean release. A mix of photolithography and e-beam lithography, lift-off and dry etching steps utilized are described, and challenges during the electrical characterization are discussed. Future design iterations focused on different beam designs are also presented.

J.O. Lee, Y.H. Song, M.W. Kim, M.H. Kang, J.S. Oh, H.H Yang, and J.B. Yoon, "A sub-1-volt nanoelectromechanical switching device", *Nature nanotechnology*, 8(1), 36-40, 2013.

Plasma Science and Technology Division
Room 104B - Session PS+AS+EL+EM+SE-WeM

Current and Future Stars of the AVS Symposium I

Moderator: Eric A. Joseph, IBM Research Division, T.J. Watson Research Center

8:20am **PS+AS+EL+EM+SE-WeM-2 Invited Talk-Future Stars of AVS Session: Ellipsometry at THz Frequencies: New Approaches for Metrology and Metamaterial-based Sensing*, Tino Hofmann*[1]*,*** University of North Carolina at Charlotte

Spectroscopic ellipsometry at terahertz frequencies has seen substantial advancements over the last several years. Now, instruments are available which allow precise measurements of the material's complex dielectric function including its anisotropy. This access to accurate electromagnetic material properties at THz frequencies is essential for the development of increasingly advanced THz optical systems and a prerequisite for the design and manufacturing of optical elements for this spectral range.

In this talk I will give an overview of recent developments in the implementation of THz ellipsometry and focus on applications where THz ellipsometry contributed valuable material parameters. In combination with external magnetic fields generalized THz ellipsometry allows the accurate measurement of the optical Hall effect. The optical Hall effect enables the precise determination of the free charge carrier properties effective mass, mobility, and density in semiconductor heterostructures at THz frequencies without the need of electrical contacts and will be discussed in detail.

The exploration of novel physical phenomena observed in artificially structured metamaterials and the application thereof is of interest due to its relevance for the design and fabrication of novel THz optical elements and sensors. Metamaterials have attracted continued interest for almost two decades due to their unique electromagnetic properties, which can differ substantially from their constituents and often do not even exist in naturally occurring materials. We have demonstrated that although being orders of magnitude smaller than the probing wavelength, metamaterials composed of highly-ordered 3-dimensional metal nanostructures exhibit a strong anisotropic optical response at THz frequencies. I will discuss how these interesting optical properties may be used for novel THz sensor and device designs.

8:40am **PS+AS+EL+EM+SE-WeM-3 Invited Talk-Future Stars of AVS Session: Remote Epitaxy – The Future for Stackable SiC Electronics*, Rachael Myers-Ward*[2]*,*** U.S. Naval Research Laboratory*; J Kim,* Massachusetts Institute of Technology*; M DeJarld,* US Naval Research Laboratory*; K Qiao, Y Kim,* Massachusetts Institute of Technology*; S Pavunny, K Gaskill,* U.S. Naval Research Laboratory

Ideally, electronic heterostructures from dissimilar materials leads to enhanced functionality. Yet, experimentally forming these heterostructures is challenging due to lattice or thermal coefficient of expansion mismatch leading to defect formation or thermally driven atomic diffusion resulting in cross-doping and gradual junction transitions. These challenges may be overcome with the discovery of remote epitaxy and 2D layer transfer [1]. Here, SiC epitaxy is performed on epitaxial graphene as the electrostatic fields from the substrate penetrate the graphene and guide adatom registry. The film is easily peeled away since the graphene is not bonded to either the substrate or epilayer; the epilayer is then van der Waals bonded to a different material enabling new functionality. We will present experimental results on the remote epitaxy of SiC, illustrating potential quantum science applications.

There are three necessary steps to create remote epitaxy. The first is to grow epitaxial graphene on SiC, followed by transferring the graphene to a desired substrate (if different from SiC), and finally the growth of the remote epitaxial layer. If the remote epitaxy is to be SiC, which is the focus of this paper, the second step is not needed. Epitaxial graphene (EG) was first synthesized on 4H- and 6H-SiC in a horizontal hot-wall CVD reactor between 1540 and 1580 °C in 10 slm of Ar and 100 mbar [2]. The growth temperature was dependent upon the offcut of the substrate, where substrates with higher offcuts require a lower growth temperature to ensure 1 ML of EG, which is desired to assist in SiC adatom registry during growth. SiC remote epitaxy was then performed on the EG using silane (2% in H_2) and propane precursors, where the SiC polytype replicated the underlying substrate. In an effort to transfer the remote SiC epi/EG to another substrate such as SiO_2/Si, a metallization step was performed. Thin Ti and/or Ni layers were initially deposited followed by a thicker high stress metal to create strain and aide in removing the remote SiC epi/EG from the SiC substrate [1]. Once transferred, the metal was removed via a metal etch.

In this work, we will discuss the important parameters needed for successful remote SiC epitaxy, such as metallization, graphene thickness and remote epitaxy growth temperature. The epitaxial morphology characterized by SEM and Nomarski microscopy and graphene coverage and transfer evaluated by Raman spectroscopy will be presented.

[1] Kim, *et al*., Nature 544, 340 (2017).

[2] L.O. Nyakiti, et al., MRS Bulletin 37, 1150 (2017).

9:00am **PS+AS+EL+EM+SE-WeM-4 Invited Talk-Future Stars of AVS Session: Low-Temperature Growth for 3D Integration of van der Waals Materials*, Christopher L. Hinkle*[3]*,*** University of Texas at Dallas

The integration of novel logic and memory devices, fabricated from van der Waals materials, into CMOS process flows with a goal of improving system-level Energy-Delay-Product (EDP) for data abundant applications will be discussed. Focusing on materials growth and integration techniques that utilize non-equilibrium, kinetically restricted strategies, coupled with in-situ characterization, enables the realization of atomic configurations and materials that are challenging to make but once attained, display enhanced and unique properties. These strategies become necessary for most future technologies where thermal budgets are constrained and conformal growth over selective areas and 3-dimensional structures are required.

In this work, we demonstrate the high-quality MBE heterostructure growth of various layered materials by van der Waals epitaxy (VDWE). The coupling of different types of van der Waals materials including transition metal dichalcogenide thin films (e.g., WSe_2, WTe_2, $HfSe_2$), helical Te thin films, and topological insulators (e.g., $Bi_{-2}Se_3$) allows for the fabrication of novel electronic devices that take advantage of unique quantum confinement and spin-based characteristics. We demonstrate how the van der Waals interactions allow for heteroepitaxy of significantly lattice-mismatched materials without strain or misfit dislocations. We will discuss TMDs, Te, and TIs grown on atomic layer deposited (ALD) high-k oxides on a Si platform as well as flexible substrates and demonstrate field-effect transistors with back-end-of-line (<450 °C) and even flexible plastics (<200 °C) compatible fabrication temperatures. High performance transistors with field-effect mobilities as high as 700 cm^2/V-s are demonstrated. The achievement of high-mobility transistor channels at low processing temperatures shows the potential for integrating van der Waals materials into new technologies.

This work was supported in part by 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. This work is also supported in part by NEWLIMITS, a center in nCORE, a Semiconductor Research Corporation (SRC) program sponsored by NIST through award number 70NANB17H041.

9:20am **PS+AS+EL+EM+SE-WeM-5 Invited Talk-Future Stars of AVS Session: Engineering the Properties at Heusler Interfaces*, Jason Kawasaki*[4]*,*** University of Wisconsin - Madison

The Heusler compounds are a ripe platform for engineering and discovering emergent electronic, magnetic, topological, and ferroic properties at crystalline interfaces, either with other functional Heuslers or with compound semiconductor or oxide substrates. In these applications,

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the ability to control interfaces with near atomic level control is of tantamount importance; however, challenges such as interdiffusion have hampered their development. Here, I will discuss our efforts to control the properties of Heusler interfaces using precision growth by molecular beam epitaxy (MBE). Results will be presented in three areas: (1) the use of epitaxial strain to stabilize the hexagonal phase of several polar metal candidates, (2) the use of monolayer graphene diffusion barriers to enable high temperature growth and performance of spintronic devices, and (3) the phase segregation of ferromagnetic FeV nanostructures from a semiconducting FeVSb matrix with coherent epitaxial interfaces. Together, these examples illustrate the power of epitaxy and interfaces in controlling the properties of Heuslers and other intermetallic compounds, and integrating them onto commonly used semiconductor substrate platforms.

9:40am **PS+AS+EL+EM+SE-WeM-6 Invited Talk-Future Star of AVS Session: Atom Probe Tomography for 3D Semiconductor Devices Applications*, Ajay Kumar Kambham*[1]*,*** GLOBALFOUNDRIES U.S. Inc.

Device structures are rapidly scaling down to the nanometer regime with the ongoing development in semiconductor device technology. Along with this, it is ever critical need to engineer dopant profiles and to define the formation of junctions in Metal-oxide field effect transistors (MOSFETs). This is increasingly challenging considering the severity of short channel effects (SCEs). Indeed, one type of SCE in MOSFET devices known to cause performance degradation is Drain Induced Barrier Lowering (DIBL). To reduce DIBL, dopant junction profiles are made more abrupt. This can be done through the introduction of Sigma/cavity, fully depleted silicon-on-insulator (FDSOI) structures and the modulation of stress through optimal engineered epitaxial buffer layers. To assess the quality over nanometer scale regions requires the use of analysis techniques such as Atom Probe Tomography (APT) and Transmission Electron Microscopy (TEM). This presentation will discuss the role of APT and how elemental distributions vary depending on process conditions along with the challenges involved in sample preparation.

11:00am **PS+AS+EL+EM+SE-WeM-10 Invited Talk-Future Stars of AVS Session: Three-Dimensional Imaging of Complex Oxide Interfaces*, Divine P. Kumah*[2]*,*** North Carolina State University

Complex oxide materials have a wide range of exciting tunable electronic and magnetic phases including ferroelectricity and superconductivity. The ability to fabricate atomic layers of complex oxides has led to the formation of novel interfaces and heterostructures of scientific and technological interest. The functional properties are usually correlated to sub-Angstrom structural perturbations at these interfaces. In this talk, a non-destructive synchrotron X-ray three-dimensional imaging technique will be applied to understand thickness-dependent electronic and magnetic transitions which occur in rare-earth manganite films with thicknesses on the order of an atomic layer. We show that structural distortions arising due to the electrostatic interfacial boundary conditions of the thin films are related to their thickness-dependent phase transitions. Based on these results, we show that heterostructures can be designed by molecular beam epitaxy to tune the atomic-scale structure of the manganite films to achieve robust ferromagnetism in atomically-thin layers. These results have important implications for the design of oxide-based spintronic devices and provide an important pathway for the realization of novel functional materials.

11:20am **PS+AS+EL+EM+SE-WeM-11 Invited Talk-Future Stars of AVS Session: lluminating Physics of Magnetron Sputtering Discharges*, Matjaz Panjan*[3]*,*** Jozef Stefan Institute, Slovenia

Magnetron sputtering is an established plasma technology for the deposition of thin films. In general, the technique is classified by the voltage supplied to the cathode; this can be continuous (DCMS), pulsed (HiPIMS) or oscillatory (RFMS). The distinction is also made with respect to the geometry of the magnetron source (e.g., circular, linear, cylindrical) and the magnetic field configuration (balanced or unbalanced). Despite the differences in the cathode operation, geometry and, magnetic field configuration, the underlying principle that forms dense magnetron plasma is the same. The central feature of magnetron sources is a crossed magnetic and electric field arrangement, which captures electrons close to the cathode. In such configuration, electrons gyrate around the magnetic field lines, bounce from the electric field of the sheath and drift in the azimuthal direction. The entrapment of electrons increases the plasma density close to the cathode (e.g., forming a ring-shaped plasma above the circular magnetron) and enhances the sputtering rate. Experiments using high-speed imaging and other techniques revealed that magnetron plasma is not azimuthally homogenous instead, it forms dense plasma structures called spokes. These structures have been extensively studied over the past few years and have changed our understanding of several physical processes in the magnetron discharges.

Spokes are observed for a wide range of discharge conditions, magnetron geometries and are an essential feature of all operational regimes [1-3]. They commonly form periodic patterns, have an arrowhead-like shape with an arrow pointing in the **E**×**B** direction, and travel with azimuthal velocities of several km/s. In the talk, I will present efforts to understand the physics of spokes and magnetron discharges in general. In particular, I will discuss spatial distribution of the plasma potential [4] and the influence it has on the transport of charged particles [5], sputtering process and overall sustainability of the discharge. I will demonstrate that electric fields associated with spokes cause localized re-energization of electrons and thus help to sustain magnetron discharge. Spokes also influence energy and spatial distribution of ions and therefore indirectly affect the thin film growth.

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

[2] A. Ehiasarian *et al.,Appl. Phys. Lett.*, **100** (2012) 11410

[3] M. Panjan *et al.*, *Plasma Sources Sci. Technol.*, **24** (2015) 065010

[4] M. Panjan and A. Anders, *J. Appl. Phys.***121** 063302 (2017)

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

11:40am **PS+AS+EL+EM+SE-WeM-12 Peter Mark Memorial Award: Plasma-bio Interactions: Investigating Mechanisms to Enable New Applications*, Peter Bruggeman*[4]*,*** University of Minnesota **INVITED**

Cold non-equilibrium atmospheric pressure plasmas (CAPs) have received a lot of attention in the last decades due to their huge potential for biomedical applications including wound healing, cancer treatment, dental treatments and disinfection and decontamination of heat sensitive materials [1]. These applications are due to the near ambient gas temperature at which CAPs can be produced and their high reactivity, involving the production of numerous reactive oxygen and nitrogen species [2]. Many applications require controlled interactions of plasma with bacteria, virus and mammalian cells or tissue that enable selectivity between healthy and cancer cells or in the treatment of bacteria on healthy tissue or food samples for which off target effects needs to be minimized. A controlled selectivity might be the greatest challenge for these applications and requires a detailed understanding of the underlying plasma-bio-interaction mechanisms. In this framework, my group in collaboration with microbiologists has performed detailed studies of the interactions of CAP with virus, bacteria and mammalian cells. Our research shows that controlling the gas phase plasma chemistry can lead to significant different biological responses of the living organisms [3-6]. The outcomes of these studies allow unraveling chemical pathways responsible for plasma-bio interactions and linking plasma kinetics to plasma-bio interactions. These insights are of invaluable importance for the development of applications in the field of plasma medicine.

References

[1] I. Adamovich, S.D. Baalrud, A. Bogaerts *et al*, J. Phys. D: Appl. Phys. **50**, 323001 (2017)

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

[3] K. Wende, P. Williams, J. Dalluge *et al.* Biointerphases, **10** (2), 029548 (2015)

[4] H.A. Aboubakr, U. Gangal, M.M. Youssef, S.M. Goyal and P.J. Bruggeman, J. Phys. D: Appl. Phys. **49**, 204001 (2016)

[5] G. Nayak, H.A. Aboubakr, S.M. Goyal and P.J. Bruggeman, Plasma Process. Polym. **15**, 1700119 (2018)

[6] V.S.S.K. Kondeti, C. Phan, K. Wende, H. Jablonowski, U. Gangal, J. Granick, R.C. Hunter and P.J. Bruggeman (submitted)

Acknowledgements

This work is partially supported by the ”Plasma Science Center on Control of Plasma Kinetics” of the United States Department of Energy, Office of Fusion Energy Science (DE-SC0001319), the Agriculture and Food Research Initiative of the USDA`s National Institute of Food and Agriculture (2017-67017-26172) and a Department of Energy Early Career Research Award (DE-SC0016053).

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[1] **Future Stars of the AVS**

[2] **Future Stars of the AVS**

[3] **Future Stars of the AVS**

[4] **Peter Mark Memorial Award Winner**

Plasma Science and Technology Division
Room 104A - Session PS+EM-WeM

Advanced Patterning

Moderators: Jeffrey Shearer, IBM Research Division, Albany, NY, Yiting Zhang, KLA-Tencor

8:00am **PS+EM-WeM-1 Study of High Selective Silicon Nitride Etching Mechanisms in Remote Plasmas: Impact of Wafer Temperature***, Emilie* ***Prevost,*** STMicroelectronics, France*; L Vallier, G Cunge,* LTM, Univ. Grenoble Alpes, CEA-LETI, France*; C De Buttet,* CEA-LETI, France*; S Lagrasta,* STMicroelectronics, France*; C Petit-Etienne,* LTM, Univ. Grenoble Alpes, CEA-LETI, France

Nowadays in the Semiconductor industry, challenging applications often requires ultra-high selectivity etching processes. Wet processes are often used but have drawbacks and show limitations in high aspect ratio features. One alternative possibility is to use chemical downstream etching plasmas. In this work, NF_3/O_2 downstream plasmas are used to etch selectively Si_3N_4 towards SiO_2 in high aspect ratio patterns (over 100).

In NF_3/O_2 plasmas, we observe that the wafer temperature (T°) has a considerable (but non linear) impact on the etching selectivity. When T° is raised from 40°C to 100°C, the selectivity first drop and then increase again, with a marked minima at 70°C. Indeed, the etching rate of Si_3N_4 and SiO_2 have a different behavior with T°: while the SiO2 etch rate increase slowly and continuously with T°, the Si_3N_4 etch rate first drop between 40 and 70 °C and then increases again at higher T°. This effect is attributed to two mechanisms in competition, the etching led by atomic fluorine and surface passivation via oxidation. To better understand the nonlinear behavior of the Si_3N_4 etch rate, the etching mechanisms of Si_3N_4 as a function of T° was investigated by plasma (VUV absorption spectroscopy) and surface diagnostics (Ellipsometry,XPS and AFM).

Angular XPS analysis show that the Si_3N_4 surface oxidation is minimal at low T° (40°C). As the wafer T° is increased, the thickness of the oxidized layer also increases rapidly until it reaches its maximum (about 5 nm) at 70°C. This is attributed to an enhanced diffusion of the O atoms produce by the plasma in the Si_3N_4 material. At higher T° the thickness stays constant but the amount of O in the layer decreases. In the NF_3/O plasma, atomic fluorine are responsible for the etching of both Si3N4 and SiO2 but with a natural selectivity. Therefore, the surface oxidation of the Si_3N_4 surface during etching is going to slow down the nitride etch rate and the thicker this layer is the smaller the etch rate will be (F atoms must diffuse through this layer to reach Si_3N_4). Therefore, when the T° is increased the Si_3N_4 etch rate initially drops because the SiO_x layer at its surface becomes thicker. Above 70°C the layer thickness stays constant but its degree of oxidation is decreasing when T° is increased: this explain why the Si_3N_4 etch rate increases again above 70°C. Hence the nonlinear behavior of the selectivity is due to a competition between the etching (by atomic fluorine) and surface oxidation, which strongly depends on T°. We highlighted via our research an important change on the etching mechanism at 70 °C, explained by the rapid formation of a thick oxidized layer.

8:20am **PS+EM-WeM-2 Mechanism of Highly Selective SiO_2 Etching over Si_3N_4 using a Cyclic Process with BCl_3 and Fluorocarbon Gas Chemistries***, **Miyako Matsui,*** Hitachi Ltd., Japan*; K Kuwahara,* Hitachi High-Technologies Corp., Japan

Multiple patterning techniques require extremely high selectivity to various materials and controllability of cross-sectional pattern profiles with atomic scale precision. In these fine patterning techniques, SiO_2 etching over Si_3N_4 requires an advanced process to form a thinner protection layer on Si_3N_4. For example, SiO_2 atomic layer etching with the fluorocarbon (FC) passivation of C_4F_8 plasma followed by Ar^+ bombardment has been investigated [1]. To achieve a high selectivity to Si_3N_4 using conventional FC plasma, the thickness and composition of the FC film should be controlled to protect only the Si_3N_4 surface from reaction with the FC film [2]. In our previous study, we proposed a cyclic SiO_2 etching process over Si_3N_4 by using BCl_3 and FC gas chemistries [3]. BCl_3 plasma was applied because it was expected to form a thin protection layer, which was suitable for selective etching at fine patterns when a low wafer bias was used. The thin protection layer formed by BCl_3 plasma was also expected to inhibit the spontaneous etching of Si_3N_4 by F radicals.

In this study, we investigated a cyclic process using BCl_3 and fluorocarbon gas chemistries for a fine pattern structure with a space width of 20 nm. The relationships between etching parameters and cross-sectional pattern profiles were also analyzed to control the pattern profiles. This process alternately performs two steps: an adsorption step using BCl_3 mixed-gas plasma and an etching step using $BCl_3/CF_4/Ar$ plasma with applying a wafer bias. The mechanism of the cyclic process was investigated by analyzing the surface chemistry at each step. At the adsorption step, a thicker BCl_x layer was formed on the Si_3N_4 surface than on the SiO_2 surface. Then, CCl_x films were formed on both surfaces at the etching step. We found that the thicker BCl_x layer formed on Si_3N_4 at the adsorption step protected Si_3N_4 from etching by reaction of BCl_x with CF_x and F radicals at the etching step. The B atoms in the BCl_x layers desorbed from the surfaces by forming BF_x, BCl_xF, and CCl_x. In contrast, the BCl_x layer became thinner on SiO_2 than that on Si_3N_4 to promote ion-assisted etching of SiO_2. This is because the BCl_x component has high reactivity with SiO_2, and the CF_x component was also consumed by the etching reaction with SiO_2. We also found that ion-flux should be controlled to etch without shoulder-loss, and ion-energy should be controlled to etch without footing shape at the bottoms of the pattern.

[1] D. Metzler et al., J. Vac. Sci. Technol. A **32**, 020603 (2014).

[2] M. Matsui et al., J. Vac. Sci. Technol. A **19**, 2089 (2001).

[3] M. Matsui et al., Jpn. J. Appl. Phys. **57**,(2018) to be published.

8:40am **PS+EM-WeM-3 DSA Patterning for and Beyond CMOS***, **Patricia Pimenta Barros,*** CEA-LETI, France*; N Posseme,* CEA, LETI, France, France*; S Barnola,* CEA-LETI, France*; R Tiron,* CEA-LETI, MINATEC, France*; A Gharbi, M Argoud, Z Chalupa, M Gusmao-Cacho,* CEA-LETI, France*; A Paquet,* Arkema, France*; F Delachat,* CEA-LETI, France*; Nicolet, Navarro,* Arkema, France **INVITED**

The continuous increase of CMOS device density has led to new 3D architectures. For the sub-7nm nodes, Leti investigates the interest of Tri-gate, Ω-gate and stacked nanowires architectures for better electrostatic control at aggressive dimensions [1, 2]. These new architectures bring a set of etching challenges at the integration level (from active, spacer, Si/SiGe removal) and require innovative etching solutions, such as gas or bias pulsing and atomic layer etching (ALE). In this paper, an overview of the main challenges and solutions for Si/SiGe stacked NW patterning will be exposed.

The active patterning of dense stacked nanowires have been already demonstrated by Leti using the Sidewall Image Transfer (SIT) technique [3]. In this paper, we will focus on the Directed Self Assembly (DSA) of block-copolymers (BCPs) that is considered as a cost-effective and complementary solution to conventional or EUV lithography [4, 5]. Herein, stacked Si nanowires are patterned using a DSA UV-assisted graphoepitaxy approach. Chemoepitaxy and graphoepitaxy approaches, which are the two ways to perform DSA, will be benchmarked. The transfer of ultra-small patterns using high-chi BCPs materials (pitch <20nm) will be also reported.

Based on LETI's FDSOI background, we are investigating new architectures such as steep slope devices, mechanical switches or single electron devices in a CMOS compatible flow. They are all studied in a CMOS co-integration perspective to enable the hybrid logic field [6]. In this paper, we will show that DSA patterning could be a good candidate for some applications beyond CMOS such as Single Electron Transistor devices or nano-membranes manufacturing.

[1] Coquand, R., et al., Symposium on VLSI Technology, pp. T226-T227 (2013)

[2] Barraud, S., et al., Symposium on VLSI Technology, Kyoto, pp. T230-T231 (2013)

[3] Gaben, L., et al., International Conference on Solid State Devices and Materials, 1108 - N-2-2, pp1108-1109 (2015)

[4] Jeong, S-J., et al., Materials today 16 (12), 468-476 (2013).

[5] Guerrero, D. J., Solid State technology (2017)

[6] Barnola, S, et al., Proc. SPIE 9054 (2014)

9:20am **PS+EM-WeM-5 Composition Modulation of SiGe for Si/SiGe Dual Channel Fin Application***, **Yohei Ishii,*** Hitachi High Technologies America Inc.*; Y Lee,* National Nano Divice Laboratories*; W Wu,* National Nano Device Laboratories*; K Maeda,* Hitachi High Technologies America Inc.*; H Ishimura,* Hitachi High-Technologies Taiwan Corp.*; M Muira,* Hitachi High-Technologies Corp.

As a consequence of downscaling to follow Moore's law, device structure was changed from conventional planar structure to Fin-type Field Effect Transistors (FinFETs) to achieve higher drive current and lower leakage current. In sub-10nm processes, it is necessary to further improve FinFETs electrical performance. A promising approach is to replace silicon fins with a new material, such as silicon germanium, which enhances carrier mobility

[1]. In Si/SiGe dual channel FinFETs, Si is used in n-FETs, while SiGe is used in p-FETs. Therefore, it is necessary to understand the difference in etching characteristics between Si and SiGe. Recently, we have developed an etching process to selectively etch Si over SiGe, and proposed the etching mechanism [2]. This etching technique proved to adjust not only the Si and SiGe pattern CDs (Si CD> SiGe CD and vice versa), but also Si and SiGe etched depth (Si etched depth < SiGe etched depth and vice versa), using Si/SiGe dual channel fin pattern samples.

As for the electrical performance of SiGe, it is important to form Si-rich SiGe surface at the SiO2/SiGe interface, because interface states play important role on sub-threshold characteristics [3]. There are several methods to form Si rich surface, such as thin Si cap epitaxial growth over SiGe fin [4] or H2 anneal-induced Si segregation [5]. However, it remains difficult to achieve the surface without the formation of a thick Si layer, which acts as a parasitic channel. In addition to that, avoiding Ge diffusion into Si cap layer is also an issue.

In this presentation, we propose a low-temperature process for achieving atomically controlled Si rich surface by utilizing plasma treatment to induce SiGe composition modulation at SiGe surface. We will also present a method to flexibly control the composition of SiGe surface (from Ge-rich surface to Si-rich surface) by utilizing plasma treatments. Details of the study will be discussed in this presentation.

[1] D. Guo, et. al., VLSI Tech. Dig., p.14, 2016

[2]. Y. Ishii et. al., Jpn. J. Appl. Phys. (Accepted)

[3]. C. H. Lee et. al., IEDM Tech. Dig., p.31.1.1., 2016

[4]. H. Mertens, et al., VLSI Tech. Dig., p.58, 2014

[5] L. Rudkevich, et. al., Phys. Rev. Lett. Vol.81 p. 3467 (1998)

9:40am **PS+EM-WeM-6 Etching Mechanisms of Si Containing Materials in Remote Plasma Source using NF3 based Gas Mixture**, ***Erwine Pargon**, V Renaud, C Petit-Etienne, L Vallier, G Tomachot, G Cunge, O Joubert,* Univ. Grenoble Alpes, CNRS, LTM, Grenoble, France*; J Barnes, N Rochat,* Univ. Grenoble Alpes, CEA, LETI, Grenoble , France

The introduction of new 3D designs (fin FETs, nanowire..) for sub-10 technological nodes bring new challenges for etch applications. Contrary to planar devices, 3D devices require more isotropic etch capabilities with high selectivity between different materials . Remote plasma source (RPS) which is based only on chemical mechanisms offers great capability for etch applications requiring high etch selectivity such as removal of SiN spacer in 3D device or fabrication of Si or SiGe horizontal nanowire for gate all around device. NF3 based gas mixtures are frequently used to etch Si containing materials in a RPS process. In this paper, we propose to investigate the etching and selectivity mechanisms of Si containing materials (SiN, SiO_2, SiGe and Si) in RPS process using NF3/NH3 or NF3/H2 gas mixture. In this study, the hydrogen content of SiN and SiO_2 materials is modulated by using different deposition techniques (LPCVD, PECVD..). The etching experiments are performed in an industrial RPS reactor. The substrate temperature can be varied between 40 and 200°C. The etching kinetics are in real time thanks to in situ kinetic ellipsometry. The results show that the etching of both SiN and SiO_2 materials in NH_3/NF_3 remote plasma proceeds through the formation of $(NH_4)_2SiF_6$ salts on the material surface that consume the pristine material. Similarly to oxidation processes, the consumed thickness of material is proportional to the thickness of the salt layer. The real time monitoring of the SiN and SiO_2 etching reveals that the etching proceeds in three phases. First, the reactive species absorb on the material surface but without consuming it. The delay before the materials starts to be etched increases with substrate temperature and decreases if the surface is rich in O and/or H, conveying that these elements act as a catalysis of the salt formation. During the second phase, the material is etched rapidly through the salt layer. During this phase, the material consumption depends on the substrate temperature and nature, as well as the plasma conditions. Finally during the third phase, the materials are consumed less rapidly because the reactive species have to go through the salt layer before reaching the salt/material interface. The etching kinetics in the third phase are almost independent on the substrate temperature, material, and plasma conditions. The key to get infinite etch selectivity of SiN over SiO_2 and SiO_2 over SiN is to tailor the substrate temperature and the surface functionalization. High etch selectivity of SiGe over Si can be easily achieved in NH3/NF3 remote plasma. Adding H2 in the mixture allows to reverse the trend.

11:00am **PS+EM-WeM-10 Precise Control of Silicon Nitride Spacer Etching Selectively to Silicon for 3D CMOS Device**, *V Ah-Leung, N Possémé, **Olivier Pollet**, S Barnola,* CEA-LETI, France

With transistors size scaling down, device processing requirements become more and more stringent. For technology node beyond 14 nm, one of the most critical step is the spacer etching. It requires a perfect anisotropy (no CD loss) without damaging [1] nor consumption of the exposed material like silicon, silicon germanium and oxide [2,3]. In planar transistor, the silicon or silicon germanium consumption is limited by the short over-etch process (30-50%). However for vertically stacked wires3D devices, the silicon fin is directly exposed during the removal of the silicon nitride on the active area sidewalls. This is the major issue since in this case, important over etch is required (>200%) to fully remove the residues at the bottom of the fin. Therefore, the spacer etch is considered today as one of the most challenging etch process for 2D but more especially 3D devices.

Today, current fluorocarbon etch chemistry (like CH3F/CH4/O2) are no longer suitable for 3D CMOS integration where long overetch is necessary.

In this context, we propose to introduce a new cyclic etch process of silicon nitride selectively to silicon to fulfill the stringent etch requirements described above [4].

This cyclic process is composed of two steps. A first step consists in silicon nitride etching till to top of the silicon fin. XPS analyses performed on blanket films (Silicon nitride and Si) reveal that a thin reactive layer is formed at the SiN surface, while an important deposition is observed at Si surface. This deposition at the Si surface is dependent of the process time. A second step (CHF3 based chemistry) allows partially removing the deposition on top of Si while etching the silicon nitride. Thanks to this new approach silicon nitride is linearly etched as a function of the number of cycles while the silicon film consumption is below 1.5nm. The selectivity reached by this new process is >100.

The impact of the different process step times and number of cycles on SiN and Si surface composition has been analyzed by XPS and will be presented. A proof of concept on vertically stacked wires patterned wafer will show that the silicon nitride spacer can be fully removed on the sidewall of the fin with limited impact on the silicon consumption/damage.

[1] N. Kuboi, T. Tatsumi, T. Kinoshita, T. Shigetoshi, M. Fukasawa, J. Komachi, and H. Ansai, J. Vac. Sci. Technol. A **33** (6), 061308 (2015).

[2] B. E. E. Kastenmeier, P. J. Matsuo, and G. S. Oehrlein, J. Vac. Sci. Technol. A **17** (6), 3179 (1999).

[3] K. Eriguchi, Y. Nakakubo, A. Matsuda, Y. Katao, K. Ono, IEEE Electr. Device L. **30** (7), 712 (2009).

[4] N.Posseme, S.Barnola, patent pending

11:20am **PS+EM-WeM-11 A Study on the Distortion of Poly Si Nano Hole Profile with High Aspect Ratio in sub X nm**, ***Jin Won Lee**, J Lee, K Seong, T Kwon, H Jeong, S Hong, D Han, B Lim, A Ji, Y Oh, J Park,* Samsung Electronics, Republic of Korea

As the Critical Dimension (CD) of Semiconductor becomes smaller, process using new materials is being developed and multi-patterning processes are required to overcome the limitations of lithography. However, only a few of them have been adapted to mass-production of the semiconductor because they costs highly and are complex. As a result, Researches on Si materials (SiN, SiO_2, Poly-Si) widely used in semiconductors have been actively conducted.

In this study, we will describe the etch process with excellent LER (~ 1) by removing the distortion which causes various problems and securing the vertical profile in the Poly-Si nano hole with the high aspect ratio (1:50) in sub X nm. HBr based Etch is favorable for Poly Si Etch because it has a high selectivity between Poly-Si and SiO_2. However it has tendency to cause clogging $Si_XBr_YO_Z$ byproducts which aggravate the open margin and profile control. By the way, the etch profile is also deteriorated due to irregularly crystallized grains, which is a character of Poly-Si and they might induce etch stop it is severe. Unlike HBr based etch, Cl2 based etch tends to be less polymerizing and less reactive thus it causes less clogging which is less effective by the poly grain and is effective to improve the profile. We adopted Cl2 based multi cycle etch over HBr based etch to secure the characteristics of the vertical profile with etch stop free.

Distortion must be solved in order to improve the LER, which is an important factor that affects not only the vertical profile but also the electrical characteristics of semiconductor of device. In general, the etch rates increases with increased process temperature and the distortion tends to be improved. However, in our study, the hole distortion is improved and more vertical profile is led at low temperature. This can be explained by the difference in the re-deposition tendency of byproduct. When the temperature is high, a large amount of byproduct, that occurs after etch, is more re-deposited on the upper part than the lower part because the convective phenomenon becomes more active and the sticking coefficient of the hole side wall decreases. As a result, the clogging becomes worse, and the hole side wall cannot be re-deposited uniformly. CD tends to be smaller. Profile tends to be positive and LER tend to be worse. On the contrary, if the process temperature is low, the sticking coefficient of the hole side wall increases, and the re-deposition is performed well. Since it is totally re-deposited in the hole side wall, it is confirmed the CD is increased and a vertical profile is foamed and the LER is improved.

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11:40am **PS+EM-WeM-12 Etching Recipe Optimization Using Machine Learning***, **Takeshi Ohmori**, H Nakada, M Ishikawa, N Kofuji, T Usui, M Kurihara,* Hitachi, Ltd., Japan **INVITED**

The development of semiconductor fabrication processes has been prolonged due to constantly evolving nano-scale 3D devices. This lengthy development period has driven up the cost of semiconductor devices, and the process development needs to be sped up in order to reduce the cost.

Along with time modulation of plasma generation and bias power and an increase in the number of gas species, continuous improvement of the control functions of a plasma etcher has been made to provide accurate nano-scale etching. A set of parameters for the control functions is called a recipe, which is used as input data for the etcher. Etching accuracy can be improved by increasing the number of parameters in the recipe. However, it is difficult to optimize the recipe for obtaining a target etch profile when there are many parameters.

In this work, we present two types of exploration method for recipe optimization using machine learning: one using etching profile data [1] and the other using feature data related to the etching profile [2]. These were developed to assist the development of the etching process and to reduce the time period of the development, respectively.

In the method using the profile data, a recipe is optimized through the repetition of an optimization cycle that consists of learning the relationship between the profiles and the recipes, predicting the recipes to obtain a target profile, performing etching experiments with the predicted recipes, and adding the experimental results to the learning data. In this cycle, kernel ridge regression is used as the learning engine and a Si trench pattern is used to examine the exploration method. By using the predicted recipe, a vertical trench profile was successfully etched, and the profile was further improved by increasing the number of cycles from one to seven.

Next, we developed the recipe exploration method based on machine learning of feature data related to the etching profile in order to accelerate the optimization. A micro/macro cavity method is used to extract the feature data. An approximate region to obtain the vertical profile can be determined in the feature data space because the feature data show the characteristics of ion assist etching and radical etching. The relationship between the feature data and the recipes was learned, and feature data were then explored to obtain the vertical profiles. After the iteration of the exploration, it enabled us to determine the optimum recipes for the vertical profile in just seven times of Si trench etching.

[1] T. Ohmori et al., Proc. of Int. Symp. Dry Process, Tokyo, pp. 9–10 (2017).

[2] H. Nakada et al., Proc. Gaseous Electronics Conf., Pittsburgh (2017).

Plasma Science and Technology Division
Room 104C - Session PS+MN-WeM

IoT Session: Enabling IoT Era

Moderators: Ankur Agarwal, KLA-Tencor, David Lishan, Plasma-Therm LLC

8:00am **PS+MN-WeM-1 A "Moore's Law" for Packaging***, **Subramanian Iyer,*** University of California at Los Angeles **INVITED**

While Silicon has scaled aggressively by over a factor of a few thousand over the last six decades the progress in packaging has been more modest – a linear factor 4-5 in most cases. In this talk, we will examine the reasons for this lag and what we are doing to fix this imbalance. Packaging is undergoing a renaissance where chip-to-chip interconnects can approach the densities of on-chip interconnects. We will discuss the technologies that are making this happen and how these can change our thinking on architecture and future manufacturing. Specifically, we will discuss two embodiments: Silicon as the next generation packaging substrate, and Flexible electronics using fan-out wafer level processing. We will describe how this is needed for the IoT era.

8:40am **PS+MN-WeM-3 Fabrication, Chemical Lift-Off and Optical Characterization of Nanoscale III-Nitride Light Emitters***, **Lesley Chan**[1], C Pynn, P Shapturenka, T Margalith, S DenBaars, M Gordon,* University of California at Santa Barbara

High density, near eye, and flexible display technologies of the future will require efficient micro- and nanoscale pixels based on light emitting diodes (LEDs). Liquid-crystal displays (LCD) and organic LEDs are currently used or envisioned for these applications, but their efficiencies and lifetimes are low. Higher efficiency III-nitride materials are promising for such displays, but manufacturing and implementing sub-micron scale InGaN/GaN structures that emit at different wavelengths into devices is currently difficult. Moreover, flexible and curved display applications require substrate thinning or separating individual devices from their growth substrates for subsequent printing or pick-and-place onto alternate substrates.

In this talk, we present an easy and scalable fabrication and chemical lift-off method to create nanoscale InGaN LEDs, along with morphological and optical characterization of the resulting structures using photo- (PL) and cathodoluminescence (CL). Active and sacrificial multi-quantum well (MQW) layers were epitaxially grown on semipolar (20-21) GaN substrates using MOCVD and patterned into large mesas (4x4 mm^2) using photolithography and Cl_2/N_2 plasma etching. Mesas were 'flip-chip' bonded to sapphire and chemically released from the GaN growth substrate by photoelectrochemical (PEC) etching of the sacrificial MQW layer, leaving behind a 1-2 µm thick p-GaN/MQW/n-GaN device layer protected with Si_3N_4. Nano-LEDs (nLEDs) were then patterned on the thin film device layer using colloidal lithography and plasma etching, released using HF vapor, and suspended in water, resulting in a colloidal solution of InGaN nLEDs. LED geometry was tuned by adjusting the SiO_2 colloid mask size (500-2000 nm) and plasma processing, e.g., using an isotropic CF_4/Ar mask reduction etch and vertical GaN etch with Cl_2/N_2. Preliminary PL results show a five-fold increase in emission for on-wafer nLEDs compared to their planar (unpatterned) counterparts. The large PL enhancement is thought to be due to increases in both IQE and EQE resulting from relaxed strain (decreasing the quantum confined Stark effect) and enhanced light extraction from increased scattering and graded index effects (i.e., non-planar geometries), respectively. CL spectroscopy and imaging of individual nLEDs also revealed strong MQW emission after processing with peak wavelengths at 430 nm. This work suggests that the 'flip-chip' approach, combined with colloidal lithography and chemical release, is a viable route to solution processable, high efficiency nanoscale light emitters.

9:00am **PS+MN-WeM-4 High Radical Flux, with Low Ion and Photon Flux, Plasma Source, for MEM'S Technology***, **Marc Segers**, Y Pilloux, D Lishan, S FERRAND,* Plasma-Therm LLC

Micro-electromechanical system (MEMS) are main constituent of a variety of sensors, that include pressure and vibration sensors, accelerometers and gyroscopes, and radiation and temperature sensors. MEMS is a technology that could answer the IoT's requirements for sensors high sensitivity.

To be able to produce MEMS with lower cost and higher quality, different steeps are necessary with preventive treatment, like substrate cleaning or sacrificial photoresist removal, with plasma.

In this work, we introduce a unique inductively coupled downstream plasma source configuration to generate high density radical concentration, for a chemical action and surface activation, but without high ion and photon fluxes, in opposition with conventional inductively coupled plasmas.

Our plasma technology provides a unique process capability for ultimate surface preparation, removal of most difficult residues formed during semiconductor and MEMS processing. System features an innovative approach to "Inductive Coupling", introducing a proprietary plasma confinement technology that is capable of a quasi-full gas dissociation inside the discharge tube, at low RF power. Although the plasma discharge tubes are isolated from the treatment chamber, with a remote plasma design, they deliver a large concentration of free radicals. That "High Density Radical Flux" technology (HDRF®) has demonstrated concentration levels up to 1,000 times higher than conventional plasma sources. HDRF® provides a damage free processing, allowing cleaning of high aspect ratio structures, preventing collapsing or stiction free of membranes, and

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[1] **Coburn & Winters Student Award Finalist**

activation of ultra-sensitive materials, that could be find in MEMS technology. Most of applications include Bosch polymer removal, low temperature photoresist stripping, descum and activation of ultrasensitive surfaces prior to bonding, like MEMS capsuling or shielding.

The low ion and photon exposure significantly reduces the opportunity for damage to sensitive layers. This inductive plasma arrangement prevents local heating and charging on the wafer. With that low local electrical potential, the HDRF® is efficient with 3D structures on the wafer (e.g. MEMS and other high AR features) where preventing ion shielding effects is important.

This work will first describe the **HDRF®** source and different advantages for MEMS processing. Second, several applications using the HDRF® technology will be discussed. These applications will include cleaning of 30:1 aspect ratio (AR) silicon vias, removal of sacrificial layers in MEMS structures, low temperature photoresist removal, and surface smoothing of Bosch generated sidewalls using micro-isotropic etching.

9:20am **PS+MN-WeM-5 Use of Plasma in Advanced Packaging**, ***Michael Seddon***, ON Semi **INVITED**

Advanced Packaging is critical for the continually evolving demands of IoT. As additional functionality is added to the final product, and as its form factor is reduced to further promote mobility and compatibility, the semiconductor package has become even more critical in the integration and overall success of the technology. Advanced IoT packaging is required to offer not only the reliably and protection required of the technology, but it needs to offer the solution with the lowest possible power usage, most efficient use of space and footprint, improved thermal performance, while at a low cost to the end customer. This presentation will discuss several uses of plasma in advanced packaging solutions to meet these demands in both improving the overall reliability performance as well as offering new technology solutions.

11:00am **PS+MN-WeM-10 Low Temperature Plasmas in Nanotechnology Applications**, ***Meyya Meyyappan***, NASA Ames Research Center **INVITED**

The versatility and low temperature processing capability has allowed the use of gas discharges in a variety of nanotechnology applications. This talk will provide an overview of our activities on the use of low temperature plasmas in printed electronics and also the growth of nanomaterials and application development. We have developed an atmospheric pressure plasma jet as an alternative to inkjet and aerosol printing to deposit nanomaterials on paper, plastic, metal foils and textiles etc. to enable flexible, printable electronics. This is a single-step process that does not require a follow-on annealing or sintering in order to get consolidated thin films as is customary with other techniques. The surface temperature is in the range of 20-80 deg C depending on the carrier gas used and the morphology of the film can be controlled by varying the carrier gas and other plasma parameters. Examples of printed materials and their applications will be discussed. The talk will also cover growth of vertical graphene or carbon nanowalls using PECVD on various substrates with interesting properties as well as carbon nanofibers for a variety of applications. The author thanks Ram Gandhiraman, Jessica Koehne, Mike Oye, Mehrdad Shaygan, Mark Rummeli and Jeong-soo Lee.

11:40am **PS+MN-WeM-12 Gas Phase Synthesis of Pure III-V Semiconductor Nanoparticles from Bulk Metals by using Low Temperature Plasma**, ***Necip Berker Uner***, *E Thimsen*, Washington University in St. Louis

III-V semiconductors are an important class of optoelectronic materials with applications that cover a broad range of the spectrum. Nanoparticles of many of the III-V materials, such as GaAs, InP and InSb, have been synthesized successfully with colloidal methods. However, high quality colloidal syntheses of stibnide and nitride nanoparticles haven't been reported yet. In this work, we present a general gas phase synthesis route for pure nanocrystals of GaSb and GaN. The method relies on reacting aerosols of different metals with help of a low temperature plasma (LTP). Aerosols of Ga, Sb and gaseous nitrogen bearing species were used as precursors. First, the aerosols of the constituent metals were generated via evaporation and condensation. Then, these aerosols were sent into a tubular argon LTP reactor, which provides continuous in-flight processing. As demonstrated in a previous study [1], particles vaporize in the LTP, and the resulting vapor may lead to nucleation of new particles or to re-condensation on the remaining clusters. During the synthesis of the III-V nanomaterials, unipolar charging prevents agglomeration, therefore free-standing particles were produced. Synthesized particles were found to be crystalline and they were mixed on an atomic scale. The stoichiometry was adjusted by manipulating input aerosol concentrations and applied plasma power. Materials were characterized *ex-situ* via high resolution transmission electron microscopy, energy dispersive x-ray spectroscopy, electron-energy-loss spectroscopy, x-ray diffraction and inductively-coupled plasma optical emission spectroscopy. The presentation will provide the results obtained through the extensive characterization methods mentioned. Furthermore, capping the synthesized particles with surfactants, effects of post-etching on the material, and photoluminescent properties will be presented. Operation of the aerosol sources and the mechanism leading to the formation of the compound materials will also be discussed.

[1] N. B. Uner and E. Thimsen, "In-Flight Size Focusing of Aerosols by a Low Temperature Plasma," *J. Phys. Chem. C*, vol. 121, no. 23, pp. 12936–12944, Jun. 2017.

12:00pm **PS+MN-WeM-13 Investigation of Fundamental Hydrocarbon Plasma Chemistry for Unraveling Film Deposition Processes on Nanomaterials**, ***Tara Van Surksum***, *E Fisher*, Colorado State University

Nanostructured materials have numerous desirable properties (e.g., electronic, optical, high surface area) making them useful for range of applications (e.g., catalysts, sensors). However, in some cases, mechanical properties of the materials are not well-suited for their intended environment. Plasma processing of nanomaterials presents an ideal route to modify bulk and surface properties and ultimately, fine tune these materials for desired applications. Hydrocarbon plasmas are often employed to deposit amorphous hydrocarbon films and have been utilized in conjunction with nanostructured materials to increase material hardness. To date, however, a lack of understanding of the fundamental interactions between the material and gas-phase hinders material development. Thus, we aim to elucidate how hydrocarbon plasma deposition processes are influenced by substrate morphology and chemistry, and conversely, how the material ultimately influences the gas-phase chemistry of the plasma.

Here, inductively-coupled hydrocarbon plasma systems (e.g., CH_4, C_2H_4) are investigated to elucidate the roles of gas-phase radicals and gas-surface interactions during film growth processes for flat (e.g., glass slides, Si wafers) and nanostructured (e.g., SnO_2, TiO_2, ZnO) substrates. Materials properties are also assessed to determine the influence of the plasma parameters on film quality. X-ray photoelectron spectroscopy confirms the deposition of amorphous hydrocarbon films on all substrates and scanning electron microscopy images show morphological differences between films deposited under different plasma conditions. Raman spectroscopy reveals that plasma processing creates oxygen vacancies in the TiO_2 lattice structure. Additionally, optical emission spectroscopy is utilized to determine relative species' densities and rotational and vibrational temperatures ($T_R$and T_V, respectively) for multiple species (e.g., CH, C_2). In CH_4 plasma systems, T_V(CH) ranges from ~2000 to ~4000 K under most plasma conditions, whereas T_R(CH) generally reaches values ranging from 1800 to 2800 K. Both values appear to correlate with system pressure and applied rf power. In some cases, the nanostructured substrates have a measurable effect on the gas-phase chemistry (e.g., presence of additional gas-phase species, elevated T_R(CH)), whereas in others, the substrate does not appreciably alter the gas-phase of the plasma. Collectively, these data help to unravel these complicated systems by providing valuable insight regarding possible mechanistic phenomena in hydrocarbon plasmas linked to film deposition on materials with complex architectures.

Plasma Biology, Agriculture, and Environment Focus Topic
Room 104A - Session PB+BI+PC+PS-WeA

Plasma Agriculture & Environmental Applications

Moderator: Deborah O'Connell, University of York, UK

2:20pm **PB+BI+PC+PS-WeA-1 Pulsed Power Applications for Farming and Food Processing***, **Koichi Takaki**,* Iwate University, Japan **INVITED**

High-voltage and plasma are useful in several stages in agriculture, fishery and food processing including contribution to the food safety. Pulsed high-voltage produces intense high-electric field which can cause some biological effects such as stress response (stimulation) and electroporation. Types of pulsed power that also have biological effects are caused with gas discharges and water discharges which include reactive species such as ROS and RNS. We developed repetitively operated compact pulsed power generators with a moderate peak power for the agricultural applications.

The pulsed repetitive discharge were used for promoting growth of the vegetables and fruits. The growth rate of the vegetables and sugar content in the strawberry harvested after the cultivation increased by the plasma irradiation to the hydroponic solution [1] . The plasma was irradiated in the drainage water for 10 and 20 minutes each day. The leaf size of the plants increased with plasma treatment time. Number of colony forming units (CFU) of *R. solanacearum* in the liquid fertilizer decreased from 10^7 to 10^2 CFU/mL using the discharge plasma treatment [2]. Seedlings with discharge plasma treatment were relatively healthy; in contrast, all seedlings in the positive control wilted and died from infection of *R. solanacearum* after 12 days. The yielding rate of Shiitake mushroom (*L. edodes*) was also improved with the high-voltage stimulation in fruit-body formation phase [3] .

Electrostatics effect were used for keeping freshness of not only agricultural products [4, 5], but also marine products [6] . In postharvest phase of agriculture, keeping freshness in storage house and in transportation container is important. The electrostatic effects can contribute to remove airborne bacteria and fungi spore from the storage house and container [4] . This removal contributes to reduce the infection risk with fungi and bacteria. Some kinds of fruit and vegetable emit the ethylene gas which accelerate a degradation of other kind fruits and vegetables. The plasma can contribute the ethylene removal via oxidization reaction [5] . The AC electric field induces a conformational change of protein. This technologies can contribute to extend the freshness of marine products [6] .

References:

1. J. Takahata *et al.*, Jpn. J. Appl. Phys., **54** (2015) 01AG07.
2. T. Okumura *et al.,* Plasma Medicine, **6** (2017) 247.
3. K. Takaki *et al.*, Microorganisms, **2** (2014) 58.
4. S. Koide *et al.*, J. Electrostatics, **71** (2013) 734.
5. K. Takahashi *et al.,* J. Jpn. Appl. Phys., **57** (2018) AG04.
6. T. Okumura *et al.,* Jpn. J. Appl. Phys., **55** (2016) 07LG07.

3:00pm **PB+BI+PC+PS-WeA-3 Stimulus Control on Organisms Using Pulsed Power Technology***, **Douyan Wang**, T Namihira,* Institute of Pulsed Power Science, Kumamoto University, Japan **INVITED**

Pulsed power is instantaneous ultra-high power with high energy density (10^5-10^7J/m^3). By controlling and utilizing it in a narrow space and an instantaneous time, phenomena and reactions that are not attained by conventional and ordinary methods can be achieved. For instance: electromagnetic field, discharge plasma, shockwaves, intense light emission, etc. By selecting or combining some of these physical phenomena, it is able to control the degree of output performance. Bioelectrics refers to the use of pulsed power, powerful pulsed electric or magnetic field for extremely short periods of time, non-thermal plasmas in gases or liquids and shock waves, in order to give novel physical stresses to biological cells, tissues and/or organisms as well as bacteria. Bioelectrics is an interdisciplinary academic field over physics, chemistry, biology, medical science, agriculture, environmental, mechanical and electrical engineering, and is expected to open up new science and technology.

By controlling the degree of electrical stimulations using pulsed power, it is possible to either inactivate biological targets or keep them alive and activate their functions. Examples of inactivation are given as: sterilization of liquids, treatment of algae and marine harmful organisms, growth inhibition of plants. On the other hand, more delicate stress control enables the activation of living organisms such as transcriptional activation of genes, substance transduction into cells, growth enhancement of plants. Both direct and indirect stimuli are useful. Here, aerial, liquidus and edaphic environmental control are examples of the indirect stimulus.

4:20pm **PB+BI+PC+PS-WeA-7 Synthesis of Nitrates by Atmospheric Microplasma in Aqueous Solution***, **Nicolas Maira**, F Reniers,* Université Libre de Bruxelles, Belgium

For many years, cold atmospheric plasma techniques have been used for a large variety of applications such as surface modification, film deposition, nanoparticles synthesis or pollutants degradation. One of their main advantage is the possibility to work with a gaseous, liquid or solid phase. In this study, the plasma water treatment is investigated for a potential application in agriculture. When water solutions are treated by plasma, in air environment, several reactive oxygen and nitrogen species (RONS) are generated [1,2]. The main RONS are hydrogen peroxide (H_2O_2), nitrites (NO_2^-) and nitrates (NO_3^-). Nitrates are one of the most essential molecules for plants because, together with ammonium, they represent an important source of nitrogen which is mandatory for DNA, RNA, enzymes, chlorophyll, ATP and many other molecules. For some applications such as hydroponics or urban agriculture, the local production of pure nitrates fertilizers directly available in the flowing water feeding system would be of great interest.

In this study, a DC atmospheric microplasma system is used for the investigation of the formation mechanism of NO_3^- in water. The liquid phase is analyzed by Ionic Chromatography (IC), UV-visible spectrometry (UV-vis) and pH-metry, whereas the gas phase is probed by Optical Emission Spectroscopy (OES) and atmospheric Mass Spectrometry (MS).

Firstly, the influence of the inner diameter of the microplasma stainless steel needle is investigated (internal diameter of 0,76 mm, 0,50 mm and 0,20 mm). The amount of NO_x^- (NO_2^- and NO_3^-) synthesized varies with the diameter and the shape of the plasma is different for a larger internal diameter. Furthermore, the total amount of NO_x^- formed in a solution shows a linear trend with the total charge injected into the plasma with, however different slopes for nitrites and nitrates.

The oxidation mechanism of NO_2^- to NO_3^- is then explored and the influence of other reactive species on this mechanism is then studied. Indeed, it is known from the literature that H_2O_2 may play a role in the process for different atmospheric plasma systems [2]. The formation of oxygenated water and its role as an oxidant is highlighted in the microplasma system. Therefore, the amount of H_2O_2 synthesized by microplasma is compared to other plasma systems. The nature of the atmosphere above the solution is modified in order to determine the species formed in the gaseous phase and their respective influence.

The authors would like to thank the financial support of NITROPLASM (EOS Project 30505023)

[1] Machala Z. *et al. Plasma Processes and Polymers*, 10, 649-659, **2013**.

[2] Judée F. *et al. Water Research* 133, 47-59, **2018**.

5:00pm **PB+BI+PC+PS-WeA-9 Design Considerations for Plasma-based Water Purification Reactor Scale-up***, **John Foster**, S Mujovic, J Groele, J Lai,* The University of Michigan-Ann Arbor **INVITED**

Plasma-based water purification has been proven viable in laboratory demonstration experiments, highlighting its effectiveness at the removal of contaminants of emerging concern and at disinfection. While these small scale experiments bolster the promise of plasma based advanced oxidation, translating demonstration experiments to practice has proven challenging. A chief challenge is the scale up of plasma-based methods to a viable water treatment technology that is both robust and usable at treatment flow rates of interest. Presented here is an attempt to frame the scope of the challenge, the current state of the art in plasma water purification, and scale up design considerations both from plasma science and engineering standpoints. The objective here is to summarize key challenges to scale-up and implementation as well as elaborate on approaches to achieving a high throughput plasma-based water treatment system. Two illustrative reactor examples amenable to scale up are highlighted along with associated performance data. The pathway from bench-top demonstration of plasma-based systems to piloting and ultimately to the reduction of the technology to practice is also elaborated upon.

5:40pm **PB+BI+PC+PS-WeA-11 Radicals and Ozone Generated in Ar/He and Ar/He/H_2O Plasma by using Atmospheric Pressure Plasma Jet Systems and their use in Methylene Blue Degradation***, J Hsieh,* ***YiJinWei Wei,*** Ming Chi University of Technology, Taiwan, Republic of China*; C Li,* National Yang Ming University, Taiwan, Republic of China

Optical emission spectroscopy (OES) and UV absorption spectrometry were first used to gather information about the excited species present near/in the plasma plume generated using Ar/He and Ar/He/H_2O gases with an atmospheric pressure plasma jet (APPJ). Afterward, the APPJ system was used to study its efficiency in degrading methylene blue as a function of radical and ozone density. According to the results, it was found that the degradation of methylene blue was directly related to the ozone concentration and, perhaps, OH radical density. Additional moisture may be used to control the ratio of ozone and OH radical density, resulting in the variation of degradation rate. Complete degradation of MB can be achieved in 80 seconds.

Plasma Science and Technology Division
Room 104C - Session PS+EM-WeA
Advanced BEOL/Interconnect Etching

Moderators: Michael Morris, Trinity College Dublin, Tetsuya Tatsumi, Sony Semiconductor Solutions Corporation

2:20pm **PS+EM-WeA-1 Etch Strategies for Reducing Defects and Pattern Roughness in BEOL EUV Patterning***,* ***Jeffrey Shearer,*** IBM Research Division, Albany, NY*; A Raley, Q Lou, J Kaminsky,* TEL Technology Center, America, LLC*; L Meli,* IBM Research Division, Albany, NY

As EUV lithography takes center stage in next-node semiconductor logic manufacturing, many challenges still need to be overcome. Of those, resist scumming, resist line breaks, and pattern roughness stand out as three of the top issues to address, especially when direct printing single levels below 36nm pitch. Previously, we have reported several methods of addressing these concerns in BEOL patterning, including introducing new material stacks and implementing new etch techniques such as resist reinforcement and quasi-atomic layer etching (QALE). This presentation will expand upon those ideas as well as introduce new etch methods that help enable direct EUV printing of single levels. Resist scumming will be addressed by exploring different types of descum etch chemistry. Data will show that line breaks can be reduced by resist reinforcement methods using pre-etch in situ deposition, increasing etch selectivity using QALE, and implementing direct current superposition (DCS). Additionally, we will show how line end pullback can be modulated with these different techniques and data will be presented that show resist reinforcement methods can recover more than 50% of line end pullback caused by more selective etch chemistries. The aspect ratio dependence of resist reinforcement and QALE will be discussed along with how aspect ratio impacts pattern roughness. The effectiveness of all of these etch strategies will be evaluated with defect characterization (bridge patterns and line breaks) and electrical testing (shorts and opens yield). Finally, we will discuss the impact of chamber configuration on EUV lithography pattern transfer. Data will be shown from chambers with the radio frequency (RF) split between top and bottom electrodes, dual RF on the bottom electrode only, and RF split between top and bottom electrodes with the addition of DCS. This work was performed by the Research Alliance Teams at various IBM Research and Development Facilities.

2:40pm **PS+EM-WeA-2 Influence of Topological Constraints on the Ion Damage Resistance of Low-*k* Dielectrics***,* ***Qing Su,*** University of Nebraska-Lincoln*; T Wang, J Gigax, L Shao,* Texas A&M University*; W Lanford,* University at Albany*; M Nastasi,* University of Nebraska-Lincoln*; L Li,* Intel Corporation*; G Bhattarai, M Paquette,* University of Missouri-Kansas City*; S King,* Intel Corporation

Low-*k* dielectric materials are well known to be sensitive to process induced damage during back-end-of-line (BEOL) patterning and metallization. This sensitivity has been largely attributed to the incorporation of terminal organic groups into the structure of low-*k* dielectric materials to lower dielectric permitivity and the subsequent loss of the terminal organic groups during BEOL processing. However, the correlations between the actual atomic structure of low-*k* dielectrics and their susceptibility to BEOL damage have been largely qualitative. A more quantitative metric for relating both the atomic structure and network topology of low-*k* dielectrics to downstream processing would allow for more efficient design and selection of materials for BEOL as well as pitch division multi-pattern applications. Toward this end, we have investigated the ion radiation damage resistance for a series of low-*k* and high-*k* dielectric amorphous hydrogenated silicon carbide (a-SiC:H) thin films, wherein atomic structure and topological constraints have been previously shown to play a remarkably fundamental role in determining the full spectrum of electrical, optical, thermal, and mechanical properties. We specifically show the response of a-SiC:H films with > 37% hydrogen content and mean atomic coordination ($<r>$) ≤ 2.7 subjected to 120 keV He^+ irradiation with damage level to 1 displacment per atom (dpa). Significant hydrogen loss, bond rearrangement, and mechanical stiffening were induced in these films. In contrast, comparatively minor changes were observed for a-SiCH films with <35% hydrogen content and $<r>$ > 2.7 also exposed to the same He^+ irradiation. The observed radiation hardness threshold at $<r>_{rad}$ > 2.7 is above the theoretically predicted rigidity percolation threshold of $<r>_c$ = 2.4. As we will show, the higher observed radiation hardness threshold can be interpreted as evidence that terminal hydrogen bonds and bond bending forces associated with two-fold coordinated motifs are too weak to function as constraints in collisions with high energy ions. Eliminating these constraints from consideration would increase $<r>_c$ to > 2.7 in agreement with the observed $<r>_{rad}$ = 2.7. These results demonstrate the key role of network coordination and topological constraints in ion damage resistance and perhaps provides new criteria for the design of new ion damage resistant / tolerant materials.

3:00pm **PS+EM-WeA-3 BEOL Patterning Challenges for 14nm and Beyond High Volume Manufacturing***,* ***Xiang Hu,*** GLOBALFOUNDRIES*; Y Ren,* GLOBALFOUDRIES*; D Medeiros, P Lee,* GLOBALFOUNDRIES **INVITED**

As the semiconductor features progressively shrink to sub 20 nm dimensions, patterning technology becomes significantly more critical. Pattern fidelity, yield, quality and cost now all incrementally become competing factors to the successful production of advanced technology nodes in high volume manufacturing. In this paper we will provide an overview on the challenges of patterning technology for single patterning, double patterning (DP), triple patterning (TP), self-aligned double patterning and EUV patterning, based on the learning of BEOL (Back End of Line) patterning technology development. We will focus on BEOL patterning technology challenges for 14nm high volume manufacturing, and demonstrate the patterning solutions for DP and TP 1D and 2D structure optimization. We will elaborate on process enhancements and controls such as CD, tip-to-tip and iso-dense loading optimization, the integrated patterning solution for open and short yield improvement and via-to-metal reliability improvement, the multi-variant APC control for process stability improvement by APC thread reduction and thread sharing among a variety of products. The success of BEOL patterning technology is dependent on patterning capability, process robustness and cost of patterning solutions.

4:20pm **PS+EM-WeA-7 Innovative Approaches for Future Challenges in MOL/BEOL Etch***,* ***Ryukichi Shimizu,*** Tokyo Electron Miyagi Limited, Japan **INVITED**

Critical dimensions (CD) continue to shrink driven by the quest for cheaper, faster and less power-consuming devices. If simple shrink was not enough, all of the back end, middle and front end of line (BEOL, MOL and MOL) also have introduced structural complexity and stringent topographic dimension, material property integrity and fundamental integration yield requirements. Self-aligned contact (SAC), high aspect ratio contact (HARC) and damascene structures in the MOL and BEOL typify challenging integrations. SAC structures are formed by oxide being etched from a nitride encasement. The oxide must be etched both beside and over thin (few nm) nitride films with near infinite selectivity as horizontal nitride layers can be exposed far before the deepest oxide in contact vias are removed. These structures are subject to “plugging” if the films get to thick, loss of nitride if the films get too thin, and etch rate or profile integrity loss elsewhere due to imbalances in ion energy flux or radical loss due to shadowing in a deep via. Obtaining the perfect balance of radical flux, ion flux and ion energy for these structures over a single die, let alone an entire wafer full of dies, is nearly impossible. Put in more general terms, fabrication challenges for plasma etch related to controlling local CD Uniformity (LCDU) and mitigating depth loading and CD loading are ever present due to difference in aspect ratio dependence (ARD) of transport of radicals and ions (and their energy) in features.

Atomic layer etching (ALE) has gained favor as an approach to extract more control over the fabrication of small CD complex topographic structures. The idea is that alternating steps of self-limiting processes (e.g., passivation layer formation) and desorption (e.g., the removal of a passivation layer) mitigate aspect ratio dependence effects that lead to the aforementioned problems. The problem is that not all passivation processes are self-limiting. Fluorocarbon based processes are not self-limiting rendering them quasi-atomic layer etch. Without special consideration, quasi-ALE has the same problems that continuous processes possess.

We have demonstrated the use of a new method of rapid advanced cyclic etch (RACE) comprising an isotropic CD trim step, mixed mode CVD, ALD and anisotropic bombardment to perform aspect ratio independent deposition and thereby eliminate CD bias effects. We show that X-Y CD control by ALD, CVD and trim can also be influenced by line-of-sight re-deposition from feature bottom. The ability to manage CD will be discussed as a means of enabling advanced patterning processes for both logic, interconnect and memory at advanced technology node.

5:00pm **PS+EM-WeA-9 Gas-phase Pore Stuffing for Low-damage Patterning of Organo-silicate Glass Dielectric Materials***, **Jean-Francois de Marneffe**,* IMEC, Belgium*; M Fujikama, T Yamaguchi, S Nozawa, R Niino, N Sato,* Tokyo Electron Technology Solutions Limited*; R Chanson, K Babaei Gavan,* IMEC, Belgium*; A Rezvanov,* IMEC, Belgium/Moscow Institute of Physics and Technology*; F Lazzarino, Z Tokei,* IMEC, Belgium

Capacitance gain remains of high value for lowering the interconnect RC delay in CMOS transistors, especially in the current design-technology co-optimization (DTCO) era where circuit density is maximized. In view of their superior mechanical properties, intermediate low-k dielectrics (sub-nanometer pore diameter, open porosity < 20%, k-value > 2.5) do attract nowadays most interest. CVD porous organo-silicate glasses are the most industry-relevant materials. They do suffer from processing damage, due to their porous and bi-component nature. As a consequence, some tailored protection strategies need to be developed. The gas-phase pore stuffing (GPPS) is a CVD method using two organic reactive precursors. Vaporized monomers (Gases A and B) are injected into the reactive chamber, supplied to the substrates and polymerized. Polymers are formed in the pores, deep in the bulk dielectrics, and can be removed by thermal annealing in controlled atmosphere. The GPPS technique is demonstrated on multiple OSG materials (various porosity), then applied to an OSG dielectric with nominal k-value 2.55, porosity ~ 16% and pore diameter ~ 0.8nm, which is embedded into a M1/V0 45nm ½ pitch vehicle. The target patterning sequence aims at creating a dual damascene structure by the fully self-aligned via approach (FSAV). The benefits of the GPPS is studied on the various plasma steps used in the FSAV patterning, allowing to reduce plasma damage up to 50% for the most damaging part of the FSAV patterning sequence (CO_2 ash, used for post-via strip, GPPS recess and GPPS unstuffing). The ability of the GPPS to form a protective plug is demonstrated, by excess polymerization in the pre-patterned via. By taking advantage of the specific properties of the GPPS approach, modifications of the FSAV patterning sequence are proposed, leading to potentially large capacitance gain. Various unsealing, unplugging and unstuffing options will be described, aiming at preparing the low-k surface for GPPS stuffing, and/or restoring the original porosity without residues, at the end of the patterning sequence. The gain in low-k dielectric properties, using the GPPS technique, is studied by k-value extraction on the various used vehicles.

Dr R. Chanson has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No 708106.

5:20pm **PS+EM-WeA-10 ALD-Sequential Etch to Address Advanced BEOL Etch/Integration Challenges***, **Xinghua Sun**, Y Lu, K Lutker-Lee, A Raley,* TEL Technology Center, America, LLC*; D O'Meara,* Tokyo Electctron, America, Inc.*; T Yamamura,* Tokyo Electron Miyagi Limited*; Y Kikuchi,* TEL Technology Center, America, LLC

As semiconductor nodes continue to scale past 7nm and beyond, control of critical dimension (CD), reactive ion etch (RIE) lag, low-k damage, material selectivity and chamfer profile becomes increasingly challenging for patterning of low-k materials in back end of line (BEOL) dual damascene processes. While modulation of plasma processing can address some of these challenges, process knobs that benefit one parameter can come into conflict with another, thereby leading to a necessity to compromise between them.

Recently, the introduction of anisotropic sequential etch, in which cyclical alternation of separated deposition and activation (etching) steps are used to decouple and control plasma chemistry, has revealed additional flexibility in profile control. However, anisotropic sequential etch tends to benefit processes that require significant boosts in etch selectivity and a controlled directional etch rate, while showing little improvement for processes where material damage is also a major concern, as in the case of low-k. As such, alternative methods to protect the low-k sidewall/corner during dual damascene processing are necessary. Introduction of a conformal, sacrificial side wall/corner protective layer through atomic layer deposition (ALD) can potentially fill this gap. Addition of an ALD-sequential etch process allows for a wide range of deposition choices, in contrast to the limited options generated through the gas chemistries typical for plasma etch. In this talk, we show how an ALD-sequential etchcan address dielectric etch challenges.

5:40pm **PS+EM-WeA-11 The Underlying Role of Mechanical Rigidity and Topological Constraints in Reactive Ion Etching of Amorphous Materials***, **Gyanendra Bhattarai**, S Dhungana, B Nordell, A Caruso, M Paquette,* University of Missouri-Kansas City*; W Lanford,* University at Albany*; S King,* Intel Corporation

In order for self-aligned multi-pattern techniques to be extended deep into the single digit nanometer range, new fab friendly material combinations with near perfect etch selectivity will need to be identified. This in turn requires a greater understanding of the interplay between plasma etching processes and the properties of the material being etched. While some qualitative correlations between dry etch rates and material properties such as composition, porosity, and density have been reported, more quantitative relationships have been generally lacking. In this regard, we demonstrate that analytical expressions derived to describe the material dependence of the yield for ion-induced sputter processes can be extended to reactive ion etch processes. Specifically, we first demonstrate a direct relationship between the atomic surface binding energy (U_{sb},), bulk modulus, and ion sputter yield for the elements, and then subsequently prove our hypothesis for amorphous multi-element compounds by demonstrating that the same relationships exist between the reactive ion etch (RIE) rate and nanoindentation Young's modulus for a series of a-SiN_x:H and a-SiO_xC_y:H thin films. The impact of a materials network topology is further revealed via application of the Phillips–Thorpe theory of topological constraints, which directly relates Young's modulus to the mean atomic coordination ($<r>$) for an amorphous solid. The combined analysis allows the observed trends and plateaus in the RIE rate versus modulus to be ultimately reinterpreted in terms of the atomic structure of the target material through consideration of $<r>$. These findings establish the important underlying role of mechanical rigidity and network topology in ion–solid interactions and provide a new consideration for the design and optimization materials for self-aligned pitch division / multi-pattern technologies.

6:00pm **PS+EM-WeA-12 Plasma Processing of Phase Change Materials for PCRAM***, N Altieri, **Ernest Chen**, J Chang,* University of California, Los Angeles*; S Fong, C Neumann, P Wong,* Stanford University*; M Shen, T Lill,* Lam Research Corporation

The manipulation of the amorphous to crystalline phase transition observed in chalcogenide glasses for non-volatile memory applications has been studied for many years since its initial conception. However, only recently has innovation in both materials development and memory device architecture enabled phase change random access memory (PCRAM) to become a promising candidate for applications such as neuromorphic computing.

Understanding the effects of plasma processing as well as post-processing damage of the phase change material (PCM) utilized in PCRAM is crucial to ensuring proper device performance. The studies presented herein focus on the behavior of $Ge_2Sb_2Te_5$ (GST-225) in conjunction with H_2 and CH_4 discharges as well as the roles of O_2 and N_2 through the use of a custom-built integrated ion beam chamber, inductively coupled plasma reactor, and *in-situ* x-ray photoelectron and quadrupole mass spectrometers.

Etch and gas phase reaction byproducts for single element Ge, Sb, and Te as well as GST-225 in hydrogen and methane have been identified through the use of quadrupole mass spectrometry and optical emission spectroscopy. X-ray photoelectron spectroscopy has been used to characterize surface bonding states and film composition across a wide parameter space, including low and high pressures as well as varying feed gas compositions.

Methane and hydrogen-based discharges were identified as capable GST etchant chemistries, resulting in rates up to 80 nm/min; however, the post-processing film composition was found to be strongly dependent on the chosen etch chemistry. Hydrogen radicals were identified as the dominant etchant species and resulted in the preferential removal of Sb and Te at low (15 mTorr) and high (75 mTorr) pressure conditions through the formation of volatile hydride products. Post-processing surface analysis indicated a substantial decrease in Sb and Te concentration from their initial 22 and 55 atomic percent to 3 and 4 atomic percent as well as an accumulation of Ge on the post-etch surface. Tuning of the etch chemistry was further explored through the use of auxiliary N_2 in order to modify the etch rate and preserve the starting 2:2:5 stoichiometry crucial to proper PCRAM device performance.

Nanometer-scale Science and Technology Division
Room 102B - Session NS+AN+EM+MI+MN+MP+PS+RM-ThM

Nanopatterning and Nanofabrication

Moderators: Brian Hoskins, National Institute of Standards and Technology (NIST), Meredith Metzler, University of Pennsylvania, Leonidas Ocola, IBM Research Division, T.J. Watson Research Center

8:00am **NS+AN+EM+MI+MN+MP+PS+RM-ThM-1 Femtosecond Laser Processing of Ceria-Based Micro Actuators***, **Jenny Shklovsky**,* Tel Aviv University, Israel*; E Mishuk,* Weizmann Institute of Science, Israel*; Y Berg,* Orbotech Ltd, Israel*; N Vengerovsky, Y Sverdlov,* Tel Aviv University, Israel*; I Lubomirsky,* Weizmann Institute of Science, Israel*; Z Kotler,* Orbotech Ltd*; S Krylov, Y Shacham-Diamand,* Tel Aviv University, Israel

The integration of piezoelectric and electrostrictive materials into micromachined Si devices is viewed as an important technological milestone for further development of Microelectromechanical Systems (MEMS). Recently, it was demonstrated that gadolinium-doped ceria (CGO) exhibits very large electrostriction effect, which results in large electrostrictive strains and high energy densities under very low frequencies (0.01 – 1 Hz). Lead-free CGO is chemically inert with respect to Si, making it an attractive candidate for implementation in MEMS actuators. However, the integration of CGO into MEMS devices is challenging due problems associated with using conventional patterning techniques involving lithography and etching.

In this work, we have successfully created functional double-clamped beam micro-actuators made of CGO films confined between the top and bottom Al/Ti electrodes. The stack containing the electrodes and the ≈ 2 µm-thick CGO film was first blanket-deposited on top of the Si wafer. Cavities were then deep reactive ion etched (DRIE) in the wafer leading to forming of the free-standing rectangular membranes, 1.5 mm × 0.5 mm in size. Finally, ≈ 1.2 mm long and ≈ 100 µm wide the double-clamped beams were cut from the membranes using a femtosecond (fs) laser, demonstrating an unharmful technique for CGO patterning. Laser pulse energies, overlaps and number of line passes were varied during the experiments, to achieve successful cuts through the suspended layer by a clean ablation process. The optimized process conditions were found at a fluence of ~0.3 J/cm^2 for a pulse width of 270 fs, where minimal damage and accurate processing was achieved with minimized heat-affected zones.

Resistivity measurements between the top and the bottom electrodes before and after fs laser cutting revealed that the cutting has no influence on the electric parameters of the device and no electrical shorts are introduced by the laser processing. Vertical displacement measurements under bipolar AC voltage (up to 10 V), at the frequency range of 0.03 – 2 Hz, demonstrated the functionality of the micro-actuator. A displacement of ≈ 45 nm at the voltage of 10 V at 50 mHz was achieved. The actuator didn't show any mechanical or electrical degradation after continuous operation. Our data confirm that fs laser cutting is a useful technique for processing CGO films. The developed techniques may be expanded to other materials used for fabrication of MEMS devices, enabling fast, high yield and high-quality patterning of materials that are challenging to pattern using conventional etching-based methods.

*Three first authors contributed equally to this abstract.

8:20am **NS+AN+EM+MI+MN+MP+PS+RM-ThM-2 Synthesis of Functional Particles by Condensation and Polymerization of Monomer Droplets in Silicone Oils***, **Prathamesh Karandikar**, M Gupta,* University of Southern California

The initiated chemical vapor deposition (iCVD) process is an all-dry, vacuum process used to deposit a wide variety of functional polymers. Typically, the monomer and initiator radicals are introduced simultaneously at process conditions leading to undersaturation of monomer vapors. In this work we report a sequential vapor phase polymerization method in which monomer droplets were first condensed onto a layer of silicone oil and subsequently polymerized via a free radical mechanism to fabricate polymer particles. The viscosity of the silicone oil was systematically varied from 100 cSt through 100,000 cSt. A heterogeneous particle size distribution was produced at low viscosities of silicone oil where the smaller particles were formed by the cloaking and engulfment of monomer droplets nucleated at the vapor-liquid interface and the larger particles were formed by coalescence inside the liquid. Coalescence could be inhibited by increasing the viscosity of the silicone oil leading to a decreased average radius and a narrower size distribution of the polymer particles. A transition to polymer film formation was observed for the 100,000 cSt silicone oil substrates. We studied the polymerization of two different monomers, 4-vinyl pyridine and 2-hydroxyethyl methacrylate, since these polymers have a variety of useful properties such as pH-responsiveness and biocompatibility. Our process enables fabrication of functional particles with average diameters ranging from 100 nm – 500 nm with fast reaction times (≈ 15 min). The advantages of our method for the fabrication of polymer particles are that it does not require surfactants or organic solvents and features short reaction times compared to conventional polymer particle synthesis methods such as emulsion polymerization.

8:40am **NS+AN+EM+MI+MN+MP+PS+RM-ThM-3 Competition Between Scale and Perfection in Self-assembling Structures***, **James Liddle**,* NIST Center for Nanoscale Science and Technology **INVITED**

Biology relies on self-assembly to form complex, highly-functional structures, inspiring the search for synthetic systems capable of forming similarly complex structures. Such systems typically operate under diffusion-limited, near-equilibrium conditions, making the problem even more challenging. Multi-functional, molecularly-addressable nanostructures of arbitrary shape can be built using DNA-mediated self-assembly. While this is a powerful method, and recent developments in DNA nanostructure fabrication have expanded the available design space, fabrication based on DNA alone can suffer from low yields and is hampered by the need to trade off size and mechanical rigidity.[1,2]

We have been working to both understand the factors that limit the yield of self-assembled structures, and to devise approaches to overcome them. As the number of discrete components used to assemble a structure increases, yield decreases exponentially. We circumvent this limit, by using a two-stage, hierarchical self-assembly process, which allows us to create large structures with high yield.[3] Our process employs a small number of discrete, sequence-specific elements to shape the structure at the nanoscale and define the large-scale geometry. A generic building block – a DNA binding protein, *RecA* – rigidifies the structure without requiring any unnecessary information to be added to the system.

Blending sequence-specific and structure-specific elements enables us to expand the self-assembly toolbox and make micrometer-scale, rigid, molecularly-addressable structures. More generally, our results indicate that the scale of finite-size self-assembling systems can be increased by minimizing the number of unique components and instead relying on generic components to construct a framework that supports the functional units.

[1] Murugan, A., Zou, J. & Brenner, M. P. Undesired usage and the robust self-assembly of heterogeneous structures. *Nat. Commun.* **6**, 6203, doi:10.1038/ncomms7203 (2015).

[2] Schiffels, D., Liedl, T. & Fygenson, D. K. Nanoscale structure and microscale stiffness of DNA nanotubes. *ACS Nano* **7**, 6700-6710, doi:10.1021/nn401362p (2013).

[3] Schiffels, D, Szalai, V. A., Liddle, J. A., Molecular Precision at Micrometer Length Scales: Hierarchical Assembly of DNA–Protein Nanostructures, *ACS Nano*, **11**, 6623, (2017)

9:20am **NS+AN+EM+MI+MN+MP+PS+RM-ThM-5 Polymer Templated Annealing of DNA Patterned Gold Nanowires***, **Tyler Westover**, B Aryal, R Davis, A Woolley, J Harb,* Brigham Young University

Using DNA origami as a bottom up nanofabrication technique, gold nanowires are formed via directed assembly of gold nanorod seeds and connected by electroless plating. This metal deposition process results in wires with low conductivities compared to bulk gold. Junctions between plated seeds are likely the cause of this low conductivity. Annealing of the nanowires could potentially improve the conductance, however, nanowire annealing at low temperatures (200° C) results in wires coalescing into beads. A polymer encapsulation layer was deposited to maintain overall nanowire shape during annealing. The polymer templated anneal resulted in a resistance reduction, in some cases, to below 1000 ohms. Resistance measurements were performed using a four point resistance configuration. Electrical contacts to the randomly oriented 400 nm long wires were made by electron beam induced deposition. Nanowire morphology was measured before and after annealing by scanning electron and high resolution transmission electron microscopy.

11:00am **NS+AN+EM+MI+MN+MP+PS+RM-ThM-10 Directed Self-assembly of Block Copolymers for Applications in Nanolithography*, Paul Nealey,*** University of Chicago **INVITED**

DSA of block copolymer films on chemically nanopatterned surfaces is an emerging technology that is well-positioned for commercialization in nanolithography and nanomanufacturing. DSA of (PS-b-PMMA) films on lithographically defined chemically nanopatterned surfaces is one focus of our activities in which the main research objectives revolve around understanding the fundamental thermodynamics and kinetics that governs assembly, and therefore patterning properties such as 3D structure, perfection, and processing latitude. A second focus is to use the physical and chemical principles that we have elucidated for DSA of PS-b-PMMA towards the development of block copolymer systems capable of self-assembling into the sub 10 nm regime and continuing to meet the stringent constraints of manufacturing. The research is enabled by the recent development of techniques to combine metrology tools (TEM tomography, GISAXS, RSoXS, high-speed APF), theoretically informed course grained models, and evolutionary algorithms to quantitatively determine and predict the independent process and material parameters that result in different 3D structures of assembled domains.

11:40am **NS+AN+EM+MI+MN+MP+PS+RM-ThM-12 Three Dimensional Mesoporous Silicon Nanowire Network Fabricated by Metal-Assisted Chemical Etching*, Deepak Ganta,*** *C Guzman, R Villanueva,* TAMIU

Mesoporous nanowires have gained huge attention due to their applications in energy and sensing. The high surface area along with the quantum confinement effect lead to improved performance of the electrochemical devices during energy conversion and storage. 3D structure or nanowire network improves the reaction site surface area even further along all the three dimensions, enhancing both light and heat absorption. There is also a huge demand for inexpensive, non-lithographic methods to fabricate 3D network of nanowires, which are also mesoporous, with better control of both dimensions and porosity, over a large surface area. They can be very useful in some broad range applications such as solar energy conversion, energy storage, water harvesting, environmental control, bio-sensing, and thermoelectrics.

To address the problem, we report a simple and inexpensive method of fabricating 3D mesoporous Si nanowire network by metal-assisted chemical etching (MacEtch). Degenerately doped p-type silicon or p+ silicon wafer (0.001 ~0.005 Ω·cm) was coated with about 22 nm silver film at 350 °C for 5~6 hours in a vacuum furnace (pressure < 3×10^{-7} Torr). Scattered silver particles with different sizes were formed as a result of the dewetting process. Then we deposited 10~11 nm of noble metal (Au) at 0.5 Å/s rate, followed by silver lift-off to obtain an Au mesh as an etching mask. The mixture of a chemical solution of HF: H_2O_2: Ethanol = 30:1:1 is used as a chemical etchant under room temperature. The time of immersion of the silicon wafer in the etchant effects the aspect ratio of the silicon nanowire array. After MachEtch, the Au is removed by immersing the sample in the aqua regia solution. The ratio of the chemicals in the etchant will affect the pore size. The aspect ratio of the silicon nanowire network can be controlled by the etching rate. The etching rate was roughly one μm/min. The 3D network is formed as the length of the 1D silicon nanowires (50 nm -100 nm) was varied, followed by critical point drying to carefully control the uniformity of 3D silicon nanowire network on the entire surface area of the 6-inch silicon wafer.

Analysis of the 3D mesoporous silicon nanowire network was conducted using Scanning Electron microscopy (SEM), and the top view image confirmed the 3D network of silicon nanowires. The pore sizing (2-50 nm) along with the crystallinity confirmed from the high-resolution transmission electron microscopy (TEM) images with the diffraction patterns.

12:00pm **NS+AN+EM+MI+MN+MP+PS+RM-ThM-13 Enhancing Light Extraction from Free-standing InGaN/GaN light Emitters Using Bio-inspired Backside Surface Structuring***, L Chan, C Pynn, S DenBaars,* ***Michael Gordon,*** University of California at Santa Barbara

A simple, scalable, and reproducible nanopatterning method to create close-packed (moth-eye like) patterns of conical nano- and microscale features on InGaN/GaN LED surfaces, and on the backside outcoupling surface of LED devices, is presented. Colloidal lithography via Langmuir-Blodgett dip-coating using silica masks (d = 170–2530 nm) and Cl_2/N_2-based plasma etching produced features with aspect ratios of 3:1 on devices grown on semipolar (20-21) GaN substrates. The resulting InGaN/GaN multi-quantum well (MQW) structures were optically pumped at 266/405 nm, and light extraction enhancement was quantified using angle-resolved photoluminescence (PL). A 4.8-fold overall enhancement in light extraction (9-fold at normal incidence) relative to a flat outcoupling surface was achieved using a feature pitch of 2530 nm. Extraction enhancement occurs due to the graded-index (GRIN) effect and breaking of the TIR condition via increased diffuse scattering and diffractive effects, the importance of which evolves with moth-eye feature size. PL results also demonstrate that colloidal roughening, which has greater geometric tunability and works on any GaN orientation, is equivalent to current, c-plane only photoelectrochemical (PEC) roughening methods. Patterning the outcoupling backside of a semipolar device, rather than the topside, is also a technologically feasible approach to fabricate electrically pumped devices because it avoids issues associated with making large area (topside) p-contacts, etching close to or into the active emitter region (destroying the MQWs), or disrupting guided modes in thin-film LEDs layers on sapphire. Because of its simplicity, range of optical control, and wide substrate compatibility, the colloidal lithography technique is a promising alternative to existing commercial processes and a future pathway for enhanced extraction engineering in free-standing polar, nonpolar, and semipolar III-nitride LEDs.

Plasma Science and Technology Division
Room 104C - Session PS+EM+TF-ThM

Atomic Layer Processing: Atomic Layer Etching

Moderators: Erwin Kessels, Eindhoven University of Technology, the Netherlands, Mingmei Wang, TEL Technology Center, America, LLC

8:00am **PS+EM+TF-ThM-1 Precise Flux Control of Ions and Radicals using Electron Beam Generated Plasmas*, David Boris,*** U.S. Naval Research Laboratory **INVITED**

Processing with atomic layer precision requires the ability to not only add, remove or modify one monolayer of material but to also leave adjacent layers unchanged. This requires fine control over the flux of species and energy deposition at the surface. In addition to the need for low damage, the complex device structures proposed for next generation nano-electronics will require control over radical to ion ratio as well. Electron beam-generated plasmas are generally characterized by high charged particle densities (10^{10}- 10^{12} cm^{-3}), low electron temperatures (0.3 - 1.0 eV), and in reactive gas backgrounds, a relatively low radical production rate compared to discharges. These characteristics provide the ability to precisely control the ion energy at adjacent surfaces and importantly, also the ability to control the ratio of ion to radical fluxes. In this work, we demonstrate this precise level of control using a variety of plasma characterization techniques and demonstrate how the applicability of these features to the processing of select materials systems. Specifically, we will discuss the processing of monolayer material systems such as graphene and MoS_2, where the material properties can be tuned without unwanted erosion or damage. Also SiN etching using pulsed, electron beam generated plasmas produced in SF_6 backgrounds is examined with particular attention paid to the etch rates, selectivity (vs. carbon films, Si and SiO_2), and patterning as function of operating parameters such as relative gas concentration, operating pressure, and substrate bias. Lastly, we address the use of electron beam generated plasmas for native oxide removal and subsequent passivation of surfaces. The processing results are compared with plasma diagnostics to gain a better understanding of the process requirements. This work is partially supported by the Naval Research Laboratory base program.

8:40am **PS+EM+TF-ThM-3 Demonstration of Self-limiting Nature and Selectivity Control in Annealing Procedures for Rapid Thermal-Cyclic ALE of W, TiN, and SiN*, Kazunori Shinoda,*** *H Kobayashi,* Hitachi, Japan*; N Miyoshi, K Kawamura, M Izawa,* Hitachi High-Technologies, Japan*; K Ishikawa, M Hori,* Nagoya University, Japan

Isotropic atomic layer etching (ALE) is expected to play an important role in semiconductor manufacturing because the next-generation devices will have miniaturized three-dimensional structures. The authors have developed isotropic ALE for SiN, TiN, and W using rapid thermal-cyclic processes, which are cyclic repetitions of plasma exposure and infrared annealing [1, 2]. Isotropic ALE ideally consists of cyclic repetitions of self-limiting formation and self-limiting desorption of the surface-modified layers. In the previous publications, the authors demonstrated self-limiting nature of the plasma exposure steps. In this paper, self-limiting nature of the infrared annealing steps are demonstrated. It is also demonstrated that etching selectivity between different materials can be controlled to be from infinitely selective to nonselective by adjusting the infrared annealing time.

The experimental apparatus used in this study is an ALE tool for 300-mm wafers. This tool is composed of a processing chamber, an inductively-coupled plasma source, infrared lamps, and in-situ ellipsometer. Films of W, TiN, and SiN deposited on Si substrates were used as sample materials. The wafers were first exposed to hydrofluorocarbon-based plasma to produce surface-modified layers on the surfaces of the materials to be etched. The wafers were then annealed by infrared irradiation to remove the surface-modified layers. The cycle of plasma exposure and infrared annealing was repeated ten times.

Firstly, infrared annealing time dependence of wafer temperature was examined. It was found that wafer temperature increased with increasing irradiation time at around 7°C /sec. Next, we examined how the annealing time affected the etched amount per cycle for W, TiN, and SiN. In the experiment, ten-cycle etching was repeated changing the annealing time in the range from 0 to 24 sec. The etched amount per cycle for W increased with the annealing time and saturated when the annealing time exceeded 10 sec. The etched amount per cycle for TiN increased when the annealing time exceeded 10 sec and saturated when the annealing time exceeded 20 sec. The etched amount per cycle for SiN saturated when the annealing time exceeded 15 sec. These results imply that the ALE process for W, TiN, and SiN are self-limiting in nature. Moreover, by choosing an optimal infrared annealing time, both highly selective and nonselective ALE for different materials was obtained. For instance, infinitely selective ALE of W over TiN was achieved when infrared annealing time was 8 sec.

[1] K. Shinoda et al., J. Phys. D: Appl. Phys. **50**, 194001 (2017).

[2] K. Shinoda et al., SPIE Advanced Lithography 10589-17 (2018).

9:00am **PS+EM+TF-ThM-4 Mechanisms for Atomic Layer Etching of Metal Films by the Formation of Beta-diketonate Metal Complexes*, Tomoko Ito, K Karahashi, S Hamaguchi,*** Osaka University, Japan

Ar^+ ion milling processes have been widely used for the fabrication of magnetic tunnel junctions (MTJ) of magnetoresistive random access memory (MRAM) devices. However, Ar^+ ion milling has a problem of surface damage caused by high energy ion bombardment, so the development oflow-energy reactive ion etching (RIE) processes is imperative for further miniaturization of MTJ cells. In recent years, beta-diketones such as acetylacetone (acac) andhexafluoroacetylacetone (hfac) have been considered as efficient etchants for thermal atomic layer etching (ALE) of metal films by the formation of volatile beta-diketonate metal complexes. Moreover, if low-energy ion incidence, rather than heating of the substrate, enhances the formation of organic metal complexes and their desorption from the metal surface, anisotropic ALE of metal films may be achieved. In this study, we explore the possibility of the development of such ion-enhanced metal surface etching using surface reactions of beta-diketones. The objectives of our research are, therefore, to understand surface reactions between gas-phase beta-diketones and metal surfaces and to clarify the beam-surface interaction between low-energy Ar^+ ions and beta-diketone adsorbed metal surfaces. To achieve these objectives, we have developed an atomic layer process (ALP) surface analysis system, which consists of a high-resolution X-ray photoelectron spectroscopy (XPS) analysis chamber and an ALP reaction chamber. The system allows *in-situ* analyses of, e.g., acac orhfac adsorbed Cu, Ni and Co surfaces and those after an exposure to low-energy Ar^+ or Xe^+ ion fluxes. The typical reactive gas exposure was in the range of 100 -10000 L (in units of L: Langmuir: 10^{-6} Torr・s) and the ion energy was in the range of 10- 50 eV. It is found that, for pre-oxidized Ni and Cu surfaces, hfac molecules adsorbed without C-O and C-F bond braking. It is also found that low-energy Ar^+ ion injection breaks down adsorbed hfac molecules even on a pre-oxidized Ni surface, fluorinating the Ni surface. The results show the difficulty of using low-energy ion exposure to enhance the formation of volatile metal complexes but also suggests a possibility of atomic-level surface modification of metal films using organic molecules, which may be used for highly controlled etching processes.

9:20am **PS+EM+TF-ThM-5 Thermal Atomic Layer Etching of Transition Metal Films*, Charles Winter,*** Wayne State University **INVITED**

Atomic layer deposition (ALD) features self-limited growth, which affords inherently conformal coatings on shaped substrates and Ångstrom-level thickness control.[1] Atomic layer etching (ALE) is a related technique, where layers in a film are removed one layer at a time and involve a self-limited mechanism.[2] Until recently, almost all ALE processes entailed either plasmas or ion beams.[2] Plasmas and ion beams require expensive equipment and the energetic species may damage sensitive layers in films. As a result, there is considerable interest in the development of purely thermal ALD processes that use chemical reactions to achieve thickness reductions. The first thermal ALE processes were only reported in 2015 for metal oxides and fluorides,[3-5] and many materials can now be etched thermally. Cobalt, copper and other first row transition metal films have wide applications in microelectronics devices.[6] The ability to carry out ALE on these metals would be very valuable. However, there has been little progress reported to date in the thermal ALD of first row transition metal films. We recently reported the ALD growth of cobalt[7] metal films and have explored these films as starting substrates in thermal ALE. In this talk, we will give an overview of the thermal ALE of cobalt metal films. These processes entail treatment of the cobalt metal films with formic acid in a first step, presumably to afford surface layers of cobalt(II) formate. These oxidized surfaces are then treated with various ligands in a second step to afford volatile cobalt(II) complexes, resulting in etching. Ligands that can be used to promote etching will be overviewed. Thermal ALE of copper and other metal films will also be presented.

1. S.M. George, Chem. Rev. 110 (2013) 111-131.
2. K.J. Kanarik, T. Lill, E.A. Hudson, S. Sriraman, S. Tan, J. Marks, V. Vahedi, R.A. Gottscho, J. Vac. Sci. Technol. A 33 (2015) 020802.
3. Y. Lee, S.M. George, ACS Nano 9 (2015)2061-2070. Y. Lee, J.W. DuMont, S.M. George, Chem. Mater. 27 (2015)3648-3657.
4. Y. Lee, J.W. DuMont, S.M. George, J. Phys. Chem. C 119 (2015) 25385-25393.
5. Y. Lee, J.W. DuMont, S.M. George, ECS J. Solid St. Sci. Technol. 4 (2015) N5013-N5022.
6. C.-C. Yang, P. Flaitz, P. Wang, F. Chen, D. Edelstein, IEEE Electron Dev. Lett. 31 (2010) 728-730.
7. M.M. Kerrigan, J.P. Klesko, C.H. Winter, Chem. Mater. 29 (2017) 7458-7466.

11:00am **PS+EM+TF-ThM-10 Gas Cluster Ion Beam Etching under Organic Vapor for Atomic Layer Etching*, Noriaki Toyoda,*** University of Hyogo, Japan **INVITED**

In our presentation, we will present our investigation of the usage of a gas cluster ion beam (GCIB) under organic vapor to irradiate a surface to produce atomic layer etchings (ALE). Gas cluster ions are aggregates of thousands of atoms or molecules that are collectively ionized and can be focused into a GCIB. The kinetic energy of a gas cluster ion is shared between the thousands of gas atoms or molecules; hence, the energy per particle in the cluster can be easily reduced to several eV. Furthermore, gas cluster ions can transfer a relatively large amount of energy to a concentrated area of the target surface; thus, a large number of target atoms can be sputtered by one gas cluster ion. As a result of the high-energy impact of gas cluster ions, low-damage surface modification takes place. Because of the features outlined above, GCIB guns are also widely used in conjunction with surface analysis techniques such as secondary ion mass spectrometry (SIMS) and X-ray photoelectron spectroscopy (XPS).

Because gas cluster ions deposit energy in a condensed manner without severe damage, surface reactions are enhanced even at room temperature, which is beneficial for ALE. In our study, we performed halogen-free ALE of Cu using oxygen-GCIB irradiation under acetic acid vapor [1]. We performed the etching process in the following steps: (1) adsorption of acetic acid on Cu, (2) evacuation of residual acetic acid vapor, and (3) reaction between acetic acid and Cu with the subsequent removal of the surface Cu layer via oxygen-GCIB irradiation. During one cycle of ALE, a very thin layer of acetic acid was adsorbed onto the Cu. Subsequently, the chemically altered Cu on the surface layer was removed with oxygen GCIB irradiation. When the Cu surface was irradiated with a 20 kV oxygen GCIB, Cu atoms beneath the surface layer were also sputtered after the removal of the chemically modified layer and as a result, this etching process was not self-limiting. On the contrary, when the surface was irradiated with a 5 kV oxygen GCIB, Cu atoms beneath the surface layer were not sputtered after the removal of the chemically modified layer. Thus, it could be concluded that halogen-free ALE could only be achieved at a lower oxygen GCIB voltage, namely 5kV. In the presentation, we will report the preliminary results of the various metal etching experiments we conducted with a GCIB under organic vapors and report their applications for ALE.

[1] N. Toyoda and A. Ogawa, Journal of Physics D: Applied Physics, 50, 184003 (2017).

11:40am **PS+EM+TF-ThM-12 Utilizing Chemical Structure of Hydrofluorocarbon Precursors to Achieve Ultra-High Selective Material Removal in Atomic Layer Etching*, Kang-Yi Lin, C Li,*** University of Maryland, College Park*; S Engelmann, R Bruce, E Joseph,* IBM Research Division, T.J. Watson Research Center*; D Metzler,* IBM Research Division, Albany, NY*; G Oehrlein,* University of Maryland, College Park

Atomic layer etching (ALE) applies sequential deposition and etching steps with short processing step length to establish selective material removal and atomic scale precision. The reactant pulsed in the ALE sequential reaction steps may behave differently from its use in continuous plasma etching, since for ALE the reactant is injected only during the deposition step and the deposited film undergoes non-steady-state surface desorption reaction during the etching step. In this work we will compare a mixture of a fluorocarbon (FC) precursor and H_2 with a hydrofluorocarbon (HFC) precursor, i.e. mixtures of octafluorocyclobutane (C_4F_8) with H_2 and 3,3,3-trifluoropropene ($C_3H_3F_3$), for SiO_2 ALE and etching of SiO_2 selective to Si_3N_4, Si and SiGe. For continuous plasma etching, process gas mixtures, e.g. C_4F_8/H_2, have been employed and enable highly selective material removal based on reduction of the fluorine content of deposited steady-state HFC films. This approach, however, is not successful for ALE since the residual hydrogen during reaction steps will induce etching and reduce the remaining thickness of the deposited HFC film. This HFC film on the surface is required for both etching of SiO_2 and passivation of the Si_3N_4, Si and SiGe, and a reduction in film thickness leads to lower material etching selectivity. $C_3H_3F_3$ with hydrogen reduces fluorine content in the precursor structure and allows deposition of fluorine-deficient HFC films without suppressing the formation of the passivation layer on the surface. Our results support that gas pulsing of complex HFC precursors in ALE provides a novel opportunity of utilizing the precursor chemical structure for achieving near-atomically abrupt selective ALE processes for SiO_2 over Si_3N_4, Si, SiGe and potentially for other materials. The authors gratefully acknowledge financial support of this work by the Semiconductor Research Corporation (2017-NM-2726).

12:00pm **PS+EM+TF-ThM-13 Etch Selectivity Mechanisms of Implanted Over Pristine SiN Materials in NH_3/NF_3 Remote Plasma for Quasi Atomic Layer Etching with the Smart Etch Concept*, Vincent Renaud,*** *E Pargon, C Petit-Etienne,* LTM, Univ. Grenoble Alpes, CEA-LETI, France*; J Barnes, N Rochat,* Cea, Leti, Minatec, France*; L Vallier, G Cunge, O Joubert,* LTM, Univ. Grenoble Alpes, CEA-LETI, France

The complexification of 3D architectures of advanced CMOS devices require to etch materials with a sub-nanometer accuracy without introducing damage to the surface and with infinite selectivity between the materials in presence. The Smart etch concept is a n original etching approach which has successfully been proposed to etch silicon nitride spacer with less than 1nm of spacer dimension loss and SiGe recess. This technic relies on a surface modification by H or He ion implantation performed in capacitive coupled plasma (CCP) reactor, followed by a selective removal of the modified layer over the pristine material. The selective removal can be achieved either by wet or remote plasma source etching. Today, the mechanisms driven the etch selectivity between the pristine and modified SiN layers in remote plasma are still misunderstood

In this paper, we propose to investigate the etching mechanisms of pristine and implanted silicon nitride layers in NH_3 /NF_3 remote plasma. The etching experiments are performed in 300mm industrial prototype of reactor, equipped with both a CCP and a remote plasma source allowing to achieve the implantation and the removal steps in the same reactor chamber. The substrate temperature can be varied from 40 to 200°C during the process. The etching kinetics are followed in real time thanks to in situ kinetic ellipsometry. The SiN layers are characterized by XPS, XRR and Tof-SIMS.

The real time monitoring of the etching reveals that there is a delay before the SiN layers are etched for any plasma conditions and wafer temperature. The incubation time increases with substrate temperature and depends on the surface state. For instance, our results show that a deoxidized SiN surface using HF wet is not etched in NH_3/NF_3 remote plasma, proving that the oxygen acts as a catalysis of the reaction, and subsequent material etching. Moreover, it is shown that the main impact of the He or H_2 implantation step is to functionalize the SiN surface by implanting residual oxygen present in the chamber and generating dangling bond. Thus, the incubation time when etching implanted SiN layers in NH_3/NF_3 plasma at 100°C is only of 30s compared to 84s for pristine SiN. This means that short duration of remote plasma is the key parameter to achieve, infinite selectivity between implanted and pristine SiN surface.

Plasma Science and Technology Division
Room 104A - Session PS-ThM

Plasma Sources

Moderators: TaeSeung Cho, Applied Materials, Geunyoung Yeom, Sungkyunkwan University, Republic of Korea

8:00am **PS-ThM-1 Model of a Radio-Frequency Low Electron Temperature Plasma Source*, Shahid Rauf,*** *L Dorf, K Collins,* Applied Materials

The time-averaged plasma potential in a partially ionized plasma is directly linked to the electron temperature (T_e). Plasmas with low T_e or plasma potential are attractive for applications that require low ion energy at surfaces. One of the most promising such applications is atomic layer etching. Reactive ion etching relies on reaction of energetic ions and chemically reactive radicals on surfaces for material removal. Ion energy in radio-frequency (RF) plasmas is typically 10s of eV or higher. Since such energetic ions can damage and modify the near-surface material, film etching with atomic precision becomes impractical using low pressure RF plasmas. On the other hand, if the plasma potential is low and capability exists to control the ion energy at the substrate using RF or DC biasing, one can etch material with Å-scale fidelity [1]. Even conventional plasma processes can benefit from low T_e as plasma potential determines the energy of ions bombarding the chamber surfaces.

This paper describes a radio frequency (RF) driven low T_e plasma source. This source utilizes two RF supplies, a higher frequency source (60 MHz) for plasma production and a lower frequency source (2 MHz) for controlling the ion energy. The plasma source is divided into two regions separated by a perforated plate. A high density ($> 10^{17}$ m^{-3}) plasma is generated in the primary region next to the RF powered electrode. The DC bias on the powered electrode is high (~ 2000 V) leading to energetic ion bombardment on it. These ions produce secondary electrons that, under the low-pressure condition under consideration, enter the plasma as a beam of energetic electrons and many of them reach the perforated plate. It is demonstrated that the slits in the perforated plate can be designed to prevent the RF primary plasma from leaking into the secondary region while still allowing the beam electrons to pass through. The plasma produced by the beam electrons has moderate density (~ 10^{16} m^{-3}) and $T_e <$ 0.5 eV. The influence of slit dimensions on the characteristics of the plasma in the secondary discharge region is examined in the paper.

[1] L. Dorf, J. C. Wang, S. Rauf, G. A. Monroy, Y. Zhang, A. Agarwal, J. Kenney, K. Ramaswamy and K. Collins, J. Phys. D 50, 274003 (2017).

8:20am **PS-ThM-2 Electron-beam Sustained Plasma with Unique Characteristic of Low Electron Temperature at Very Low Pressure*, Zhiying Chen,*** Tokyo Electron America, Inc.*; K Nagaseki,* Tokyo Electron Miyagi, Ltd., Japan*; J Blakeney, M Doppel, P Ventzek,* Tokyo Electron America, Inc.*; A Ranjan,* TEL Technology Center, America, LLC.

Low electron temperature plasmas have recent interest because of their potential applications in atomic layer etching, etch of non-volatile materials and polymer processing. Electron-beam sustained plasmas (ESP) are primarily sustained by an electron beam. In this presentation we describe one kind of ESP system consisting of two plasmas separated by a dielectric injector. The electron-source plasma is generated by an inductively coupled source (ICP), on the boundary walls of which a negative DC voltage is applied. The main plasma is the ESP itself, which is generated by the electron beam extracted from ICP through a dielectric injector by an accelerator located inside the ICP. The electron temperature and electron energy distribution functions (EED*f*) are measured by Langmuir Probe. We show the ESP plasma is characterized by a low electron temperature (less than 1eV) at very low pressure (1-10mT) measured. This unique characteristic is unavailable to conventional plasmas, in which pulsing or high pressure is required to obtain low electron temperature. The plasma also illustrates the controllable EED*f* especially when superposed on an additional plasma such as a simple ICP source. The electron temperature of the ICP source can be significantly dropped with the addition of an ESP. The presentation includes a discussion regarding the uniformity and scalability of the ESP system. In particular, the generation of a sheet electron beam without the aid of a magnetic field and the impact of externally coupled capacitive power are discussed.

8:40am **PS-ThM-3 Hydrid Plasma Source with Inductive and Capacitive Fields: Fundamental Understanding and Nano-applications***, **Hyo-Chang Lee,*** Korea Research Institute of Standards and Science (KRISS), Republic of Korea **INVITED**

Hybrid plasma source with inductive and capacitive fields, which is often called RF-biased inductively coupled plasma (ICP) or reactive ion etcher, has been widely used in semiconductor, display, and solar-cell etching processes [1]. The original concept for the hybrid plasma source is an expectation that the antenna coil of the ICP controls the plasma density while the RF bias controls the ion energy independently. However, the RF bias can act as plasma source like an asymmetric capacitively coupled plasma (CCP) and directly affect plasma parameters such as electron temperature, plasma density, and electron energy distribution. In this talk, I will present effects of inductive and capacitive fields of the hybrid plasma source on the plasma parameters, electron heating, and processing result [2-9]. This invited talk will find the fundamental understanding of the hybrid plasma source and give open possibilities for applications to various applied fields to find novel control knob and optimizing processing conditions for improvement of the device quality and processing results.

[1] H.C. Lee, Appl. Phys. Rev. 5, 011108 (2018).

[2] Lee et al., Appl. Phys. Letts. 96, 071501 (2010).

[3] Lee et al., Phys. Rev. E 81, 046402 (2010).

[4] Lee et al., Thin Solid Films 519 7009 (2011).

[5] Lee et al., Appl. Phys. Letts. 101, 244104 (2012).

[6] Lee et al., J. Appl. Phys. 111, 093301 (2012).

[7] Lee et al., Plasma Sources Sci. Technol. 21 035003 (2012).

[8] Lee et al., Plasma Sources Sci. Technol. 22 032002 (2013).

[9] Lee et al., Plasma Sources Sci. Technol. 24 0240 (2015).

9:20am **PS-ThM-5 Improving RF Power Delivery for Pulsed Operation***, J Brandon, C Smith, K Ford,* North Carolina State University*; S Nam,* Samsung Electronics*; **Steven Shannon,*** North Carolina State University

The increased reliance on pulsed RF power delivery for manufacturing applications has greatly expanded the process window and performance capability of state-of-the-art process equipment. Power delivery under pulsed conditions rely mainly on static impedance matching conditions, delivered power compensation, or optimization algorithms that minimize power reflection due to impedance mismatch over multiple pulse cycles. On time scales within the RF pulse, power delivery can significantly impact process performance, particularly as devices approach the sub 10nm regime, as it can impact electron temperature spikes at ignition and the formation of electric potentials in and around the plasma and substrate. Options to improve power delivery efficiency within the pulse can provide mechanisms to control or mitigate these conditions for process optimization, but have practical limitations due to the ms time scale response needed to capture electrical transients under pulsed conditions.

Using standard match topologies found in pulsed RF systems, methodologies for impedance matching optimization for plasma transient control are presented. Using a simple global plasma model with equivalent circuit module for capturing power delivery circuitry and a cylindrical ICP reactor, the interaction between power coupling (specifically impedance matching) and plasma conditions during the power-on transient of a pulsed ICP system are studied. Control of electron temperature spiking at the power onset as well as rate of rise of plasma density are demonstrated using a static p-type match topology. The impact of dissipative losses in the matching network are also explored, and suggest that the standard insertion loss, or "equivalent series resistance" characterization of impedance match power dissipation may present an incomplete picture of match performance under transient conditions and that dissipation in the shunt elements play a significant role with regard to the transient plasma conditions during the power on cycle of a pulsed RF system, and may provide a pathway for improving the efficiency of power delivery during pulsed operation. Finally, a synergistic approach where match topology, source antenna design, and plasma load are considered can provide pathways for within-pulse impedance matching and power delivery control. We will present examples where this approach may enable within-pulse active tuning of pulsed RF systems with existing technologies. This work is supported by the Samsung Mechatronics R&D Center.

9:40am **PS-ThM-6 Optimizing Transients Using Low-High Pulsed Power in Inductively Coupled Plasmas***, **Chenhui Qu**, S Lanham,* University of Michigan*; T Ma, T List, P Arora, V Donnelly,* University of Houston*; M Kushner,* University of Michigan

Pulsed inductively coupled plasmas (ICPs) are widely used for etching in semiconductor device fabrication. Pulse repetition frequencies (PRFs) of up to 10s kHz are commonly used for the high power density provided during the pulse-on period and the unique chemistry during the pulse-off period. The use of highly attaching halogen gases produces low electron densities during the pulse-off period, which can produce instabilities, E-H transitions and ignition delays when applying power. To mitigate these issues, a low-level power could be maintained during "pulse-off" to limit the minimum plasma density, therefore reducing ignition delays and enhancing plasma stability.

In this work, ICPs sustained by 1-5 kHz pulsed power using Ar/Cl_2 mixtures at tens of mTorr were computationally and experimentally studied. The computations were performed with the 2-D Hybrid Plasma Equipment Model. The experiments include measurements of electron density (n_e), temperature (T_e) and electron energy distributions. The power is modulated during the pulse-off period and the transient behavior of the ICP was studied.

The computed T_e reaches a quasi-steady state for both high and low power excitation. Some experimental results agree well with the predictions from the model while others show a reproducible delay in plasma ignition. The model predicts that within the skin-depth, T_e spikes to a high value during the low-to-high power modulation and a low value during a high-to-low power modulation. Due to some averaging and energy loss that occurs during transit from the skin depth, both measurements and model results show little modulation in T_e a few cm above the substrate. The influence of the power, pressure, PRF and duty cycle of the pulse profile on the bulk plasma properties will be discussed.

* Work supported by Samsung Electronics Co. Ltd., National Science Foundation and the DOE Office of Fusion Energy Sciences.

11:00am **PS-ThM-10 Silicon Nitride Film Formations Using Magnetic-Mirror Confined New Plasma Source***, **Tetsuya Goto,*** Tohoku University, Japan*; S Kobayashi,* Kotec Company, Ltd., Japan*; S Sugawa,* Tohoku University, Japan

Realization of high-quality silicon nitride film formation at low temperature was strongly required for various fields such as the Si CMOS devices, the solar cells, as well as the micro electro mechanical systems (MEMS). In this study, a magnetic-mirror confined electron cyclotron resonance plasma source for low-damage plasma processings was newly developed, and applied to the silicon nitride film formations. The mirror-confined plasma is the well known concept in a field of fusion plasmas where high-density and high-temperature plasmas are produced by confining plasmas using the magnetic field. We applied this concept to plasma enhanced chemical vapor depositions. In a magnetically confined plasma, neutral reactive species produced by the plasma can escape from the confined plasma without the restriction of motion by the magnetic field, contrary to the confined charged particles of ions and electrons. Thus, when the substrate is placed at the neighborhood of the confined plasma, a large amount of reactive species will be supplied to the substrate with low irradiation of ion flux, suggesting the realization of low-damage and high-quality processes. It was found that the magnetic mirror confinement method worked well to excite the high-density plasma larger than 10^{11} cm^{-3} with low plasma excitation power of 10 W or less. SiN films were deposited by exciting $Ar/SiH_4/N_2/H_2$ plasmas. It was found that, in the optimized condition, an impurity concentration of oxygen in the film could be suppressed less than 1%, which was even smaller than that in the controlled low-pressure chemical-vapor deposited film at 750◦C, suggesting the realization of high-quality nitridation process. Next, wet etching stability was investigated by dipping the films into the 5% HF solution. For the 400◦C-deposited film, the etching rate was approximately 3 nm/min which was the same level to that of 750◦C-LPCVD film. Although the etching rate of the 200◦C-deposited film increased to approximately 10 nm/min, this rate was much smaller than that of thermally-grown SiO_2 film (approximately 40 nm/min).

It was also confirmed that the excellent step coverage could be obtained for the 0.5 micron trench pattern.

The developed plasma source has a potential to realize high-quality film deposition processes of the plasma CVD, the plasma ALD, and the reactive sputtering.

Acknowledgement

The deposition process was carried out in Fluctuation-Free-Facility in Tohoku University.

1. T. Goto, K. Sato, Y. Yabuta and S. Sugawa, Rev. Sci. Instrum. vol. 87 (2017) 123508.

2. T. Goto, K. Sato, Y. Yabuta, S. Hara and S. Sugawa, Journal of the Electron Devices Society, vol. 6, (2018) 512.

11:20am **PS-ThM-11 Resonant Element Microwave Plasma Source***, **Barton Lane**, P Ventzek, A Bhakta,* Tokyo Electron, America, Inc.*; K Nagaseki,* Tokyo Electron Miyagi, Ltd., Japan*; A Ranjan,* Tokyo Technology Center America

We report here the use of resonant elements for plasma generation. The resonant elements are realized as metal structures embedded in alumina using a metal printing and lamination process. The embedded structures present a flat featureless alumina face to the plasma which is optimal for reducing particle generation. The structures are chosen to be resonant in the microwave frequency range and thus have geometric sizes of approximately 10 mm, although this can be chosen for the particular application. The structures can be viewed as LC circuits which have a number of resonances in the microwave band each with a corresponding spatial electric field eigenmode. The geometry of the structures reported here positions the inductive portion near to the plasma and in one eigenmode produces inductively generated circular mirror currents in the plasma which have a spatial dimension of 10 mm. The LC structures which we report on have a quadrupole symmetry in order to minimize the coupling to surface waves which tend to propagate away from the launch structure and are difficult to control. The fields responsible for plasma generation are the near fields of the resonant structure and these die away quickly from the structure giving a localized plasma generation region. The alumina blocks in which the resonant element structures are embedded are pierced by cylindrical holes through which gas is injected into the generated plasma. For one eigenmode of this system at low pressures (~ 10 mTorr) the electric fields are such that the plasma concentrates in the supersonic gas jet and has a size of approximately 1 mm. The structures can also be used to sustain a plasma in a high pressure cavity which then serves as a source of radicals through jet outlets. In this case the cavity pressures are in the several Torr or higher range. With the addition of small permanent magnets operation in the 0.1 mTorr regime is possible by exploiting the electron cyclotron phenomenon. The resonant elements can be arranged in an array. We report on a linear array which is coupled by TEM parallel plate transmission lines embedded in the alumina. Because the presence of plasma tends to detune the structures from resonance there is a natural negative feedback which helps to balance the multiple elements producing a reasonably uniform “curtain” of plasma. The ability to extend such an array to cover the entire upper electrode of a semiconductor reactor has been noted as well as the ability to control the spatial distribution by choosing different natural resonances for different regions of the reactor.

11:40am **PS-ThM-12 Microwave Plasma Enabling Efficient Power-To-X Conversion***, **Gerard van Rooij**,* DIFFER, The Netherlands, Netherlands **INVITED**

Sustainable energy generation by means of wind or from solar radiation through photovoltaics or concentrated solar power will continue to increase its share of the energy mix. Intermittency due to e.g. day/night cycle, regional variation in availability, and penetration of sustainable energy into sectors other than electricity such as the chemical industry necessitates means of storage, transport and energy conversion on a large scale. A promising option is the synthesis of chemicals and artificial fuels using sustainable energy. A truly circular economy requires that the raw materials are the thermodynamically most stable ones such as CO_2 and N_2. In this contribution it will be highlighted how plasma chemistry can potentially combine compatibility with e.g. intermittency and localized production to activate these molecules with maximum energy efficiency, essentially due to preferential vibrational excitation (causing inherently strong out-of-equilibrium processing conditions that achieve selectivity in the reaction processes). Examples will be discussed of research carried out at DIFFER to ultimately enable a scale up to chemical industrial applications.

A common microwave reactor approach is evaluated experimentally with laser Rayleigh and Raman scattering (to assess gas and vibrational temperatures) and Fourier transform infrared spectroscopy (yielding conversion and efficiency). For example, 50% energy efficiency was observed in pure CO_2 (forming CO and O_2) in a thermodynamic equilibrium conversion regime governed by gas temperatures of ~3500 K. These results are interpreted on basis of Boltzmann solver based plasma dynamics estimates, indicating that intrinsic electron energies are higher than what is favourable for preferential vibrational excitation. Pulsed experiments (1-5 kHz) in which gas temperature dynamics are revealed confirm this picture. In pure N_2, vibrational temperatures are observed in excess of 10000K and up to five times higher than the gas temperature. The signature of the Treanor effect (overpopulation of higher levels) is confirmed. These observations are promising in view of economic localized production of fertilizer. Finally, an outlook is given to novel reactor approaches that tailor the plasma dynamics to optimally promote vibrational excitation and to achieve the desired non-equilibrium.

Thin Films Division
Room 102A - Session TF+AS+EL+PS-ThM
In-situ Characterization and Modeling of Thin Film Processes

Moderator: Thomas Riedl, University of Wuppertal

8:00am **TF+AS+EL+PS-ThM-1 Defects in Thin Films: A First Principles Perspective***, **Douglas Irving**, J Harris, J Baker, S Washiyama, M Breckenridge,* North Carolina State University*; P Reddy,* Adroit Materials*; R Collazo, Z Sitar,* North Carolina State University **INVITED**

Realization of next-generation power and optoelectronic devices depends on the ability to controllably donor dope thin films of AlN and Al-rich AlGaN. The challenge in donor doping these materials begins with the donor dopant itself, Silicon. While it is a common shallow donor dopant in GaN, it exhibits a deeper ionization level in AlN due to the formation of a DX center near the conduction band minimum. Compensation in both the low and the high doping regime also presents a significant technical challenge to the doping of AlN thin films. In this talk, we explore the mechanisms for compensation in Si-doped AlN in the low and high doping regimes. For this purpose, we have implemented first principles density functional theory calculations with screened hybrid exchange-correlation functionals to determine the properties of individual defects in AlN. The formation energies of each defect are used within a grand canonical equilibrium model to identify the predominant defects as a function of growth conditions. In the low doing regime, important to drift layers in power electronics, we find unintentional impurities and unintentional impurity complexes are often responsible for free carrier compensation. Compensation in films that are doped to higher impurity concentration is found to be related to vacancy-dopant complexes. Possible solutions unique to thin films have also been explored and will be presented. Results from these methods are compared with complementary experimental data that includes below band gap optical absorption and photoluminescence, electrical measurements, dopant implantation, and available SIMS measurements.

8:40am **TF+AS+EL+PS-ThM-3 Advances in Numerical Simulation of SiN ALD***, **Paul Moroz**,* TEL Technology Center, America, LLC

Atomic layer deposition (ALD) includes a fast growing area of applications and could be foreseen as becoming one of the leading semiconductor technologies. In many cases, it allows accurate atomic-scale deposition of films with almost conformal profiles. Here we present new results on the Monte Carlo feature-scale simulations of ALD conducted with a feature-profile simulator, FPS3D [1-5], as well as comparison of obtained simulation results with the corresponding experiments. The ALD processes are often complex, involving large molecules and, to our knowledge, have not been addressed by other feature-profile simulations except FPS3D. The main factor of all of ALD schemes is the cyclic change in flux parameters and in the corresponding surface chemistry, which results in a single monolayer or, most typically, in a fraction of a monolayer of a film deposited after application of a cycle. Here, we consider a case of ALD with two time-steps: (1) dichlorosilane gas and (2) ammonia plasma. The SiN deposition rate in this case is about a half of a monolayer per cycle. A set of surface reactions is considered which emphasize the steric hindrance effect that was found to be an important factor in explaining deposition rates for this ALD process.

References:

[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, J. Physics: CS 550 012030 (2014).

[4] P. Moroz, 15th Int. Conf. on Atomic Layer Deposition, Portland, OR (2015).

[5] P. Moroz, D. J. Moroz, Japan. J. Appl. Phys. **56**, 06HE07 (2017).

9:00am **TF+AS+EL+PS-ThM-4 Diffusion Kinetics Study of Adatom Islands: Activation Energy Barriers Predicted using Data-driven Approaches***, **ShreeRam Acharya**, T Rahman,* University of Central Florida

The Self-Learning Kinetic Monte Carlo (SLKMC) method [1] with a pattern recognition [2] and a diffusion path finder scheme enables collection of a large database of diffusion processes including single- and multiple-atoms, and concerted island motion and their energetics. The databases collected from adatom-island (2-8 atoms) diffusion characteristics for a large set of homo- and hetero-epitaxial metallic systems (Cu, Ni, Pd and Ag) are used to extract a set of easily accessible features, geometrical and energetic, using physical insight which are then encoded. Those features along with activation energy barrier are used to train and test linear and non-linear statistical models. A non-linear model developed based on neural network technique predicts the diffusion energy barriers with high correlation with the calculated ones. In this talk, we present the results of kinetics study of these homo or hetero-epitaxial metallic systems some of whose barriers are used for training of the model and are compared to the corresponding quantities obtained from KMC simulation using energy barriers calculated from computationally intensive interatomic interaction potential based approach.

[1] O. Trushin, et al., *Phys. Rev. B***72**, 115401 (2005).

[2] S.I. Shah, et al., *J. Phys.: Condens. Matt.***24**, 354004 (2012).

Work supported in part by MMN-1710306.

9:20am **TF+AS+EL+PS-ThM-5 Using Ellipsometry and XPS to Understand the Degradation of Thin-film Aluminum Mirrors Protected by Ultrathin Fluorides***, M Linford, **Brian I. Johnson**, R Turley, D Allred,* Brigham Young University

The LUVOIR (Large, UV-optical-IR) telescope is a potential NASA flagship space-based observatory of the 2020’s or 30’s. It will utilize the largest mirrors ever put into space. The reflective coating for the mirrors will be aluminum, since there is no material with comparable reflectance at shorter wavelengths. However, to achieve high reflectance over the broadest energy range, the top surfaces of such Al mirrors must be protected against the formation of oxide layers that form quickly in air using wide-bandgap fluoride coatings, traditionally about 25 nm of MgF_2. Researchers have been endeavoring to use fluorides which are transparent further into the VUV (vacuum ultraviolet) like LiF and AlF_3, and to make these barriers more continuous by depositing them on heated surfaces and making the barriers thinner. However, when the barriers are thinner and when materials like LiF are exposed to moist air, degradation of VUV reflectance is observed. Thus, studying fluoride barrier-coated mirrors is vital. We have recently reported on the time dependent growth of apparent aluminum oxide thickness for two Al mirrors protected by ultrathin fluoride layers. These measurements were based on variable-angle, spectroscopic ellipsometric (VASE) measurements. (Allred, Thomas, Willett, Greenburg, & Perry, 2017) (Miles, 2017) . VASE, however, does not provide chemical composition data. An independent analytical technique which is sensitive to surface composition is required. We have undertaken such investigations using X-ray photoelectron spectroscopy (XPS), and now report on correlations between optical properties and XPS for fluoride-coated aluminum mirror test structures.

9:40am **TF+AS+EL+PS-ThM-6 Model for Amorphous Thin Film Formation and Validation***, **Rahul Basu**,* VTU, India

A coupled set of equations describing heat and mass transfer during phase transformation is formulated The model is extended to incorporate surface convective effects. These equations which are non linear due to the moving interface are linearized and decoupled. Effects of various heat transfer parameters are analyzed through small parameter expansions. Solutions obtained via this artifice allow closer examination of surface effects on the boundary layer of the phase transformation. A relation is found for the effect of the glass transition temperature versus the boundary layer thickness for several alloys in various groups of the Periodic Table. Earlier work and results are analyzed in light of the present analysis.

11:00am **TF+AS+EL+PS-ThM-10 2D TMD Monolayer of MoS_2 BY ALD and Insight in the Mechanism by Surface Organometallic Chemistry***, **Elsje Alessandra Quadrelli**,* CNRS CPE Lyon, France **INVITED**

Atomically-thin crystalline domains of MoS_2 [1] or WS_2 [2] are obtained from an organometallic amorphous deposit obtained by ALD/MLD. This original result with respect to the state of the art has been mechanistically rationalized with in situ and in operando modelling studies on the oxide nanobeads at different annealing temperatures. This contribution will present the surface organometallic method, the characterization of the 2D layers (among which the first in-plane micrographs of ALD-grown MoS_2 samples)[1] and the proposed surface coordination chemistry mechanism at hand obtained with model studied on 3D silica beads. These model studies couple in operando infra-red spectroscopy, gas-chromatography detection of the released by-products and atomic composition of the deposit at each cycle, leading to molecular level understanding of the growth process.

***Acknowledgments** : This work was carried out within the framework of the partnership between the C2P2 research unit (UMR 5265 CNRS CPE Lyon University Claude Bernard Lyon 1) and CEA's Directorate of Technological Research (DRT) on the nanochemistry platform installed in CPE Lyon. The authors of the papers below thank CPE Lyon, CNRS, CEA / LETI (Silicon Technology Department and nanocharacterization platform) for the support and the DRF / INAC for the collaboration in the framework of the "2D Factory" project.*

***Ref** : [1] Cadot et al.Nanoscale , **2017**, 9, 467. [2] Cadot et al. JSVT A **2017**, 35, 061502 .*

11:40am **TF+AS+EL+PS-ThM-12 A Novel Fourier Transform Ion Trap Mass Spectrometer for Semiconductor Processes***, **Gennady Fedosenko**, H Chung, R Reuter, A Laue, V Derpmann, L Gorkhover, M Aliman, M Antoni,* Carl Zeiss SMT GmbH, Germany

Real-time inline control of process gas compositions with high sensitivity has been of particular importance in recent years in the semiconductor industry and beyond. Commonly quadrupole residual gas analyzers (RGA) are used, together with Optical Emission Spectroscopy (OES) for process control and process development. However, most RGAs are not capable of measuring a whole mass spectrum fast enough to monitor etch or deposition processes of a few seconds. A new process control mass spectrometer, based on Fourier-Transform 3D Quadrupole Ion Trap technology, is more appropriate for real-time inline process monitoring.

The 3D-Quadrupole Ion Trap mass spectrometer *iTrap*® by ZEISS is installed in a vacuum chamber (~ 120mm x 120mm x 500mm) with a fast switching valve for pulsed gas sample injection (pulse duration ~ 50ms or less). An electron gun is used for ionization of the gas pules. The Ion Trap achieves ion trapping and accumulation by means of a radio frequency applied to the ring electrode of the trap. With the aid of advanced electronic amplifiers and selective ion excitation technique the ion oscillations can be measured electrically by means of the induced current on the cap electrodes without using any separate particle detector. The mass spectrum can be finally obtained in less than one second.

Real-time measurements of the hydrogen plasma cleaning process of Sn contaminated samples were performed with the *iTrap* mass spectrometer. The working pressure of the plasma cleaning process was 0.5 mbar. Decreasing signal of SnH_4 and other contaminations from the samples which are directly correlated to the cleaning process were observed with *iTrap*. This result is extremely useful for the process control of plasma processes and inline real-time contaminations control for high-end applications.

Inline measurement at a MOCVD chamber showed that *iTrap* is capable to detect reaction products, contaminations on the wafer holder and dopant memory in real-time. These results demonstrate that *iTrap* is a very sensitive and fast process mass spectrometer suitable for real-time inline process monitoring.

Many etch processes take place in 10 to 30 s process steps. Different processes were examined with e.g. HBr or BCl_3 chemistry together with several wafer materials such as Silicon, Hafnium Oxide or Titanium Nitride. The obtained mass spectra show the etch plasma chemistry together with etch reaction products (HfClx, SiClx, etc.). This data gives new insight into the etch processes, which until now were rarely understood on a chemical level. First wafer effects related to the chamber cleaning and pre-coating steps prior to the etch step were also examined.

12:00pm **TF+AS+EL+PS-ThM-13 Realization of Shifts in Threshold Voltage and Subthreshold Swing in Atomic Layer Deposited Zinc Oxide As Channel Layer through *in-situ* Half-Cycle Analysis***, **Harrison Sejoon Kim**, A Lucero, S Kim, J Kim,* University of Texas at Dallas

Thin film process monitoring of atomic layer deposition (ALD) has been adopted as the versatile technique to identify both chemical and physical properties of ALD films. Their *in-situ* characterization technique includes mostly Fourier-transform infrared spectroscopy, X-ray photoelectron spectroscopy, and quartz crystal microbalance analysis. [1–3] However, currently there are no reports on monitoring the results of sub-nm device physics even if we are already in the era of beyond 10 nm node semiconductor processes. Moreover, even if there are a few initial studies, demonstrating *in-situ* electrical characterization with ALD, it requires device packaging, which ultimately limits the flexibility to be further characterized. [4]

In this current work, we have developed an ultra-high vacuum (UHV) cluster tool equipped with thermal processing, plasma surface treatment, thin film deposition, and electrical characterization which can be performed *in-situ* (Figure 1). With this feasibility, we demonstrate the deposition of semiconducting zinc oxide (ZnO) in inverted-coplanar structured thin film transistors (TFT). Diethylzinc (DEZ) and water (H_2O) is used as ALD precursors at 100°C. DEZ and H_2O half-cycle analysis is carried out to monitor the interface states of ZnO/dielectric (Figure 2). Initially, 45 ALD cycles of ZnO have shown switching behavior with an on/off ratio of ~10^2 in vacuum. Subsequent ALD cycle shifts the threshold voltage (V_{th}). V_{th} shifts associated with each ALD cycle are assumed to be attributed to the changes in interface trap density as a result of interface state passivation in ZnO during its growth, especially passivating fixed oxide charges (Q_{ox}). To understand interface states of ZnO and the bulk of oxide better, further analysis of shift of subthreshold swing (SS) is demonstrated. Since shifts in SS best represents changes in interface trap density, [5] it is worthwhile to note the changes in SS in metal-oxide-semiconductor transistors.

This work was supported by the Creative Materials Discovery Program on Creative Multilevel Research Center (2015M3D1A1068061) through the National Research Foundation(NRF) of Korea funded by the Ministry of Science, ICT & Future Planning.

[1] D. N. Goldstein *et al*., *J. Phys. Chem. C.112*, 19530, **2008**.

[2] M. D. Groner *et al*., *Chem. Mater.16*, 639, **2004**.

[3] C. L. Hinkle *et al*., *Appl. Phys. Lett.91*, 1, **2007**.

[4] S. Jandhyala *et al*., *ACS Nano.6*, 2722, **2012**.

[5] P. J. McWhorter *et al*., *Appl. Phys. Lett.48*, 133, **1986**.

Thin Films Division

Room 104B - Session TF+PS-ThM

Deposition Processes for 3D and Extreme Geometries

Moderators: Richard Vanfleet, Brigham Young University, AnnaMaria Coclite, Graz University of Technology

8:00am **TF+PS-ThM-1 ALD and Diffusion in High Aspect Ratio Carbon Nanotube Forests***, **David Kane**, R Davis, R Vanfleet,* Brigham Young University

Very high aspect ratio or nanostructured materials have numerous applications. In many of those applications, the surface is decorated by atomic layer deposition or other vapor phase deposition techniques. In these extreme geometries the uniformity of deposition is a function of the interplay between transport (diffusion) and reaction rates. The A-B cycling in Atomic Layer Deposition (ALD) separates the deposition reaction from the transport. We have observed a limited penetration depth which decreases with cycle number in ALD on vertically aligned multiwall carbon nanotube (MWCNT) forests with an effective aspect ratio of 1000. Models of ALD in high aspect ratio features based on Knudsen diffusion transport combined with a simple geometric model of nucleation and growth on surfaces with a low nucleation site density can qualitatively reproduce the observed deposition. Fitting the models to the data allows extraction of the diffusion coefficients for these confined geometries.

8:20am **TF+PS-ThM-2 Nanoporous Reference Substrates for ALD on High Aspect Ratio High Surface Area Materials***, **Dmitri Routkevitch**,* InRedox

Deposition of conformal and uniform coatings onto high aspect ratio high surface area substrates and materials is a unique domain of ALD impacting many important applications, including energy generation and storage, semiconductor device manufacturing, chemical and biosensing and many others. However, ALD process development on such substrates is hindered by complex material geometry leading to poorly understood transport conditions and high cost of real substrates, such as large Si wafers at later staged of processing. In addition, modern ALD reactors, designed and optimized for high speed processing of flat substrates, require validation of uniformity and conformality of ALD coatings both inside the pores and laterally across the high surface area substrates with complex multiscale topology.

Nanoporous Anodic Aluminum Oxide (AAO) – a self-organized material resembling nanoscale honeycomb – is a controllable, well-defined, inexpensive and convenient nanomaterial platform to support the development and validation of high surface area ALD. The combination of ALD with AAO enables control of both the nanoscale geometry and chemistry with unprecedented precision to provide new avenues for design and engineering of functional materials and devices.

Some of the benefits of AAO as a reference ALD substrate are:

1. Highly uniform and parallel cylindrical pores, complex pore structures (modulated, branched, etc) available to emulate different pore size distributions of other materials.
2. A broad spectrum of transport conditions (pore diameters from 2 nm to 500 nm and pore lengths from <100 nm to >300 µm for aspect ratio (L/D) from 1 to as high as 50,000) that could be tested to aid better understanding and rapid development of new ALD processes.
3. Reproducible and well-understood surface chemistry of alumina makes it nearly universally suitable for many binary reactions involved in ALD.
4. High pore densities (10^{12} to 10^7 cm^{-2}) allow straightforward characterization of elemental depth profiles by EDS even for very thin (5-10 nm) coatings.
5. Available in different form factors and on different substrates (flexible foils and tapes, rigid plates, Si wafers, glass blanks, etc) to accommodate different types of ALD reactors, such reel-to-reel reactors for coating battery electrodes or reactors designed to process stacks of Si wafers or PV substrates.

Scaleable to large sizes, low cost.

Several case studies will be presented where AAO was used as a reference substrate to aid the development of ALD for high surface area materials.

8:40am **TF+PS-ThM-3 Fine-tuned Resistive Coatings for Detector Applications***, **Maximilian Gebhard**, A Mane, D Choudhury, S Letourneau, D Mandia, Y Zhang, J Elam,* Argonne National Laboratory

An important building block for detector devices are amplifiers, such as microchannel plates (MCPs). Due to the geometry of several periodically arranged microchannels, incident electrons or irradiation can be amplified by several orders of magnitude, making MCPs highly efficient in several applications such as neutron detectors and night-goggles. The efficiency of state-of-the-art MCPs is strongly related to functional coatings, acting as resistive coating and secondary electron emission (SEE) layer. While the SEE material (*e.g.* Al_2O_3 or MgO) should exhibit a high SEE coefficient, the resistive coating must facilitate a uniform and stable electrostatic field along the pores and during operation. It was shown previously that atomic layer deposition (ALD) is capable to produce highly efficient SEE coatings (MgO) as well as a fine-tuned resistive coating directly on the MCP substrate, thereby improving the overall performance of the detector devices.[1,2] By producing highly conformal thin films over large areas and on large aspect ratios, ALD is the method of choice to produce functionalized MCPs.

One challenge in manufacturing reliable MCPs for advanced applications are external conditions like ambient temperature. With temperature gradients of 100 K or higher, the thermal coefficient of resistance (TCR) of the resistive coating plays a major role with respect to electrical transport phenomena. Positive TCRs can cause increased resistance at elevated temperatures and in due turn a collapse of the MCP's performance. Similar determining factors are on hand for strongly decreased temperatures. A second challenge is the fluorine-based chemistry, which is currently often employed to produce ALD-functionalized MCP coatings.

We present here the development of ALD-fabricated materials, being free of fluorine chemistry and exhibiting tailored electric resistance over a broad temperature range as well as promising performance as resistive coating in MCPs. Apart from thorough process development, those transition metal-based materials were analyzed regarding their composition, structure and electrical behavior employing XPS, SEM, XRD and extended IV-measurements. Furthermore, the coatings were applied to MCPs, which were tested for their performance.

[1] A. U. Mane and J. W. Elam, *Chem. Vap. Deposition*, **2013** (19), 186-193

[2] M. J. Minot, B. W. Adams, M. Aviles, J. L. Bond, C. A. Craven, T. Cremer, M. R. Foley, A. Lyashenko, M. A. Popecki, M. E. Stochaj, W. A. Worstell, A. U. Mane, J. W. Elam, O. H. W. Siegmund, C. Ertley, H. Frisch and A. Elagin, *Proceedings Volume 9968, Hard X-Ray, Gamma-Ray, and Neutron Detector Physics XVIII*, **2016**, DOI: 10.1117/12.2237331

9:00am **TF+PS-ThM-4 Tungsten Atomic Layer Deposition on Vertically Aligned Carbon Nanotube Structures***, **Ryan Vanfleet**, R Davis, D Allred, R Vanfleet,* Brigham Young University

Carbon Nanotubes (CNTs) can be grown from 2D patterns into high aspect ratio, 3D MEMS structures. These porous structures can then be filled solid with different materials in order to impart specific and unique properties to the MEMS device. Tungsten, with its conductivity, high density and high temperature resistance, could be of special interest for many MEMs devices. Due to the high packing density and high aspect ratios of vertically aligned CNT forests, it is difficult to uniformly deposit films throughout the entirety of the structure. Atomic Layer Deposition (ALD) has been shown to uniformly coat structures with extreme geometries using sequential, self-limiting surface reactions. This in an inherently slow process, especially on geometries where the deposition is diffusion-limited such as in CNT forests. Approximately 50 nm of tungsten is required to fill a CNT-patterned structure solid where the individual CNTs grow roughly 100 nm apart. The tungsten ALD process has been shown to be able to deposit more than a single atomic layer per cycle so that the necessary number of cycles to fill the CNT structure is reduced. The process parameters that facilitate this increased deposition rate will be discussed. Tungsten-filled CNT beams were subjected to three-point bending tests to determine material properties of the composite structures. Preliminary tests on beams with about 35 nm of as-deposited tungsten give an ultimate strength of 11 MPa and a Young's Modulus of 1.7 GPa. The microstructure of the as-deposited tungsten is extremely fine and annealing studies will also be addressed.

9:20am **TF+PS-ThM-5 ALD in Metal Organic Frameworks: Toward Single Site Synthesis and Sinter-Resistant Catalysts***, **Alex Martinson**,* Argonne National Laboratory **INVITED**

Reproducibly and homogeneously synthesizing single-site transition metal catalysts on exceedingly high surface area supports with stability under catalytic conditions remains a grand challenge. To address this challenge, we utilize atomic layer deposition (ALD) in metal-organic frameworks (MOFs), a process we call AIM. Here, ALD provides a straightforward gas phase route to access a wide variety of small precision clusters with spatial and dimensional homogeneity. The well-defined structure of MOF NU-1000 framework and nodes allows for detailed characterization of their size and uniforming as well as insight into their inherent stability. This talk will discuss several classes of ALD precursors and processing conditions that have been identified to be compatible with few-atom cluster deposition in Zr-based MOF NU-1000.

11:00am **TF+PS-ThM-10 Alumina Deposition by Atomic Layer Deposition (ALD) on Flat Surfaces and High Aspect Ratio Structures***, **Dhruv Shah**, D Patel, D Jacobsen, J Erickson, M Linford,* Brigham Young University

Atomic layer deposition (ALD) involves layer-by-layer deposition due to sequential exposure of two precursors to as substrate . ALD was developed in the late 1970s by Suntola and co-workers as a modification of chemical vapor deposition (CVD). In ALD, the dosing and purging steps are separated to ensure that each precursor saturates the surface before the other precursor enters the chemical reactor. ALD is widely used in the semiconductor and microelectronics industry to deposit thin films of various oxides on different substrates. ALD can be operated in two modes: plasma assisted and thermally assisted. Thermally assisted ALD has been widely used due to its high uniformity and conformality in depositing thin films on a variety of substrates.

Here we report alumina deposition by ALD using trimethylaluminum and water as precursors on silicon substrates. We optimized the process on flat surfaces like silicon shards, and extrapolate the process to high aspect ratio devices and powders, ultimately confirming the deposition on these high aspect ratio materials. Achieving high degrees of consistency and uniformity for deposition on powders through a frit using ALD has been difficult. We tried multiple recipes for alumina deposition, optimizing the dose time, purge time and effective exposure of the precursor on the substrate to achieve uniform results. Our thin films are characterized by spectroscopic ellipsometry (SE), water contact angle goniometry, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and/or transmission electron microscopy (TEM). The thin films we have obtained on planar substrates using ALD vary in thickness from 0.5 – 41.0 nm. These thin films were used to conduct a multiple sample analysis (MSA) in SE to obtain the optical constants of alumina. Since alumina is one of the most commonly used material in microfabrication, its optical constants will be useful in the field.

11:20am **TF+PS-ThM-11 Resistivity of the Alumina Diffusion Barrier in Catalytic Carbon Nanotube Growth***, **Berg Dodson**, G Chen, R Davis, R Vanfleet,* Brigham Young University

By using photolithography techniques and catalytically grown carbon nanotubes (CNTs) it is possible to fabricate high aspect ratio structures that can be used as scaffolds for MEMS devices. The drawback of making CNT structures this way is it is difficult to electrically connect to them since they are grown on an insulating alumina layer. However, previous work demonstrates that the alumina layer becomes conductive during CNT growth. Two-point probe measurements from tungsten to a CNT post in a 100 nm tungsten/alumina 50 nm/CNT stack yielded 580 ± 65 Ω. I present TEM based data showing how this change in conductivity correlates with iron and carbon diffusing into the alumina layer during CNT growth. I will also show how the observed diffusion in these samples compares with what is predicted by diffusion models as well as how the change in resistivity compares to what is expected in doped alumina.

11:40am **TF+PS-ThM-12 High Temperature Active CeO_2 Nanorods Generated via Diffusion Limited Atomic Layer Deposition***, **Haoming Yan**, X Yu, Q Peng,* University of Alabama

CeO_2 has attracted lots of attention due to its superior oxygen storage and donating ability as a catalyst support. CeO_2 nanorods has the best donating ability than all the other types of CeO_2 materials. However, the nanorods change its morphology and lose its activity at 400°C or above. Therefore, improving the thermal stability of CeO_2 nanorods can unlock the potential applications of CeO_2 nanorods in the high temperature applications. In this work, we introduce a diffusion-limited Al_2O_3 atomic layer deposition to selectively passivate the surface site of CeO_2 nanorods, largely enhancing its thermal stability and its oxygen storage capacity simultaneously.

Electronic Materials and Photonics Division
Room 101A - Session EM+2D+NS+PS+RM+TF-ThA

IoT Session: Flexible Electronics & Flash Networking Session

Moderators: Shalini Gupta, Northrop Grumman ES, Sang M. Han, University of New Mexico

2:20pm **EM+2D+NS+PS+RM+TF-ThA-1 Epitaxial Electrodeposition of Electronic and Photonic Materials onto Wafer-size Single Crystal Gold Foils for Flexible Electronics*, Jay Switzer,*** Missouri University of Science and Technology **INVITED**

Single-crystal silicon (Si) is the bedrock of semiconductor devices due to the high crystalline perfection that minimizes electron-hole recombination, and the dense SiO_x native oxide that minimizes surface states. There is interest in moving beyond the planar structure of conventional Si-based chips to produce flexible electronic devices such as wearable solar cells, sensors, and flexible displays. Most flexible electronic devices are based on polycrystalline materials that can have compromised performance due to electron-hole recombination at grain boundaries. In order to expand the palette of electronic materials beyond planar Si, there is a need for both an inexpensive substrate material for epitaxial growth, and an inexpensive and scalable processing method to produce epitaxial, grain-boundary-free films of metals, semiconductors, and optical materials. Recently, in our laboratory, we have developed a process for producing wafer-size, flexible, and transparent single-crystal Au foils by an electrochemical processing method.[1] Au is epitaxially electrodeposited onto Si using a very negative applied potential. An interfacial layer of SiO_x is then produced photoelectrochemically by lateral undergrowth. The Au foil is then removed by epitaxial lift-off following an HF etch. We will report on the electrodeposition of epitaxial films of metal oxide semiconductors such as Cu_2O and ZnO onto the highly-ordered and flexible Au foils. We will also present new, unpublished results in which we spin-coat epitaxial films of perovskites, such as $CsPbBr_3$, directly onto these Au foils and onto other single crystals.

Acknowledgement: This presentation is based on work supported by the U.S. Department of Energy, Office of Basic Sciences, Division of Materials Science and Engineering under grant No. DE-FG02-08ER46518.

[1] Mahenderkar N., Chen Q., Liu Y.-C., Duchild, A., Hofheins, S. Chason E., Switzer J (2017). Epitaxial lift-off of electrodeposited single-crystal gold foils for flexible electronics. Science, **355**, 1203-1206.

3:00pm **EM+2D+NS+PS+RM+TF-ThA-3 Flexible Electronic Devices Based on Two Dimensional Materials***, R Kim, N Glavin,* Air Force Research Laboratory*; R Rai, K Gliebe, M Beebe,* University of Dayton; Air Force Research Laboratory*; J Leem,* University of Illinois at Urbana-Champaign, Republic of Korea*; S Nam,* University of Illinois at Urbana-Champaign*; R Rao,* Air Force Research Laboratory*; **Christopher Muratore**,* University of Dayton

Low temperature synthesis of high quality 2D materials directly on flexible substrates remains a fundamental limitation towards realization of robust, strainable electronics possessing the unique physical properties of atomically thin structures. Here, we describe room temperature sputtering of uniform, stoichiometric amorphous MoS_2, WSe_2, and other transition metal dichalcogenides and subsequent large area (>2 cm^2) photonic crystallization to enable direct fabrication of two-dimensional material photodetectors on large area flexible PDMS substrates. Fundamentals of crystallization kinetics for different monolithic and heterostructured TMDs are examined to evaluate this new synthesis approach for affordable, wearable devices. The photodetectors demonstrate photocurrent magnitudes and response times comparable to those fabricated via CVD and exfoliated materials on rigid substrates and the performance is unaffected by strains exceeding 5%. Other devices and circuits fabricated from crystallized 2D TMDs deposited on large area flexible substrates are demonstrated.

3:20pm **EM+2D+NS+PS+RM+TF-ThA-4 Contact Resistances and Schottky Barrier Heights of Metal-SnS Interfaces***, **Jenifer Hajzus**, L Porter,* Carnegie Mellon University*; A Biacchi, S Le, C Richter, A Hight Walker,* National Institute of Standards and Technology (NIST)

Tin(II) sulfide (SnS) is a natively p-type, layered semiconductor that is of interest for two-dimensional and optoelectronic applications. Understanding the behavior of contacts to SnS is essential for its use in devices. In this work, contact metallizations with a range of work functions were characterized on both solution-synthesized, p-type SnS nanoribbons and electron-beam evaporated, polycrystalline SnS thin films. The structure and properties of electron-beam evaporated SnS films were dependent upon deposition temperature and post-deposition annealing. A deposition temperature of 300 °C followed by vacuum annealing at 300 °C resulted in p-type, orthorhombic SnS films. Specific contact resistances of Ti/Au, Ru/Au, Ni/Au, and Au contacts were measured on SnS films using circular transfer length method (CTLM) patterns prior to and after annealing the contacts at 350 ° C in argon. All metallizations on SnS thin films were ohmic prior to annealing. A trend of decreasing average specific contact resistance with increasing metal work function was observed for the as-deposited contacts. Annealed Ru/Au exhibited the lowest average specific contact resistance of ~1.9×10^{-3} Ω -cm^2. Contacts were additionally patterned onto individual, solution-synthesized SnS nanoribbons. In contrast to the behavior of contacts on electron-beam evaporated films, low work function metals (Cr/Au and Ti/Au) formed Schottky contacts on SnS nanoribbons, whereas higher work function metals (Ni/Au and Pd/Au) formed ohmic or semi-ohmic contacts. Ni/Au exhibited a lower contact resistance (~10^{-4} Ω cm^2 or lower) than Pd/Au (~10^{-3} Ω cm^2 or lower). Schottky barrier heights and ideality factors of Cr/Au and Ti/Au contacts were extracted by fitting current-voltage measurements to a back-to-back Schottky diode model. The ohmic behavior for Ni/Au and Pd/Au and the calculated Schottky barrier heights (0.39 and 0.50 eV for Cr/Au and Ti/Au, respectively) on SnS nanoribbons agree well with behavior predicted by Schottky–Mott theory and suggest a lack of Fermi level pinning.

Plasma Science and Technology Division
Room 104C - Session PS+EM+TF-ThA

Atomic Layer Processing: Integration of ALD and ALE

Moderator: Scott Walton, Naval Research Laboratory

2:20pm **PS+EM+TF-ThA-1 Atomic-Layer Etching (ALE) of Nickel or Nickel Oxide Films by Hexafluoroacetylacetone (HFAC) Molecules***, **Abdulrahman Basher**, M Isobe, T Ito, K Karahashi,* Osaka University, Japan*; M Kiuchi,* National Institute of Advanced Industrial Science and Technology (AIST), Japan*; T Takeuchi,* Nara Women's University, Japan*; S Hamaguchi,* Osaka University, Japan

Atomic layer etching (ALE) is one of the most promising technologies and a prospective solution to various technical problems in nanometer-scale device fabrication processes. ALE consists of a series of processing cycles and, in each cycle, a transition step to form a reactive thin layer on the material surface is followed by a removal step to take off only this modified layer. For a metallic film, the formation of volatile organic metal complexes may be used to establish low-damage ALE processes. In this study, to explore the possibility of establishing new etching processes for the manufacturing of magnetoresistive random access memories (MRAMs), we examine possible etching reactions of magnetic materials with organic molecules. In this study, we select Ni as a sample of ferromagnetic materials. An earlier studies [1,2] indicated that hexafluoroacetylacetone (hfac) may be used for etching of Ni due to the possible formation of nickel(II) hexafluoroacetylacetonate $Ni(hfac)_2$. According to [2], if a Ni surface is oxidized and then exposed to gas-phase hfac, $Ni(hfac)_2$ are formed when the substrate temperature is increased. It is pointed out that, without the oxidation process, $Ni(hfac)_2$ is not formed under similar conditions. Therefore, the expected single cycle of Ni ALE by gas-phase hfac is as follows; a Ni surface is first exposed to oxygen and then to hfac. This step is then followed by the increase of substrate temperature. In this study, however, the goal of this study is to understand the interaction mechanisms between hfac and a Ni or NiO surface and we use the first principles calculation to examine the interaction of a hfac molecule with a Ni or NiO surface atoms. The simulation results based on Gaussian 09 that we have obtained so far suggest that the transfer of a proton from an enol hfac molecule to the Ni or NiO surface generates its deprotonated anion, whose oxygen atoms strongly interact with a positively charged Ni atom on the surface and thus form a precursor of a highly volatile metal complex. Difference in charge distribution between Ni and NiO surfaces affects the likelihood of the formation of such precursors. Surface roughness may also affect such surface reactions.

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[1] Chen J. K., Altieri N. D., Kim T., Chen E., Lill T., Shen M., and Chang J. P., " Direction etch of magnetic and noble metals. II. Organic chemical vapor etch," *J. Vacuum Sci. & Tech. A***35**, 05C305 (2017).

[2] Nigg H. L. and Masel R. I., " Surface reaction pathways of 1,1,1,5,5,5-hexafluoro-2,4-pentandione on clean and pre-oxidized Ni(110) surface," *J. Vacuum Sci. & Tech. A***17**, 3477 (1999)

2:40pm **PS+EM+TF-ThA-2 Thermal Atomic Layer Etching of HfO_2 Using HF for Fluorination and $TiCl_4$ for Ligand-Exchange***, Y Lee,* ***Steven George,*** University of Colorado at Boulder

Thermal atomic layer etching (ALE) can be accomplished using sequential fluorination and ligand-exchange reactions. HF has been a typical fluorination reactant. Various metal precursor s have been used for ligand-exchange such as $Sn(acac)_2$, $Al(CH_3)_3$ and $AlCl(CH_3)_2$ and $SiCl_4$. This study explored $TiCl_4$ as a new metal chloride precursor for ligand-exchange. Thermal HfO_2 ALE using $TiCl_4$ and HF as the reactants was studied using i*n situ* quartz crystal microbalance (QCM) measurements from 200 - 300 °C. The HfO_2 films were etched linearly versus number of $TiCl_4$ and HF reaction cycles. The sequential $TiCl_4$ and HF reactions were also self-limiting versus reactant exposure. The QCM studies observed a mass change per cycle (MCPC) of -10.2 ng/(cm^2 cycle) at 200 °C and -56.4 ng/(cm^2 cycle) at 300 °C. These MCPCs correspond to HfO_2 etch rates of 0.11 Å/cycle at 200 °C and 0.59 Å/cycle at 300 °C. To explore the selectivity of thermal ALE using $TiCl_4$ and HF as the reactants, spectroscopic ellipsometry (SE) measurements were also employed to survey the etching of various materials. The SE results revealed that HfO_2 and ZrO_2 were etched by $TiCl_4$ and HF. In contrast, Al_2O_3, SiO_2, Si_3N_4, and TiN were not etched by $TiCl_4$ and HF. QCM studies also revealed that $TiCl_4$ and HF were able to etch Ga_2O_3. The etching selectivity can be explained by the reaction thermochemistry and the stability and volatility of the possible etch products. Al_2O_3 can also serve as an etch stop for HfO_2 ALE.

3:00pm **PS+EM+TF-ThA-3 Rapid thermal-cyclic Atomic Layer Etching of SiO_2 Using Infrared Annealing***,* ***Nobuya Miyoshi,*** Hitachi High-Technologies, Japan*; H Kobayashi, K Shinoda, M Kurihara,* Hitachi, Japan*; K Kawamura, K Ookuma, Y Kouzuma, M Izawa,* Hitachi High-Technologies, Japan

Device structures are changing from planar-types to three-dimensional types, such as fin-type field-effect transistors and gate-all-around transistors, in order to reduce leakage current and power consumption. Furthermore, fabricating these devices requires both high selectivity and precise control of device dimensions below the 10 nm scale. Atomic layer etching (ALE), which involves the layer-by-layer removal of thin films, is expected to meet these requirements. In a conventional ALE process for SiO_2[1], HF and NH_3 molecules are exposed to the surface simultaneously. In this case, the etching amount per cycle is proportional to square root of the exposure time of HF and NH_3, indicating that the process is quasi-self-limiting (not self-limiting).

We have been investigating a thermal ALE of SiO_2 in which ammonium fluorosilicate-based surface modified layer is formed after exposure to HF and NH_3 gas, and removed by using infrared annealing. Etching depth of blanket SiO_2 samples were measured by using in-situ ellipsometry. We found that self-limiting formation of the modified layer was achieved with separate exposure of HF and NH_3 gas. In addition, we successfully demonstrated that this etching process was highly selective with respective to poly-Si and SiN. Comparison between experimental results and Langmuir adsorption model for dependence of etching rate on partial pressure of HF and NH_3 clarified that the SiO_2 surface during the gas exposure is in adsorption-desorption equilibrium.

In addition to HF/NH_3 gas chemistry, we developed an ALE process utilizing plasma to generate HF molecule in stead of using HF gas. This process consists of plasma discharge for HF exposure, evacuation of the residual gas, NH_3 exposure, and infrared annealing. In the plasma discharge, fluorine based gases, such as CF_4, NF_3, and SF_6 were diluted by H_2 gas. The etching rate of SiO_2 saturated at 2.8 nm/cycle in regard to the discharge time, which indicates self-limiting behavior of the modification step. In contrast, the etching rates of poly-Si and SiN were below the detection limit of in-situ ellipsometry, demonstrating that this etching process for SiO_2 is highly selective to poly-Si and SiN.

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

3:20pm **PS+EM+TF-ThA-4 The Smoothing Effect in Atomic Layer Etching (ALE)***,* ***Keren Kanarik,*** *S Tan, W Yang, I Berry, T Lill, Y Pan, R Gottscho,* Lam Research Corporation

Since the 1970s, the semiconductor industry has fabricated electronic circuits using a pattern-transfer approach that is remarkably reminiscent of the etching artform used centuries ago. Only, now, the patterns are a million times smaller, and require etching to within a few atoms on features less than 40 atoms wide. The most advanced etching technique in production today is called atomic layer etching (ALE). To the extent that an ALE process behaves ideally – with high ALE synergy and self-limiting behavior – the primary benefit is improved uniformity across all length scales: at the surface, between different aspect ratios, and across the full wafer. The focus here will be on the atomic-scale topography of the surface left behind after etching.

The purpose in this presentation is to introduce a new ALE benefit – the smoothing effect. By this, we mean that, beyond maintaining surface topography, ALE can improve the surface smoothness (ref 1). We will show that the effect in directional ALE is pervasive across different material systems, including Si, C, Ta, and Ru. We will propose explanations for the ALE smoothing phenomenon, and identify possible applications for this effect both inside and outside the semiconductor industry.

Ref 1: Kanarik, Tan, and Gottscho. *J. Phys. Chem. Rev.* submitted April 1, 2018.

4:00pm **PS+EM+TF-ThA-6 Prospects for Combining ALD and ALE in a Single Chamber***,* ***Mike Cooke,*** Oxford Instruments, UK **INVITED**

There are obvious similarities between the process cycles of atomic layer deposition (ALD) and atomic layer etching (ALE), so could one machine do both? It is already the case that plasma enhanced chemical vapour deposition (PECVD) tools also perform etching, for the purpose of chamber cleaning. Deposition can also be performed in a tool configured for plasma etching, whether accidentally by creating a plasma with net deposition of fluorocarbon polymer, or by deliberately introducing gases such as silane. However, the wafer is usually heated above ambient in the range 100C – 400C for deposition, in both parallel plate PECVD and when using a high density plasma, while the wafer is typically cooled for etching.

There are also clear overlaps between the hardware requirements for atomic layer deposition and thermal atomic layer etching. The overlaps are more restricted for plasma enhanced ALD and ALE, because both the wafer temperature range and the character of the plasma can differ. In ALD there are benefits from using a remote plasma, because the plasma primarily creates a flux of radicals, while in ALE the plasma delivers both radicals and an ion bombardment flux. However, there is potential for combining plasma ALD and ALE in a chamber with an RF biased table. Thermal ALE and plasma ALE can be combined if the wafer table has a wide temperature range, and the tool can deliver doses of low vapour pressure ALE precursors.

The motivation for combining processes is less clear outside the academic community. Researchers wanting to access both precision etching and deposition under tight constraints of space and budget may be attracted to it, but the combination of halogen chemistry for ALE and organometallic precursors for ALD may make it difficult to change quickly between etching and deposition.

Results from ALE and ALD are presented to explore the overlap, including recent work on ALE and ALD for III-V power devices.

4:40pm **PS+EM+TF-ThA-8 Low Temperature Surface Preparation of GaN Substrates for Plasma Assisted-Atomic Layer Epitaxial Growth***,* ***Samantha G. Rosenberg,*** U.S. Naval Research Laboratory*; D Pennachio,* University of California, Santa Barbara*; M Munger,* SUNY Brockport*; C Wagenbach,* Boston University*; V Anderson,* U.S. Naval Research Laboratory*; S Johnson,* U. S. Naval Research Laboratory*; N Nepal, A Kozen, J Woodward,* U.S. Naval Research Laboratory*; Z Robinson,* SUNY Brockport*; K Ludwig,* Boston University*; C Palmstrøm,* University of California, Santa Barbara*; C Eddy, Jr.,* U. S. Naval Research Laboratory

We have previously shown that using our low temperature plasma-assisted atomic layer epitaxy (ALEp) method we can grow AlN and InN for various applications.$^{1-3}$ The materials we have grown using our ALEp method have shown good crystalline quality, but suffer from an incorporation of carbon. Theory has led us to believe that the substrate preparation plays a significant role in the remediation of carbon, as that surface becomes the interface for the growth of the III-N film. Therefore, using surface science techniques, we strive to develop not only a fundamental understanding of the ALEp growth process but also atomic layer processes that will result in the best preparation method for a pristine GaN starting surface for ALEp.

In-situ surface studies of *in-situ* and *ex-situ* GaN substrate preparation and InN ALEp growth were conducted to advance fundamental understanding of the ALEp process. We conduct *in-situ* grazing incidence small angle x-ray scattering (GISAXS) experiments at the Cornell High Energy Synchrotron Source to investigate growth surface morphological evolution during sample preparation including a gallium-flash-off atomic layer process (ALP) at varying temperatures and number of cycles. GISAXS information is complemented with *in-vacuo* x-ray photoelectron spectroscopy, reflection high-energy electron diffraction, and *ex-situ* atomic force microscopy studies conducted at the Palmstrøm Lab at UCSB, where we consider different *ex-situ* sample preparation methods to produce the most suitable GaN surface for our ALP/ALEp-based approach. We have determined that a combination of UV/ozone exposure followed by an HF dip produces the cleanest and smoothest GaN surface. We have further determined with GISAXS that ALP-based gallium-flash-off experiments performed at higher temperatures (500°C) produce a smoother starting surface than lower temperatures. Additionally we have determined that we should only perform ~10 cycles of ALP gallium-flash-off instead of 30 as was empirically chosen previously. Due to the sensitivity of the GISAXS experiment, we are able to observe the effect of individual components of the ALP process cycle (pulse vs purge), leading us to insights on the underlying chemical process of the gallium-flash-off ALP. Combining these two results, *ex-situ* and *in-situ* cleaning preparation, should lead us to the best GaN starting surface to grow high quality crystalline InN films.

[1] N. Nepal, et al., Appl. Phys. Lett. 103, 082110 (2013)

[2] C. R. Eddy, Jr, et al., J. Vac. Sci. Technol. A 31(5), 058501 (2013)

[3] R. S. Pengelly, et al., IEEE Trans. Microwave Theory Tech. 60, 1764 (2012)

5:00pm **PS+EM+TF-ThA-9 Chemical Interactions with Alkali Compounds for Controlling the Transition between Thermal HF-based Atomic Layer Etching and Deposition***, **John Hennessy**,* Jet Propulsion Laboratory, California Institute of Technology

The use of anhydrous hydrogen fluoride (HF) as a precursor can result in a variety of atomic layer deposition (ALD) processes for thin films like MgF_2, AlF_3 and LiF, with good optical properties in the deep ultraviolet. Cyclic exposure to HF and several organoaluminum compounds including trimethylaluminum (TMA), can also result in the thermal atomic layer etching (ALE) of some oxide films like Al_2O_3. In this work we show that the introduction of alkali halide compounds (such as LiF or KBr) into the reactor during this cyclic exposure can dramatically alter the deposition and etch conditions at a given substrate temperature. This occurs via the formation of an intermediate complex between the metalorganic precursor and the alkali compounds, that then enhances the removal of the surface fluoride created during the preceding HF exposure. Although the etch rate can be enhanced via this interaction at a given substrate temperature, the process remains self-limiting overall.

This approach provides a pathway to the low temperature (~100 °C) thermal ALE of Al_2O_3. This can be useful for substrate-sensitive applications where exposure to high temperature or energetic plasmas is undesirable. The interaction of TMA and the alkali halide also results in approaches for the spatially-selective deposition of AlF_3, or the spatially-selective etching of Al_2O_3.

We have utilized this combination of ALE and ALD to gently remove the native oxide from metallic aluminum and replace it with AlF_3 for a variety of optics and sensing applications at JPL. This can be performed by variation of the substrate temperature to switch continuously from ALE-mode to ALD-mode, or by variation of the aluminum precursor to tune the chemical interactivity with the alkali compounds. Fabricated devices made with this concept are relevant for a variety of NASA astrophysics and planetary science applications at ultraviolet wavelengths.

5:20pm **PS+EM+TF-ThA-10 Selective Processing to Enable High Fidelity Control for the 5 nm Node***, **Benjamen Rathsack**,* Tokyo Electron America, Inc.*; A Ranjan,* TEL Technology Center, America, LLC.*; P Ventzek,* Tokyo Electron America, Inc.*; H Mochiki,* Tokyo Electron Miyagi, Ltd., Japan*; J Bannister,* Tokyo Electron America, Inc. **INVITED**

Selective processing through the integration of Etch and ALD is critical to enable high fidelity control for 5 nm node structures. The complexity of multi-step integrations and processes has caused edge placement error (EPE) to become a critical challenge. The enablement of further scaling requires the utilization of self-aligned processing to address overlay variation as well as highly selective processing to address localized fidelity control. Fidelity control has become complex on multi-step processes integrated for SAQP, self-aligned block (multi-color) and high-aspect ratio structures. Localized fidelity control is highly dependent on both the material stacks and selective processing capabilities. This includes stringent selectivity, profile, loading and uniformity requirements. To meet these requirements, the fusion of Etch and ALD enables atomic level precision with minimal impact from CD loading effects. The fusion of Etch and ALD processing also improves across wafer CD control and LWR. The use of selective processing is demonstrated to be a key enabler of 5 nm node fidelity control.

Plasma Science and Technology Division
Room 104A - Session PS-ThA

Plasma Diagnostics, Sensors and Controls
Moderator: Steven Shannon, North Carolina State University

2:20pm **PS-ThA-1 In-situ Measurement of Electron Emission and Electron Reflection Yields***, **Mark Sobolewski**,* National Institute of Standards and Technology (NIST)

Bombardment of plasma-exposed surfaces by energetic particles causes electrons to be emitted, which in turn influence the plasma. Accurate plasma simulations require knowledge of the flux or yield of emitted electrons. Yields can be measured directly in beam studies, but it is impractical to produce a beam of each possible energetic particle produced by typical plasmas. In contrast, in-situ measurements, performed during plasma exposure, provide useful values for effective or total electron emission yields, summed over all the energetic particles present for given plasma conditions. Here, measurements were performed at 5-10 mTorr in a radio-frequency (rf) biased, inductively coupled plasma (icp) system. The rf voltage and current across the sheath adjacent to the rf-biased electrode are measured, along with Langmuir probe measurements of ion current density and electron temperature. The measurements are analyzed by a numerical sheath model, which allows the current of electrons emitted from the surface to be distinguished from other mechanisms of current flow. An insulating cap placed on the rf-biased electrode exposes a small, off-center portion of its area. The cap, combined with the azimuthal electric field generated by the icp source, allows outgoing, emitted electrons to be distinguished from electrons reflected at the counterelectrode surface. Thus we obtain values for the total yield or flux of electrons emitted at the rf-biased surface and the reflection coefficient at the counterelectrode. The technique is validated by comparing measurements made in argon discharges with literature results and then is applied to characterize yields at practical surfaces in inert gas plasmas and fluorocarbon etching plasmas.

2:40pm **PS-ThA-2 Electron Energy Distribution Measurements in Dusty Non-thermal Plasmas***, **Austin Woodard**, L Mangolini,* University of California, Riverside

Dusty plasmas are a peculiar class of plasmas characterized by the presence of charged solid particles. Understanding the properties of these environments, ever-present in laboratory discharges, represent a crucial requirement for the engineering and optimization of several plasma-based processes employed in industrial manufacturing, such as thin film fabrication and etching. Langmuir probe measurements represent a well-established method used for the investigation of the properties of plasma discharges, such as the electron density, the ion density, the electron temperature and the electron energy distribution function (EEDF). In dust-rich plasmas, however, the application of the Langmuir probe method is quite challenging as the dust particles quickly form an insulating film on the probe surface which may hinder a reliable measurement. In this contribution, Langmuir probe measurements are performed in an inductively coupled RF Ar-H_2 primary plasma which is dosed with conductive nanoparticles produced in a secondary RF plasma reactor. To avoid the formation of an insulating coating, graphitic carbon nanoparticles, obtained in the secondary reactor from the dissociation of C_2H_2 in an Ar-H_2 plasma, are used for this study. The conductive graphitic nanoparticle coating formed on the probe tip does not negatively impact EEDF measurements in a pristine Ar-H_2 plasma, allowing a more forgiving environment in which to study the effect of dust on plasma properties. The EEDF is obtained through the Druyvesteyn method, via the second-derivative of I-V probe characteristics. Electron densities and temperatures are obtained from the EEDF measurements, while ion densities are calculated from the I-V characteristics. The role of process parameters such the nanoparticle density and the primary plasma input power is carefully mapped. The nanoparticle density is measured through the mass injection rate into the primary reactor, allowing for the particle charge to be measured across the parameters. In the dust-free pristine Ar-H_2 plasma, a transition in the primary ion is observed as a function of the applied RF power: H_3^+ appears to dominate at low powers, transitioning to Ar^+ at higher values. In dusty environments, the measured plasma power is much lower than in pristine, prompting H_3^+ as a likely choice for the primary ion in ion density calculations. As expected from theory and previous literature, nanoparticles act as electron sinks, reducing the electron density inside the plasma volume, resulting in an increased electron temperature to maintain ionization events; contrary to theory, however, the electron temperature increases with increasing input plasma power.

3:00pm **PS-ThA-3 The Surface Plasmon Energy and the Secondary Electron Emission on an Oxidized Aluminum Surface***, J Li, J Qiu,* ***Yi-Kang Pu,*** Tsinghua University, China **INVITED**

The energy evolution of surface plasmons and the apparent secondary electron yield on an aluminum surface during the oxidation process are investigated in an experiment under a controlled environment. The surface plasmon energy is determined from the location of the surface plasmon loss peak in the EELS spectra; at the same time, the total oxygen coverage (in the submonolayer regime) and the oxide layer thickness (in the multilayer regime) are obtained from the peak profiles of O 1s and Al 2p photoemission lines in the XPS spectra. The apparent secondary electron yield is deduced from the breakdown voltage between two parallel plate electrodes in a 360 mTorr argon environment using a Townsend breakdown model. In the submonolayer regime, both the surface plasmon energy and secondary electron yield decrease with the total oxygen coverage. In the multilayer regime, the surface plasmon energy continues to decrease with the oxide layer thickness although the rate of decrease is lower. However, the secondary electron yield sharply increases with the oxide layer thickness. In this presentation, we will discuss possible mechanisms for the variation of these quantities and compare the measured results with that from the models.

4:00pm **PS-ThA-6 Transient Phenomena in Power Modulated Chlorine Plasma***,* ***Priyanka Arora,*** *T List, T Ma,* University of Houston*; S Shannon,* North Carolina State University*; S Nam,* Samsung Electronics Co., Ltd., Republic of Korea*; V Donnelly,* University of Houston

Power-modulated plasmas (i.e. rapid switching from high to low power) could have some potential advantages over conventional pulsed plasmas (where power is periodically turned completely off) for plasma processing in that a larger parameter space is available between fully pulsed and continuous power. In the present study, power at 13.56 MHz applied to a mostly chlorine inductively-coupled plasma was modulated between a high power and low power state. Time-resolved optical emission, Langmuir probe, and forward and reflected power measurements were performed. Two distinct types of transient phenomena were found upon switching from the high power to low power state. In a “normal” mode, electron temperature (T_e) remains constant, while electron and ion number densities (n_e and n_i^+) and optical emission intensities smoothly drop to a level roughly equal to the fractional drop in power. In a second “anomalous” mode, n_e, T_e and optical emission intensities rapidly drop and stay low for an extended period before rising to values commensurate with the drop in power. Under many circumstances, a single delay time is found that depends on pressure and power duty cycle. In some cases, two delay times can be found, with subtle changes in matching network settings causing one delay time or the other. The anomalous mode can exhibit complex behavior such as two or three phases in the low power period, and periodicity at half the pulsing frequency. The anomalous mode will be discussed in terms of negative ion-driven instabilities.

4:20pm **PS-ThA-7 Measurements of RF Magnetic Fields and Plasma Current in Coupled Low and Very High Dual-Frequency Plasma Sources***, J Zhao, P Ventzek, B Lane,* Tokyo Electron America, Inc.*;* ***Toshihiko Iwao,*** *K Ishibashi,* Tokyo Electron Technology Solutions Ltd., Japan

Plasma processing systems capacitively driven at very high frequencies (VHF, e.g. 100MHz) have attracted much interest for semiconductor and flat panel display processing. VHF has the advantage of generating plasma with more efficiency as power is coupled more into electrons and less into ions in the sheath. Benefits are seen for processes requiring reduced ion energy, ostensibly to minimize damage, high ion and radical flux to the substrate. The benefits of VHF are accompanied by challenges. The short wavelength associated with VHF power is reduced even further in the presence of high density plasma. The wavelengths are comparable to the RF electrode dimension. As a result, spatial variations in plasma density and sheath voltage can arise and lead to undesired non-uniformities in process parameters. Skin effects associated with high plasma density and plasma-sheath local resonances are other destroyers of plasma uniformity. Previously, we have reported[1] a detailed investigation on the spatial and temporal evolution of RF magnetic field and plasma current in a 100MHz plasma source performed with a magnetic field probe (B-dot loop). The probe translated across the diameter of the VHF plasma measured the magnitude and phase of the fundamental and harmonics of the plasma excitation frequency as a function of radial position. The measured magnetic fields displayed a transition from simple to complex behaviors depending on plasma conditions. The spatiotemporal resolved magnetic field exhibits a series of fast current reversals and subsequent circulation driven by inward wave propagation that are electromagnetic in nature. We showed how the onset, frequency and amplitude of the current reversal and subsequent circulation were strongly related to applied plasma conditions. We also showed that plasma current derived from the magnetic field distribution was closely correlated to the plasma density profile measured by a plasma absorption probe. In order to further understand these fundamental electromagnetic structures in VHF plasma, in the current study, we apply LF on top of the VHF aimed to modify the electromagnetic structures. Performed with B-dot probe, we report the spatial and temporal evolution of VHF magnetic field and plasma current as a function of different LF phases as well as the detailed correlation of VHF electromagnetic structure and the LF modulated plasma sheath variation. We show that the coupling of the VHF electromagnetic field to the plasma strongly depends on the phase of the LF driven source. Measurements are compared against different theories for how the VHF power couples to the plasma.

[1] PS+VT-ThA12, 64th AVS Symposium, Tampa FL

4:40pm **PS-ThA-8 Self-neutralized Nearly Monoenergetic Positive Ion Beam Extracted From a Pulsed Plasma***,* ***Ya-Ming Chen,*** *R Sawadichai,* University of Houston*; S Tian,* Lam Research Corporation*; V Donnelly, D Economou, P Ruchhoeft,* University of Houston

Space charge neutralization of an ion beam extracted from a plasma is crucial for advanced plasma processes which require precise control of the ion flux and the width of the ion energy distribution (IED). In previous studies, filaments thermionically emitting electrons were used for neutralizing the space charge, which would otherwise cause the ion beam to diverge owing to Coulomb explosion.[1, 2] However, the performance of the neutralizing filaments is restricted by their limited lifetime and required extra power supplies. This work reports that a self-neutralized positive ion beam can be extracted from a pulsed plasma. In particular, a nearly monoenergetic ion beam was realized by applying a synchronous DC bias in the afterglow (plasma-off) of the plasma. A mechanism of the self-neutralization process is proposed based on space-time resolved ion and electron current (I_i and I_e) measurements done by a movable Faraday cup. The measurements revealed that electrons from a low-density plasma immediately downstream of the ion extraction grid neutralize the space charge in the beam transport region. Time-resolved plasma potential measurements suggest that there could be two periods for low-energy ions and electrons to leave the source and form the low-density plasma in the downstream of the ion extraction grid. Among the observations are 1) with increasing distance, d, from the grid $I_e > I_i$ at d = 1-5 cm, $I_e = I_i$ at d ≈ 20 cm, and $I_e << I_i$ at d > 30 cm; 2) I_i decays by less than $1/r^2$; 3) electron energy peaks at ~30 eV, ascribed to acceleration by the 100 eV ion beam transiting through the downstream plasma. Ion flux and IEDs were also studied using a retarding field energy analyzer (RFEA). Detailed explanations for the self-neutralization process will be described.

Work supported by NSF.

References

[1] R. G. Jahn, *Physics of Electric Propulsion*. (Courier Corporation, 2006).

[2] J. P. Chang, J. C. Arnold, G. C. H. Zau, H.-S. Shin and H. H. Sawin, *J. Vac. Sci. Technol A*:

15 (4), 1853-1863 (1997).

5:00pm **PS-ThA-9 Diagnostics of Plasma Neutral Species in a Very High Frequency Oxygen Plasma with High Sensitivity Broadband Absorption Spectroscopy***,* ***Jianping Zhao,*** *P Ventzek, B Lane,* Tokyo Electron America, Inc.*; T Iwao, K Ishibashi,* Tokyo Electron Technology Solutions Ltd., Japan*; J Booth,* CNRS, Ecole Polytechnique, France

As advanced memory and logic critical dimensions shrink and stack complexity, film quality and yield requirements increase, precision plasma processes including plasma enhanced atomic layer deposition (PEALD) and atomic layer etch (ALE) experience more demand. Ideally infinite selectivity and damage-free process results with sub-angstrom control are sought. Plasma enhanced processes, particularly PEALD rely on plasma generated radicals for much of their perceived benefit. Furthermore, in both atomic layer etch and deposition processes, low or nearly zero energy ions are required. Large-area plasma processing systems capacitively driven at very high frequencies (VHF, e.g. 100MHz) have attracted much interest for semiconductor device and flat panel display processing. VHF has the additional advantage of generating plasma with more efficiency as power is coupled more into electrons and less into ions in the sheath. Benefits are seen for processes requiring reduced ion bombardment energy, ostensibly to minimize damage and high radical flux to the substrate. Unfortunately, it has been a challenge to measure the neutral plasma species of interest. It would be desirable to use plasma absorption spectroscopy to study plasma neutral species because it can provide direct measurement of the absolute densities of species in their ground state as well as vibrational and rotational properties of neutrals. Lack of intense and stable light sources with wide wavelength coverage and the lack of optical aberration-free spectrographs and detectors with true high resolution has rendered plasma absorption spectroscopy impractical as a solution for industry. Emission based diagnostics such as actinometrical methods are far too imprecise. A recent advance, broadband plasma absorption spectroscopy[1] (BPAS) has been proven to be a very practical improvement of plasma absorption spectroscopy with capability to detect absorbance as low as 1×10^{-4}. In order to understand the fundamental plasma chemistry property of VHF plasma, we present here the measurement of the plasma neutral properties with a high sensitivity BPAS technology. Illustrative measurements were performed in a 100MHz plasma source with pure oxygen plasma spanning a wide RF power and pressure range. Vibrational and rotational properties of O_2 molecules are derived from a theoretical fitting to the experimental spectra. Density of O_2 molecule at different vibrationally excited levels are also derived. Effects of VHF power and pressure on these plasma neutral properties are reported.

[1] Mickaël Foucher, Daniil Marinov, Emile Carbone, Pascal Chabert, and Jean-Paul Booth, Plasma Sources Sci. Technol. 24 (2015) 042001

5:20pm **PS-ThA-10 Development of the Virtual Metrology Using a Plasma Information Variable (PI-VM) for Monitoring SiO_2 Etch Depth***, **Yunchang Jang**, H Roh, S Ryu, J Kwon, G Kim,* Seoul National University, Republic of Korea

Advanced process control (APC) has been attracting attention as a technology to enhance process yield and it requires accurate and reliable virtual metrology (VM). Accuracy of VM is determined by how sensitively the input variables reflect the drift and changes of the process environment. Many previous approaches to improve the performance of VM have been focused on development of the statistical methods to select the valuable input variables from the equipment data and additional sensor data such as optical emission spectroscopy (OES) and plasma impedance monitors (PIM). In this study, the noble variables, named plasma information (PI) variables are introduced, which are obtained by phenomenological analysis and they are added into the VM development. Then we evaluated its contribution to improve the accuracy of VM. It notes that PI variables represents the state of etch plasma so it can be used to monitor the variation of process results in plasma-assisted semiconductor fabrication process. Effect of PI variables on improving VM accuracy has been investigated through following conventional (or standard) VM development procedures as follows; 1. preprocess of input dataset, 2. data exploration, 3. variable selection, 4. training of a model, and 5. Validation of the model. We added PI variables in the steps (i) in-between 2 and 3 steps (called PI-VM_{STA}) and (ii) in-between 3 and 4 steps (called VM_{STA}+PI). Each VM model are developed and evaluated by using 50 sets of SiO_2 etching depth data, having 20:1 aspect ratio and less than 5 % of variation. PI_{EEDF}, representing variation of electron energy distribution function (EEDF) is obtained from analysis of OES, which is based on the argon excitation kinetics. Pearson's correlation filter, principal component analysis (PCA), and stepwise variable selection are used for the variable selection methods. Results show that VM models using PI_{EEDF} have better performance than any other conventional VM models because PI_{EEDF} has much higher correlation with output variable than the other equipment and sensor variables. Especially, PI-VM_{STA} using stepwise variable selection method shows the highest accuracy where PI_{EEDF} provides a basis to select other OES variables. This study shows that a phenomenological-based, statistically tuned VM can be developed by using PI variables as input. It has advantages for management of dataset and selection of control variables in APC application.

5:40pm **PS-ThA-11 Model Predictive Control of Plasma Density in Ar/SF_6 Capacitively Coupled Plasma Source***, **Sangwon Ryu**, H Roh, Y Jang, D Park, J Koo, J Lee, G Kim,* Seoul National University, Republic of Korea

Advanced Process Control (APC) of plasma assisted processes has drawn interests because the reproducibility of process results is degraded by continuous deterioration of the equipment. To control the process drift, the process plasma should be maintained by in-situ controller. Some earlier researches handled real-time feedback proportional integral derivative (PID) controllers for plasma density which is coupled to generation of the reactive species in plasma assisted processes. However, since PID had no knowledge of the controlled system, PID couldn't guarantee optimal control especially for systems with long dead time. Thus, we proposed model predictive controllers (MPC) for plasma density in Ar/SF_6 etching plasma as the control model of the MPC contains information of the system. To provide plasma density to the controller in real-time, we developed plasma density monitoring module which used light emissions from Ar measured by a spectrometer. The method showed $R^2 = 0.99$ with plasma density measured by Langmuir probe. The control model of the MPC was set as First Order Plus Dead Time (FOPDT) model which consisted of the linear gain and the time constants. We trained the control model with sensitivity tests; observing variation of plasma density as changing RF power. Compared to PID, MPC showed 6 times shorter settling time in set point tracking tests. Also, the integral of the absolute error for the MPC was 4 times lower than that of PID in same tests. The experimental results showed that MPC could control plasma more effectively than PID could by predicting the dead time of the system included in the control model. From the analysis on the parameters of the control model, we explained the control model as function of system parameters; the linear gain represented the balance between the power absorbed by electron and the power lost by electron impact collisions and the time constants were composed of the data transfer time between devices and the actuation time of the devices. This study showed that MPC could be used as the etching process plasma controller which would be a part of APC.

Surface Science Division
Room 102A - Session SS+EM+PS+TF-ThA
Deposition, Etching and Growth at Surfaces

Moderator: Bruce E. Koel, Princeton University

2:20pm **SS+EM+PS+TF-ThA-1 Controlled Deposition and High-Resolution Analysis of Functional Macromolecules in Ultrahigh Vacuum***, **Giovanni Costantini**,* University of Warwick, UK **INVITED**

The ultimate spatial resolution of scanning tunnelling microscopy (STM) has allowed to gain an exceptional insight into the structure and the intra- and inter-molecular bonding of a huge number of adsorbed molecular system. Unfortunately, these remarkable analytical capabilities are achieved only under ultrahigh vacuum (UHV) conditions and therefore cannot be directly applied to more interesting systems composed of functional (bio)molecules or complex synthetic compounds. In fact, thermal sublimation is the strategy of choice for preparing ultrathin films of small and heat-resistant molecules in UHV but larger, complex (bio)molecules are not compatible with this process.

This challenge has been overcome in recent years by adapting soft-ionisation techniques developed in mass spectrometry (mainly electrospray ionisation, ESI) to transfer intact fragile molecules into the gas phase and to soft-land them onto atomically flat and clean substrates. When combined with advanced scanning probe microscopes operating under UHV conditions, these novel set-ups allow the surface deposition and high-resolution characterisation of a wide range of functional organic molecules and inorganic nanoparticles.

This talk will present recent advances in the development of ESI-deposition techniques and their combination with UHV-STM to analyse complex (bio)molecule-surface systems. It will start by reviewing the limits that standard molecular deposition imposes on the size of (bio)molecules that can by studied in surface science. It will continue by presenting a recently developed ESI-deposition setup based on a simple, efficient and modular design with a high intensity and mass selectivity. The discussion will then proceed to the application of ESI-STM to the characterisation of adsorbed polypeptides and polymers. In particular, it will be shown that this technique allows the imaging of individual macromolecules with unprecedented detail, thereby unravelling structural and self-assembly characteristics that have so far been impossible to determine.

3:00pm **SS+EM+PS+TF-ThA-3 Unconventional Nucleation and Growth Kinetics: *in situ* Variable-temperature Scanning Tunneling Microscopy Studies of Chemical Vapor Deposition of Inorganic Monolayers on Metallic Substrates***, **Pedro Arias**,* University of California, Los Angeles*; A Abdulslam,* Colorado School of Mines*; A Ebnonnasir,* University of California at Los Angeles*; C Ciobanu,* Colorado School of Mines*; S Kodambaka,* University of California, Los Angeles

The growth of thin films from atoms and/or molecules deposited from the gas phase onto solid substrates is a non-equilibrium phenomenon where the structure, composition, and crystallinity of the films are determined by kinetic and thermodynamic processes. Over the past few decades, vast and fruitful efforts have been devoted to understanding the kinetics of thin film growth. As a result, conventions of the kinetic factors have been developed to predict the growth mechanism and, hence, microstructure of the as-grown films: for example, nucleation at terraces (steps) is expected to occur when surface diffusion of adsorbed species is significantly lower (higher) compared to the deposition flux and is observed at higher (lower) fluxes and lower (higher) substrate temperatures. Here, we report an unconventional growth mode of inorganic monolayers on metallic substrates.

Using in situ ultra-high vacuum scanning tunneling microscopy (UHV STM), we investigated the chemical vapor deposition (CVD) kinetics of hexagonal boron nitride (hBN) monolayers on Pd(111). In each experiment, STM images are acquired while exposing Pd(111) to borazine (10^{-7} – 10^{-6} Torr) at temperatures 573 K and 673 K and for times up to 2500 s. The STM images reveal the nucleation and growth of two-dimensional islands on the Pd surfaces. From the images, we measure the areal coverage, island sizes, and island density as a function of time, temperature, and borazine flux. We find that the rates of areal coverage and island density increase ten-fold with increasing borazine pressure from 10^{-7} to 10^{-6} Torr at 573 K and three-fold with increasing temperature from 573 K to 673 K and borazine pressure of 10^{-7} Torr. Our STM images reveal an unusual nucleation and growth mode: at lower deposition flux and higher temperature, islands form on terraces; increasing the flux and/or lowering the temperature result in preferential nucleation and growth at the step edges. Interestingly, the step-edge growth of borazine islands is observed on *both* up and down steps. We attribute this phenomenon to the structure and the highly anisotropic bonding of borazine on Pd(111). Our results provide new insights into the growth dynamics of two-dimensional layered materials.

3:20pm **SS+EM+PS+TF-ThA-4 Redox-Active Ligands for Single-Site Metal-Organic Complexes on Surfaces as Heterogeneous Catalysts***, **Tobias Morris**,* Indiana University*; D Wisman,* Indiana University, NAVSEA Crane*; I Huerfano, N Maciullis, K Caulton, S Tait,* Indiana University

The utilization of single-site transition metal centers at surfaces is of growing interest in the heterogenous catalysis community. One advantage of single-site metal centers is the high dispersion so that a much higher fraction of atoms contribute to chemical activity compared to nanoparticle catalysts. Our approach to forming single-site metal centers is on-surface complexation with a redox-active ligand, which allows a high degree of ordering on the surface as well as intimate chemical contact of the metal center with the support surface. The ligand design enables us to tailor the coordination geometry and oxidation state of the metal and thus affect the cooperation between metal and ligand and the chemical reactivity. Several ligands, differing in backbone, binding pocket, design, and peripheral units were examined in this study. Tetrazine-based ligands are known for their redox activity. The on-surface two-electron redox process utilizes vapor deposition of 3,6-di-2-pyridyl-1,2,4,5-tetrazine (DPTZ) with vanadium cations onto an Au(100) surface. The metal-organic complexation leads to the growth of 1D chains consistent of one metal per ligand due to the divergent binding pockets created by the tetrazine core and pyridine rings. Exposing the V-DPTZ chains to oxygen results in a dissociative reaction of molecular oxygen to form a terminal oxo species on the vanadium, while allowing the metal-organic complex to remain intact. Interestingly, the dioxygen activation contributes adsorbed oxygen to the support surface by a spillover mechanism. The stable V-oxo species is the only oxidation product, unlike the unselective oxidation of V nanoparticles. A newly synthesized ligand, tetraethyltetra-aza-anthraquinone (EtTAAQ), utilizes a quinone backbone with adjacent pyrazine rings to generate four symmetric binding pockets. Quinones are one of the oldest studied redox-active ligands. EtTAAQ has the capacity for up to a four-electron reduction, enabling the possibility for multiple metal sites per ligand. Continued work on redesigning ligands is showing promise in increasing the cooperativity of the ligand and the metal which could lead to heightened reactivity.

4:00pm **SS+EM+PS+TF-ThA-6 Oxidation and Ablation of HOPG Using Supersonic Beams of Molecular Oxygen Combined with STM Visualization***, **Ross Edel**, T Grabnic, B Wiggins, S Sibener,* University of Chicago

Graphite is widely studied due to its importance in high-performance materials applications such as high velocity flight systems as well as its key role as a model system for other carbonic materials such as graphene and carbon nanotubes. Our research focuses on the reaction of highly oriented pyrolytic graphite (HOPG) with molecular oxygen, the mechanism of which is not yet fully understood. Utilizing a one-of-a-kind instrument that combines a supersonic molecular beam and scanning tunneling microscope (STM) in ultra-high vacuum, we are able to tightly control the energy and angle of impinging oxygen and examine the nanoscopic and mesoscopic evolution of the surface. We have found that different oxygen energies, incident angles, and surface temperatures produce morphologically distinct etching features: Anisotropic channels, circular pits, and hexagonal pits faceted along crystallographic directions. The faceted and circular etch pits were formed at low O_2 energy, with faceting only apparent below a critical surface temperature, while anisotropic etching was observed with exposure to higher energy oxygen. Comparison of low- and high-grade reacted samples show that anisotropic channels likely result from the presence of grain boundaries. Reaction probability increased with beam energy and demonstrated non-Arrhenius behavior with respect to surface temperature, peaking at around 1375 K. Beam impingement angle had only minor effects on the reaction probability and etch pit morphology. Reactivity was enhanced by natural grain boundaries and artificially created point defects, showing the critical influence of small structural imperfections. Our combination of STM imaging with well-defined and controlled oxidation conditions connects interfacial reaction kinetics with time-evolving nanoscopic surface morphology, providing new insight into the oxidation of graphitic materials under high-temperature conditions. Spatio-temporal correlations obtained in this manner shed new light on interfacial erosion mechanisms, and provide an incisive complement to the information obtained using spatially-averaged gas-surface reactive scattering measurements.

4:20pm **SS+EM+PS+TF-ThA-7 Kinetically Trapped Molecular Growth during the Self-assembly of ZnTPP on Ag(100)***, **Sylvie Rangan**, P Kim, C Ruggieri, R Bartynski,* Rutgers, the State University of New Jersey*; S Whitelam,* Lawrence Berkeley National Laboratory

The result of the self-assembly of organic molecules on a noble metal surface is often analyzed in terms of equilibrium configurations, implicitly assuming that molecular adsorbates are mobile enough to reach global thermodynamic equilibrium. For example, tetraphenylporphyrins (TTPs), which have a 4-fold symmetry and a high surface mobility, generally assemble on surfaces in highly-ordered nearly-square arrays, locked in-place by phenyl T-stacking. Here, using scanning tunnel microscopy, a highly ordered metastable phase is observed for a monolayer of ZnTPP molecules self-assembled at 300 K on Ag(100). This phase is composed of two rows of the expected nearly-square phase, alternated with a row of rotated molecules. The usually reported square phase is found only after higher temperature anneal. Using a Kinetic Monte Carlo model, molecular self-assembly is simulated and reveals that this system is an unusual example of 2D molecular growth, where kinetic factors could be the limiting process directing self-assembly.

4:40pm **SS+EM+PS+TF-ThA-8 Early Stage Oxidation and Evolution of Surface Oxides in Ni(100) and Ni-Cr(100) Thin Films***, **William H. Blades**, P Reinke,* University of Virginia

The interaction of molecular oxygen with Ni(100) and Ni-Cr(100) thin films has been studied through a synergetic experimental and computational effort. The physical and chemical processes behind the initial stages of oxidation prior to the formation of a full oxide layer are not well understood. By oxidizing Ni(100) and Ni-Cr(100) thin films and studying the growth of the surface oxides with Scanning Tunneling Microscopy and Scanning Tunneling Spectroscopy, the evolution of oxides grown within the pre-Cabrera-Mott regime can be captured. The data collected are combined with Bandgap and Density of States maps and statistical distributions of the surface's electronic structure are generated. Pure Ni(100) and Ni-(8-12)wt.%Cr(100) thin films were prepared on MgO(100) in UHV and exposed to oxygen up to 400 L. Under these oxidation conditions the Ni(100) prefers the Ni(100)-c(2x2)O reconstruction, which drives step faceting into {100} segments subsequently limiting the growth of NiO at elevated temperatures. Our experiments demonstrate that once a nominal amount of Cr is added to Ni(100), the Ni-Cr(100) surface will undergo a different oxidation reaction pathway. After just 14 L of O_2 exposure we observe NiO growth across the surface, the presence of large oxide nodules and three distinct chemisorbed phases. Initial NiO nucleation and growth occurs along the step edges of the Ni-Cr surface. The superlattice and modulation of tip bias has revealed a NiO-Ni(6x7) cube-on-cube interfacial relationship. NiO wedge-like features are also observed and have characteristically different superlattice spacing, which offers insight into the manner in which metal-oxides mitigate strain within the pre-Cabrera-Mott regime. One of the chemisorbed phases we observe has been identified as Cr(100)-c(2x4)O, suggesting surface segregation and subsequent phase separation of BCC Cr. Two other chemisorbed domains are present and possess distinct electronic signatures that have been captured by STS. Density Functional Theory is used to develop an understanding of the effect of Ni and Cr on the local bonding environment of the prevalent chemisorbed phases of Ni-Cr(100). This combined experimental and theoretical approach has offered greater insight into alloy-oxide interface structure, and the role of transition metal dopants in the oxidation process in the pre-Cabrera-Mott regime. This work is supported by the Office of Navel Research MURI “Understanding Corrosion in Four Dimensions,” Grant N00014-14-1-0675.

5:00pm **SS+EM+PS+TF-ThA-9 DLC Films by Modified HiPIMS with Effect from Pulse Parameters on Plasma Parameters and Film Quality**, ***David Ruzic****, I Haehnlein,* University of Illinois at Urbana-Champaign*; B Wu,* Southwest Jiaotong University*; D Barlaz,* University of Illinois at Urbana-Champaign*; B Jurczyk,* Starfire Industries

Diamond like carbon (DLC) films have made waves as of late in many industries. DLC provides a high strength low friction surface with the potential for high chemical resistivity. High Power Impulse Magnetron Sputtering (HiPIMS) is a promising physical vapor deposition (PVD) that creates high ionization fractions at the substrate using high power pulses over low duty factors. The resulting high plasma densities (as high as 10^{19} m^{-3}) creates ionization fractions of sputtered material at the target surface. The increase in energy of atoms due to high ionization rates at the substrate yields higher density and smoother films. In combination with a positive polarity pulse to drive ions to the substrate surface, the DLC film hardness can be increased while producing a smoother film surface.

By introducing a larger ion flux, determined through a gridded energy analyzer, the ratio of sp^3 bonded carbon to sp^2 is presented for a multitude of parameters. This work explores not only the use of positive polarity pulses, but the effect of pulse parameters, has on film hardness and morphology. By controlling the deposition rate through pulse width and repetition rate while controlling deposition energy increases by approximately 5% in sp^3 fraction were observed while surface roughness decreased by a factor of 4 for a non-hydrogenated amorphous carbon film by just the introduction of a positive polarity pulse. Further increases are reported through fine tuning the discharge parameters while looking at plasma densities, ion fraction, surface roughness, sp^3 fraction, and hardness for DLC on silicon substrates.

5:20pm **SS+EM+PS+TF-ThA-10 Adsorption and Reactions on Topological Insulators Surfaces Probed by Low Energy Ion Scattering**, ***Haoshan Zhu***[1]*, W Zhou, J Yarmoff,* University of California - Riverside

Bi_2Se_3 and Bi_2Te_3 are two-dimensional topological insulators (TIs) that have attracted intense interest in recent years. TIs are promising candidates for superconductor, spintronics and quantum computing applications due to topological surface states (TSS) that connect the conduction and valence bands. The clean $Bi_2(Se,Te)_3$ surfaces prepared under ultra-high vacuum (UHV) are terminated with Se or Te, but the termination can change if exposed to air or prepared under non-ideal conditions. The adsorption and reactions of various atoms and molecules with $Bi_2(Se,Te)_3$ have thus been studied extensively, as they can result in changes to the TSS, doping and surface reconstruction. Here, TI surfaces are exposed to Cs, Bi, and halogens (Cl_2 and Br_2) in UHV and investigated by low energy electron diffraction (LEED), work function measurements and low energy ion scattering (LEIS). It is found that Cs lowers the work function and remains stable at small coverages but becomes mobile at larger coverages. Bi grows in a quasi bilayer-by-bilayer mode with the first Bi bilayer being strongly bonded to the TI surface. Both clean TI surfaces and Bi-covered surfaces are exposed to halogens. The clean surfaces are relatively inert to halogens, but they readily adsorb onto Bi films . The Bi is etched away when the samples are lightly annealed, restoring the clean Se- or Te-terminated surfaces.

5:40pm **SS+EM+PS+TF-ThA-11 Atomically Controlled Metallation of Porphyrinoid Species with Lanthanides on Surfaces**, ***Borja Cirera,*** IMDEA Nanoscience, Spain*; J Björk,* Linköping University, Sweden*; G Bottari, T Torres,* Universidad Autonoma Madrid, Spain*; R Miranda, D Ecija,* IMDEA Nanoscience, Spain

Metallation of surface confined porphyrinoid architectures have emerged as an important research topic due to its importance for biological phenomena and potential applications including optoelectronics, nanomagnetism, sensing and catalysis.

Hereby, the in-situ design of mutant porphyrinoids, either by selection of unconventional metal centers like lanthanides or by choosing different backbones, is attracting great attention. In this talk we report our latest research regarding the metallation by dysprosium, an archetype lanthanide metal for magnetic applications, of porphyrinoid species of distinct cavity size.

On one hand, the deposition of Dy on top a submonolayer of fluorinated tetraphenyl porphyrin species on Au(111) affords the expression of three different Dy-derived compounds, which are identified as the: initial, intermediate and final metallated states. Importantly, the initial metallated complexes exhibit a narrow zero bias resonance at the Fermi level that is assigned to a molecular Kondo resonance with $T_k \approx 120$ K, which can be switched off by means of vertical manipulation.

On the other hand, the adsorption on Au(111) of an expanded hemiporphyrazine with 27 atoms in its internal cavity is investigated, showing a long-range orientational self-assembly. Furthermore, a spatially controlled “writing” protocol on such self-assembled architecture is presented, based on the STM tip-induced deprotonation with molecular precision of the inner protons. Finally, the capability of these surface-confined macrocycles to host lanthanide elements is assessed, introducing a novel off-centered coordination motif.

The presented findings represent a milestone in the fields of porphyrinoid chemistry and surface science, revealing a great potential for novel surface patterning, opening new avenues for molecular level information storage, and boosting the emerging field of surface-confined coordination chemistry involving f-block elements.

Thin Films Division
Room 104B - Session TF+AS+EL+EM+NS+PS+SS-ThA
IoT Session: Thin Films for Flexible Electronics and IoT

Moderators: Jesse Jur, North Carolina State University, Siamak Nejati, University of Nebraska-Lincoln

2:20pm **TF+AS+EL+EM+NS+PS+SS-ThA-1 Ultraflexible Organic Electronics for Bio-medical Applications**, ***Tomoyuki Yokota****, T Someya,* The University of Tokyo, Japan **INVITED**

Recently, flexible electronics has much attracted to realize bio medical application for their flexibility and conformability [1-3]. To improve these characteristics, reducing the thickness of the device is very effective [4]. We have developed ultra-flexible and lightweight organic electronics and photonics devices with few micron substrates. We fabricated the 2-V operational organic transistor and circuits which has very thin gate dielectric layers. The gate dielectrics were composed of thin aluminium oxide layer and self-assembled monolayers (SAMs). Due to the very thin substrate and neutral position, our device shows the highly flexibility and conformability. The device doesn’t be broken after crumpling.

And also we fabricated highly efficient, ultra-flexible, air-stable, three-color, polymer light-emitting diodes (PLEDs) have been manufactured on one-micrometer-thick parylene substrates. The total thickness of the devices, including the substrate and encapsulation layer, is only three micrometers, which is one order of magnitude thinner than the epidermal layer of the human skin. The PLEDs are directly laminated on the surface of skin and are used as indicators/displays owing to their amazing conformability as their superthin characteristics. Three-color PLEDs exhibit a high external quantum efficiency (EQE) (12, 14, and 6% for red, green and blue, respectively) and large luminescence (over 10,000 candelas per square meter at 10 V). The PLEDs are integrated with organic photodetectors and are used as pulse oximeter.

References

[1] D. Khodagholy et al., Nature Commun. **4** 1575 (2013).

[2] G. Schwartz et al., Nature Commun. **4**, 1859 (2013).

[3] L. Xu et al., Nature Commun. **5** 3329 (2014).

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[1] **Morton S. Traum Award Finalist**

[4] D. H. Kim et al., Nat. Mater., **9**, 511 (2011).

3:00pm **TF+AS+EL+EM+NS+PS+SS-ThA-3 Molecular Surface Chemistry for Improved Interfaces in Organic Electronics***, **Jacob W. Ciszek**,* Loyola University Chicago

Organic optoelectronic devices (OLED, OFETs, etc.) contain at least one, if not multiple instances of overlayers deposited onto organic semiconductors. The generated interface is inherently flawed with issues such as non-ohmic contact, overlayer delamination, or deposition induced damage arising. Traditionally, this is addressed by physical vapor deposition of yet another layer or by reengineering the materials in the device stack. In contrast, a reaction based approach allows for a wider range of function to be installed via molecular components in an organized and oriented manner, all while take advantage the inherent reactivity of the organic molecules which comprise the semiconducting layer. We have developed this approach via a “click-like” Diels-Alder chemistry whereby prototypical acene films (tetracene or pentacene) can be appended with a variety of small molecules to form an interfacial layer only ~5 Å thick. This chemistry is then applied towards improving the metal on semiconductor contact. As a demonstration of principle, Diels-Alder chemistry is utilized to form covalent bonds linking the organic semiconductor with a deposited metal contact thereby eliminating the poor adhesion present in this system. Application of the chemistry towards contact potential shifts is presented, while work towards sensing applications concludes the talk.

3:20pm **TF+AS+EL+EM+NS+PS+SS-ThA-4 Investigation of Low Temperature ALD-deposited SnO_2 Films Stability in a Microfabrication Environment***, **Tony Maindron**, S Sandrez, N Vaxelaire,* CEA/LETI-University Grenoble Alpes, France

For applications such as displays (LCD, OLED) or solar cells, it is mandatory to use Transparent Conductive Oxides (TCOs) so as to allow light to extract out of the circuit or for light harvesting, respectively. In display technology, TCOs are also studied so as to replace the silicon technology developed to make the semiconducting channel in thin-film transistors. The mainstream TCO today is indium tin oxide (ITO), (90% indium oxide and 10% tin oxide). It has the advantage of having a high conductivity and a low surface resistivity, of the order of 10 ohm/square, while having a transmittance greater than 85% over the entire visible spectrum. However, it has several drawbacks, including the scarcity of indium and the high cost associated to its extraction process, which has prompted the scientific community to look for alternative TCOs. Among all TCOs, ZnO has been widely studied as a low cost single-metal oxide alternative material to ITO, as well as its multi-metal oxide derivatives using a dedicated metal dopant to control its electrical conductivity, as for instance with Al (ZnO:Al or AZO). One issue however with ZnO films lays in their relative chemical stability to water. It has been shown that films of ZnO or AZO change their physical properties when exposed to moisture: electrical conductivity decreases, roughness can increase, and optical characteristics are modified. By extension, when ZnO-based TCOs have to be finely patterned by photolithography, their high sensitivity to water-based solutions can be a severe issue. In our laboratory, we have noticed that ZnO and AZO films made by ALD at 150 °C typically are not stable in a microfabrication process: a large decrease (~ 20 %) of AZO thickness after the development step of photoresists used to pattern the TCO film has been noticed. One way to stabilize ZnO-based compounds is to anneal the films at high temperatures. However for some dedicated applications that use fragile substrates (plastic films for flexible organic electronics for instance), such post annealing processes at high temperature (typ. > 150 °C) cannot be applied. An alternative is to explore alternative materials to AZO: we found out that SnO_2 ALD (150 °C) shows very promising features regarding the stability under a microfabrication environment, while having good electrical and optical characteristics.

4:00pm **TF+AS+EL+EM+NS+PS+SS-ThA-6 Dopant Distribution in Atomic Layer Deposited ZnO:Al and In_2O_3:H Films Studied by Atom Probe Tomography and Transmission Electron Microscopy***, Y Wu, B Macco,* Eindhoven University of Technology, The Netherlands, Netherlands*; D Giddings, T Prosa, D Larson,* CAMECA Instruments Inc.*; S Kölling, P Koenraad,* Eindhoven University of Technology, The Netherlands*; F Roozeboom, **Erwin Kessels**,* Eindhoven University of Technology, The Netherlands, Netherlands*; M Verheijen,* Eindhoven University of Technology, The Netherlands

Transparent conductive oxides (TCOs) are ubiquitous in many of today’s electronic devices, including solar cells. Atomic layer deposition (ALD) is a promising method to prepare high quality TCO films due to its well-known virtues – i.e., precise growth control, excellent conformality and uniformity – combined with its damage-free character. Here we report on two types of TCO films that we have studied by a combination of atom probe tomography (APT) and high-resolution transmission electron microscopy (TEM). The aim was to get more insight into how the dopants are distributed in the films.

The first study was carried out on ZnO:Al prepared by alternating cycles of $Zn(C_2H_5)_2$ and H_2O with cycles of $Al(CH_3)_3$ and H_2O in a supercycle fashion at 250 °C. For this material it is known that the maximum conductivity achievable is limited by the low doping efficiency of Al. To better understand the limiting factors for the doping efficiency, the 3-dimensional distribution of Al atoms in the ZnO host material matrix has been examined at the atomic scale by the aforementioned techniques [1]. Although the Al distribution in ZnO films prepared by so-called “ALD supercycles” is often presented as atomically flat δ-doped layers, in reality a broadening of the Al-dopant layers was observed with a full-width-half-maximum of ~2 nm. In addition, an enrichment of the Al at grain boundaries was seen.

The second study involved In_2O_3:H prepared by InCp and a mixture of O_2 and H_2O at 100 °C. This material provides a record optoelectronic quality after post-deposition crystallization of the films at 200 °C. Since both the H dopant incorporation and the film microstructure play a key role in determining the optoelectronic properties, both the crystal growth and the incorporation of H during this ALD process were studied [2]. TEM studies show that an amorphous-to-crystalline phase transition o ccurs in the low temperature regime (100-150 °C), which is accompanied by a strong decrease in carrier density and an increase in carrier mobility. Isotope studies using APT on films grown with D_2O show that the incorporated hydrogen mainly originates from the co-reactant and not from the InCp precursor. In addition, it was established that the incorporation of hydrogen decreased from ~4 at. % for amorphous films to ~2 at. % after the transition to crystalline films.

[1] Y. Wu, A. Giddings, M.A. Verheijen, B. Macco, T.J. Prosa, D.J. Larson, F. Roozeboom, and W.M.M. Kessels, Chem. Mater. 30, 1209 (2018).

[2] Y. Wu, B. Macco, D. Vanhemel, S. Kölling, M.A. Verheijen, P.M. Koenraad, W.M.M. Kessels, and F. Roozeboom, ACS Appl. Mater. Interfaces, 9, 592 (2017).

4:20pm **TF+AS+EL+EM+NS+PS+SS-ThA-7 Roll-to-Roll Processable OTFT Sensors and Amplifier***, **Kai Zhang**,* University of Oxford, Department of Materials, UK*; C Chen, B Choubey, H Assender,* University of Oxford, UK

The high flexibility and relatively low cost of organic electronics are gradually providing more possibility for their application. Compared with conventional silicon based electronics, organic electronics have relatively short lifecycles and processor speed, but they are more promising in the market of wearable and flexible devices, for example, wearable health care devices, simple memory devices and flexible displays. In recent years, some flexible and wearable sensors have been developed, e.g. skin-touching sensors embedded in a sports suit can detect the change of heart rate, blood pressure, ion concentration of perspiration, or infrared radiation from the human body.

In most sensors based on organic thin film transistors (OTFT) made to date, the semiconductors are employed directly to detect analytes. However, (1) the lifecycles of this design is short due to the low stability of organic semiconductors; and (2) any modification for selectivity needs to be compatible with the semiconductor.

In this paper, we present sensors based upon an extended floating gate in order to separate the sensory area from the semiconductor. Transistors are manufactured, using our roll-to-roll vacuum webcoating facility, using a high-throughput all evaporation process (Ding et al., 2016, Taylor et al., 2015). We have demonstrated the principle of operation of a floating gate sensor integrated with the vacuum-deposited OTFT, by means of a simple strain sensor, using ferroelectric PVDF on the extended floating gate to directly act as a sensory material. To amplify the sensor signal further, a series of current mirrors and differential amplifiers have been designed based on the properties of single OTFTs. The combination of organic amplifier and OTFT sensor will be helpful to transduce sensing signal to a suitable level for wireless signal reading from flexible devices.

Reference:

DING, Z., ABBAS, G. A. W., ASSENDER, H. E., MORRISON, J. J., YEATES, S. G., PATCHETT, E. R. & TAYLOR, D. M. 2016. Vacuum production of OTFTs by vapour jet deposition of dinaphtho[2,3-b:2’,3’-f]thieno[3,2-b]thiophene (DNTT) on a lauryl acrylate functionalised dielectric surface. *Organic Electronics,* 31**,** 90-97.

TAYLOR, D. M., PATCHETT, E. R., WILLIAMS, A., DING, Z., ASSENDER, H. E., MORRISON, J. J. & YEATES, S. G. 2015. Fabrication and simulation of organic transistors and functional circuits. *Chemical Physics,* 456**,** 85-92.

4:40pm **TF+AS+EL+EM+NS+PS+SS-ThA-8 Functionalization of Indium Gallium Zinc Oxide Surfaces for Transparent Biosensors***, X Du, S John, J Bergevin,* ***Gregory Herman,*** Oregon State University

Amorphous indium gallium zinc oxide (IGZO) field effect transistors (FETs) are a promising technology for a wide range of electronic applications including implantable and wearable biosensors. We have recently evaluated the functionalization of IGZO back channel surfaces with a range of self-assembled monolayers (SAM) to precisely control surface chemistry and improve stability of the IGZO-FETs. The SAMs evaluated include, n-hexylphosphonic acid (n-HPA), (3,3,4,4,5,5,6,6,6-nonafluorohexyl) phosphonic acid (FPA), and (3-aminopropyl) trimethoxysilane (APTMS). A comparison of the surface chemistry is made for bare and SAM functionalized IGZO back channel surfaces using X-ray photoelectron spectroscopy and electronic device measurements in air and phosphate buffer solution (PBS). We find significantly improved device stability with the SAMs attached to the IGZO back channel surface, both in air and PBS. We related this to the reduction of traps at the back channel surface due to SAM passivation. To further evaluate the IGZO-FETs as biosensors we have immobilized glucose oxidase (GOx) to the APTMS functionalized IGZO back channel surface using glutaraldehyde. We find that both the FPA functionalized and the GOx immobilized surfaces are effective for the detection of glucose in PBS. Furthermore, the GOx immobilized IGZO-FET based glucose sensors have excellent selectivity to glucose, and can effectively minimize interference from acetaminophen/ascorbic acid. Finally, we will discuss fully transparent IGZO-FET based glucose sensors that have been fabricated directly on transparent catheters.These results suggest that IGZO-FETs may provide a means to integrate fully transparent, highly-sensitive sensors into contact lenses.

5:00pm **TF+AS+EL+EM+NS+PS+SS-ThA-9 Large Area Atmospheric Pressure Spatial ALD of IZO and IGZO Thin-film Transistors***, C Frijters, I Katsouras, A Illiberi, G Gelinck,* Holst Centre / TNO, Netherlands*;* ***Paul Poodt***, Holst Centre / TNO and SALDtech B.V., Netherlands

Atmospheric pressure Spatial ALD is able to deliver high deposition rates while maintaining the advantages of conventional ALD, such as low defect density, high conformality and thickness uniformity. An emerging application for Spatial ALD is flat panel (OLED) display manufacturing. Examples include oxide semiconductors and dielectric layers for use in thin-film transistors (TFT's), and thin-film encapsulation for flexible OLED displays. As today's displays are fabricated on glass plate sizes in the order of several square meters, a remaining challenge is the development of large-area Spatial ALD deposition technology that is able to combine high throughput with uniform performance across very large areas.

We are developing large area Spatial ALD technology, and as a first step between the lab and the display fab, we have installed a large area Spatial ALD sheet-to-sheet tool which can handle up to 400x325 mm^2 sized substrates. With this tool we are able to deposit uniform films across a deposition width of 400 mm and thickness non-uniformities of ~ 1%. The whole tool is operated under an atmospheric pressure but inert N_2 environment. The tool can be used to deposit a variety of materials using both thermal and plasma-enhanced Spatial ALD.

We will present about the fabrication and performance of 30 cm x 30 cm TFT backplanes with $InZnO_x$ (IZO) and $InGaZnO_x$ (IGZO) oxide semiconductors deposited by spatial ALD. The IZO and IGZO films were deposited by plasma enhanced Spatial ALD using co-injected In-, Ga- and Zn-precursors and an atmospheric pressure N_2/O_2 plasma. The deposition process has been optimized in terms of film composition and electrical properties on a lab-scale reactor before being translated to the large area spatial ALD rector. We will report on the yield and performance of the 30 cm x 30 cm TFT backplanes, including electrical properties such as the field effect mobility, V_{on} and bias stress stability and compare it with state-of-the-art sputtered IGZO TFT's. Finally, the challenges in up-scaling Spatial ALD to plate sizes of 1.5 m and beyond will be discussed.

5:20pm **TF+AS+EL+EM+NS+PS+SS-ThA-10 Thin Film Ink-Jet Printing on Textiles for Flexible Electronics***,* ***Jesse Jur****, I Kim, H Shahariar,* North Carolina State University

Inkjet printing of thin film flexible electronics on textiles is an emerging field of research with advances in wearable technology. In this study we describe for the first-time a reliable and conformal inkjet printing process of printing particle free reactive silver ink on textile surfaces. Reactive silver ink is printed on fibers with eclectic polymers ranging from polyester and polyamide, and different structures of textiles such as knitted, woven, and nonwoven fabrics. The conductivity and the resolution of the inkjet-printed tracks are directly related to the fiber structures in the fabrics. Multiple passes of printing layers are needed to confirm the percolation of the metal network on porous, uneven surfaces. The conformity and the electrical conductivity of the inkjet-printed conductive coating on PET textiles are improved by in-situ heat curing the substrate during printing and surface modification, for example, by atmospheric oxygen plasma treatments. The in-situ heat curing potentially minimizes wicking of the ink into the textile structures. We have achieved the minimum sheet resistance of 0.2 Ohm/sq on polyester knit fabric, which is comparable to the conductive thick-paste used in the screen-printed process, as well as other traditional physical and chemical deposition processes on textile fabrics/yarns. Additionally, we have constructed textile knit structures which changes electric percolation depending on structural deformations of the knit loops, providing positive and negative gauge factors upon stretching. The printed patterns are post-treated with diluted silicone/UV curable aliphatic water-soluble polyurethane coating to improve the durability during washing. These findings open up the possibility of integrating inkjet printing in the scalable and automated manufacturing process for textile electronic applications.

5:40pm **TF+AS+EL+EM+NS+PS+SS-ThA-11 Flexography Oil Patterning for In-line Metallization of Aluminium Electrodes onto Polymer Webs: Commercial Roll to Roll Manufacturing of Flexible and Wearable Electronics***,* ***Bryan Stuart****, T Cosnahan, A Watt, H Assender,* University of Oxford, Department of Materials, UK

Vacuum metallisation of aluminium through shadow masks has been commercially used for decades for depositing electrodes on rigid semiconductor devices, however recent developments have enabled large area, continuous deposition of patterned metallization in the aesthetic printing industry and has the potential for electrode interconnects for devices on flexible substrates such as Polyethylene Terephthalate (PET) and Polyethylene Naphthalene (PEN). Flexible polymer webs of PET were coated (*SeeSupplementary Figure*) with 50 nm thick, 165 um wide aluminium electrodes by commercially compatible manufacturing at roll-to-roll web speed of 2.4 m min^{-1} showing tremendous potential for large scale manufacturing of wearable electronic devices in transistors, low level energy generation (Thermoelectric generators), energy storage (thin film batteries) or display technologies (LED displays) [1].

The in-line patterning process relies on adaptation of flexography ink printing which typically transfers ink to a rubber patterned plate for printing images onto polymer webs. The flexibility of the printing plate accommodates for irregularities in the surface of the substrate making this process desirable for large area manufacturing. Metallization has been used to deposit aluminium onto a flexography applied pattern by replacing ink with a low vapor pressure oil (e.g. Perfluropolyether, Krytox®). The radiative heating of aluminium metallization causes simultaneous evaporation of the oil pattern, thereby rapidly forming the desired metal pattern onto the un-patterned regions. Currently we are scaling-up the oil flexography/metallization process into an industrial-scale roll-to-roll coater with potential web widths of 350 mm and roll speeds of 100 m min^{-1}, in order to increase web speeds, and to expand the range of materials deposited and the functional devices to which they are applied.

This paper reports on in-line pattern deposition of aluminium and other materials as applied to functional devices, for example organic thin film transistors and thermoelectric devices. In particular we are able to demonstrate how the process can be compatible with other functional layers. We will report our studies of electrode precision (shapes/sizes) by patterned metallization and our first studies of sputtering with flexography patterning. The long term view is integration of this technology along the R2R production path for single pass/high speed production of low cost and flexible integrated circuits.

References

1. Cosnahan, T., A.A. Watt, and H.E. Assender, *Modelling of a vacuum metallization patterning method for organic electronics.* Surface and Coatings Technology, 2017.

Nanometer-scale Science and Technology Division
Room 102B - Session NS+AM+AS+MN+PC+PS+SS+TR-FrM

SPM – Probing Chemical Reactions at the Nanoscale

Moderators: Phillip First, Georgia Institute of Technology, An-Ping Li, Oak Ridge National Laboratory

8:20am **NS+AM+AS+MN+PC+PS+SS+TR-FrM-1 Using Self-Assembly to Engineer Electronic Properties in 1D and 2D Molecular Nanostructures***,* ***Michael F. Crommie,*** University of California at Berkeley Physics Dept. **INVITED**

Control of chemical reactions at surfaces has created new opportunities for on-surface synthesis of low-dimensional molecular nanostructures. By designing precursor molecules it is possible to engineer new bottom-up structures with atomic precision and predetermined electronic properties. We have used this technique to confirm recent predictions that quasi-1D graphene nanoribbons (GNRs) have well-defined electronic topology. This means that when “topologically non-trivial” GNRs are fused to “topologically trivial” GNRs then a singly-occupied, topologically-protected interface state occurs at the boundary between them. This has allowed us to engineer new GNRs with unique electronic structure. We have also engineered molecular precursors to control the behavior of 2D polymers. By tuning the coupling reaction between monomers it is possible to create 2D covalent organic frameworks (COFs) that exhibit novel electronic superlattice behavior.

9:00am **NS+AM+AS+MN+PC+PS+SS+TR-FrM-3 Chemical and Electronic Structure of Aniline Films on Silica Surfaces***,* ***Christopher Goodwin,*** University of Delaware*; A Maynes,* Virginia Polytechnic Institute and State University*; Z Voras,* University of Delaware*; S Tenney,* Center for Functional Nanomaterials Brookhaven National Laboratory*; T Beebe,* University of Delaware

The use of silica as a substrate for polyaniline is highly appealing since silica is a common component in photovoltaics. To this end we have developed a vacuum technique for the deposition and functionalization of silica with aniline, without the need for wet chemistry. To study the chemistry of the reaction, X-ray Photoelectron Spectroscopy (XPS), Time-of-Flight Secondary Ion Mass Spectroscopy (TOF-SIMS), and Atomic Force Microscopy (AFM), among other techniques, have been used. To determine the electronic structure if the resulting films, scanning tunneling microscopy and evaluation of valance band data collected by XPS was performed. By controlling the temperature of the gas-phase reaction, two states of aniline were found to exist on the silica surface. Our interest is in determining how the two states affect the electronic band structure of the surface.

9:20am **NS+AM+AS+MN+PC+PS+SS+TR-FrM-4 Electric Field Driven Chemical Reaction of Individual Molecular Subunits by Scanning Tunneling Microscopy***,* ***Tomasz Michnowicz,*** Max Planck Institute for Solid State Research, Germany, Deutschland*; B Borca,* Max Planck Institute for Solid State Research, Germany*; R Pétuya,* Donostia International Physics Centre, Spain*; M Pristl, R Gutzler, V Schendel, I Pentegov, U Kraft, H Klauk,* Max Planck Institute for Solid State Research, Germany*; P Wahl,* University of St Andrews, UK*; A Arnau,* Donostia International Physics Centre, Spain*; U Schlickum, K Kern,* Max Planck Institute for Solid State Research, Germany

Understanding of elementary steps and control in chemical reactions on the atomic scale might improve significantly their efficiency and applicability. Scanning tunneling microscopy (STM) allows both investigating and stimulating chemical reactions of individual organic subunits, for example via the tunneling current, electric field or a mechanical interaction. Here we present a study of an STM stimulated desulfurization process of the thiophene functional group embedded in a tetracenothiophene (TCT) molecule on a Cu(111) surface. Precise positioning and applying stimuli with the STM tip apex allows determination of a two-step process responsible for this chemical reaction. High resolution STM images, supported by the DFT calculations, help us to correlate the first reaction step to the breaking of one the carbon-sulfur bonds and the second to the breaking of the second carbon-sulfur bond. The latter reaction also results in a significant increase of the bond strength of the broken thiophene part to Cu surface atoms. The chemical reaction is triggered by positioning the tip apex above the thiophene part and applying a threshold voltage that depends linearly on the tip-molecule distance. This linear dependence is a hallmark of an electric field driven process. In addition, conduction measurements through single TCT molecules before and after the reaction have been performed. Compared to the intact molecule we observed a 50% increase of conductance after the chemical reaction, which is in agreement with the finding of a much stronger bond formation between the molecule and Cu surface atoms.

9:40am **NS+AM+AS+MN+PC+PS+SS+TR-FrM-5 Characterising Conjugated Polymers for Organic Electronics by High-resolution Scanning Probe Microscopy***,* ***Giovanni Costantini,*** University of Warwick, UK

The structure of a conjugated polymer and its solid-state assembly are without a doubt the most important parameters determining its properties and performance in (opto)-electronic devices. A huge amount of research has been dedicated to tuning and understanding these parameters and their implications in the basic photophysics and charge transporting behaviour. The lack of reliable high-resolution analytical techniques constitutes however a major limitation, as it hampers a better understanding of both the polymerisation process and the formation of the functional thin films used in devices.

Here, by combining vacuum electrospray deposition and high-resolution scanning tunnelling microscopy (STM) we demonstrate the ability of imaging conjugated polymers with unprecedented detail, thereby unravelling structural and self-assembly characteristics that have so far been impossible to determine.

Applying this novel technique to prototypical DPP- and thiophenes-containing polymers, we show that sub-molecular resolution STM images allow us to precisely identify the monomer units and the solubilising alkyl side-chains in individual polymer strands. Based on this, it becomes possible to determine the molecular number distribution of the polymer by simply counting the repeat units. More importantly, we demonstrate that we can precisely determine the nature, locate the position, and ascertain the number of defects in the polymer backbone. This unique insight into the structure of conjugated polymers is not attainable by any other existing analytical technique and represents a fundamental contribution to the long-discussed issue of defects as a possible source of trap sites. Furthermore, the analysis of our high-resolution images, also reveals that the frequently assumed all-trans-conformation of the monomers in the polymer backbone is actually not observed, while demonstrating that the main driver for backbone conformation and hence polymer microstructure is the maximization of alkyl side-chain interdigitation.

10:00am **NS+AM+AS+MN+PC+PS+SS+TR-FrM-6 Probing Electrical Degradation of Lithium Ion Battery Electrodes with Nanoscale Resolution***,* ***Seong Heon Kim,*** Samsung Advanced Institute of Technology, Republic of Korea*; S Park, H Jung,* Samsung Advanced Institue of Technology, Republic of Korea

The high performance of lithium-ion batteries (LIBs) is in increasing demand for a variety of applications in rapidly growing energy-related fields, including electric vehicles. To develop high-performance LIBs, it is necessary to thoroughly understand the degradation mechanism of LIB electrodes. The investigation of the electrical conductivity evolution during cycling can lead to a better understanding of the degradation mechanism in cathode and anode materials for Li-ion batteries. Here, we probed the electrical degradation of LIB electrodes with nanoscale resolution via quantitative and comparative scanning spreading resistance microscopy (SSRM). First, the electrical degradation of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) particles which are representative LIB cathode materials was studied [1]. After 300 charge/discharge cycles, stepwise-increasing resistance distributions toward the centers of the secondary particles were observed. These distributions correspond to the degenerated granular structures of the secondary particles caused by the formation of micro-cracks. Second, the electrical degradation of LIB anodes, the blended Si-C composites with graphite (Gr) particles, was investigated using SSRM [2]. From the SSRM measurements, it was obviously demonstrated that the electrical conductivity of the Si-C composite particles is considerably degraded by 300 cycles of charging and discharging, although the Gr particles maintain their conductivity. Our approach using SSRM techniques can be a good tool to study the electrical properties of various LIB electrode materials with nanoscale resolution.

[1] S.Y. Park, W.J. Baek, S.Y. Lee, J.A. Seo, Y.-S. Kang, M. Koh, S.H. Kim, Probing electrical degradation of cathode materials for lithium-ion batteries with nanoscale resolution, Nano Energy 49 (2018) 1–6.

[2] S.H. Kim, Y.S. Kim, W.J. Baek, S. Heo, D.-J. Yun, S. Han, H. Jung, Nanoscale electrical degradation of silicon-carbon composite anode materials for lithium-ion batteries, Submitted.

Friday Morning, October 26, 2018

Plasma Science and Technology Division
Room 104A - Session PS-FrM

Plasma Modeling

Moderators: Venkattraman Ayyaswamy, University of California Merced, Premkumar Panneerchelvam, KLA-Tencor

8:20am **PS-FrM-1 Investigation of Electrical Asymmetric Effect in Very High Frequency Plasma Source using Electromagnetic Plasma Model*, Xiaopu Li*,** *K Bera, S Rauf, K Collins,* Applied Materials

Capacitively coupled plasmas (CCP) are widely used for semiconductor material processing. One usually strives to obtain uniform fluxes of active neutrals and ions and ion energies at the substrate for optimum process uniformity. As technology is accelerating, advanced processing application requires not only uniformity but also flexible control of species fluxes and energies. Recently, electrical asymmetric effect (EAE) has been extensively studied in the literature [1-3], where separate control of ion flux and ion energy is achieved by applying a fundamental frequency and its higher harmonics in a high frequency CCP source. In the present study, EAE is systematically investigated by tailored-waveform excitations in the very high frequency (VHF) regime where electromagnetic effect becomes significant. A fully coupled electromagnetic plasma model is used to consider both EAE and electromagnetic effects. The fluid plasma model computes species densities and fluxes, as well as the plasma current density. Drift-diffusion approximation is used for species fluxes in the continuity equations for all charged species. Neutral species densities are determined by solving the continuity equations with diffusion coefficients computed using the Lennard-Jones potentials. The electromagnetic phenomena are described by the Maxwell equations with the plasma current density updated from the fluid model. The finite difference time domain (FDTD) technique is used to discretize the Maxwell equations, which are solved explicitly in time. A geometrically asymmetric discharge is excited using the VHF source and its harmonics. The phase between the excitation frequency and its harmonics has been modulated to control the electrical asymmetry. Ar discharge is studied based on the reaction mechanism similar to the previous study [4]. This study provides a fundamental understanding of EAE, that is important to achieve flexible control of ion fluxes and energies in VHF capacitively coupled plasmas.

1. U Czarnetzki *et al*, *J. Phys.: Conf. Ser.* **162** 012010 (2009)
2. E. Schüngel *et al*, *J. Appl. Phys.* **112,** 053302 (2012)
3. T Lafleur, 2016 *Plasma Sources Sci. Technol.* **25** 013001 (2016)
4. S. Rauf and M. J. Kushner, *J. Appl. Phys.* **82**, 2805 (1997)

8:40am **PS-FrM-2 Simulation of Pulsed Inductively Coupled Plasmas*, Jun-Chieh Wang*,** *W Tian, S Rauf, S Sadighi, J Kenney, P Stout, V Vidyarthi, J Guo, K Delfin, N Lundy,* Applied Materials

Pulsed plasma processing has gained more attention lately in semiconductor industry due to its advantages over continuous wave (CW) plasmas processing. Pulsed plasma provides us with extra knobs to tailor the etching process to the desired specification, such as improved uniformity and depth loading. In this talk, a typical electronegative plasma at several mTorr with ICP source (W_s) + RF bias (W_b) of a few hundred Watts has been studied. The pulsing frequency of 1-10 KHz and duty cycle (DC) of 10% - 90% are used to investigate three pulsing schemes: source pulsing (pulsed source W_s + CW bias W_b), bias pulsing (pulsed bias W_b + CW source W_s), and their synchronized pulsing.

The plasma modeling code used in this talk, CRTRS, is a multi-dimensional hybrid plasma model. The model simultaneously solves the Poisson's equation and continuity equation for all charged species; the drift-diffusion approximation and momentum equations are solved for electron and ion fluxes. After the potential, flux and charged density have been updated, the electron energy conservation equation is solved for electron temperature. A Monte Carlo model is used to compute the ion energy and angular distribution (IEAD) at the wafer over a pulse period. The time evolution of IEAD, as well as the fluxes of relevant ions and neutral radicals at the wafer, are recorded and coupled to a 3-dimensional feature scale model for later evaluation of different pulsing modes during the Si etch step. We found that when the source power is pulsed (pulsed W_s + CW W_b), plasma extinguishes during the pulse-off period, higher sheath voltage is produced up to a few kV at lower DC as a result of lower electron density to maintain the constant W_b. When the bias power is pulsed (pulsed W_b + CW W_s), plasms density is slightly modulated by the bias power, while sheath voltage increases up to the kV level during the pulse-on period. When the source and bias powers are synchronized, IEADFs are sensitive to the phase between powers. The simulation results from plasma and feature scale model provide guidance for further experimental testing. By focusing only on the promising concepts, we are able to speed up the research cycle and gain competitive advantages.

9:00am **PS-FrM-3 The Important Role of Metal Vapour in Arc Welding: New Insights from Modelling*, Anthony Murphy*,** *J Xiang, H Park, F Chen,* CSIRO, Australia **INVITED**

Arc welding is very widely used in manufacturing industry to join metals. The process relies on the intense heat flux from the arc plasma to partially melt metal. This also produces metal vapour, which can be transported into the arc by diffusion and convection. Metal vapour plasmas emit radiation much more strongly than those in standard welding gases such as argon and helium. The presence of metal vapour therefore leads to increased radiative cooling of the arc, which decreases the heat flux to the workpiece and leads to shallower welds.

It is well known that metal vapour dominates the arc plasma in the case of in metal inert gas / metal active gas (MIG/MAG) welding, in which the upper electrode is a metal wire whose tip melts to form droplets. Large amounts of metal vapour are produced from the wire tip, and the strong downward convective flow in the arc ensures that the central region of the arc contains around 50% metal vapour.

In contrast, the upper electrode in tungsten inert gas (TIG) welding is tungsten, which does not melt or vaporize. Metal vapour is produced only from the weld pool (the molten region of the workpiece). Computational models have predicted that the strong downward convective flow in the arc confines the metal vapour close to the workpiece. The models therefore predicted that the strong radiative cooling of the arc that is observed in MIG/MAG welding does not occur in TIG welding.

We have developed a computational model of TIG welding that treats the diffusion of the metal vapour in the arc plasma accurately for the first time. Previous treatments only considered ordinary diffusion (driven by concentration gradients); we now also take into account diffusion driven by temperature gradients and the applied electric field (cataphoresis). Our results demonstrate that cataphoresis causes upward diffusion of the metal vapour into the centre of the arc, despite the strong downward convective flow, leading to substantial radiative cooling of the arc.

We also report intriguing results obtained for TIG welding of stainless steel, in which we treat the diffusion of iron and chromium vapours separately. Our results show that the iron and chromium vapours have different trajectories through the arc, explaining the surprising measurements of Tanaka and Tsujimura (*Quart. J. Japan Weld. Soc.* **30** 164, 2012), which found that iron vapour reached only as far as the tungsten electrode tip, whereas chromium vapour was deposited on the tungsten well above its tip.

Finally, we examine the substantial influence of the choice of welding gas, arc current and other parameters on the influence of metal vapour on the arc and the weld.

9:40am **PS-FrM-5 Molecular Dynamics Study on Collision Cascade Dynamics for Sputtering of Lennard-Jones Particles*, Nicolas Mauchamp*,** *M Isobe, S Hamaguchi,* Osaka University, Japan

Plasma etching techniques have been widely used to manufacture semiconductor devices. The sizes of typical silicon (Si) based semiconductor devices are now reaching atomic sizes. The further development of plasma etching techniques to fabricate such small devices requires a better understanding of plasma-surface interactions between the material surface and impacting plasma species. Especially when the device sizes are in the range of nanometers, a high precision in plasma control is one of the key challenges for the manufacturers to obtain desired results and avoiding unwanted effects in manufactured devices. For example, during an etching process with energetic ions impacting on the material surface, surface damages caused by energetic ion bombardment may lead to the formation of non-functional regions in manufactured devices. For nanometer scale semiconductor devices, nanometer-scale plasma-induced defects in their electrically active regions typically impair the device performance. Since the last century, the interaction between a surface and an energetic incident particle as well as the collision cascade resulting from it has been widely studied, which has led to the establishment of several theories. However sputtering phenomena are highly non-linear and the system is not in thermal equilibrium, so none of these theories provides a comprehensive description of collision cascade dynamics, even for a simple case of two-body interactions such as the Lennard-Jones (LJ) interaction. In this study, as a model system, physical sputtering of a cool Lennard-Jones solid, i.e., a solid that consists of particles interacting with two-body LJ interactions and is in thermal equilibrium at a temperature sufficiently below its melting temperature, is examined with the use of Molecular Dynamics (MD) simulations. The goal of this study is to understand how the interatomic potential function of a material affects its sputtering yield, a macroscopic and non-thermodynamical property of the material. Self-sputtering of a LJ material and physical sputtering of a LJ material by the incidence of energetic non-reactive particles with different sizes and masses were examined. A non-reactive particle in this study is the one that interacts with other particles via a repulsive part of a LJ potential. From MD simulation, dependence of the sputtering yield on the normalized incident energy and the incidence angle has been obtained for different mass ratios and atomic-radius ratios between the substrate and impacting particles.

10:00am **PS-FrM-6 Surface Reaction Analysis by Molecular Dynamics (MD) Simulation for SiO2 Atomic Layer Etching (ALE)**, ***Satoshi Hamaguchi***, *Y Okada, M Isobe, T Ito, K Karahashi,* Osaka University, Japan

Alternating application of fluorocarbon plasmas with no bias energy and Ar plasma with low bias energy to a SiO2 film is known to cause atomic layer etching (ALE) of its surface. In this ALE process, it is assumed that a thin layer of fluorocarbon is deposited on the SiO2 surface in the first step and low-energy Ar+ ion irradiation causes mixing of deposited fluorocarbon with atoms of the underlying SiO2 surface in the second step, promoting desorption of volatile SiFx and CO from the surface until fluorocarbon on the surface is completely exhausted. In this study, we have examined the surface reactions of such processes, using molecular dynamics (MD) simulations. It has been found, however, the actual surface reactions are not as simple as described above. In the Ar+ ion irradiation step, preferential sputtering of O atoms occurs even at low ion incident energy, which makes the surface more Si rich and also promotes the formation of Si-C bonds in the presence of a deposited fluorocarbon layer. In other words, in deficiency of O atoms on a SiO2 film surface, low-energy Ar+ ion irradiation may not be able to remove C atoms completely from the surface. Under such conditions, more carbon atoms may remain on the surface after each ALE cycle and etch stop may eventually occur after several ALE cycles. On the other hand, our simulation results indicate that a small amount of oxygen added to Ar+ ion irradiation may contribute to more efficient removal of carbon from the surface and also supplement the deficiency of oxygen caused by the preferential sputtering of oxygen from the surface. Simulation results are also compared with experimental observations of SiO2 ALE based on fluorocarbon plasmas.

10:20am **PS-FrM-7 Atomistic Simulations of He Plasma Modification of SiO2 Thin Films for Advanced Etch Processes**, ***Florian Pinzan***, *R Blanc, F Leverd,* STMicroelectronics, France*; E Despiau-Pujo,* LTM, Univ. Grenoble Alpes, CEA-LETI, France

Due to high ion bombardment energies and significant fragmentation rates, conventional continuous wave (CW) plasma processes are not able to selectively etch ultra-thin films without damaging the underlying layers of advanced nano-devices. Used as dielectric film in Flash memory devices, inter-poly Oxide-Nitride-Oxide (ONO) stack layer is directly impacted by this issue. Its bottom SiO2 layer (40Å) etching is challenging as it must be performed with nanoscale-precision in order to avoid damaging the underlayer substrate, which would lead to device performance loss. To achieve this nanometric precision etching, one possible solution may be the use of a recently developed two-step etch technology, which has already proved its worth for nitride spacers etching in terms of both anisotropy and selectivity [1]. In the first step, the material to be etched is exposed to a hydrogen (H2) or helium (He) ICP or CCP plasma; in the second step, the modified material is chemically etched by wet cleaning (HF bath) or exposure to gaseous reactants only (NH3/NF3 downstream plasmas).

Due to the complexity of plasma-material interactions, the development of such a new etch approach requires a more detailed understanding of the fundamental mechanisms involved in the process. Therefore, we develop Molecular Dynamics (MD) simulations to study the implantation step in Si-O-N-He and Si-O-N-H systems and provide an overview of the reaction processes at the atomic scale. The objective is to understand precisely the role of the ion energy and ion dose in the implantation, and to determine the relationship between the flux/energy of plasma species (He+, Hx+, H) bombarding the surface and its structural/chemical modifications.

In this paper, we investigate specifically the interaction between low energy He+ ions and SiO2 thin films via MD simulations. We study in particular the influence of the ion energy (5-100eV) and ion dose on the substrate modification. Cumulative bombardment leads to a self-limited ion implantation followed by the formation of a modified He-implanted layer at steady state. The modified layer thickness is shown to increase with the incident ion energy, and only few sputtering of the SiO2 layer is observed in the ionic energy range considered here. Mechanisms of helium retention and desorption, as well as the detailed structure of the material at steady state, will be discussed during the presentation.

10:40am **PS-FrM-8 Plasma Characteristics in a Capacitively Coupled System at Moderately High Pressure: Model and Experiment Comparison**, ***David J. Peterson***, *S Shannon,* North Carolina State University*; W Tian, P Kraus, K Bera, S Rauf, T Chua, T Koh,* Applied Materials Inc.

Plasma parameters including electron density, effective collision frequency, effective electron temperature, voltage & current characteristics, neutral gas temperature, ion temperature and sheath thickness around the probe are measured over different pressures and powers ranging from 0.1-4.0 Torr and 20-150 W in Ar, He, Ar-He, and N_2 plasmas. Both grounded and fully floating hairpin resonator probes are used in a parallel plate capacitively coupled system driven at 27 MHz. Probe measurements are made in the axial and radial directions. Probe sheath thickness is measured using a time resolved measurement system capable of ~100 ns time resolution. Effective collision frequency is measured using the resonance full width half max. Effective electron temperature can determined from the effective collision frequency through the plasma conductivity equation but requires assuming an electron energy distribution function (EEDF). Effective electron temperatures are presented for three different EEDFs: Maxwellian, Bi-Maxwellian, and Druyvesteyn. Neutral gas temperature is measured by assuming rotational-translational equilibrium in N_2 where the second positive system is used to determine rotational temperatures. Ion temperatures are also determined through this method via the 1st negative system in N_2^+. Spatial profiles of plasma parameters along with voltage & current characteristics are compared with 2-dimensional fluid plasma simulation results. The detailed model-experiment comparison proved useful for improving understanding of plasma chemistry mechanisms in these low temperature plasmas at moderately high pressure. The possibility of inferring plasma potential from comparing floating and grounded probe measurements is discussed as well as the possibility of inferring dissociation fractions in N_2 from effective collision frequency. A new technique for manufacturing hairpin probes is discussed, which is capable of producing quality factors ~400. All analysis and data acquisition is done with open source python scripts which are freely available to the public.

11:00am **PS-FrM-9 Numerical Modeling of Capacitively Coupled Plasma Process Chamber using CCPFoam**, ***Abhishek Kumar Verma***[1], University of California Merced*; K Bera, S Rauf,* Applied Materials*; A Venkattraman,* University of California Merced

Plasma etching and deposition of thin films on Silicon wafers are an integral part of the microelectronics manufacturing process. To facilitate design and development of such systems, plasma modeling is of immense importance. In this work, we intend to perform computer simulations of a typical radio-frequency plasma processing system used for plasma enhanced chemical vapor deposition. Details of the rounded wafer edge and process kit geometry have been well resolved using our high performance computational framework. The 2D and representative 3D continuum simulations will be performed using widely recognized fluid model implementation in our in-house developed plasma solver library "CCPFoam" which uses robust finite volume library, OpenFOAM. The solver is capable of performing parallel multiphysics simulation using scalable algorithms and software tools for the simulation of complex physical phenomenon governed by plasma dynamics. An in-depth analysis has been performed on the usefulness and applicability of this solver in a competitive R&D work environment. Considerable emphasis is being placed on plasma modeling techniques, mainly assessing accuracy and efficiency of numerical schemes, utility of high performance numerical tools and sensitivity to input parameters. The simulations intend to show detailed analysis on the influence of physical parameters for capacitively coupled plasmas and dependence of characteristics of generated plasma on various physical parameters (e.g., process kit geometry and material properties), power supplied and operating pressure. The results will give insight into the applicability and future scope of this framework for high fidelity plasma product R&D.

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[1] **Coburn & Winters Student Award Finalist**

11:20am **PS-FrM-10 Silicon Carbide Nanoparticles for Thermoelectric Composites and Graphene Coatings for Plasmonics***, **Devin Coleman,*** University California, Riverside*; A Hosseini, A Greaney,* University of California, Riverside*; S Bux, J Fleurial,* Jet Propulsion Laboratory, California Institute of Technology*; L Mangolini,* University of California, Riverside

Beta phase silicon carbide nanoparticles are produced by a two step non-thermal plasma process. The surface morphology of the particles is tunable from bare silicon carbide, and between monolayers or few-layers of graphitic or "graphene-like" shells

The bare silicon carbide particles are used as an additive for bulk n-type silicon thermoelectrics. Silicon carbide is mixed with silicon nanopowders, produced by high energy ball milling, and the composite is consolidated by conventional hot pressing into bulk pucks. 99+% density is achieved at volume fractions ranging from 0-5% silicon carbide in silicon. The addition of these nanoinclusions results in a modest decrease in both electrical and thermal conductivities. Most notably, there is also an enhancement in the magnitude of the Seebeck coefficient by up to 40%, resulting in an 80% improvement of the figure of merit, ZT, compared to the parent silicon. This effect is modeled as an energy filtering process, courtesy of Prof. Alex Greaney and his student Aria Hosseini.

The particles with graphene-like shells exhibit a broadband IR absorbance as measured by ATR-FTIR. The peak position, width, and intensity varies as a function of particle size, shell thickness, and surface coverage. A similar phenomenon has been predicted in computational work by F. Abajo for free-standing graphene structures. The computational results show narrow absorbance peaks, compared to broad features in the experimental. This is attributed to a distribution in shell size and number of layers. Additionally, Raman characterization of as-produced powders yields spectra most similar to "damaged" or "defective" graphene. A comparison of previous works, experimental results, and FDTD modeling using Lumerical software will be presented.

11:40am **PS-FrM-11 Electromagnetic Effects in Wide Area Very High Frequency Linear Plasma Source***, **Kallol Bera**, X Li, S Rauf, K Collins,* Applied Materials

Wide area very high frequency (VHF) capacitively coupled plasmas (CCP) are used for materials processing in the semiconductor and display industries. Electromagnetic effects can play significant role in plasma distributions for VHF plasma source. In this study, a VHF linear plasma source is considered, which consists of parallel conductive bars enclosed within ceramic insulator tubes. The linear source is immersed inside the discharge volume, which is enclosed by perfect conductors on the front, back, top, and bottom boundaries except for the input and output ports. Periodic boundary conditions are used on the left and right side boundaries parallel to the conductive bars in order to represent an array of conductive bars over a wide area. A full three dimensional electromagnetic plasma model is used to understand the interactions between the external radio-frequency source and the plasma. The fluid plasma model computes species densities and fluxes, as well as the plasma current density. Drift-diffusion approximation is used for species fluxes in the continuity equations for all charged species. Neutral species densities are determined by solving the continuity equations with diffusion coefficients computed using the Lennard-Jones potentials. The electromagnetic phenomena are fully described by the Maxwell equations with the plasma current density updated from the fluid model. The RF source in the model excites a transverse electromagnetic (TEM) wave through the input ports. The CPML absorbing boundary condition is applied for the termination port that avoids electromagnetic wave reflections back into the plasma. The finite difference time domain (FDTD) technique is used to discretize the Maxwell equations, which are solved explicitly in time. Ar discharge is studied based on the reaction mechanism similar to the previous study [1]. The plasma density distribution is found to be dependent on excitation frequency, pressure and power. The spatial distribution of plasma also depends on excitation phases from the ports as well as the port terminations (using either short or perfect absorption).

1. S. Rauf and M. J. Kushner, J. Appl. Phys. **82**, 2805 (1997)

12:00pm **PS-FrM-12 External Circuitry Models for PIC Simulations of Cylindrical Magnetron Sputtering Chamber***, **Nate Crossette**, T Jenkins, D Smithe, J Cary,* Tech-X Corporation

Simulations provide a means of virtually prototyping devices before building expensive physical prototypes. Virtual prototyping by means of simulation has the additional advantage of allowing rapid testing of parametric and configurational modifications. In this study, we use the highly parallelized particle-in-cell/finite-difference time-domain modeling code VSim [1] to model a 2D planar cylindrical magnetron sputtering chamber. The magnetic field of a set of permanent magnets is determined by means of a magnetostatic solver and imported into the simulation. Particle-wall interactions include sputtering and secondary electron emission. Monte Carlo interactions model collisions within the chamber. We test the effects of modifying the external circuitry on the formation of the glow discharge inside the device. We consider constant voltage and constant current circuitry. Constant current circuitry is modeled by feeding back absorbed currents from the plasma to the walls into the determination of the cathode potential. In some models we include the capacitance of the chamber, which is calculated from simulation.

1. C. Nieter and J. R. Cary, “VORPAL: a versatile plasma simulation code”, J. Comp. Phys. **196**, 2004, pp. 448-473.

* Work supported by U.S. Department of Energy, SBIR Phase II award DE-SC0015762

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