2D Materials Focus Topic
Room 201B - Session 2D+EM+MI+NS+TF-MoM

2D Materials Growth and Fabrication

Moderator: Jing Xia, University of California Irvine

8:20am **2D+EM+MI+NS+TF-MoM1 Wafer Scale Epitaxial Growth of Monolayer and Few-Layer WS_2 by Gas Source Chemical Vapor Deposition**, ***Mikhail Chubarov***, *T.H. Choudhury, J.M. Redwing,* The Pennsylvania State University

Tungsten disulfide (WS_2) has been widely investigated due to its outstanding properties compared to other 2D TMD including a bandgap of 2 eV, relatively high theoretical electron mobility, valley spin polarization, among others. Commonly, the films are grown on amorphous substrates like SiO_2 and, consequently, consist of high angle grain boundaries after coalescence due to the random orientation of domains. These can act as scattering and recombination centers for charge carriers limiting device performance. To avoid this, a crystalline substrate and epitaxial growth is typically employed for general thin film deposition although this approach has not been extensively investigated for 2D TMD monolayers. Large area growth is also crucial to show technological feasibility of the material for wafer-scale device fabrication.

In this work, we employ cold wall gas source chemical vapor deposition for the growth of WS_2 films on 2" (0001) α-Al_2O_3. To achieve coalesced monolayer growth over the entire substrate, we implemented a multi-step growth process modulating the metal precursor concentration during each of the steps. $W(CO)_6$ and H_2S were used as precursors in H_2 carrier gas. The deposition experiments were conducted over the temperature range from 750 °C to 1000 °C at a pressure of 50 Torr. Characterization of resulting samples was conducted using atomic force microscopy (AFM), in-plane X-ray diffraction (XRD) and room temperature Raman and photoluminescence (PL) measurements.

Initial studies showed that the WS_2 films exhibit multiple crystal orientations which evolve with growth temperature. At lower deposition temperature (750 °C), two orientations rotated 30° one from another were observed. At the high deposition temperature (1000 °C), five different crystal orientations were present. Among others, orientation with epitaxial relation of (10-10)WS_2//(10-10)α-Al_2O_3 was present at all temperatures. It was established that the unwanted orientations can be suppressed by increasing the H_2S concentration. Further adjustment of the growth and use of the multi-step growth process led to the formation of a coalesced epitaxial monolayer WS_2 on α-Al_2O_3 with XRD FWHM of 10-10 peak in ω being 0.09°. This value suggests well in-plane oriented domains with low edge dislocation density. A high intensity, narrow (FWHM=40 meV) PL peak positioned at 2.01 eV was observed for WS_2 films. Monolayer formation was confirmed from the AFM height profile (D =0.9 nm) and Raman measurements by observing spectral region where layer breathing and shear modes would appear. A fully coalesced, monolayer film was achieved using the multi-step growth process in a total time of 80 minutes.

8:40am **2D+EM+MI+NS+TF-MoM2 Wafer Scale Deposition of Monolayer Transition Metal Dichalcogenides**, ***Kortney Almeida***, *M. Wurch, G. Stecklein, L. Bartels,* University of California, Riverside

Monolayer transition metal dichalcogenide (TMD) films are promising materials in the continuing development of nanoscale devices. Methods to produce wafer-scale monolayer TMD films have included tube-furnace chemical vapor deposition (CVD), liquid-phase exfoliation, and metal-organic CVD. These methods suffer from issues with particulate contamination, pyrophoric precursors, and high cost. Here we demonstrate the growth of homogeneous wafer-scale monolayer molybdenum disulfide (MoS_2) using solid inorganic and liquid organic precursors in a high-vacuum environment. These results are achieved using an amorphous SiO_2substrate and without any powder or metal-organic precursors. Growth proceeds by the decomposition of carbon disulfide at a hot molybdenum filament, which yields volatile MoS_xprecursors that precipitate onto a heated wafer. The continuous and homogeneous single-layer film of $MoS_2$is deposited at wafer scale with a total growth time of fifty minutes. Various thicknesses of the thin films are also demonstrated by the manipulation of the filament power. Optical and electrical characterization indicates performance comparable to or better than MoS_2film grown by other wafer-scale growth techniques. Our method provides a scalable process to deposit thin TMD films in a high vacuum environment.

9:00am **2D+EM+MI+NS+TF-MoM3 Crystal Growth of 2D Materials: From Model Systems to Integrated Manufacturing**, ***Stephan Hofmann,*** University of Cambridge, UK **INVITED**

In order to serve the industrial demand for "electronic-grade" 2D materials, we focus on chemical vapour deposition (CVD), and in this talk I will review our recent progress in scalable CVD [1] and device integration approaches of highly crystalline graphene, hexagonal boron nitride (h-BN) and transition metal dichalcogenide films. The systematic use of in-situ metrology, ranging from high-pressure XPS to environmental electron microscopy, allows us to reveal some of the key growth mechanisms for these 2D materials that dictate crystal phase, micro-structure, defects, and heterogeneous integration control at industrially relevant conditions [2,3]. I will focus on tailored CVD processes to achieve large monolayer h-BN domains with lateral sizes exceeding 0.5 mm. Importantly we show that depending on the process catalyst as-grown h-BN mono-layers can be easily and cleanly transferred using an entirely exfoliation-based approach.[4] We demonstrate sequential h-BN pick-up, opening a pathway to integrate CVD films in high quality 2D material heterostructures. Progress in growth reached a level where adequate characterisation of such 2D crystal layers over large areas has become a key challenge. Hence we also explore new non-contact characterisation methods [5,6]. We work on applications ranging from magentic tunnel junctions [7] to sensing and single molecule analysis [8,9], and the talk will focus on some of the diverse yet connected integration challenges for CVD 2D films that present a key bottleneck towards reliable scale-up manufacturing and commercialisation.

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9:40am **2D+EM+MI+NS+TF-MoM5 Understanding the Edge-Controlled Growth and Etching in Two-Dimensional Materials**, ***Kai Xiao***, *X. Li, X. Sang,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory; *W. Zhao, J. Dong,* Center for Multidimensional Carbon Materials (CMCM), Institute for Basic Science (IBS), Ulsan,44919, South Korea; *A. Purektzy,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory; *C. Rouleau,* Center for Functional Nanomaterials Brookhaven National Laboratory; *F. Ding,* Center for Multidimensional Carbon Materials (CMCM), Institute for Basic Science (IBS), Ulsan,44919, South Korea; *R.R. Unocic, D.B. Geohegan,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

Understanding the atomistic mechanisms governing the growth and etching of two-dimensional (2D) materials is of great importance in guiding the synthesis of large area, single-crystalline, high quality 2D crystals and heterostructures. In this talk, the growth-etching-regrowth process of monolayer 2D crystals by a CVD method will be discussed. We found that switching from growth to etching formed pores with various shapes in the single crystal domains which can be explained by edge-structure dependent growth process. In addition, combined with first principles theory, and ab initio simulations, in situ STEM imaging was used to understand the evolution of edge structure around pores in monolayers as a function of temperature and Mo chemical potential. Our results demonstrate that by varying the local chemical environment, we can trigger formation of 2D monolayer nanostructures terminated by different edge reconstructions during in situ heating and electron beam irradiation and form edge structures with metallic and/or magnetic properties. The ability to synthesize 2D nanostructures with metastable NW edges having predictable atomic structures opens the door to a wide range of novel 2D materials and heterosturctures with electrical and magnetic properties as revealed by DFT, which could potentially act as functional building blocks for next-generation nano-devices.

References:

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10:00am **2D+EM+MI+NS+TF-MoM6 Synthesis and Characterization of 1T, 1T', and 2H $MoTe_2$ Thin Films**, ***Thomas Empante***, University of California, Riverside; *Y. Zhou,* Stanford University; *S.A. Naghibi Alvillar,* El Camino College; *E.J. Reed,* Stanford University; *L. Bartels,* University of California, Riverside

Transition metal dichalcogenides (TMDs) have been of interest over the past few decades for their intriguing structural, electronic, and optoelectronic properties, particularly when scaled down to thin films. One of the most interesting TMD materials is molybdenum ditelluride ($MoTe_2$) because of its relative ease to attain multiple phases at room temperature, namely the metallic 1T' phase and the semiconducting 2H phase. Here we show a facile chemical vapor deposition process to synthesis not only the aforementioned phases but the elusive unreconstructed 1T phase by regulating the cooling rate and the addition of carbon dioxide during the reaction. Our experimental Raman spectroscopy results were compared to theoretical density functional theory calculations which verify the synthesis of all three phases. Electronic transport measurements were also used to characterize the films and show that the newly synthesized 1T phase is in good agreement with theoretical models depicting semi-metallicity as the material shows increased conductivity with elevated temperatures. In addition to the pure phase materials, mixed phase materials, such as 2H/1T, can be synthesized with slight alterations to the parameters leading to enhancements of the 2H phases' conductivity.

11:20am **2D+EM+MI+NS+TF-MoM10 Low-Defect, High-Uniformity Transfer-Free Graphene on SiO_2 by Thermal Chemical Vapor Deposition**, ***Leslie Chan***, *D.S. Tsai, Z. Wang, C. Carraro, R. Maboudian,* University of California, Berkeley

Chemical vapor deposition (CVD) has emerged as the customary approach for scalable, controllable production of graphene for integrated devices. Standard CVD graphene must be transferred from a generic metal growth substrate onto the desired substrate (*e.g.*, SiO_2), but this extra transfer often leads to wrinkles, contamination, and breakage that ultimately result in poor device performance. Several groups have demonstrated metal-catalyzed direct CVD-graphene growth on insulating substrates, but the final graphene products are deficient in quality and uniformity. This work details an expansion of the parameter space that enables lower-defect, higher-uniformity graphene than previously reported using nickel and copper catalysts, respectively. We introduce a mechanism based on carbon permeability that provides deeper insight into the growth process. Ultimately, these studies seek to inform the judicious choice of process parameters that will lead to large-area, high-quality, layer-controlled graphene directly on target substrates.

Spectroscopic Ellipsometry Focus Topic
Room 202A - Session EL+AS+EM-MoM

Application of SE for the Characterization of Thin Films and Nanostructures

Moderators: Alain C. Diebold, SUNY Polytechnic Institute, Mathias Schubert, University of Nebraska-Lincoln

8:20am **EL+AS+EM-MoM1 Stealth Technology-based Terahertz Frequency-domain Ellipsometry**, ***Vanya Darakchieva,*** Linköping University, Sweden **INVITED**

We present the newly designed Terahertz (THz) frequency-domain spectroscopy (FDS) ellipsometer at the Terahertz Material Analysis Center (THeMAC) at Linköping university and demonstrate its application to a variety of technologically important materials and heterostructures. We show that employing concepts used in stealth technology for the instrument geometry and scattering anti-static coating, and modulation of the backward wave oscillator (BWO) THz source allows for effective suppression of standing waves enabling accurate ellipsometry measurements with high spectral resolution (of the order of MHz). We further demonstrate an etalon-based method for frequency calibration in THz FDS ellipsometry. The instrument can incorporate various sample compartments, such as a superconducting magnet, in-situ gas cells or resonant sample cavities, for example. Reflection and transmission ellipsometry measurements over a wide range of angles of incidence for isotropic (Si) and anisotropic (sapphire) bulk samples are presented together with determination of the material dielectric constants. We further demonstrate results from cavity enhanced THz optical Hall effect experiments on an AlGaN/GaN high electron mobility transistor structure (HEMT), determining the free charge carrier density, mobility and effective mass parameters of the 2D electron gas (2DEG) at room temperature. We show through in-situ experiments on epitaxial monolayer graphene exposed to different gases and humidities that THz FDS ellipsometry is capable of determining free charge carrier properties and following their changes upon variation of ambient conditions in atomically thin layers. Exciting perspectives of applying THz FDS ellipsometry for exploring low-energy excitation phenomena in condensed and soft matter, such as the vibrational, charge and spin transport properties of magnetic nanolaminates, polymers and hybrid structures for photovoltaics and organic electronics; and determination of THz optical constants and signatures of security and metamaterials are envisioned.

9:00am **EL+AS+EM-MoM3 Spectroscopic Ellipsometry and Finite Element Modeling based Optical Characterization of Highly Coherent Au-Si Slanted Columnar Periodic Nanostructures**, ***Ufuk Kilic,*** University of Nebraska-Lincoln; *A. Mock,* Linköping University, Sweden; *R. Feder,* Fraunhofer IMWS, Germany; *D. Sekora, M. Hilfiker, R. Korlacki, E. Schubert, C. Argyropoulos, M. Schubert,* University of Nebraska-Lincoln

An unprecedented and phenomenal control of anisotropic optical properties of a material is reported here by utilizing periodic arrangement of nanostructures. These artificially engineered structures exhibit distinct optical, mechanical, and magnetic properties when they are compared with their bulk counterparts which has recently gained a growing interest due to its potential applications in various optical and optoelectronic systems such as lenses, solar cells, photodetectors, and sensors [1-3]. In addition to the material choices (ie. elemental composition), the size and shape of these artificial structures also play a key role in tailoring the aforementioned inherent properties.

Unraveling the mechanisms that influence and control the optical properties of highly-porous, periodic, and three-dimensional arrangements of nanoplasmonic structures can offer new approaches for the development of next generation sensors. Glancing angle deposition and atomic layer deposition can be used to create periodic nanostructures with multiple constituent materials, so-called heterostructured metamaterials.[4] In this study, we employ a two-source (ie. Au and Si) electron-beam-evaporated, ultra-high-vacuum glancing angle deposition which allows for the fabrication of highly-ordered and spatially-coherent super-lattice type Au-Si slanted columnar heterostructured thin films. We perform a combinatorial spectroscopic generalized ellipsometry and finite-element method calculation analysis to determine anisotropic optical properties. We observe the occurrence of a strong locally enhanced dark quadrupole plasmonic resonance mode (bow-tie mode) in the vicinity of the gold junctions, with a tunable and geometry dependent frequency in the near-infrared spectral range. In addition, inter-band transition-like modes are observed in the visible to ultra-violet spectral regions. We demonstrate that changes in the index of refraction due to the concentration variation of a chemical substance environment (gaseous or liquid) within a porous nanoplasmonic structure can be detected by transmitted intensity alterations down to 1 ppm sensitivity.

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9:20am **EL+AS+EM-MoM4 Temperature Dependent Dielectric Function and Critical Point Comparison of bulk Ge and α-Sn on InSb**, ***Rigo Carrasco***, *C. Emminger, N. Samarasingha, F. Abadizaman, S. Zollner,* New Mexico State University

Germanium is an indirect bandgap semiconductor with a bandgap of 1.55 µm at room temperature. Its band gap can be shifted to longer wavelengths and becomes direct by adding 5-20% Sn, which allows to detect efficiently in the IR range. Alloys of Ge and Sn are therefore of interest for photovoltaics, detectors and room temperature lasers (2-7 µm). Alpha-tin on the other hand, is a semimetal that, when under strain,

has a very small band gap at the Gamma point of the Brillouin zone. We compare this direct band gap (E_0 peak) occurring in the infrared region of strained α-Sn on InSb to the absorption edge of Ge.

We investigate the temperature dependence of the complex dielectric function (DF) and interband critical points (CPs) of bulk Ge between 10 and 738 K using spectroscopic ellipsometry in the spectral range from 0.5 to 6.3 eV at a 70° angle of incidence [1]. The complex dielectric function at each temperature is fitted using a parametric oscillator model. Figure 1 shows that variations in temperature influence structures in the spectra of the DF. Furthermore, we analyze CPs in reciprocal space by studying Fourier coefficients as described in [2]. The peaks of the E_0 and $E_0+\Delta_0$ CPs are relatively narrow (Fig. 2) which makes the analysis of their broadenings difficult. A small excitonic peak is visible at the absorption edge E_0, also shown in Fig. 2.

Spectroscopic ellipsometry measurements were also performed on several epitaxially grown α-Sn layers on InSb in the spectral range of 0.03 to 6.5 eV. Comparing the results of the pseudo-dielectric function of Sn to the one of Ge shows a remarkable difference of both spectra in the IR- region, as demonstrated in Fig. 3. While structures at higher energies, such as the E_1 and $E_1+\Delta_1$ CPs, are similar in shape and amplitude for both materials, the E_0-peak in α-Sn is significantly larger than in Ge. Therefore, we believe that the E_0 peak in the spectrum of Sn is not due to excitons but can probably be explained by other parameters which influence the band structure, such as strain, composition, or free carrier concentration. The large peak between E_0 and E_1 is an interference fringe. We also compare the temperature dependence of the E_0 gap in Ge and alpha-tin.

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9:40am **EL+AS+EM-MoM5 Elastomer Thin Films and Conducting Nanostructures for Soft Electronics and Dielectric Elastomer Transducers***,* ***Bert Müller****, B. Osmani, T. Töpper,* University of Basel, Switzerland

Nanometer-thin polymer films are essential components of low-voltage dielectric elastomer transducers and will, for example, play a vital role in future artificial muscles [E. Fattorini et al.: Ann. Biomed. Eng. 44 (2016) 1355]. Organic molecular beam deposition (MBD) is a versatile technique to prepare silicone films under well-defined conditions [F. M. Weiss et al.: Mater. Design 105 (2016) 106; T. Töpper et al.: APL Mater. 4 (2016) 056101], but the achievable growth rates of about 1 µm per hour are too low for the fabrication of multi-layer devices. Therefore, we have developed electro-spraying as an alternative deposition method with one or two orders of magnitude faster rates [F. M. Weiss et al.: Adv. Electron. Mater. 2 (2016) 1500476; F. Weiss et al.: Langmuir 32 (2016) 3276]. For the two approaches, spectroscopic ellipsometry (SE) has been employed for in situ monitoring the film's optical properties, the film thickness and the surface morphology during deposition and ultra-violet (UV) light irradiation. The derived quantities were verified by means of atomic force microscopy (AFM). Subsequent to the silicone deposition and the cross-linking by UV light curing, Au has been deposited using MBD and sputtering. This deposition process was also quantitatively characterized using SE and controlled by means of the plasmonic fingerprints of the metal nanostructures [T. Töpper et al.: Adv. Electron. Mater. 3 (2017) 1700073]. The ex situ AFM measurements revealed well-known modulations characteristic for strained surface layers [B. Osmani et al.: Eur. J. Nanomed. 9 (2017) 69]. Recent nano-indentation tests have demonstrated that the Au-layers on the silicone near the critical stress regime hardly contribute to the overall elastic modulus and are, therefore, a sound basis for smart electrodes [B. Osmani et al.: Adv. Mater. Technol. 2 (2017) 1700105]. The nano-mechanical probing of the powered thin-film dielectric elastomer transducers evidenced the importance of the thickness homogeneity for such devices [B. Osmani et al.: Appl. Phys. Lett. 111, (2017) 093104]. The function of planar thin-film dielectric elastomer transducers can be precisely determined taking advantage of the cantilever bending approach [B. Osmani et al.: Rev. Sci. Instrum. 87 (2016) 053901]. Spectroscopic ellipsometry and advanced atomic force microscopy with nano-indentation capability enables us to thoroughly characterize the film morphology as well as the optical and local mechanical parameters of silicone and Au/silicone nanostructures.

10:00am **EL+AS+EM-MoM6 Spectroscopic Ellipsometry Investigation of Temperature Effects in Heated Self-organized 2D Arrays of Au Nanoparticles***,* ***Michele Magnozzi****, M. Ferrera, M. Canepa,* Università di Genova, Italy*; F. Bisio,* CNR-SPIN, Italy

Metal nanoparticles (NPs) have the interesting property of behaving as efficient converters of EM radiation into heat. While this can occur via interband photoexcitation, the presence of a Localized Surface Plasmon Resonance provides an extra degree of freedom to tune and optimize the heating [1].

Assessing the temperature of plasmonic NPs during or immediately after illumination is not an easy task, and typically involves the use of models that necessarily have to simplify the complex temperature-dependent dielectric and thermodynamic response of nanosystems; for this reason, a measurement of the T-dependent optical behavior of the NPs at well-defined, externally controlled T would greatly contribute towards a better understanding of the thermoplasmonic properties of metal NPs.

Spectroscopic ellipsometry (SE), being a high-sensitive and non-destructive technique, is an ideal tool to investigate the optical response of NPs systems, provided that a proper model is used for data analysis.

We report a T-dependent investigation of the optical response of densely-packed 2D arrays of gold nanoparticles supported on an insulating nanopatterned substrate [2]. SE measurements were acquired in the 245-1450 nm spectral range, under high-vacuum conditions and in the 25-350 °C temperature interval [3]. Using a dedicated effective medium approximation developed for this kind of systems [2], we are able to reproduce the complex anisotropic optical response of this system employing morphological parameters deduced by *ex-post* AFM analysis; the temperature-dependent dielectric functions of Au, required as input in the model, was obtained in a dedicated SE measurement. The model yields a very good agreement with experimental data at relatively low T; however, though the appropriate T-dependent dielectric function of Au is systematically employed, the model is no longer able to reproduce the data obtained at the highest T. Indeed, a satisfactory agreement is attained introducing an effective correction to the Drude term of the dielectric function of Au, that keeps into account morphological effects affecting the NPs surface - such as softening or melting - that enhance the surface electron scattering rate. Our analysis thus shows that the T-dependent optical properties of metal NPs deviate from simplified expectations, and validate SE as valuable tool to study the complex, anisotropic properties of plasmonic NPs systems.

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10:40am **EL+AS+EM-MoM8 Spectroscopic Ellipsometry of 2D WSe_2 Films***,* ***Baokun Song****, H.G. Gu, M.S. Fang,* Huazhong University of Science & Technology, China*; Y.L. Hong, W.C. Ren,* Shenyang National Laboratory for Materials Science Institute of Metal Research Chinese Academy of Sciences, China*; X.G. Chen, S.Y. Liu,* Huazhong University of Science & Technology, China

Recently, two-dimensional (2D) WSe_2 has become a popular choice for nanoelectronic, optoelectronic, and valleytronic devices due to its layer-modulated bandgap, high mobility (~200cm^{2}V^{-1}s^{-1}) and on-off ratio (10^8), and large spin-orbit coupling effect. The performance of those novel WSe_2-based devices strongly depends on the intrinsic optical properties of WSe_2, which exhibit an intriguing layer dependency. Therefore, the accurate and quantitative characterization of the layer-dependent optical properties of WSe_2 is essential to the optimal design of those related devices.

In this work, the dielectric function, bandgaps, and critical points (CPs) of WSe_2 ranging from monolayer to bulk have been comprehensively investigated and analyzed by spectroscopic ellipsometry over an ultra-broad band (0.73-6.42eV). The dielectric function of high-quality uniform WSe_2 specimens prepared by chemical vapor deposition were firstly obtained from the ellipsometric spectra. Then the bandgaps of the WSe_2 films were determined from their corresponding absorption coefficient spectra. We experimentally observed that the bandgaps of the WSe_{-2} films change from 1.63eV in monolayer to 1.21eV in bulk. Moreover, by using the CPs analysis, a series CPs (A-H) in the dielectric function spectra were precisely distinguished and many of them were rarely reported before. The positions of CPs (A-E) exhibit an obvious red shift when the layer number increases, while the CPs (F-H) exhibit a slight blue shift. The former

phenomenon can be partly interpreted as the decaying geometrical confinement of excitons, while the underlying reasons for the latter merit further studies. These novel and advanced optical features will promote the fundamental understanding of the electronic structures and the development of WSe_2-based devices.

11:00am **EL+AS+EM-MoM9 Thermal Evolution Process of $MaPbI_3$ Film Based on Spectroscopic Ellipsometry**, *X.Q. Wang, X.Y. Shan, H. Siddique,* ***Rucheng Dai****, Z.P. Wang, Z.J. Ding, Z.M. Zhang,* University of Science and Technology of China

Thermal Evolution Process of $MaPbI_3$ Film Based on Spectroscopic Ellipsometry

Xiangqi Wang, Xueyan Shan, Hassan Siddique, Rucheng Dai, Zhongping Wang, Zejun Ding, and Zengming Zhang*

University of Science and Technology of China, Hefei 230026, China;

*Corresponding author: zzm@ustc.edu.cn

Abstract

During the last few years, the hybrid organic-inorganic methylammonium lead halide perovskite $CH_3NH_3PbI_3$ ($MaPbI_3$) has received great interest in the field of photovoltaics [1,2]. The relevant researches develop rapidly since the first realization of organic-inorganic hybrid solar cell, due to the excellent performance of $MaPbI_3$, such as high charge mobilities, suitable band gap and long carrier diffusion length. However the stability of MaPbI has been a key issue hinder the practical application [3]. Here we present in-situ spectroscopic ellipsomety measurement to understand the nature of thermal degradation process of MaPbI . The dynamic evolution process of dielectric constants of the as-prepared $MaPbI_3$ film through heating is obtained by an effective medium approximation model fitting. The proportion of $MaPbI_3$ and PbI is also obtained from the analysis of the ellipsometry data. The thickness of the film decrease in two-step, which is explained as the collapse of the PbI_2 frame. Our work provide the first in-situ detection of the optical properties through the degradation process of $MaPbI_3$ film, which can be consulted for further improving the stability of $MaPbI_3$.

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11:20am **EL+AS+EM-MoM10 a-Si as a Protective Layer to Block the Oxidization of Al mirrors**, ***Yhoshua Wug****,* University of California at Los Angeles*; D.D. Allred, R.S. Turley,* Brigham Young University

Arguably, the best path to produce a truly broadband, e.g., an IR-optical-UV-EUV (extreme ultraviolet) mirror, for a future space observatory is an EUV multilayer mirror coated by a very thin bare aluminum layer. However, using a bare Al layer presents challenges that first must be overcome. Al oxidizes rapidly when contact with the atmosphere occurs. The customary solution is to cover the mirror with a protective evaporated fluoride layer. Unfortunately, these are opaque under ~110 nm, whereas, bare Al itself is highly reflective down to 85nm and could be used as a mirror to that wavelength if a barrier were not required. Once the mirror is in space far from the Earth, where there is no oxygen, Al would no longer need a barrier layer. Could a barrier be removed in space? Neither fluorides nor aluminum oxide can be removed once they are deposited without damaging the mirror's surface and destroying VUV reflectance. a-Si could be used as a protective layer that is potentially removable without roughening the Al surface. Dry hydrogen etching processes exist that could remove a silicon barrier as silane gas which would dissipate quickly in space. Such a process would use the Al layer as an etch stopping barrier in removing the a-Si protective layer. But is a-Si a suitable barrier for Al? We report our variable-angle spectroscopic ellipsometry studies of evaporated a-Si thin films on evaporated Al films. We discuss the conditions where a-Si can act as a protective layer to block aluminum oxidation.

11:40am **EL+AS+EM-MoM11 Terahertz to Mid-infrared Dielectric Response of Poly-methacrylates for Stereolithographic Single Layer Assembly**, *D.B. Fullager,* ***Serang Park****, Y. Li, J. Reese,* University of North Carolina at Charlotte*; E. Sharma, S. Lee,* Harris Corporation*; S. Schöche, C.M. Herzinger,* J.A. Woollam Co. Inc*; G.D. Boreman, T. Hofmann,* University of North Carolina at Charlotte

Producing THz optical components with arbitrary shapes using additive manufacturing is receiving considerable interest because it offers a rapid, low-cost avenue for THz imaging system development. In order to design such THz optical components appropriately, accurate knowledge of the complex dielectric function of the materials used for stereolithographic 3D fabrication, is crucial. In this presentation we report on the complex dielectric function of several poly-methacrylates which are frequently used for stereolithographic fabrication. Spectroscopic ellipsometry data sets from the THz to mid-infrared spectral range were obtained from isotropically cross-linked poly-methacrylate samples. The data sets were analyzed using stratified layer optical model calculations using parameterized model dielectric functions. While the infrared spectral range is dominated by several strong absorption features with Gaussian profiles, these materials are found to exhibit only weak absorption in the THz range. In conclusion we find that thin transmissive THz optics can be easily achieved using poly-methacrylate-based stereolithographic fabrication. Possible origins of the observed absorption in the THz spectral range are identified and pathways to reduce it are discussed.

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, Taiwan Semiconductor Manufacturing Company (TSMC)

8:20am **EM+MP+PS-MoM1 Aluminum Gettering Gate for Improving Defect Density in SiGe MOSCAP Devices**, ***Emily Thomson****, M. Kavrik, A.C. 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-MoM2 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_{-4}, TiO_2, and $Al_{-2}O_3$), 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.

10:00am **EM+MP+PS-MoM6 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-MoM8 The Role of Selective Processes in the Atomic Scale Era***, **Robert Clark**, J. Smith, K.-H. Yu, K. Tapily, G. Pattanaik, S. Consiglio, T. Hakamata, C.S. Wajda, A. Raley, G.J. 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-MoM10 Selective Patterning of Silicon/Germanium Surfaces and Nanostructures via Surface Initiated Polymerization***, **Amar Mohabir**, T. Weiss, G. Tutuncuoglu, E.M. Vogel, M.A. 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-MoM11 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).

Materials and Processes for Quantum Computing Focus Topic
Room 203A - Session MP+EM+MN+NS-MoM
Systems and Devices for Quantum Computing I

Moderator: Vivekananda Adiga, IBM, T.J. Watson Research Center

9:00am **MP+EM+MN+NS-MoM3 Quantum Supremacy: Checking a Quantum Computer with a Classical Supercomputer***, **John Martinis**,* Google Inc **INVITED**

As microelectronics technology nears the end of exponential growth over time, known as Moore's law, there is a renewed interest in new computing paradigms such as quantum computing. A key step in the roadmap to build a scientifically or commercially useful quantum computer will be to demonstrate its exponentially growing computing power. I will explain how a 7 by 7 array of superconducting xmon qubits with nearest-neighbor coupling, and with programmable single- and two-qubit gate with errors of about 0.2%, can execute a modest depth quantum computation that fully entangles the 49 qubits. Sampling of the resulting output can be checked against a classical simulation to demonstrate proper operation of the quantum computer and compare its system error rate with predictions. With a computation space of 2^49 = 5 x 10^14 states, the quantum computation can only be checked using the biggest supercomputers. I will show experimental data towards this demonstration from a 9 qubit adjustable-coupler "gmon" device, which implements the basic sampling algorithm of quantum supremacy for a computational (Hilbert) space of about 500. We have begun testing of the quantum supremacy chip.

9:40am **MP+EM+MN+NS-MoM5 Active Protection of a Superconducting Qubit against Josephson Amplifier Backaction***, **Baleegh Abdo**, N.T. Bronn, O. Jinka, S.B. Olivadese, A. Corcoles, M. Brink,* IBM T. J. Watson Research Center*; R. Lake, D.P. Pappas,* National Institute of Standards and Technology*; J.M. Chow,* IBM T. J. Watson Research Center

Nonreciprocal microwave devices, e.g., isolators and circulators, are key components in high-fidelity, quantum-nondemolition (QND), measurement schemes. They separate input from output and protect the quantum systems from unwanted backaction originated by the output chain. However, state-of-the-art, cryogenic circulators and isolators are disadvantageous in scalable architectures because they are lossy, bulky and use magnetic materials and strong magnetic fields, which are not compatible with superconducting circuits. In this work, we realize and characterize nonreciprocal, superconducting devices suitable for qubit readout, which are formed by coupling two nondegenerate Josephson mixers in interferometric schemes. Nonreciprocity is generated by applying a phase gradient between the same-frequency pumps feeding the devices, which play the role of the magnetic field in a Faraday medium. We incorporate these Josephson-based, nonreciprocal devices into a qubit setup and demonstrate fast, high-fidelity, QND measurements of the qubit while actively protecting it against Josephson amplifier backaction.

10:00am **MP+EM+MN+NS-MoM6 Nonlinear Light-matter Interaction: From Superconducting Qubits to Spins in Diamond***, **Eyal Buks**,* Israel Institute of Technology, Israel

Cavity quantum electrodynamics (CQED) is the study of the interaction between matter and photons confined in a cavity. In the Jaynes-Cummings model the matter is described using the two-level approximation, and only a single cavity mode is taken into account. The interaction has a relatively large effect when the ratio $E/\hbar\omega$ between the energy gap E separating the two levels and the cavity mode photon energy $\hbar\omega$ is tuned close to unity.

The talk is devoted to the study of the light-matter interaction in the nonlinear regime using three different CQED systems. In the first experiment a Josephson flux qubit serves as a two-level system and a superconducting resonator as the cavity [1]. We experimentally find that the cavity response exhibits higher order resonances (called superharmonic resonances) in the nonlinear regime when the ratio $E/\hbar\omega$ is tuned close to an integer value larger than unity. In the second experiment the interaction between a spin ensemble of diphenylpicrylhydrazyl (DPPH) molecules and a superconducting resonator is explored in the region where $E/\hbar\omega \gg 1$ [2]. We find that the cavity response is significantly modified when the spins are intensively driven close to their Larmor frequency. Retardation in the response of the spin ensemble gives rise to effects such as cavity mode cooling and heating. In the third experiment the interaction between localized spins in diamond (nitrogen-vacancy and nitrogen substitutional) and a superconducting resonator is studied [3]. We find that nonlinearity imposes a fundamental limit upon sensitivity of CQED-based spin detection.

References

1. Eyal Buks, Chunqing Deng, Jean-Luc F.X. Orgazzi, Martin Otto and Adrian Lupascu, Phys. Rev. A 94, 033807 (2016).

2. Hui Wang, Sergei Masis, Roei Levi, Oleg Shtempluk and Eyal Buks, Phys. Rev. A 95, 053853 (2017).

3. Nir Alfasi, Sergei Masis, Roni Winik, Demitry Farfurnik, Oleg Shtempluck, Nir Bar-Gill and Eyal Buks, arXiv:1711.07760.

10:40am **MP+EM+MN+NS-MoM8 Variations in Surface Dipole-Moment Density with Coverage for C/Au(110) – (2 × 1) and Electroplated Au Ion-trap Electrodes***, **Dustin Hite**, K.S. McKay,* National Institute of Standards and Technology (NIST)*; H.Z. Jooya,* ITAMP, Harvard-Smithsonian Center for Astrophysics*; E. Kim,* University of Nevada, Las Vegas*; P.F. Weck,* Sandia National Laboratories*; H.R. Sadeghpour,* ITAMP, Harvard-Smithsonian Center for Astrophysics*; D.P. Pappas,* National Institute of Standards and Technology (NIST)

Ion traps, designed to test the feasibility of scalable quantum information processing, suffer from excessive electric-field noise that increases strongly as the ion-electrode spacing decreases in progressively smaller traps. This noise couples to the charge of the ions in the trap causing motional heating, which can result in the decoherence of quantum logic gates. This heating can be reduced by orders of magnitude with the use of cryogenic trap electrodes or by in-situ surface cleaning with ion bombardment in traps with room-temperature electrodes. Many experiments over the past two decades have supported theories that model this noise source as being caused by fluctuations in the dipole moments of contaminant adsorbates on the metallic trap electrode surfaces. Gold electrodes are often used to avoid oxidation and other contaminants, nevertheless a thin carbonaceous layer of approximately 3 monolayers (ML) develops on Au, even due to air exposure alone. In this work, we have studied the model system of C/Au(110) – (2 × 1) to understand the mechanisms for the variations in the surface dipole-moment density as a function of the degree of carbon coverage. We have implemented Kelvin probe force microscopy, along with x-ray photoelectron spectroscopy, to determine an average dipole-moment density with increasing carbon coverage, and have compared the results to density functional theory aided by ab-initio molecular dynamics techniques. We find a nearly linear decrease in the work function with a rate of approximately -0.7 eV/ML for sub-monolayer coverages, a regime in which trapped ions have been observed to have a maximum rate of heating. Finally, we compare the results for the model system to those for a microfabricated ion-trap chip with electroplated Au electrodes contaminated with a native hydrocarbon layer incrementally removed by ion bombardment.

11:00am **MP+EM+MN+NS-MoM9 A Compact Cryogenic Setup for Quantum Computing with Trapped Atomic Ions***, **Ismail Inlek**, R. Spivey, G. Vrijsen, Z. Jia, J. Kim,* Duke University

Trapped atomic ions are standard qubits for quantum computing with their long coherence times and high-fidelity qubit operations for universal quantum logic gates. However, conventional trapped ion systems often utilize bulky vacuum and optics setups, hindering scalability and ease of use. We aim to address these infrastructure issues by packaging micro-fabricated ion traps in an ultra-high vacuum (UHV) environment and designing optics to be an integral part of the overall system. Additionally, small footprint of the sealed UHV package allows users to easily install it on

a cryostat to benefit from lower heating rates and further reduced vacuum levels. Moreover, these ion trap packages can be conveniently swapped to benefit from micro-fabricated ion trap manufacturing improvements without external UHV maintenance requirements. Towards achieving this goal, we report successful ion trapping in a compact cryogenic setup and characterize the performance of our apparatus for quantum computing applications.

11:20am **MP+EM+MN+NS-MoM10 Advances in Trapped Ion Quantum Computing*, Jungsang Kim,*** Duke University **INVITED**

Trapped ions provide a highly desirable physical substrate on which to construct a scalable quantum computer. All qubits are exactly identical by nature, can be well isolated from the environment to establish long coherence times, and high fidelity quantum logic gates have been readily available. Furthermore, the long-range Coulomb interactions used for multi-qubit gates in a chain allows for highly connected network of qubits that are fully programmable, opening up opportunities for advanced and flexible quantum computer architectures. Some of the most advanced and complex quantum algorithms have been implemented in trapped ion systems leveraging these features. On the other hand, the ion trap systems so far have mainly relied upon conventional methodology used in atomic physics labs to set up the lasers, vacuum chambers and their optical alignments to realize the system. Novel integration technologies, including micro-fabrication, micro-electromechanical system (MEMS), and advanced packaging approaches have been adopted in the past decade to push the integration level for trapped ion systems. In this presentation, I will summarize the state-of-the-art systems used to implement quantum computing applications in the laboratories today, and also outline system design approach currently undertaken to improve the stability, reliability, and programmability of trapped ion quantum computers. Then, I will discuss the opportunities and challenges ahead for reaching a scalable quantum computer capable of executing useful tasks.

Nanometer-scale Science and Technology Division
Room 102B - Session NS+2D+AN+EM+MN+MP+PC+RM-MoM

IoT Session: Nanostructured Devices and Sensors

Moderators: David Czaplewski, Argonne National Laboratory, Liya Yu, NIST Center for Nanoscale Science and Technology

8:20am **NS+2D+AN+EM+MN+MP+PC+RM-MoM1 Integrating Nanodiamonds with Augmented Artificial Intelligence and Digital Health to Optimize Combination Therapy*, Dean Ho,*** UCLA **INVITED**

Dean Ho, Ph.D.

Nanodiamonds have emerged as promising candidates for clinical drug delivery due to their ability to carry a wide range of candidate therapies, unique surface properties, and biological tolerability. This lecture will highlight our recent clinical trial to validate a nanodiamond-embedded biomaterial for root canal therapy indications [1]. We will discuss the broad spectrum of efficacy, safety, characterization, and other studies that bridged in vitro with preclinical and downstream in-human studies. This lecture will also discuss upcoming clinical nanodiamond-based drug carrier studies, as well as our work in augmented artificial intelligence (AI) to develop globally optimized nanodiamond-modified therapy. Pairing nanodiamond platforms with augmented AI will lead to major advances in drug development and markedly improve response rates and treatment outcomes for a broad spectrum of disorders. Our recent clinical trials using these powerful combination therapy optimization technologies and digital health platforms to scale their implementation to usher in a new era of nanomedicine-based treatment will also be discussed [2].

1. Lee et al., Proceedings of the National Academy of Sciences, 2017

2. Zarrinpar et al., Science Translational Medicine, 2016

9:00am **NS+2D+AN+EM+MN+MP+PC+RM-MoM3 Morphology-Controlled Large-Scale Tin Oxide Nanostructures for Highly Sensitive Room Temperature Gas Sensor*, Amrit Sharma,*** Norfolk State University

Highly sensitive large-scale tin oxide (SnO_2) nanostructures were grown on a glass substrate by vapor-liquid-solid (VLS) process using a mixture of anhydrous tin (II) chloride ($SnCl_2$) and zinc chloride ($ZnCl_2$) powders. We demonstrate a new kind of single cell vapor deposition system to precisely control nanostructural morphology by changing the weight ratio of $SnCl_2$ and $ZnCl_2$ and growth temperature. The morphology and structural property of as-grown nanostructures were characterized using scanning electron microscopy (SEM) and X-ray diffraction (XRD). The SEM images revealed that the SnO_2 nanostructures with different densities, sizes, and shapes can be achieved by adjusting the weight ratio of $SnCl_2$ and $ZnCl_2$. SnO_2 nanostructures with diameter ~20 nm and length ~100 nm showed ~85% sensitivity and 53 seconds of response time, whereas the nanorods with diameter ~100 nm and length ~ 1mm showed ~50% sensitivity with 198 seconds response time. The nanostructured material with small size and shape showed better sensitivity on sensing at room temperature compared to previously reported SnO_2 based sensors.

9:20am **NS+2D+AN+EM+MN+MP+PC+RM-MoM4 Improving the Localized Surface Plasmonic Resonance Sensing Properties by Composite Metal/Dielectric Mixtures*, Steven Larson*[1]*,*** *Y. Zhao,* University of Georgia

Localized surface plasmon resonance (LSPR)-based sensors, whose resonance absorbance wavelength responds to the change in the local dielectric environment have attracted great attention and have been widely studied over the past decade. These sensors are traditionally improved by modifying the shape, size, and gap in the plasmonic nanostructure of the sensor. The sensitivity can also be tuned by the dielectric constant of the plasmonic material, such as noble metal alloys, but the improvements are not significant. Here we show that using a metal-dielectric composite, one can significantly improve the sensitivity of a LSPR sensor. Regular nanotriangle pattern samples composed of a mixture of Ag and MgF_2 with different composition ratios are prepared by combining nanosphere lithography and electron beam co-deposition. The plasmon resonance of these composite nanostructures at high Ag composition (C_{Ag})are shown to redshift with C_{Ag} until a composition threshold ($C_{Ag} \leq 90\%$) is met, where the resonance wavelength is nearly constant, slightly blue shifting. Multiple morphological and compositional characterization techniques are used to confirm that the shifts in the plasmonic properties are due to the change in composition and not a change in the morphology. The resulting LSPR sensor at C_{Ag} = 90 at.% can achieve a sensitivity of 696 RIU/nm, as compared to 312 RIU/nm for the same nanotriangle with pure Ag. This significantly improved sensitivity is due to the modified dispersion relationship of the dielectric constant by the composite and will play an important role in future plasmonic material design and applications.

9:40am **NS+2D+AN+EM+MN+MP+PC+RM-MoM5 Improving the Selectivity of Tin (IV) Oxide Paper Based Gas Sensors with Plasma Surface Modification*, Kimberly Hiyoto,*** *E.R. Fisher,* Colorado State University

Metal oxide nanomaterials are desirable for solid-state gas sensors because of their ability to detect a wide variety of gases through changes in resistance resulting from gas-surface interactions. When optimizing these sensors, the supporting substrate is rarely considered, resulting in devices that are often brittle and have a fixed amount of nanomaterial that can be exposed to target analytes. Recent work using paper as the supporting substrate yields more affordable sensors that are flexible, allowing for a more robust device. Furthermore, the porous morphology of the paper also provides a larger surface area to attach metal oxides when compared to a traditional flat substrate of the same dimensions. Another limitation of these metal oxide sensors is inherent in the detection method. The lack of selectivity and required operating temperature of ≥300 °C limits the widespread use of metal oxide sensors. Dopants or the addition of a filter in the device design are typical approaches to address these problems; however, this increases fabrication complexity and cost. Plasma processing is a promising strategy to address these issues because it maintains desirable bulk properties but modifies the surface of the material to enhance gas sensor performance.

Here, we describe the Ar/O_2 plasma modification of paper based, tin (IV) oxide (SnO_2) nanoparticle devices as a function of applied rf power and precursor pressure. After plasma modification, the paper-based sensors exhibited improved response to carbon dioxide, ethanol, and benzene when compared to the untreated material on a more traditional substrate, zirconium dioxide. Additionally, sensor response to a target gas changed depending on the plasma modification parameters used, indicating the selectivity of these SnO_2 sensors can be easily tailored via plasma processing. Response and recovery studies of both the treated and untreated sensors will be discussed to demonstrate the dynamic behavior of these devices to the target gases as another measure of gas sensor performance and durability. Along with sensing behavior, optical emission spectroscopy and X-ray photoelectron spectroscopy provide insight into how the plasma modified the material, ultimately elucidating the

[1] **NSTD Student Award Finalist**

relationship between material surface chemistry and sensor selectivity. Finally, preliminary work using this same fabrication process with another type of metal oxide gas sensor will be discussed to demonstrate the applicability of this method for other types of materials. Ultimately, these data work toward improved understanding of the gas sensing mechanism to design better performing gas sensors.

10:00am **NS+2D+AN+EM+MN+MP+PC+RM-MoM6 TiN@Si_3N_4 Core-shell Heterostructures as Nanoantennas for Photocatalytic Reforming of Methanol***, **Alejandro Alvarez Barragan**, L. Mangolini,* University of California, Riverside

The light-harvesting capacity of plasmonic nanoparticles has recently garnered attention in the synthesis of nanoantennas for photocatalysis. Aluminum, gold, and silver have been used to successfully drive hydrogen dissociation and CO oxidation reactions by injecting hot electrons into chemically active catalysts —such as platinum and palladium— adsorbed to their surface. However, the low response of aluminum at visible-near infrared (vis-NIR) wavelengths, the high cost of silver and gold, and the low thermal stability of these three metals, inspire the quest for alternative plasmonic materials that could potentially expand the field towards more ambitious and cost-effective applications. Titanium nitride (TiN) is a conductive ceramic with high hardness and bulk melting point (2930 °C). Its plasmon resonance located in the vis-NIR region, low cost relative to gold and silver, and well-understood properties as a thin film in the semiconductor industry, make it a strong alternative to mainstream plasmonic metals. The present work encompasses a comprehensive study of the oxidation kinetics of TiN particles at the nanoscale and an exploration of its role as nanoantennas for light-induced methanol reformation. TiN particles are synthesized via a scalable, modular, non-thermal plasma method. Titanium and nitrogen precursors are transported into a RF frequency plasma where TiN particles nucleate and grow. The high surface area and nitrogen deficiency of the particles facilitate the oxidation of the material and weaken its plasmonic response. The introduction of a secondary reactor with an input of SiH_4 as precursor gas leads to the formation of a Si_3N_4 coating. STEM and XPS analyses show that Si_3N_4 acts as a diffusion barrier, dramatically reducing the oxidation of the ~8 nm TiN particles. UV-vis-NIR spectrophotometry data show that the core-shell heterostructures experience a substantial blue-shift of the plasmon peak and an increase in intensity compared to the bare TiN. Platinum nanoparticles were subsequently deposited on the TiN@Si_3N_4 by photo-induced reduction of an aqueous solution of chlorplatinic acid. After rinsing and centrifuging, the Pt/TiN@Si_3N_4 heterostructures were diluted in a 50:50 water/methanol solution. Upon photoexcitation via white light illumination, hydrogen generation was readily detected by gas chromatography. This work also highlights the wide range of applications available for light-induced processes, ranging from materials processing (deposition of Pt particles) to photocatalysis (methanol reforming). It also strengthens the case for alternative plasmonic materials in a field dominated by precious metals.

10:40am **NS+2D+AN+EM+MN+MP+PC+RM-MoM8 Nanostructured Sensor and Device Applications of Infiltrated Zinc Oxide***, **Leonidas Ocola**,* Argonne National Laboratory*; Y. Wang, J. Chen,* University of Wisconsin-Milwaukee*; P. Blaisdell-Pijuan,* California State University-Fullerton*; R. Divan,* Argonne National Laboratory **INVITED**

With the increased portfolio of materials deposited using atomic layer deposition (ALD) there has been an increased interest in infiltrated metal oxides such as zinc oxide for novel applications. We find that ZnO metal oxide ALD infiltration can be useful for nanoscale resolution imaging of biological samples and to fabricate novel UV and gas nanosensors with high sensitivity. The ALD infiltration utilizes similar concepts of the ALD coating process with the significant difference in process exposure times, pressure, and purpose. The purpose is to allow the precursor gases infiltrate a porous media (such as a dry biological sample or a photoresist polymer) and allow the reaction to occur inside the material matrix.

In terms of device fabrication we use SU8 as a negative resist that allows for localization of the infiltration process. We have used this property to make a device that is UV sensitive, and that is sensitive to ppm concentrations of gases by using infiltrated zinc oxide. The large bandgap and semiconductor properties of ZnO allow for a visible-blind ultra violet light sensor. We used a standard UV flashlight that emits at 408 nm as the UV source. We also tested the same device for sensing gases like nitrous oxide and formaldehyde. We show that the device can detect these gases with concentrations of 5 ppm. The change in current for such low concentrations was measured to be between 25% and 35 %.

With the purpose of investigating quantum applications of infiltrated ZnO, we also have characterized the growth of ZnO in PS-b-PMMA block copolymers (BCP) of spherical and cylindrical sub-20 nm morphologies and studied how the photoluminescence of these nanostructures varies per its seed layer. We report blue-shifted photoemission at 335nm (3.70eV), suggesting quantum confinement effects. Samples of ZnO prepared with an alumina seed layer showed additional defect state photoemission at 470nm and 520nm for spherical and cylindrical BCP morphologies, respectively. Defect photoemission was not observed in samples prepared without a seed layer. No Raman peaks were observed for any samples with less than four cycles of ZnO, implying the absence of phonons and the functionality of these ZnO nanostructures as isolated emitters. To that effect we have demonstrated a fabrication path to isolate single infiltrated cylinders, paving the way for further studies of optical properties of individual 20 nm ZnO nanostructures.

- Use of the Center for Nanoscale Materials an Office of Science user facility, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

11:20am **NS+2D+AN+EM+MN+MP+PC+RM-MoM10 Templates for the Investigation of Size-Selected Nanocluster Networks***, **Patrick Edwards**, V.V. Kresin,* University of Southern California

The study of metal nanoclusters has revealed quantum nanoscale effects unique to the fully size-resolved regime. A highly notable example is electronic shell structure, akin to that in atoms and nuclei, which arises when confined conduction electrons organize into discrete energy levels. One consequence is the possibility of dramatic enhancement in electron Cooper pairing. Recent research from our group has provided evidence of this enhancement in certain free Al nanoclusters, with the electronic transition taking place at a temperature two orders of magnitude above that of bulk aluminum. We now aim to take advantage of this phenomenon by exploring the pairing transition in size-selected nanoclusters soft-landed on an appropriate substrate. Of particular interest are graphene and nanotube device architectures which provide unique templates for organizing nanocluster arrays. For example, a network of such superconducting nanoislands may induce superconductivity in graphene even at low coverages. Theory also predicts that an array of nanoclusters will not only support, but even enhance the Josephson current by 2-3 orders of magnitude. Carbon allotropes offer two distinct advantages for our system. First, the weak out-of-plane bonding provides a surface with less potential to disturb the structure of the soft-landed nanoclusters. Second, the tunability of graphene and carbon nanotube-based field effect transistors offers a versatile probe of nanocluster properties. We are also investigating the use of biological nanowires (bacterial flagella) as potential scaffolds upon which to deposit such nanocluster networks. These abundant and naturally occurring nanowires could serve as low cost and highly reproducible alternatives to the more common metallic or semiconductor templates.

Research supported by the Army Research Office (W911NF-17-1-0154).

11:40am **NS+2D+AN+EM+MN+MP+PC+RM-MoM11 High Performance Detection for X-ray and g -ray with $MAPbX_3$ Perovskite Single Crystals***, X. Wang, Z. Zhu, Q. Li, J. Wu, X. Zhang, B. Wang, **Wei Lei**,* Southeast University

Recently, organometallic lead trihalide perovskites have emerged as a new generation of opto-electronic materials. However, the high performance detection for x-ray and gamma-ray with $MAPbX_3$ is still a big challenge. For x-ray and gamma-ray detections, the detectors should have high sensitivity. If the photon counting method is adopted, the high energy resolution and high time resolution are also required. In this work, the large area $MAPbBr_3$ single crystal has been fabricated with a facile methodology. Due to the quite thick active material and large carrier mobility, the x-ray photons and gamma-ray photons can be absorbed with high efficiency. The photo generated electrons and holes can also be collected effectively with the large electric field. To decrease the dark current in the detection, a novel photo-diode structure is proposed here. In crystallization process of $MAPbI_3$ single crystal, the p-n junction can be formed with doping of selenium atoms into $MAPbI_3$ single crystal.

With various temperature method, the 30mm×30mm×7mm $MAPbBr_3$ single perovskite crystal is fabricated. As the experimental results shown, almost all of the 100 keV x-ray photons are absorbed when the $MAPbBr_3$ SPC is 7mm thick. The detection sensitivity is as high as 305 µC $Gy_{air}^{-1}cm^{-2}$ when the anode voltage of x-ray tube is 30 kV .

To reduce the dark current in the detection, two type of photo diode structures have been proposed here. Firstly, a photo diode with structure of Au/TPD/$MAPbBr_3$ PSC/C_{60}/PCBM/Ag has been fabricated with spin

coating and sputtering methods. Although the dark current density can be reduced to 20 nA/cm^2 with -30V bias voltage, the temporal response time is nearly 50 µs due to the defects on the interfaces between PSC and carriers transport layers. Then, by doping selenium (Se) in $MAPbI_3$ perovskite single crystals (DPC) crystallization process, low dark current p-n junctions were fabricated without any organic layers. This photodiodes gives the high detection sensitivity as 21000 mC $Gy_{air}^{-1}cm^{-2}$ and 41 mC $Gy_{air}^{-1}cm^{-2}$ for 60 keV x-ray and 1.33 MeV gamma-ray respectively. In this photodiode, the transition time becomes shorter under higher electric field, and the carrier lifetime also becomes shorter due to the dopant of Se atoms. Finally, the temporal response time is measured as 3 µs by experiments. The FWHM width of energy spectrum is decreased to 3.2%@1330 keV.

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

Plasma-Surface Interactions

Moderator: Yohei Ishii, Hitachi High Technologies America Inc.

8:20am **PS+AS+EM+SS-MoM1 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-MoM2 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.A. FILONOVICH,* Total SA Renewables, France*; E.V. 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-MoM3 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

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

9:20am **PS+AS+EM+SS-MoM4 Decay of Hydrogen in NF_3/Ar and O_2/Ar Cleaning Process by Optical Emission Spectroscopy***, **Hanyang Li**, Y. Zhou, V.M. 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

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

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-MoM5 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.

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10:40am **PS+AS+EM+SS-MoM8 Tailoring the Surface Properties of Porous Zeolite Constructs using Plasma Processing*, Angela Hanna*[1]*,*** *E.R. 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 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-MoM9 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-MoM10 Evolution of Photoresist Layer Structure and Surface Morphology under Fluorocarbon-Based Plasma Exposure*, Adam Pranda,*** *S.A. Gutierrez Razo, J.T. Fourkas, G.S. 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

[1] **National Student Award Finalist**

variations in fundamental plasma parameters such as the ion energy or exposure time.

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11:40am **PS+AS+EM+SS-MoM11 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.L.G. 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).

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Spectroscopic Ellipsometry Focus Topic
Room 202A - Session EL+EM-MoA

Spectroscopic Ellipsometry: Novel Applications and Theoretical Approaches

Moderators: Vanya DarakchievaStefan Zollner, New Mexico State University,

1:20pm **EL+EM-MoA1 The Physics of Low Symmetry Metal Oxides with Special Attention to Phonons, Plasmons and Excitons and their Potential for Uses in Power Electronics and Quantum Technologies***, **Mathias Schubert**,* University of Nebraska - Lincoln, Linköping University, Sweden, Leibniz Institute for Polymer Research, Dresden, Germany*; A. Mock, R. Korlacki, S. Knight,* University of Nebraska - Lincoln*; V. Darakchieva,* Linköping University, Sweden*; B. Monemar,* Linköping University, Sweden, Tokyo University of Agriculture and Tech., Japan*; H. Murakami, Y. Kumagai,* Tokyo University of Agriculture and Technology, Japan*; K. Goto,* Tokyo University of Agriculture and Technology, Tamura Corporation, Japan*; M. Higashiwaki,* National Institute of Information and Communications Technology, Japan **INVITED**

We discuss analysis of the dielectric function tensor for monoclinic metal oxides. We derive the dispersions of transverse, longitudinal and plasmon coupled modes in gallium oxide [M. Schubert et al., Phys. Rev. B 93, 125209 (1-18) (2016); Editors' Suggestion], the Lyddane-Sachs-Teller relation for monoclinic and triclinic semiconductors [M. Schubert, Phys. Rev. Lett. 117, 215502 (2016)], the identification of transverse and longitudinal phonons in scintillator material cadmium tungstate [A. Mock, M. Schubert et al., Phys. Rev. B 95, 165202 (1-15) (2017)], the band-to-band transitions and excitons and their eigenvectors in gallia [A. Mock, M. Schubert et al., Phys. Rev. B 96, 245205 (1-12) (2017)], the effective electron mass tensor measurement using the optical Hall effect in gallium oxide [S. Knight, A. Mock, M. Schubert et al., Appl. Phys. Lett. 112, 012103 (2018); Editors' Pick], the temperature dependence of band-to-band transitions energies in gallium oxide [A. Mock, M. Schubert et al., Appl. Phys. Lett. 112, 041905 (2018)], and the dielectric and inverse dielectric tensor analysis method for transverse and longitudinal phonon mode dispersion characterization in high-power laser material yttrium silicon oxide [A. Mock, M. Schubert et al., Phys. Rev. B, 97 165203 (1-17) (2018)].

2:00pm **EL+EM-MoA3 Mueller Matrix Spectroscopic Ellipsometry Based Scatterometry of Nanowire Gate-All-Around (GAA) Transistor Structures***, M. Korde, **Alain C. Diebold**,* SUNY Polytechnic Institute

One of the most difficult measurement challenges facing semiconductor research and development is determining the feature dimensions and shape for complicated 3D structures. GAA transistors are fabricated from fins etched from a $Si/Si_{1-x}Ge_x/Si/\ Si_{1-x}Ge_x/Si$.. multilayer.(1, 2) At one point in the fabrication process, the nanowires used in GAA transistors have the nanowire transistor structures suspended between the source and drain. Considering the close spacing of neighboring transistors, measuring the nanowires is a significant challenge. In this talk, we present simulations aimed at understanding the sensitivity to changes in feature shape and dimension for the structures used to fabricate GAA transistors. Simulations of the multi-layer fins shown a clear sensitivity to fin shape and Si layer thickness which is enhanced by the use of the full Mueller Matrix capability vs traditional spectroscopic ellipsometry.

1. Optical measurement of feature dimensions and shapes by scatterometry, A.C. Diebold, A. Antonelli, N. Keller, APL Mat., (2018), in press.
2. Muller matrix spectroscopic ellipsometry based scatterometry simulations of Si and $Si/Si_xGe_{1-x}/Si/Si_xGe_{1-x}/Si$ fins for sub 7-nm node gate-all-around transistor metrology, S. Dey, N. Keller, M. Korde, and Alain C. Diebold, SPIE, Metrology, Inspection, and Process Control for Microlithography XXXII, SPIE Advanced Lithography, San Jose, Feb 25-Mar. 1, 2018. To be published in conference proceedings.

2:20pm **EL+EM-MoA4 Anomaly in the Optical Constants of Ni near the Curie Temperature***, **Farzin Abadizaman**, S. Zollner,* New Mexico State University

Magnetized Ni demonstrates an anomaly in its optical constants near the Curie temperature (T_c = 627 K). Experiment shows that this anomaly does not depend on the morphology of the sample. To investigate this feature, we have carried out a series of ellipsometry measurements in the energy range of 0.5 to 6.5 eV as a function of temperature from 80 to 800 K in 25 K steps. Furthermore, temperature dependent Mueller Matrix (MM) measurements have been performed on the magnetized Ni at a single energy of 1.97 eV as a series of four runs, up and down, between 300 and 800 K. The MM data of magnetized Ni reveal slight changes in the anisotropic portion of the MM while passing T_c. However, vast changes in the isotropic MM elements are found, indicating that the anomaly is not due to the induced anisotropy of the sample. The anomaly occurs only in the first run when the temperature passes T_c, which suggests that it stems from magnetization. On the other hand, magnetizing the sample again and repeating the experiment do not demonstrate any anomaly as passing T_c, which disproves our previous suggestion. In fact, the anomaly happens only once for each sample, regardless of its morphology.

No observable variation in the out-of-plane grain sizes were found in the XRD data before and after the temperature measurement. This and the fact that the anomaly occurs for a single crystalline sample as well as for a polycrystalline one indicate that it cannot be due to the grain growth. This turned our attention to the surface effects: Several experiments have been conducted to investigatehow the surface of sample changes around T_c and how cleaning the surface affects the optical constants of Ni. The authors believe that the anomaly around T_c originates from the surface changes. Yet the question of why it occurs near T_c is still open. The same series of experiments have been performed on cobalt and the results are compared to Ni.

2:40pm **EL+EM-MoA5 Phonon Confinement and Excitonic Absorption in the Optical Properties of ZnO Films***, **Nuwanjula Samarasingha**, S. Zollner,* New Mexico State University*; D. Pal, A. Mathur, A. Singh, R. Singh, S. Chattopadhyay,* Indian Institute of Technology Indore, India

Wide band gap materials like ZnO, which have drawn much attention for optoelectronic devices, have a large excitonic binding energy of 60 meV at room temperature. These excitons directly influence the dielectric function (**ε**) of ZnO. Hence investigation of excitonic absorption on the optical properties is very important. Wurtzite type ZnO shows three excitonic peaks in the ordinary dielectric function which are directly related to the electronic band structure. Due to the spin orbit and crystal field splitting the top valence band of ZnO is split into three sub bands . The corresponding free exciton transitions between these three valence bands and the lowest conduction band are denoted by A, C, and B. We also observe an exciton-phonon complex.

We explore the behavior of phonons and excitons in c-oriented ZnO thin films grown on Si (smaller band gap than ZnO) and SiO_2 (larger band gap than ZnO) using variable angle UV spectroscopic ellipsometry and FTIR ellipsometry. In order to characterize the structural properties of our ZnO films we performed X-ray diffraction (XRD), X-ray reflectivity (XRR), and atomic force microscopy (AFM) measurements.

According to the UV ellipsometry data the real and imaginary parts of **ε** in thin ZnO films on Si are much smaller than in bulk ZnO. We find that the excitonic enhancement decreases monotonically with decreasing film thickness. A similar behavior can be seen for ZnO films on SiO_2 as a function of thickness. The impact of this excitonic absorption on the **ε** was described by Tanguy [1]. We will fit our ellipsometric spectra by describing the dielectric function of ZnO using the Tanguy model. We will investigate the dependence of the excitonic Tanguy parameters on film thickness and substrate material.

Wurtzite type ZnO has 12 phonon branches, 9 optical and 3 acoustic modes. Among these 9 optical modes, only $1A_1$ and $1E_1$ polar phonon modes are IR active. According to the IR ellipsometry data these IR active phonon mode frequencies of ZnO films are consistent with bulk ZnO. We find a small redshift and increasing broadening with decreasing ZnO film thickness on a Si substrate. We will analyze the thickness dependence of the phonon oscillator strength of ZnO films on Si and SiO_2 substrates..

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Supported by NSF (DMR - 1505172).

3:00pm **EL+EM-MoA6 High Aspect Ratio Etch Tilt Detection with Full 4x4 Mueller Matrix Spectroscopic Ellipsometry and Its Application to 3DNAND Channel Hole Etch Process and Chamber Monitoring**, *P. Ong,* Micron Semiconductor Asia Pte. Ltd., Singapore; ***Shilin Ng****,* Nanometrics Incorporated; *G.B. Chu,* Micron Semiconductor Asia Pte. Ltd., Singapore; *P. Murphy,* Nanometrics Incorporated; *L.C. Liong, W. Fu,* Micron Semiconductor Asia Pte. Ltd., Singapore; *Y. Wen,* Nanometrics Incorporated; *L.W. Ho,* Micron Semiconductor Asia Pte. Ltd., Singapore

Full 4x4 Mueller Matrix Spectroscopic Ellipsometry (MMSE)[1] is a widely-used technique for measuring cross-sectional profile, critical dimensions (CD) and material thicknesses of repeating structures created as part of microelectronic device manufacturing processes. In this paper, it will be shown that its application can be extended to measuring asymmetries in such structures with off-diagonal Mueller Matrix Elements[2]. These asymmetries, such as tilt of etched holes, and lines or trenches, are typically caused by inhomogeneity in the etch plasma sheath at the wafer edge. This paper will focus on one of the most important use-cases: tilt of high aspect ratio (HAR) etched 3D-NAND channel holes. Full 4x4 MMSE can be used to provide fast, accurate, non-destructive measurements of the channel hole tilt, both in direction and magnitude.

Furthermore, in contrast to CD and thickness measurements which are typically done in metrology test keys, this tilt measurement is in-die and on-device. This allows us to characterize the tilt at all locations on the wafer edge, as well as the variation in tilt as the wafer edge is approached. In addition, we also show how the measurements can be used to monitor the condition of the etch chamber for equipment control and/or to trigger preventive chamber maintenance.

3:40pm **EL+EM-MoA8 Ultra-High-Speed Spectroscopic Ellipsometry and its Applications**, ***Gai Chin****,* ULVAC Inc., Japan

As a comprehensive manufacturer of metrology tools and deposition tools, ULVAC developed an innovative high-speed spectroscopic ellipsometer for some thin-film deposition applications, such as PVD, CVD, ALD and others.

This novel spectroscopic ellipsometry can measure the thickness and optical constants of thin films at a dramatically fast speed. Its data acquisition time is as short as 10ms. It does not require any active components for polarization-control, such as a rotating compensator or an electro-optical modulator. The Fourier analysis of channeled spectrum obtained from the spectrometer allows determining the four spectroscopic ellipsometry parameters of the samples simultaneously.

It created great opportunities for new applications of the spectroscopic ellipsometry in which the compactness, the simplicity and the rapid response are extremely important. It can be integrated into the deposition tool and successfully measured thin films in-situ to realize the Advanced Process Control (APC). Obviously, those from PVD, CVD and ALD are some promising applications for this novel spectroscopic ellipsometry.

This paper describes the principle, system configuration and creative efforts on developing a series of high-speed spectroscopic ellipsometers. Some of its new applications will be also introduced, such as the PVD, CVD, ALD, EUV, OLED, MEMS and some measurement data of thin films from the semiconductor, flat panel display and other industries.

4:00pm **EL+EM-MoA9 Use of Ellipsometry to Monitor Implant Damage in Methane Plasma Implant**, ***Nicholas Bateman****,* Varian Semiconductor Equipment, Applied Materials

The Applied Materials PLAD tool consists of an inductively couple plasma source and a pulsed direct current (DC) bias coupled to a platen upon which a wafer is e-chucked. This tool architecture enables high throughput for high dose implants. Unlike a standard beamline implant, which will not lead to any deposition on the wafer, the plasma implant process directly exposes the wafer to the plasma leading to both deposition and implant damage. Standard industrial metrologies like Thermawave [1] are sensitive only to the implant damage. Process control could be enhanced if both the implant damage and the deposition thickness could be monitored online.

Ellipsometry is extensively used in the semiconductor industry to measure and monitor film thickness and optical properties [2]. It would be the ideal industrial technique to measure the deposition left by a plasma implant process, but has not been used to evaluate the damage caused by ion implant.

This work presents the development of an ellipsometry model that can be used to simultaneously monitor the deposited layer thickness and the implant damage caused by a methane plasma implant. The dispersion function for the deposited layer was determined by fitting multi-angle, broad wavelength ellipsometry data for different process times and bias conditions. The extracted thickness of the damage layer is shown to be well correlated to Thermawave across a wide range of process parameters, and through an extended 'marathon' test. As the implant voltage is reduced to zero the model trends continuously to match the results of a 'deposition only' ellipsometry model that matches SEM thickness measurements.

These results suggest that for plasma doping applications, ellipsometry can be used to monitor both implant damage and deposition simultaneously to allow improved process control.

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4:20pm **EL+EM-MoA10 Study of the Thickness-dependent Optical Constants of Metallic Thin Films based on Ellipsometry and Reflectivity**, ***Jiamin Liu****, H. Jiang, S.Y. Liu,* Huazhong University of Science and Technology, China

Metallic thin films have been widely used in various plasmonic and nanophotonic applications, such as bio-chemical sensors, meta-materials and nanolasers, benefiting by their size-dependent optical constants which are different from that of bulk materials. Considering that the performances of these films are sensitive to their thicknesses and optical constants, it is highly desirable to precisely characterize the thicknesses and the optical constants of such thin films for better applications.

In this work, a synergic analysis method based on ellipsometric parameters and reflectivity has been proposed, which enables the simultaneous determination of both the thickness and the optical constants for the metallic thin film. Both the ellipsometric parameters, including the amplitude ratio tan(ψ) and the phase difference Δ between p- and s-components, as well as the reflectivity are acquired using one ellipsometer. The proposed method consists of a point-by-point synergic regression analysis on the reflectivity and the ellipsometric parameters as well as an oscillator-parametrization regression analysis on the ellipsometric parameters. The former analysis allows for the accurate determination of the thickness of metallic thin films, while the latter enables the acquisition of the optical constants. Both virtual and practical experiments of measuring a series of Cu thin films deposited on Si substrates have been sequentially carried out for demonstration. The results clearly show the coupling effect between the thickness and optical constants of these samples. And by comparing with the thicknessses reported by AFM and TEM, the validity and the accuracy of the proposed method have been verified. Further analysis on the optical constants of Cu thin films has been carried out using the oscillator-parametrization we proposed, in which the thickness dependency of the Drude term, the plasma energy and the relaxation time has also been analyzed.

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-MoA1 Area-Selective Deposition of Crystalline Perovskites**, *E. Lin,* ***Brennan Coffey****, Z. Zhang, P.Y. Chen, B. Edmondson, J.G. 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 x 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-MoA2 A Dry NF_3/NH_3 Plasma Clean for Removing Si Native Oxide and Leaving a Smooth Si Surface**, ***Christopher Ahles**, J.Y. Choi,* University of California, San Diego*; A.C. 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-MoA3 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-MoA5 The Interconnect Resistivity Bottleneck**, ***Daniel Gall**, T. Zhou, E. Milosevic,* Rensselaer Polytechnic Institute*; P.Y. 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-MoA6 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.

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3:40pm **EM+AM+NS+PS-MoA8 The Effect of Metal Diffusion on Contacts to Semiconducting Chalcogenides: Examples for 2D and 3D Materials**, ***Suzanne E. Mohney**, K.A. Cooley, M. Abraham, A.C. Domask, H. Simchi, L. Kerstetter, C. Lawrence, T.N. 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-MoA10 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.C. 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.

Magnetic Interfaces and Nanostructures Division
Room 201A - Session MI+2D+EM+NS-MoA

IoT Session: Symposium on new Magnetic Materials, Devices and Concepts for the Information Society

Moderator: Hendrik Ohldag, SLAC National Accelerator Laboratory

1:20pm **MI+2D+EM+NS-MoA1 "ZOOMING in on Data Storage and the Superb HDD"**, ***Roger Wood,*** Western Digital **INVITED**

Get ready for a wild ride starting with the vast distances of outer space and ending with the tiny

distances that separate atoms. For a very different perspective on data storage, each slide in the

presentation looks at things on a scale that is a factor of ten smaller than the previous slide. The

common thread is the technology of information storage. Information storage is what defines human

history and it is the machine-readable data storage developed in the last half-century that provides the

foundation of the modern information age. More than anything, data storage implies magnetic

recording and the hard disk drive. The humble Hard Disk Drive contains such exquisite technologies

and operates at such astounding precision that it almost defies belief. Yet, our industry churns out

these devices by the hundreds of millions and sells them for a few tens of dollars each. Please enjoy

this light-hearted logarithmic romp through storage technology from interstellar space to interatomic

spacings.

(The presentation is based on a talk given at the annual ASME ISPS banquet in Santa Clara, California, in June 2016, while the author was with Western Digital Corporation.)

2:00pm **MI+2D+EM+NS-MoA3 Physics and Applications of Spin-transfer Torques**, ***Andrew Kent,*** New York University **INVITED**

The magnetization of a magnetic material can be reversed by using electric currents that transport spin angular momentum [1]. This was predicted in magnetic tunnel junctions—two metallic ferromagnetic layers separated by a thin insulating barrier—by John Slonczewski in 1989 and demonstrated experimentally about a decade later. This discovery has had an enormous impact on magnetism research and technology [2], as prior to this the primary means to reorient the magnetization of a magnet was by applying magnetic fields (dating to 1819 and Oersted!). In this talk I will highlight some of the physics and applications enabled by the discovery of spin-transfer torques. This includes recent experiments that create localized spin-wave excitations (magnons droplets) in thin films with uniaxial magnetic anisotropy [3]. Spin-transfer torques also permit study of magnetic analogues of superconductivity, superfluidity and the Josephson effect that promise to increase our understanding of collective quantum effects. They may even enable braiding Majorana fermions [4]. Finally, I will discuss spin-torque switching of perpendicularly magnetized magnetic tunnel junctions [5], the basic device used in spin-transfer torque magnetic random access memories.

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*Work done in collaboration with Dirk Backes, Gabriel Chaves, Daniel Gopman, Christian Hahn, Jinting Hang, Yuming Hung, Ferran Macia, Daniele Pinna, Laura Rehm, Debangsu Roy, Javad Shabani and Volker Sluka at NYU; Georg Wolf, Bartek Kardasz, Steve Watts and Mustafa Pinarbasi at Spin Transfer Technologies Inc.;and Hendrik Ohldag at SSRL

2:40pm **MI+2D+EM+NS-MoA5 Hybrid Magnetic Heterostructures*, Ivan K. Schuller*,** *A. Basaran,* University of California, San Diego*; J. de la Venta,* Colorado State University*; J.G. Ramirez,* Universidad de los Andes, Colombia*; T. Saerbeck,* Institute Laue-Langevin, France*; I. Valmianski,* University of California, San Diego*; X. Batlle,* University of Barcelona, Spain **INVITED**

Hybrid materials allow the engineering of new material properties by creative uses of proximity effects. When two dissimilar materials are in close physical proximity the properties of each one may be radically modified or occasionally a completely new material emerges. In the area of magnetism, controlling the magnetic properties of ferromagnetic thin films without magnetic fields is an on- going challenge with multiple technological implications for low- energy consumption memory and logic devices. Interesting possibilities include ferromagnets in proximity to dissimilar materials such as antiferromagnets or oxides that undergo metal-insulator transitions. The proximity of ferromagnets to antiferromagnets has given rise to the extensively studied Exchange Bias[1].

In a series of recent studies, we have investigated the magnetic properties of different hybrids of ferromagnets (Ni, Co and Fe) and oxides, which undergo metal-insulator and structural phase transitions. Both the static as well as dynamical properties of the ferromagnets are drastically affected. Static properties such as the coercivity, anisotropy and magnetization [2-3] and dynamical properties such as the microwave response are clearly modified by the proximity effect and give raise to interesting perhaps useful properties.

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3:40pm **MI+2D+EM+NS-MoA8 Organismic Materials and Intelligence*, Shriram Ramanathan,*** Purdue University **INVITED**

Intelligence in the natural world is panspermic to life, ranging from basic survival skills in non-neural organisms to co-operative foraging and complex mating strategies in higher level animals. We ask the question whether such remarkable features can be implemented in the physical world utilizing adaptive matter. We have identified strongly correlated semiconductors, one class of quantum materials as particularly suited for this effort, owing to their remarkable electronic plasticity. One may refer to these systems as organismic materials that display certain well-defined characteristics of living beings. In this presentation, we will present examples from the animal kingdom focusing on intelligence and episodic memory. Then we will discuss recent collaborative studies on correlated oxides demonstrating ancestral intelligence. We will conclude with examples of neural networks that can be designed with quantum materials that can replicate fundamental animal learning traits. The role of defects, strain and orbital occupancy control in design of electronic plasticity will be highlighted.

Materials and Processes for Quantum Computing Focus Topic
Room 203A - Session MP+AM+EM+NS-MoA

Systems and Devices for Quantum Computing II

Moderator: Josh Mutus, Google Inc

1:20pm **MP+AM+EM+NS-MoA1 Quantum Engineering of Superconducting Qubits*, William Oliver,*** MIT Lincoln Laboratory **INVITED**

Superconducting qubits are coherent artificial atoms assembled from electrical circuit elements and microwave optical components. Their lithographic scalability, compatibility with microwave control, and operability at nanosecond time scales all converge to make the superconducting qubit a highly attractive candidate for the constituent logical elements of a quantum information processor. Over the past decade, spectacular improvement in the manufacturing and control of these devices has moved superconducting qubits from the realm of scientific curiosity to the threshold of technical reality. In this talk, we review this progress and our own work at MIT that are creating a future of engineered quantum systems.

2:00pm **MP+AM+EM+NS-MoA3 The Quantum Socket: A Wiring Method for Superconducting Quantum Computing*, Matteo Mariantoni,*** University of Waterloo, Canada **INVITED**

I will provide a brief introduction to the main technological and scientific challenges to be faced in order to build a practical quantum computer, with emphasis on the case of superconducting quantum computing. I will then delve into a detailed explanation of a method to address the wiring of a two-dimensional array of superconducting quantum bit (qubits): The quantum socket [1]. Next, I will show how the quantum socket can be extended to a medium-scale quantum computer and how it can help mitigate coherent leakage errors due to qubits interacting with spurious cavity modes [2]. I will then show thermocompression bonding technology [3], a method that allows us to further protect qubits from the environment. In particular, I will propose a new qubit design based on our experimental implementation of thermocompression bonded chips, where vacuum gap capacitors are used to reduce dissipation due to so-called two-level state defects in amorphous dielectrics, which are the insulators presently use in our qubits.

[1] J.H. Béjanin, T.G. McConkey, J.R. Rinehart, J.D. Bateman, C.T. Earnest, C.H. McRae, Y. Rohanizadegan, *D. Shiri*, B. Penava, P. Breul, S. Royak, M. Zapatka, A.G. Fowler, and **M. Mariantoni**, Three-Dimensional Wiring for Extensible Quantum Computing: The Quantum Socket, Phys. Rev. Applied **6**, 044010 (2016)

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[3] C.R.H. McRae, J. H. Béjanin, Z. Pagel, A.O. Abdallah, T.G. McConkey, C.T. Earnest, J.R. Rinehart, and **M. Mariantoni**, Thermocompression Bonding Technology for Multilayer Superconducting Quantum Circuits, Appl. Phys. Lett. **111**, 123501 (2017)

3:00pm **MP+AM+EM+NS-MoA6 50 Ohm Superconducting Kinetic Inductance Traveling-Wave Amplifier with flexible pump frequency for Four Wave Mixing and Three Wave Mixing*, Xian Wu*,** *M. Bal, J. Long, H.S. Ku, R. Lake, D.P. Pappas,* National Institute of Standards and Technology

We developed a 50 Ohm transmission-line based superconducting kinetic inductance traveling-wave (KIT) amplifier using high inductance material NbTiN. The nonlinearity originates from the kinetic inductance of the superconductor and enables amplification. Often, the impedance of the transmission line is significantly higher than the 50 Ohm microwave environment due to the dominance of kinetic inductance over geometric inductance at micron size scales. To address this impedance mismatch, we engineered “fingers” on each side of the original coplanar waveguide KIT [1] to introduce extra capacitance that decreases the impedance to approximately 50 Ohm [2,3]. Those extra “fingers” also function to create a band stop at higher frequency to bend the dispersion relation between wave vector (k) and frequency (f), which allows us to apply the pump frequency within a wide span of a few GHz and achieve several GHz gain bandwidth for chosen pump frequency. Another advantage of this structure is that it significantly reduces the phase velocity, hence shortening the physical length of this device. Gain measurements based on both four wave mixing and three wave mixing will be presented.

[1] Appl. Phys. Lett. **108**, 012601 (2016); https://doi.org/10.1063/1.4937922

[2] Journal of Applied Physics **119**, 083901 (2016); https://doi.org/10.1063/1.4942362

[3] Appl. Phys. Lett. **110**, 152601 (2017); https://doi.org/10.1063/1.4980102

3:40pm **MP+AM+EM+NS-MoA8 Near Term Development of Short Depth Quantum Processors***, J.M. Chow,* IBM Research Division, T.J. Watson Research Center*; **Martin Sandberg**,* IBM, T.J. Watson Research Center **INVITED**

Quantum processors are currently in their infancy though the community is poised to explore bringing them to a state where they can outperform classical computations in relevant application. The challenges that lie ahead

are plentiful and touch all aspects of the quantum computer, ranging from finding algorithms to building control software and control hardware as well as engineering and fabricating and testing the quantum hardware. In an effort to accelerate the development of quantum computing IBM launched the IBM Q experience. The Q Experience is a cloud-based platform which allows anyone to get familiar with quantum computing. It allows users to run experiments on actual quantum hardware.

In this talk I will focus on the development and characterization of short depth superconducting quantum hardware. Crosstalk and decoherence are some of the most pressing issues that we face today. Decoherence limits the number of operations that can be performed on the hardware (the depth of the circuit) whereas crosstalk can limit what operations can be performed in parallel on the circuit. The processors featured on the IBM Q experience are based on fixed frequency transmon qubits with a cross-resonance based two qubit gate. For this platform only a very narrow frequency range for the qubits is possible. This leads to problems related to frequency crowding and spurious interactions. Methods for characterizing and addressing both the frequency allocation and characterizing crosstalk will be discussed.

4:20pm **MP+AM+EM+NS-MoA10 Frequency Crowding in Lattices of Transmon Qubits**, *S. Rosenblatt, **Jared Hertzberg**, J. Chavez-Garcia, N.T. Bronn, H. Paik, M.O. Sandberg, E. Magesan, J. Smolin, J.B. Yau, V.P. Adiga, M. Brink, J.M. Chow,* IBM, T.J. Watson Research Center

A key goal in quantum computing is to develop scalable fault-tolerant quantum logic circuits. One promising architecture involves lattices of fixed-frequency transmon qubits coupled via cross-resonance gates. Fixed-frequency qubits offer high coherence and the all-microwave gate reduces circuit complexity. To optimize gate performance, excitation energies of neighboring qubits must be similar but non-degenerate. This architecture is thus sensitive to any variation in device parameters affecting transmon frequency. In this talk we will discuss a statistical model for the resulting 'frequency crowding' behavior, and suggest improvements in both architecture design and qubit fabrication in order to achieve scalable circuits with good gate fidelity.

*We acknowledge support from IARPA under Contract No. W911NF-16-0114.

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

Moderator: Robert Grubbs, Micron Technology

1:40pm **TF+EM+MI+PS-MoA2 ---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.P. 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 μC/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-MoA3 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 °C. 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 °C) 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-MoA4 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-MoA5 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-MoA8 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-MoA9 Atomic Layer Deposition of Co/Pt Multilayer films for Perpendicular Magnetic Anisotropy*, Devika Choudhury,*** *A.U. Mane, C.M. Phatak, A.K. Petford Long, J.W. 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:

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

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2D Materials Focus Topic
Room 201B - Session 2D+EM+MI+NS-TuM

Properties of 2D Materials including Electronic, Magnetic, Mechanical, Optical, and Thermal Properties

Moderator: Johannes Jobst, Leiden University

8:00am **2D+EM+MI+NS-TuM1 Effect of Lattice Stacking Orientation and Local Thickness Variation on the Mechanical Behavior of Few Layer Graphene Oxide**, ***Teng Cui***, *S. Mukherjee, C.H. Cao, P.M. Sudeep, J. Tam,* University of Toronto, Canada*; P.M. Ajayan,* Rice University*; C.V. Singh, Y. Sun, T. Filleter,* University of Toronto, Canada

Investigation of few layer 2D materials is fundamentally important to bridge the gap between monolayer and bulk properties, and practically meaningful for applications as reinforcement nanofillers and layered electronic devices. Few layer introduces differences from intrinsic properties of monolayers due to the complexity of structural heterogeneities, such as lattice stacking orientation and local thickness variation. In this work [1], few layer graphene oxide (GO) with different structural heterogeneities were studied using atomic force microscopy-based deflection measurements and transmission electron microscopy (TEM). Direct TEM evidence of fracture surfaces and molecular dynamics (MD) simulations revealed decoupled and dissimilar layer crack patterns (i.e., different cracking pathway of top and bottom layers) for misaligned bilayer GO. In contrast, aligned GO bilayers generally fractured with a larger portion of common cracks shared by both layers, indicating stronger interlayer interaction than its misaligned counterpart. MD results also revealed insignificant effect of lattice alignment on the strength and toughness of GO bilayers, which is ~23.5 GPa and $\sim 1.71\times10^{-18}$ J/nm^3, respectively, for both aligned and misaligned cases. Scaling up to ~5 layers and above revealed more significant local thickness heterogeneity and consequently a ~60% reduction of the normalized fracture force and toughness with respect to the average number of layers. MD simulations on partially intercalated few layer GO revealed anisotropic and heterogeneous stress distributions, as well as stress concentration near the inner edges, which may account for the significant reduction of strength and toughness.

[1] T. Cui, S. Mukherjee, C. Cao, P. M. Sudeep, J. Tam, P. M. Ajayan, C. V. Singh, Y. Sun, and T. Filleter, "*Effect of Lattice Stacking Orientation and Local Thickness Variation on the Mechanical Behavior of Few Layer Graphene Oxide*", **Carbon**, accepted.

8:20am **2D+EM+MI+NS-TuM2 Out-of-Plane Mechanical Properties of 2D Hybrid Organic-Inorganic Perovskites by Nanoindentation**, ***Qing Tu***, *I. Spanopoulos, S. Hao, C. Wolverton, M. Kanatzidis, G. Shekhawat, V. Dravid,* Northwestern University

2D layered hybrid organic-inorganic perovskites (HOIPs) have demonstrated improved stability and promising photovoltaic performance. The mechanical properties of such functional materials are both fundamentally and practically important to achieve both high performance and mechanically stable (flexible) devices. Here we report the static, out-of-plane mechanical properties of a series of 2D layered lead iodide HOIPs with a general formula of $(R\text{-}NH_3)_2(CH_3NH_3)_{n-1}Pb_nI_{3n+1}$, and investigate the role of structural sub-units (*e.g.*, the length of theorganic spacer molecules -R and the number of inorganic layer -n) on the mechanical properties by nanoindentation. We find that the 2D HOIPs are softer than their 3D counterparts due to the replacement of the strong inorganic layer and ionic bonds by the soft organic layers and the weak Van der Waals interactions. As n increases from 1 to 5, the relative amount of these weak factors in the crystals are decreasing and both the out-of-plane Young's modulus E and hardness H increase, approaching to the reported values of corresponding 3D crystals. DFT simulations showed a similar trend to the experimental results. Furthermore, we show that increasing the alkyl chain spacer molecule -R from $-C_4H_9$ to $-C_{12}H_{25}$, E first decreases and eventually plateaus while no clear trend in H is observed. Our results reveal that the competition between the stiff inorganic layers, the soft organic layer and the weak Van der Waals interfaces determines the mechanical properties of 2D HOIPs. Finally, we compare these findings with those in other 2D layered materials such as h-BN, MoS_2 and MXene, and shed light on routes to further tune the out-of-plane mechanical properties of 2D layered HOIPs.

8:40am **2D+EM+MI+NS-TuM3 Mechanical Properties of Many-layer CVD Graphene**, ***Kyle Larsen***, *S. Lehnardt, J.T. Rowley, B. Anderson, R.R. Vanfleet, R.C. Davis,* Brigham Young University

Graphene, a monoatomic layer of carbon atoms, has a reported Young's modulus of 1 TPa and a tensile strength of 130 GPa. These values make it both the strongest and one of the stiffest materials ever reported. The mechanical properties of multilayer graphene grown by chemical vapor deposition have been reported for films of up to 10 layers (3.35 nm). Films thicker than about 10 layers (sometimes considered graphite rather than multilayer graphene) are of interest as membranes and in MEMS applications. We have characterized CVD grown many-layer graphene films with thicknesses of about 50 nm by Raman spectroscopy, burst testing, and atomic force microscopy. The atomic force microscope was used to map the local compliance over suspended regions containing cantilevers cut out of the many-layer graphene with a focused ion beam. Analytical and finite element modeling were used in the analysis of the deflection of the many-layer graphene cantilevers to extract Young's modulus. The many-layer graphene is high quality (little or no D peak in the Raman spectrum) and has a Young's modulus in the range reported for graphene (0.5 TPa to 1 TPa).

9:20am **2D+EM+MI+NS-TuM5 Discovering and Visualizing Ferromagnetism in Intrinsic Two Dimensional Materials**, ***Jing Xia***, University of California Irvine **INVITED**

In this talk, I will discuss our recent results on discovering and visualizing in 2D magnetism using a unique scanning Sagnac MOKE microscope, which is based on a Sagnac interferometer technique and has achieved unprecedented nano-radian level Kerr and Faraday sensitivity even at DC. In exfoliated Cr2Ge2Te6 (CGT) atomic layers, we report the discovery of intrinsic ferromagnetism in 2D van der Walls crystals, defying the well-known Mermin-Wagner theorem. Unlike 3D magnetism, the ferromagnetic order in this 2D system is stabilized by magnetic anisotropy from the CGT structure, which is not present in graphene. As a result, changing the magnetic anisotropy with a small external magnetic field was found to strongly enhance the Curie temperature, which is a feature unique to 2D magnetism.

11:00am **2D+EM+MI+NS-TuM10 Onset of Buckling Folding and Slipping Instabilities in 2D Materials under Compressive Strain**, ***Jaehyung Yu***, *E. Ertekin, A.M. van der Zande,* University of Illinois at Urbana-Champaign

Atomic membranes of monolayer 2D materials represent the ultimate limit in size of nanoelectromechanical systems. These materials have high mechanical strength, yet low bending modulus leading to high pliability. Adding in the diverse active electronic properties of different 2D materials, atomic membranes will allow new next generation technologies like highly strainable crumpled or folded electronics, or 3D origami devices based on 2D materials. In order to realize these new technologies it is important to understand how the rules of continuum membrane mechanics break down on the atomic scale and how these deformations will affect the electronic properties, including the role of compressive stress, bending, adhesion and interlayer shear.

Here, we present a combined experimental and theoretical study of the onset of instabilities such as buckling, folding and slip on the properties of 2D materials and heterostructures under compression. We generate periodic fold structures of the graphene, MoS2, and their heterostructures by introducing the compressive stresses with the pre-strained stretchable substrate. We analyzed then measured the membrane morphology using atomic force microscopy (AFM) under increasing levels of uniaxial compression up to 30%. We observed that the strain-relaxation mechanism of atomic membranes could be varied from generating and growing standing folds to collapsing to generate trifolds based on the mechanical properties including 2D modulus, bending stiffness, adhesion and interlayer shear energies. The onset of these instabilities depends on the 2D material or heterostructure making up the membranes. In graphene folds grow then collapse at compressive strain of ~5%. In monolayer MoS2 standing folds grow to a fixed height of ~20 nm but do not collapse. Instead, new folds are generated in between the existing folds.

We use density functional theory (DFT) to model the morphology of the same structures under compressive slack. We find that, in multi-layer 2D materials, the onset of slip between the layers is crucial parameters to decide the bending stiffness of the material. We found that the superlubricity between the layers allows the linear scaling of bending stiffness with the number of layers, which violates the conventional cubic scaling of bending stiffness in continuum mechanics.

We unite the atomic scale simulation with the experiment through a continuum model to compare the period, shape, and transition strains extract the variations in adhesion and bending energy of different 2D materials and heterostructures to find the deformation of 2D materials under the compressive strain.

11:20am **2D+EM+MI+NS-TuM11 Title: Spatially-Resolved Contact-Free Electrical Characterization of Transition Metal Dichalcogenide Films Grown by Chemical Vapor Deposition.**, ***Miguel Isarraraz***, *L. Bartels*, University of California, Riverside

Surface Acoustical Waves (SAWs) and Transition Metal Dichalcogenides (TMDs), separately, are topics of current research due to their present and future use in telecommunications and beyond-CMOS technology. The interaction between a SAW and a 2D electron gas has been previously studied by measuring the absorption of the SAW by GaAs and, more recently, graphene[i,ii,ii]. Here, the interaction between a SAW and a TMD is studied using MoS_2 directly grown by chemical vapor deposition on 128°YX-cut $LiNbO_3$. By focusing a 532 nm laser on the sample, the generation of electron-hole pairs is found to enhance the attenuation of the SAW as expected, and this technique can be used to spatially resolve variations inside triangular MoS_2 islands. Furthermore, the time dependence of the SAW attenuation with laser exposure is used to distinguish between heating and electronic effects. The induced acoustoelectric current, laser power, and SAW excitation power dependence are discussed. This technique provides a means of electrically characterizing atomically thin semiconducting film that avoids the limitations of metallic contacts.

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11:40am **2D+EM+MI+NS-TuM12 Electronic, Thermal, and Unconventional Applications of 2D Materials**, ***Eric Pop***, *E. Yalon, C. McClellan, K. Smithe, C. English, M. Mleczko, M. Muñoz Rojo, N. Wang, S. Suryavanshi, I. Datye, C. Bailey, A. Gabourie, M. Chen, V. Chen, K. Schauble, R. Grady,* Stanford University **INVITED**

This talk will present recent highlights from our research on two-dimensional (2D) materials and devices including graphene, boron nitride (h-BN), and transition metal dichalcogenides (TMDs). The results span from fundamental measurements and simulations, to devices, to system-oriented applications which take advantage of unusual 2D material properties. On the fundamental side, we have measured record velocity saturation in graphene [1,2], as well as the thermal properties of graphene nanoribbons [3]. These are important for electronic applications, which can exhibit substantial self-heating during operation [4]. Taking advantage of low *cross-plane* thermal conductance, we found unexpected applications of graphene as ultra-thin electrode to reduce power consumption in phase-change memory [5]. We have also demonstrated wafer-scale graphene systems for analog dot product computation [6].

We have grown monolayer 2D semiconductors by chemical vapor deposition over cm^2 scales, including MoS_2 with low device variability [7], WSe_2, $MoSe_2$ – and multilayer TMDs $MoTe_2$ and WTe_2 [8]. Importantly, $ZrSe_2$ and $HfSe_2$ have native high-K dielectrics ZrO_2 and HfO_2, which are of key technological relevance [9]. Improving the electrical contact resistance [10], we demonstrated 10 nm transistors using *monolayer* MoS_2, with the highest current reported to date (>400 µA/µm), approaching ballistic limits [11]. Using Raman thermometry, we uncovered low thermal boundary conductance (~15 $MW/m^2/K$) between MoS_2 and SiO_2, which could limit heat dissipation in 2D electronics [12]. We are presently exploring unconventional applications including thermal transistors [13], which could enable nanoscale control of heat in "thermal circuits" analogous with electrical circuits. Overall, these studies reveal fundamental limits and new applications that could be achieved with 2D materials, taking advantage their unique properties.

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Materials and Processes for Quantum Computing Focus Topic
Room 203A - Session MP+EM+NS-TuM
High Coherence Qubits for Quantum Computing

Moderator: Robert Ilic, National Institute of Standards and Technology

8:00am **MP+EM+NS-TuM1 MBE Grown Nitride Superconductors for Quantum Circuits**, ***Christopher Richardson***, *A. Alexander, C. Weddle,* Laboratory for Physical Sciences

Low microwave loss superconducting capacitors and inductors are critical circuit components of superconducting qubits. For transmon qubits, the ability to make high-quality planar resonators is an essential part of fabricating highly coherent qubits. Plasma assisted Molecular beam epitaxy (PAMBE) is used to grow niobium titanium nitride alloys ($Nb_xTi_{1-x}N$) directly on silicon (111) wafers. Using a structure first approach to design optimization, the structural, surface topology, chemical characteristics, and superconducting critical temperature of these films are used for optimization of the growth conditions before resonators are fabricated and tested. Here focus will be on the optimization of PAMBE-TiN films grown under slightly nitrogen rich conditions and high growth temperatures. Using films grown on high resistivity wafers, resonators are fabricated from coplanar waveguides with a narrow 6-µm wide center conductor and nominal 500-nm deep trench etch. Cryogenic testing at 100mK demonstrate low microwave loss that is evident from measured internal quality factors that are over 1M in the single photon regime and approach 10M at high powers. The motivation of using PAMBE to grow superconductors and the favorable comparison with resonators made from leading films synthesized with sputter deposition will also be discussed.

8:20am **MP+EM+NS-TuM2 Towards Improved Coherence Times in Transmon Qubits**, ***Sam Stanwyck***, Rigetti Computing

The depth of the circuit a quantum computer can perform depends directly on the coherence times of its qubits. There are many sources of decoherence in superconducting qubits, and identifying and minimizing dominant sources is a critical step in improving the performance of quantum computers. By measuring the internal quality factor of resonators and deliberately coupling to different loss mechanisms, we identify dominant sources of resonator loss in our systems, as well fabrication process changes to ameliorate these losses. Additionally, defects and materials present on the chip surface are correlated with process changes and coherence metrics.

8:40am **MP+EM+NS-TuM3 Design and Fabrication for High Coherence Quantum Circuits**, ***David Pappas***, *X. Wu, R. Lake, M. Bal, J. Long, C.R. McRae, H.S. Ku,* National Institute of Standards and Technology (NIST) **INVITED**

In this talk we focus on achieving high coherence in multi-component quantum circuits [1,13]. We will discuss geometric and electrical design strategies that mitigate energy loss while maintaining sufficient coupling to the qubit. Materials considerations -including dielectric losses in the substrate and various interfaces -play a central role in the implementation of these circuits. We will present a summary of our studies of the various participation factors and processing techniques to reduce dielectric loss in the capacitance of the qubits and resonators for readout and coupling. We also review our methods of integration for the key nonlinear component, the overlap tunnel junctions. In particular, techniques for achieving smooth surfaces for the junctions in a back-end process will be shown.

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9:20am **MP+EM+NS-TuM5 Effect of Surface Treatment on Superconducting Qubit Coherence**, ***Bradley Christensen***, University of Wisconsin-Madison; *P. Kumar,* University of Wisconsin - Madison; *J.J. Nelson, Y. Liu, A. Ballard, B.L.T. Plourde,* Syracuse University; *R. McDermott,* University of Wisconsin - Madison

Superconducting qubits are an attractive candidate for quantum information processing in the solid state . The fidelity of two-qubit gates for superconducting qubits is one of the more challenging limitations toward scalable quantum computing. A promising approach to perform these gates uses flux-tunable qubits to bias the qubit pairs into resonance to perform the necessary entangling operations. While this approach has many advantages over competing techniques, there are still significant issues that limit the fidelity of the gates. For example, since the two-qubit gate requires flux-biasing of a qubit, this also necessarily requires one of the qubits to operate at a flux-sensitive point, and as such, 1/f flux noise will restrict the possible gate fidelity. In addition to flux noise, flux-tunable qubits also suffer from microscopic two-level system (TLS) defects that reside in the high field areas on the qubit capacitor pad. These TLS cause an enhanced decay through both resonant interactions with the qubit and Landau-Zener transitions as the qubit frequency is biased through a TLS. While one could perform spectroscopy of the TLS to map out the inoperable space, this becomes an inefficient solution for large scale systems as the TLS resonance frequencies are not stable, and will significantly drift over time.

Recent experiments on SuperconductingQUantum Interference Devices (SQUID) point to adsorbed molecular O_2 as the dominant contributor to magnetism in superconducting thin films, and demonstrate that improvements in the sample vacuum environment lead to significant reductions in surface spin susceptibility and magnetic flux noise power. Furthermore, TLS defects have been shown to reside in surface oxides and interfaces, where the TLS dipole couples to the qubit electric field, and experiments on microwave resonators have shown that high-temperature annealing can yield a reduction in surface TLS defects.

Here, we present our results on improving the vacuum environment of superconducting qubits with an ultra-high vacuum (UHV) bake to remove the adsorbates. We measure flux noise power spectral densities (PSD) using Ramsey-based, CPMG filtering, and dressed-dephasing techniques, allowing the flux PSD measurements to span 10 decades. Furthermore, by measuring qubit lifetime as a function of frequency (swap spectroscopy), we can map out the coupling strength, lifetime, and density of the TLS defects. We present a comparison of treated and untreated devices to demonstrate the improvement to qubit coherence through a UHV bake.

9:40am **MP+EM+NS-TuM6 Metrology of Dielectric Loss using Lumped-Element Microwave Resonators**, ***Corey Rae McRae***, *X. Wu, M. Bal, J. Long, H.S. Ku, D.P. Pappas, R. Lake,* National Institute of Standards and Technology

Reducing the overall concentration of TLSs in dielectric materials remains at the forefront of materials research in quantum information science. In this work, we measure a lumped element resonator fabricated from a superconductor-dielectric-superconductor trilayer to determine the TLS loss of various dielectrics of interest in superconducting quantum computing. The deposition of the trilayer prior to fabrication allows control of the metal-dielectric interfaces, and the fabrication process is generalized so that resonators containing different dielectrics can be compared easily. This lithography method enables the measurement of trilayer capacitors and junctions that have been prepared entirely in situ in an ultrahigh vacuum environment. In future work, we will interrogate a new class of low-loss dielectrics grown with epitaxial methods using the measurement capabilities developed here.

11:00am **MP+EM+NS-TuM10 Direct Observation of Atomic Structure of Ultra Thin AlO_x Barriers in $Al/AlO_x/Al$ Josephson Junctions for Quantum Devices**, ***Eva Olsson***, Chalmers University of Technology, Gothenburg, Sweden **INVITED**

The atomic structure of tunnel barriers in Josephson junctions for quantum devices and the corresponding interfaces determine the properties of the junction. The thinnest region in the barrier of a junction will be the preferential tunneling channel for charge carriers and the highest current. The current increases exponentially with decreasing barrier thickness. As a consequence, a variation on the individual atom plane length scale results in inhomogeneity of the tunnel current across the barrier. There are several earlier experimental indirect indications that only a small fraction of the junction area is active.

We are using high resolution annular dark field (ADF) scanning transmission electron microscopy (STEM) imaging to obtain high resolution (better than 1 Å) and high precision (better than 1 pm) information about the local atomic structure [1]. We use ADF STEM imaging to directly determine the thickness distribution along the oxide barrier in $Al/AlO_x/Al$ Josephson junctions [2]. The barrier thickness is about 1-2 nm. The thickness distribution shows that less than 10% of the junction area dominates the electron tunneling. We also study the influence of oxygen pressure and oxidation time on the thickness distribution. In addition, we determine the atomic structure and coordination of Al atoms within the oxide barrier layer using electron energy loss spectroscopy and nanobeam electron diffraction [3]. A lower Al coordination is observed at the metal/oxide interface compared to the interior of the oxide barrier. We also study the structure of the interfaces between the Al contact and the substrate [4,5].

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11:40am **MP+EM+NS-TuM12 Metrology of Tunnel Junctions for Superconducting Qubits**, ***Russell Lake***, National Institute of Standards and Technology (NIST); *X. Wu, H.S. Ku, J. Long, M. Bal, C.R. McRae,* National Institute of Standards and Technology (NIST) and University of Colorado Boulder; *D.P. Pappas,* National Institute of Standards and Technology (NIST)

Superconducting tunnel junctions make up the key non-linear circuit component in many implementations of quantum electrical circuits, including superconducting qubits. Therefore, controllable fabrication of superconducting junctions has taken a central role in the realization of quantum computers. In this talk we discuss fabrication and characterization of a wafer-scale process for nanoscale superconducting tunnel junctions (Al-AlOx-Al) [1]. We present the distribution of normal-state resistances across a wafer for different junction sizes. We have applied an analytical method of accounting for the current crowding in the junction leads [2] in order to give accurate predictions of the supercurrent from the room-temperature raw data. These corrected resistances can be input into the Ambegaokar-Baratoff formula to predict the critical current of the tunnel junctions in the superconducting state [3], and the corresponding non-linear effective inductance. These results are immediately relevant to the task of qubit frequency allocation in multi-qubit systems.

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Nanometer-scale Science and Technology Division
Room 102B - Session NS+AN+EM+MN+MP+RM-TuM

Nanophotonics, Plasmonics, and Metamaterials

Moderators: Alokik Kanwal, NIST Center for Nanoscale Science and Technology, Nikolai Klimov, National Institute of Standards and Technology

8:00am **NS+AN+EM+MN+MP+RM-TuM1 Parametric Nonlinear Interactions in Nanofabricated Silicon-based Photonics***, Amy Foster,* Johns Hopkins University **INVITED**

High optical confinement waveguides on integrated platforms enable nonlinear optical interactions with low power levels. The third-order nonlinear susceptibility, a modification of a material's permittivity due to an applied optical field, exists in all materials, and is an intensity-dependent process leading to third-order parametric effects. Harnessing the high optical intensities enabled by high confinement waveguides allows standard semiconductor materials to become power-efficient parametric nonlinear optical devices that can operate with powers in the mW range. The optical confinement of a waveguide also enables control over the waveguide's dispersion, allowing for phase-matching of the parametric processes thereby improving its operating bandwidth. Using standard nanofabrication techniques, integrated photonic devices can be tailored in both geometry at the nanoscale, and in magnitude of their third-order susceptibility through modification of their material properties. In this talk, we will discuss a variety of parametric nonlinear optical demonstrations in silicon-based waveguides including optical parametric amplification and oscillation, phase-sensitive amplification, and frequency conversion and comb generation. Furthermore, we will discuss these devices for a variety of applications including optical signal processing, spectroscopy, and security.

8:40am **NS+AN+EM+MN+MP+RM-TuM3 Ultrafast Optical Pulse Shaping using Dielectric Metasurfaces***, **Amit Agrawal**, S. Divitt, W. Zhu, C. Zhang, H.J. Lezec,* NIST Center for Nanoscale Science and Technology **INVITED**

Since the invention of femtosecond pulsed lasers, the field of ultrafast optical science and technology has seen significant progress in the generation and characterization of ultrashort optical pulses. Complimentary to development in generation and characterization techniques, arbitrary temporal shaping of optical pulses has become an integral part of the field. Fourier-transform pulse shaping is the most widely adopted approach that entails parallel modulation of spatially separated frequency components to achieve the desired pulse shape. Recently, dielectric metasurfaces have emerged as a powerful technology for arbitrary control over the amplitude, phase, or polarization of light in a single, compact optical element. Here, we experimentally demonstrate shaping of sub-10 fsec ultrafast optical pulses using a centimeter-scale silicon metasurface acting as both amplitude and phase modulation mask. The deep-subwavelength silicon nanostructures, positioned with nanometer precision, are individual optimized to provide accurate amplitude and phase modulations to each frequency component. Masks of this type offer a lower cost, larger size, higher resolution, high diffraction efficiency, high damage threshold method for controlling ultrafast pulses.

9:20am **NS+AN+EM+MN+MP+RM-TuM5 Single-Particle Nanophotonics and Materials Investigations with Optical Microresonator Spectrometers***, **Erik Horak**,* University of Wisconsin - Madison*; K.D. Heylman, K.A. Knapper, M.T. Rea, F. Pan, L.T. Hogan, R.H. Goldsmith,* University of Wisconsin-Madison **INVITED**

Optical microresonators have achieved impressive sensitivities in a range of experimental modalities. We leverage the exquisite sensitivity of microresonators to enable highly sensitive spectroscopic characterization of objects on the surface of the resonator. In this way, not only can single particles be detected and identified, but fundamental properties of interrogated systems can be studied, opening a path to mechanistic studies and label-free chemical identification.

Our photothermal-based technique employs a two-beam geometry. A fiber-coupled (probe) beam records the whispering-gallery mode (WGM) resonance wavelength via evanescent coupling through a tapered fiber, while a second free-space (pump) beam heats absorbing particles or molecules on the surface of the microresonator, shifting the WGM resonance. In essence we use the microresonator as a nearfield thermometer to measure dissipated heat upon optical excitation. To circumvent the photothermal background of the popular SiO_2 on Si toroidal resonators, we have developed an all-SiO_2 microtoroidal resonator, unlocking visible wavelengths to interrogation. We further employed a double-modulation technique through simultaneous Pound-Drever-Hall locking of the probe beam and amplitude modulation of the pump beam to reach sub-100 Hz or single attometer resonance shift resolution. This corresponds to signals much smaller than that predicted from a single-molecule, and thus represents an avenue toward single-molecule absorption spectroscopy.

We demonstrate this technique by examining gold nanorods (AuNR), which validate our experimental setup with near-diffraction limited photothermal maps, Lorentzian absorption spectra with stochastic center wavelengths, and single dipole polarization dependences. Further, AuNRs in close proximity to microresonator WGMs display signatures of photonic-plasmonic interactions, a forest of Fano resonances decorating the plasmonic absorption feature. This platform offers a facile methodology to study these complex interactions, with thermal annealing of the AuNRs producing highly controllable tuning of Fano resonances. Applying our platform to conductive polymers (CP), we have begun to understand the fundamental properties that enable the high conductivity from a bottom-up nanoscale perspective. We examine the interplay between homogeneous and heterogeneous broadening, measure the long-range ordering, and determine relative surface orientation of CPs. These examples firmly demonstrate the utility of our platform to go beyond sensing allowing exploration of novel characteristics in complex systems and potentially the observation of chemical and biochemical dynamics.

11:00am **NS+AN+EM+MN+MP+RM-TuM10 Optomechanical Interactions for Metrology and Signal Processing***, **Karen Grutter**,* The Laboratory for Physical Sciences **INVITED**

Imprinting radio-frequency (RF) signals on optical carriers has a broad range of applications from metrology to communication and has been accomplished in bulk components using a variety of techniques. Achieving this functionality on a chip could broaden the potential application space, but the bulk frequency generation methods do not translate directly to the nanoscale. A number of methods have been proposed for on-chip frequency generation, including various sources of electro-optic modulation, comb generation via material nonlinearities in microresonators, and optomechanical/opto-acoustic interactions. In this talk, we will discuss the features of these sources, with particular focus on optomechanical interactions.

One potential phenomenon enabling opto-acoustic frequency generation is stimulated Brillouin scattering (SBS), which is essentially an interaction between propagating phonons and photons. This effect has been demonstrated in optical fibers, and recent results in on-chip waveguides show promise. One of the challenges with SBS on chip is that gain is dependent on long interaction lengths.

This interaction can be enhanced by moving to a different domain of phonon/photon interaction: cavity optomechanics. In an optomechanical cavity, the characteristics of the generated frequency are dependent on the mechanical eigenmode. We will demonstrate the relationship between mechanical quality factor and phase noise in ring optomechanical oscillators.

The optomechanical interaction can be optimized beyond that of ring resonators by further confining optical and mechanical modes using photonic and phononic crystals. We have designed and fabricated Si_3N_4 nanobeam optomechanical crystals with ~4 GHz mechanical breathing modes. The increased optomechanical coupling of these nanobeams confers high sensitivity to displacement, which could be exploited for various metrology applications, which we will discuss.

Further enhancement of the optomechanical coupling can be achieved by modifying the optomechanical crystal geometry to support an optical slot mode. We have designed and fabricated ~3 GHz-frequency slot-mode optomechanical crystals in Si_3N_4. In addition to increasing the optomechanical coupling compared to the single-nanobeam device, this structure has increased versatility, enabling interaction with other stimuli and modalities. We have integrated NEMS actuators with a slot-mode optomechanical crystal, and used these actuators to tune the optical mode and lock it to an external, fixed laser wavelength. This increases the practicality of this device, enabling longer-term measurements and stabler frequency sources.

11:40am **NS+AN+EM+MN+MP+RM-TuM12 Cold-atom based Sensors and Standards***, **Stephen Eckel**, D.S. Barker, J.A. Fedchak, N.N. Klimov, E. Norrgard, J. Scherschligt,* National Institute of Standards and Technology **INVITED**

In this talk, I will describe our recent efforts to merge nanophotonics, ultra-high vacuum, and atomic physics together to build a new generation of

cold atom sensors and standards. In particular, I will focus on our recent realization of a single-beam system for cooling lithium atoms, an atomic species recently identified as an excellent candidate for a primary vacuum standard. Our system uses a triangular-shaped nanofabricated diffraction grating to produce the necessary beams for a magneto-optical trap that cools and slows the atoms. Unlike systems that use rubidium or cesium, which can be loaded from a vapor, lithium introduces additional complications because it must be produce from a thermal source requiring loading of the magneto-optical trap from behind the chip. Finally, I will conclude by talking about other trap geometries that we are pursuing, how they benefit vacuum and inertial sensors, and what the synergy of integrated nanophotonics, high-vacuum and atomic physics might be able to bring.

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-TuM1 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*; J.M. 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.

* *Corresponding author e-mail: sana.rachidi @cea.fr [mailto:sana.rachidi@cea.fr]*

8:20am **PS+EM+SE-TuM2 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-TuM3 Feature Scale Modeling of Etching of High Aspect Ratio Silicon Structures in Pulsed Plasmas**, ***Wei Tian***, *J.-C. 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.

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9:00am **PS+EM+SE-TuM4 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-TuM5 Etch Profile Evolution in Poly-silicon using Halogen Containing Plasmas for Next Generation Device Fabrication***, **Shyam Sridhar**, S.A. 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-TuM6 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.J. 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-TuM10 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.

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11:40am **PS+EM+SE-TuM12 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.

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12:00pm **PS+EM+SE-TuM13 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.

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Thin Films Division
Room 104B - Session TF+AM+EM+PS-TuM
Atomic Layer Processing: Area Selective Deposition

Moderators: Christophe Vallee, LTM, Univ. Grenoble Alpes, CEA-LETI, France, Steven George, University of Colorado at Boulder

8:00am **TF+AM+EM+PS-TuM1 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.

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8:40am **TF+AM+EM+PS-TuM3 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-TuM4 Topographical Selectivity with BN Electron-Enhanced ALD**, ***Jaclyn Sprenger**, A.S. Cavanagh, H. Sun,* University of Colorado at Boulder*; A. Roshko, P. Blanchard,* National Institute of Standards and Technology*; S.M. 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.

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9:20am **TF+AM+EM+PS-TuM5 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*; N. 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.

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9:40am **TF+AM+EM+PS-TuM6 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.H. Choudhury, J.M. Redwing,* The Pennsylvania State University*; T.N. Jackson, S.E. 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-TuM10 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, J.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

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

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-TuM12 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.

2D Materials Focus Topic
Room 201B - Session 2D+EM+MI+MN+NS-TuA

2D Device Physics and Applications

Moderator: Roland Kawakami, The Ohio State University

2:20pm **2D+EM+MI+MN+NS-TuA1 Spin Relaxation and Proximity Effect in WS_2/Graphene/Fluorographene Non-local Spin Valves**, ***Adam Friedman***, Laboratory for Physical Sciences; *K.M. McCreary, J.T. Robinson, O.M.J. van 't Erve, B.T. Jonker,* US Naval Research Laboratory

The mechanisms leading to spin relaxation in graphene and its heterostructures continue to be debated. Control of the spin relaxation in graphene-based structures is necessary to achieve the envisioned utility of graphene in future spintronic devices beyond Moore's law. Proximity induced spin relaxation caused by contact to a high spin-orbit material, such as WS_2, offers a promising avenue to manipulate the spin lifetime [1]. We demonstrate the operation of WS_2/graphene/fluorographene non-local spin valves and extract the spin lifetimes for a range of carrier concentrations by Hanle effect measurements. Four-terminal charge transport measurements allow us to calculate the momentum relaxation time as a function of carrier concentration and compare it to the spin lifetime. These data show that the D'yakonov-Perel' mechanism is the dominant spin relaxation mechanism for WS_2/graphene/fluorographenedevices, while, for reference graphene/fluorographene devices, linear scaling between the spin and momentum lifetimes points to spin-flip scattering during strong elastic scattering events where the scattering event is strongly coupled to the electron spin. We attribute the change in spin relaxation type in part with the inclusion of WS_2 as a substrate to proximity induced spin-orbit coupling due to the adjacent WS_2 layer, and we compare our data to the literature.

[1] A.L. Friedman, et al. Carbon 131, 18-25 (2018).

2:40pm **2D+EM+MI+MN+NS-TuA2 Two-dimensional Field-effect Light Emitting Transistors**, ***Junyoung Kwon***, *H. Ryu,* Yonsei University, Republic of Korea; *J.Y. Lee, C.H. Lee,* Korea University, Republic of Korea; *G.H. Lee,* Yonsei University, Republic of Korea

Two dimensional (2D) materials and their heterostructures hold great promises in various applications due to their unique properties and newly discovered physics. Especially, high exciton binding energy and emergence of charged excitons, *i.e.* trions, have shown that 2D semiconductors, such as transition metal dichalcogenides (TMDs), are promising candidates for new concept optoelectronics. Although lots of optoelectronic devices based on the van der Waals heterostructures of 2D materials, such as photodetectors, solar cells, and light emitting devices, have been demonstrated, development of novel optoelectronic devices is still required to fully utilize unique properties of 2D materials and enable multi-functions and versatile applications. Here we demonstrate 2D filed-effect light emitting transistors (2D-FELET) consisting of monolayer WSe_2 (light-emitting channel layer) and graphene contacts (tunable carrier injection electrodes). We encapsulated monolayer WSe_2 with two pieces of hexagonal boron nitride and fabricated graphene contacts to two ends of WSe_2. To selectively inject different types of charge (electrons and holes) at two graphene contacts, two separate top gates on top of WSe_2-graphene overlap regions were fabricated. By independent modulation of two top gates, Schottky barrier heights for electrons and holes can be tuned, which enables the selective charge injections. When two top gates are oppositely biased, electrons can be injected from one end of WSe_2 channel and holes can be injected from the other end. These opposite charges are recombined at the middle of WSe_2 channel, leading to strong light emission. The performance of the 2D-FELETs is tunable by additional electrical field from back gate. Furthermore, the devices produced in this work can be used as polarity-tunable FETs and photodetectors, simultaneously, which are beneficial for further CMOS integration. Our study shows great potential of 2D-FELETs toward future optoelectronic applications, which request ultra-thinness, transparency, flexibility, high efficiency, multi-functions, and high integration.

3:00pm **2D+EM+MI+MN+NS-TuA3 Quantum Devices with 2D Materials**, *H. Overweg, M. Eich, R. Pisoni, T. Ihn, P. Rickhaus,* ETH Zurich, Switzerland; ***Klaus Ensslin,*** ETH Zürich, Switzerland **INVITED**

Quantum dots in graphene have been mostly realized by etching. This leads to localized states at the uncontrolled edges dominating the transport properties of these quantum devices. [1] It is well known that in bilayer graphene gaps can be opened by vertical electrical fields. [2] This approach has been used with limited success to define quantum devices [3]. The pinch-off characteristics are typically limited by leakage currents often thought to occur at the physical sample edges [4].

Here we demonstrate that electrostatically tunable barriers can be fabricated on bilayer graphene devices with graphite as a back gate. We measure pinch-off resistances exceeding GOhms and observe quantized conduction plateaus for one-dimensional constrictions. [5] With suitable gate arrangements few carrier hole and electron quantum dots can be electrostatically defined. We measure the controlled occupation of quantum dots with single holes and electrons. Four-fold level bunching is observed in Coulomb blockade spectroscopy which is understood in terms of valley and spin states. Magnetic field dependence allows to investigate orbital and spin/valley degrees of freedom.

We further demonstrate quantum devices build on MoS2.

1. For a review see Bischoff et al., Applied Physics Reviews 2, 031301 (2015)

2. Oostinga et al., Nat. Materials 7, 151 (2007)

3. Allen et al., Nat. Comm. 3, 934 (2012)

4. [https://www.nature.com/articles/ncomms14552#auth-1] et al., Nat. Comm. 8, 14552 (2017)

5. Overweg et al., [https://arxiv.org/abs/1707.09282], [https://arxiv.org/abs/1709.00870]

4:20pm **2D+EM+MI+MN+NS-TuA7 GaN Microdisk Light-emitting Diode Display Fabricated on Graphene**, ***Youngbin Tchoe***, *K. Chung, K. Lee, M.S. Song, J.B. Park, H. Kim, J.Y. Park, G.-C. Yi,* Seoul National University, Republic of Korea

Microdisplay with high resolution, brightness, and efficiency with long-term stability and reliability are highly required for advanced display technologies. Inorganic semiconductors LEDs best suits this purpose because they can emit very high density of light from a small area and they have very high efficiency and long-term stability. To use inorganic LEDs for display applications, various lift-off and transfer techniques of inorganic thin films grown on single crystal substrates, such as sapphire or Si, were developed. However, achieving display devices using inorganic semiconductor thin films is still very challenging because of the limited size and high manufacturing cost of the single crystal substrates, as well as the complicated processes required for lift-off and assembly. To resolve this problem, growths of inorganic semiconductor nanostructures and thin films on graphene substrates have recently been proposed, since graphene has great scalability and extremely thin layered hexagonal lattice structure as an excellent substrate for GaN growth. Moreover, the inorganic semiconductors prepared on large-area graphene can be transferred easily to or grown on elastic substrates to meet the flexibility demand. Here, we suggest a method of fabricating ultrathin, high-resolution inorganic microdisplay based on individually addressable GaN microdisk LED arrays grown on graphene dots.

Here, we report on the fabrication and EL characteristics of ultrathin and individually addressable GaN microdisk LED arrays grown on graphene dots for microdisplay applications. GaN microdisks were prepared by epitaxial lateral overgrowth on patterned graphene microdots on SiO_2/Si substrates using MOVPE. After preparing the GaN microdisk arrays, *p*-GaN and InGaN/GaN multiple quantum well, and *n*-GaN layers were heteroepitaxially grown on the surface of the GaN microdisks. Ultrathin layers composed of GaN microdisk LED arrays on graphene dot were prepared by coating a polyimide layer and lifting-off the entire layers from the substrate. Then, single-walled carbon nanotubes (SWCNTs)/Ni/Au and SWCNTs/Ti/Au multiple electrode lines were formed on the top and bottom surface of GaN microdisk arrays in an aligned manner and crossing each other. The electrical and optical characteristics of the individually addressable GaN microdisk array on graphene dots were investigated by measuring their *I–V* curves and EL characteristics at various bending conditions. We also confirmed that the ultrathin micro-LED display worked reliably under flexible conditions and continuous operation mode.

4:40pm **2D+EM+MI+MN+NS-TuA8 Room Temperature Magnetron Sputtering and Laser Annealing of Ultrathin MoS_2 for Transistor Device Fabrication on Flexible Polymer Substrates**, ***Benjamin Sirota,*** University of North Texas; *N.R. Glavin,* Air Force Research Laboratory; *C. Arnold, A.A. Voevodin,* University of North Texas

Pulsed magnetron sputtering and subsequent laser annealing provide technologically attractive scalable route for producing two-dimensional (2D) semiconducting grade MoS_2 materials directly on the surface of flexible polymer substrates. In this study the room temperature magnetron sputtering was used to deposit 10 nm thick, amorphous MoS_2 films on

flexible PDMS as well as rigid SiO_2/Si substrates. This was followed by 248 nm pulsed laser annealing to produce polycrystalline 2H-MoS_2 over large areas. Raman and XPS analysis confirmed that pulsed laser annealing with about 1 mJ/cm^2 energy density had induced film crystallization from amorphous to hexagonal, while preserving MoS_2 chemical composition, and avoiding formation of oxide phases or damage to the temperature-sensitive polymer surface. Electrical measurements confirmed an order of magnitude improvement in electrical conductivity of the laser annealed films as compared to amorphous MoS_2. Top-gated field effect transistor (FET) devices with laser annealed sputter grown MoS_2 were directly fabricated on PDMS surfaces. Oxygen substitution of sulfur in sputter deposited MoS_2 and polycrystallinity of the laser annealed 2H-MoS_2 films resulted in low mobility values when compared to mechanically exfoliated and chemical vapor deposition grown single-crystal 2D MoS_2. However, the described approach is intrinsically scalable and provides a direct growth route for the fabrication of 2D transition metal dichalcogenide semiconducting devices on the surface of flexile and stretchable polymers.

5:00pm **2D+EM+MI+MN+NS-TuA9 Black Phosphorus: Fundamental Properties and Emerging Applications***, **Han Wang**,* University of Southern California **INVITED**

In this talk, I will discuss our recent work in developing novel electronic and photonic devices based on the anisotropic properties of black phosphorus (BP) and its isoelectronic materials such as the monochalcogenides of Group IV elements. High mobility, narrow gap BP thin film (0.3 eV in bulk) fill the energy space between zero-gap graphene and large-gap TMDCs, making it a promising material for mid-infrared and long wavelength infrared optoelectronics. Most importantly, its anisotropic nature within the plane of the layers allow for the realization of conceptually new electronic and photonic devices. Here, I will first present our work in understanding the fundamental electronic and optical properties of black phosphorus using a newly developed scanning ultrafast electron microscopy (SUEM) technique and photoluminescence spectroscopy. Our recent the study of bandgap tuning in BP and the demonstration of a polarization sensitive BP mid-IR detector will then be presented. In the second half of my talk, I will discuss our work on developing two dimensional materials based artificial synaptic devices for neuromorphic electronics, including emulating the heterogeneity in synaptic connections using the anisotropic properties of BP and a tunable memristive device as a reconfigurable synapse. I will conclude with remarks on promising future research directions of low-symmetry electronics based on anisotropic 2D materials and how their novel properties is expected to benefit the next-generation electronics and photonics technologies.

5:40pm **2D+EM+MI+MN+NS-TuA11 Patterned Growth of Hybrid Bulk-2D Tungsten Diselenide for Transistor Applications***, **Quinten Yurek**, I. Liao, D. Barroso, A.E. Nguyen, N. Duong, G. Stecklein, L. Bartels,* University of California, Riverside

As device dimensions shrink, surfaces and interfaces between materials make up a larger volume fraction of a device leading to degrading device properties in 3D materials. One solution is to use 2D materials, however these materials introduce additional challenges. For instance, high resistance Schottky barriers and a small number of free charge carriers in comparison to bulk materials. The effective mobility of field effect transistors (FETs) based on two-dimensional (2D) single-layer transition metal dichalcogenide (TMD) films is frequently limited by barriers at the contacts, as opposed to the native properties of the TMD material. Specifically, high resistance Schottky barriers form at the TMD/metal interface because of the film's thinness and resulting small number of carriers. Here we demonstrate a scalable single-step deposition method for nanoscale hybrid 2D/3D TMD structures encoded by lithographic patterning prior to deposition. By confining the metal contact to the bulk regions of WSe_2, the effective mobility is increased to nearly 100 cm^{2}V^{-1}s^{-1} with an on/off ratio >10^5 for bottom-gated devices (through 300nm of oxide), even for comparatively long channels (>5 microns) and absent other contact optimization. Our process involves lithographic patterning of a hafnium (IV) dioxide film onto the SiO_2/Si substrate prior to TMD growth. Bulk-like 3D WSe_2 is observed to grow at the location of the hafnia, while 2D single-layer material is grown in regions of bare SiO_2. Systematic evaluation of transport data allows us to extract Schottky barrier heights and other fundamental properties of our hybrid devices. We demonstrate that this process can be used to create devices with metal/3D TMD contacts, which exhibit a reduced Schottky barrier height, while continuing to use 2D TMD channels, which result in an excellent on-off ratio.

6:00pm **2D+EM+MI+MN+NS-TuA12 Enhanced Ionic Sensitivity in Solution-Gated Graphene-Hexagonal Boron Nitride Heterostructure Field-Effect Transistors***, A.D. Radadia, **Nowzesh Hasan**, B. Hou, A.L. Moore,* Louisiana Tech University

The charge transport in solution-gated graphene devices is affected by the impurities and disorder of the underlying dielectric interface and its interaction with the solution. This paper reports advancement in field-effect ion sensing by fabricating a dielectric isomorph, hexagonal boron nitride between graphene and silicon dioxide of a solution-gated graphene field effect transistor. Ionic sensitivity of Dirac voltage as high as -198 mV/decade for K^+ and -110 mV/decade for Ca^{2+} were recorded. Increased transconductance due to increased charge carrier mobility was accompanied with larger ionic sensitivity of the transconductance due to larger ionic sensitivity of the charge carrier mobility. These findings define a standard to construct future graphene devices for biosensing and bioelectronics applications.

Electronic Materials and Photonics Division
Room 101A - Session EM+2D+AN+MI+MP+NS-TuA

Solar/Energy Harvesting and Quantum Materials and Applications

Moderators: Yohannes Abate, Georgia State University, Nicholas Strandwitz, Lehigh University

2:20pm **EM+2D+AN+MI+MP+NS-TuA1 Plasmonic Metasurface Electrodes for Excitonic Solar Cells.***, **Deirdre O'Carroll**,* Rutgers, the State University of New Jersey **INVITED**

Excitonic organic solar cell technologies, while not currently competitive with inorganic-semiconductor analogues, can exhibit very small device embodied energies (due to comparatively low temperature and low energy-use fabrication processes), which is of interest for minimizing overall device cost and energy-payback time. To improve energy conversion efficiency in thin-film excitonic organic solar cells, light management using nanophotonic structures is necessary. Here, our recent work on improving light trapping in deeply-subwavelength excitonic organic semiconductor films using plasmonic metasurfaces will be presented. Numerous exciton-metasurface interaction phenomena, such as absorption-induced scattering, exciton-plasmon coupling and morphology-dependent surface plasmon light-trapping are observed to give rise to improved light trapping at different regions of the solar spectrum. Additionally, an approach to achieve the theoretical limits to the efficiency of excitonic organic photovoltaics (~22%) will be proposed that involves control of radiative recombination rate, and optimization of both photoluminescence quantum efficiency and photon recycling in organic semiconductor thin-films.

3:00pm **EM+2D+AN+MI+MP+NS-TuA3 Photoemission Electron Microscopy as a New Tool to Study the Electronic Properties of an Inhomogeneous Semiconductor for Photovoltaics***, M. Berg,* Sandia National Laboratories*; J. Kephart, A. Munshi, W.S. Sampath,* Colorado State University*; **Taisuke Ohta**, C. Chan,* Sandia National Laboratories

The energy positions of the valence and conduction electronic states with respect to the vacuum level are essential parameters to evaluate how the band gaps of semiconductors or Fermi-levels of metals line up with respect to each other. Such electronic structures of materials can be determined using photoemission spectroscopy (PES). PES measurements, however, remain challenging for inhomogeneous materials with nano- to micrometer lateral dimensions due to its mesoscopic probing area, typically no less than several microns. Photoemission electron microscopy (PEEM) is a cathode lens electron microscopy technique that combines photoemission imaging with spectroscopic modes of operation to provide PES spectra from areas less than one micron in size. Here, we present PEEM studies of the electronic structure of polycrystalline cadmium telluride (CdTe) thin films, a test case to examine the applicability of this new microscopic approach to photovoltaic materials. Post-deposition $CdCl_2$ treatment of CdTe is known to increase photovoltaic efficiency. However, the precise chemical, structural, and electronic changes that underpin this improvement are still debated. In this study, PEEM was used to spatially map the vacuum level and ionization energy of CdTe films, enabling the identification of electronic structure variations between grains and grain boundaries. *In vacuo* preparation and inert environment transfer of oxide-free CdTe surfaces isolated the separate effects of $CdCl_2$ treatment and ambient oxygen exposure. Qualitatively, grain boundaries displayed lower

work function and downward band bending relative to grain interiors, but only after air exposure of $CdCl_2$-treated CdTe. This study highlights the importance of probing the spatially varying electronic structure, elucidating the concurrent impacts of processing steps ($CdCl_2$ treatment and oxygen exposure) to develop a comprehensive picture of local electronic structure in an inhomogeneous semiconductor.

The PEEM work was performed at the Center for Integrated Nanotechnologies, an Office of Science User Facility (DE-AC04-94AL85000). M. B. & C. C. were supported by a U.S. DOE-EERE SunShot BRIDGE award (DE-FOA-0000654 CPS25859). T. O. was supported by the CINT user program and Sandia LDRD. 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-NA0003525. The views expressed in the article do not necessarily represent the views of the US DOE or the US Government.

3:20pm **EM+2D+AN+MI+MP+NS-TuA4 Modification of Bandgap for Lead-Free Double Perovskite $Cs_2AgInCl_6$ with Bi Doping***, **Hassan Siddique**, H. Da, X.Q. Wang, R.C. Dai, Z.P. Wang, Z.J. Ding, Z.M. Zhang,* University of Science and Technology of China

Lead halide perovskites have the excellent luminescent properties but exist some vital disadvantages such as instability and Pb toxicity. Lead-free double perovskites draw attention due to a possible candidate for environment-friendly materials. Direct bandgap lead-free halide of $Cs_2AgInCl_6$ is one of them. [1] In this work Bi doping $Cs_2AgInCl_6$ (CAIC) was successfully prepared. Bi dopant above 15% CAIC can restrict the parity forbidden transition responding to sub absorption peak around 600 nm.[2] On the other hand, the intensity of photoluminescence enhances with the increasing Bi dopant and touches the maximum around 30% doping, then gradually loses its intensity with further doping due to the mechanism of the concentration quenching at room temperature. Bi doping in CAIC can also modify the band gap. The absorption spectra indicate that the band gap reduces from 3.10eV without Bi doping to 2.68eV for $Cs_2AgIn_{0.30}$ $Bi_{0.70}Cl_6$. PL decay life time reveals the good intrinsic excitonic feature with less defect trappers [3]. Average life time for $Cs_2AgIn_{0.70}$ $Bi_{0.30}Cl_6$ is 490 ns which is least among all other $Cs_2AgIn_{(1-x)}Bi_xCl_6$ doping. Thermogravimetric analysis (TGA) result reveals thermal stability of $Cs_2AgIn_{0.30}$ $Bi_{0.70}Cl_6$ for the high-temperature 506°C. The Bi doping can decrease the band gap, restrict defect states, enhance PL and improve stability; these good performances make $Cs_2AgIn_{(1-x)}Bi_xCl_6$ more suitable for optoelectronic properties.

4:20pm **EM+2D+AN+MI+MP+NS-TuA7 Optimized (Quantum) Photonics***, **Jelena Vuckovic**,* Stanford University **INVITED**

Photonics has numerous applications ranging from optical interconnects, classical and quantum computing, to sensing (such as LIDAR and AR), and imaging. However, the state of the art photonics is bulky, inefficient, sensitive to environment, lossy, and its performance is severely degraded in real-world environment as opposed to ideal laboratory conditions, which has prevented from using it in many practical applications. Therefore, it is clear that new approaches for implementing photonics are crucial.

We have recently developed a computational approach to inverse-design photonics based on desired performance, with fabrication constraints and structure robustness incorporated in design process [1,2]. Our approach performs physics guided search through the full parameter space until the optimal solution is reached. Resulting device designs are non-intuitive (see Figure), but are fabricable using standard techniques, resistant to temperature variations of hundreds of degrees, typical fabrication errors, and they outperform state of the art counterparts by many orders of magnitude in footprint, efficiency and stability. This is completely different from conventional approach to design photonics, which is almost always performed by brute-force or intuition-guided tuning of a few parameters of known structures, until satisfactory performance is achieved, and which almost always leads to sub-optimal designs.

Apart from integrated photonics, our approach is also applicable to any other optical and quantum optical devices and systems. In recent years, color centers in diamond and silicon carbide (SiC) have emerged as a possible platform for implementation of quantum circuits [3,4]. We demonstrate how such quantum hardware can also be optimized to be robust, efficient, and scalable.

References

[1] A. Piggott et al, *Nature Photonics* 9, 374–377 (2015)]

[2] L. Su et al, *ACS Photonics* ASAP (2018)

[3] J.L. Zhang et al, Nano Letters 18 (2), 1360-1365 (2018)

[4] M. Radulaski et al, Nano Letters 17 (3), 1782-1786 (2017)

5:00pm **EM+2D+AN+MI+MP+NS-TuA9 Optical Properties of Single Silicon Vacancies in 4H-SiC***, H.B. Banks,* National Research Council Postdoc residing at the Naval Research Laboratory*; O. Soykal,* Sotera Defense Solutions, Inc, residing at the Naval Research Laboratory*; S.P. Pavunny, R.L. Myers-Ward, D.K. Gaskill, **Samuel Carter**,* U.S. Naval Research Laboratory

Defects in wide bandgap materials have generated substantial interest as promising systems for quantum information and quantum sensing due to bright, stable optical emission that is often coupled to long-lived spin states. One promising defect system is the silicon monovacancy in SiC (V_{Si}), which has a spin-3/2 ground state that can be optically polarized and maintain long spin coherence times even at room temperature. SiC is an attractive material in terms of mature growth and fabrication technology and also has a low natural abundance of nuclear spins, which reduces spin dephasing. While significant work has been performed to study the spin properties of V_{Si} for ensembles and even single defects, the optical properties and their connection to the spin system are less developed. Here we report on high resolution optical spectroscopy of single V_{Si} defects, specifically V2 defects, at low temperatures. Using laser excitation spectroscopy, the zero phonon line (ZPL) transitions corresponding to the $m_s=\pm1/2$ and $m_s=\pm3/2$ spin states are resolved, with a linewidth down to 70 MHz and a splitting of 1 GHz. While there is significant variation in the transition energies from one defect to another, the splitting of these lines is very uniform. We also find that emission from the V2 defect under resonant excitation of these lines rapidly decays on two very different timescales. Slow decay on a 10 ms timescale is attributed to photoionization of V_{Si} and can be prevented by periodically exciting the defect with a second laser at 745 nm. Fast decay on a µs or shorter time scale occurs due to a combination of intersystem crossing and spin polarization of the ground state. A significant difference in the decay rates of the two transitions is observed, which gives rise to spin-dependent photoluminescence intensity and non-resonant optical spin polarization. These results further our understanding of the connection between the optical and spin properties of this defect system that are necessary to optically control and readout the spin system as well as to develop a spin-photon quantum interface.

5:20pm **EM+2D+AN+MI+MP+NS-TuA10 Photoluminescence Studies on Patterned Silicon Vacancy Defects in Li Ion Implanted 4H-SiC for Scalable Quantum Device Applications***, **Shojan Pavunny**,* U. S. Naval Research Laboratory*; S.G. Carter, H.B. Banks, R.L. Myers-Ward, P. Klein,* U.S. Naval Research Laboratory*; E.S. Bielejec,* Sandia National Laboratories*; M.T. DeJarld, A.S. Bracker, E.R. Glaser, D.K. Gaskill,* U.S. Naval Research Laboratory

Recently, silicon vacancy defect centers (V_{Si}) in the CMOS compatible wide bandgap semiconductor SiC hexagonal polytypes have drawn great research interest for future applications in scalable quantum information and quantum sensing mainly due to their high electronic spin (S = 3/2) with a long coherence time at room temperature. Realization of future densely integrated quantum devices will greatly benefit from the ability to deterministically induce the desired V_{Si} density at the optimal location in the three-dimensional solid-state matrix with nanometer accuracy and excellent optical properties. With this motivation, we demonstrate targeted formation of arrays of V_{Si} ensembles as well as single defects in high-quality 4H-SiC epilayers by a direct, maskless focused ion beam implantation technique with a designed lateral separation of ~5 µm and a ~25 nm spot size. We have carried out high-resolution optical spectroscopy studies (E⊥c and E‖c) on these arrays, in which lithium ions are implanted at doses varying from 10^{12} – 10^{15} Li/cm^2 at a fixed energy of 100 keV to a depth of ~400 nm from the surface. Photoluminescence intensity and defect conversion yield with dose, photostability, fluorescence saturation, and V_1:V_1' intensity evolutions with temperature and excitation power were investigated. Results obtained from temperature dependent photoluminescence studies can provide key insights in the design and fabrication of scalable and reproducible three dimensional SiC quantum hybrid devices including photonic crystal cavities.

5:40pm **EM+2D+AN+MI+MP+NS-TuA11 Processing of Cavities in SiC Material for Quantum Technologies***, Rachael Myers-Ward, K. Hobart, K.M. Daniels, A.J. Giles, M.J. Tadjer, L.E. Luna, F.J. Kub, S.P. Pavunny, S.G. Carter, H.B. Banks, E.R. Glaser,* U.S. Naval Research Laboratory*; P.B. Klein,* Sotera Defense Solutions*; K. Qiao, Y. Kim, J. Kim,* Massachusetts Institute of Technology*; D.K. Gaskill,* U.S. Naval Research Laboratory

Silicon carbide is a material of interest for quantum computing and sensing applications owing to deep point defect centers with long spin coherence times (which characterizes the lifetime of the qubit), specifically the V_{Si} [1], divacancies [2] and nitrogen-vacancy centers [3]. These spin qubits have been isolated and coherently controlled, where V_{Si} have T_2 coherence times up to 100 µs [4] and divacancies to 1 ms [2], making these two defects of most interest to date. While the current spin coherence times have been shown to be as long as 1 ms, further improvements are needed to fully realize the potential of SiC for quantum applications. In this work, we create V_{Si} in epitaxial SiC and investigate fabricating the layers into microstructures suitable for using the V_{Si} photoluminescence (PL) emission. We have found 4H-SiC epitaxial layers grown under standard growth conditions and with varying doping densities from 10^{14} to 10^{18} cm^{-3} have no measureable V_{Si} present, as determined by confocal PL. To introduce V_{Si}, we used 2 MeV electron irradiation in doses ranging from 0.75 to 75 kGy. This results in V_{Si} PL ranging from single to ensemble emission within the confocal volume. Hence, we are able to tune the vacancy concentration.

In order to improve the indistinguishable photons from the V_{Si} and/or divacancies for real applications, photonic crystal cavities (PCC) are used to tune the emission energy [4]. Our PCC design consists of a planar array of cylindrical holes approximately 220 nm wide in a slab of SiC, ~300-500 nm thin having an area 50 x 50 μm^2, similar to [4]. To maximize the PCC quality factor, the slab should have a large index of refraction difference on the top and bottom; i.e., an air gap is desired under the slab. To achieve this goal, we have identified four fabrication methods to create the PCC. One of these techniques is to use remote epitaxy as an innovative approach which entails growing epitaxial graphene on a SiC substrate by means of Si sublimation. Silicon carbide is then grown on a monolayer of graphene to the desired film thickness [5]. This thin SiC layer is then transferred, facilitated by the weak van der Waal forces at the graphene/SiC substrate interface, to a substrate more amenable to cavity fabrication. All four fabrication methods will be presented in detail.

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6:00pm **EM+2D+AN+MI+MP+NS-TuA12 Investigation of Localized Electronic structures of PbSe Quantum Dot Superlattice on a Highly Oriented Pyrolytic Graphite (HOPG)***, Il Jo Kwak, S. Ueda,* University of California at San Diego*; A. Abelson, C. Qian, M. Law,* University of California, Irvine*; A.C. Kummel,* University of California at San Diego

Lead-Chalcogenide quantum dots are of interest due to the facility of adjustment of their electrical and optical properties. Using a colloidal self-assembly technique, extended arrays of nanocrystal QDs superlattices can be generated. The quantum confinement within individual QDs in the superlattice is relaxed and delocalization of wave functions occurs due to coupling of the QDs. In the QD solids, bulk-like electronic bands with a bandwidth of 100~200 meV are expected to form which yield much higher carrier mobility and diffusion length compared to weakly-coupled QDs; however, the electronic properties of such highly ordered QD arrays are not fully understood. The local density of state of a highly ordered monolayer PdSe superlattice was investigated by low temperature scanning tunneling microscopy.

A monolayer of PbSe QDs was prepared using the Langmuir Schaefer deposition technique. First, oleate-capped PbSe QDs dispersed in hexane were drop casted onto diethylene glycol surface. After the hexane was evaporated, a (111) in-plane oriented polycrystalline FCC superlattice was formed on the diethylene glycol surface. NH_4SCN solution was applied onto the oleate-capped PbSe superlattice film. The injection of NH_4SCN initiates the ligand exchange and phase transformation from an FCC to a simple cubic structure superlattice. A monolayer QD superlattice was prepared on a HOPG substrate. Afterward, the HOPG sample was loaded into a commercial UHV scanning tunneling microscopy chamber with a base pressure of $1x10^{-10}$torr. The sample was annealed to remove hydrocarbons and ligands from the surface. The topography of the QDs was observed with a tungsten tip. The STM images were acquired in constant current mode.

STM imaging showed the PbSe QD monolayer had 4-fold symmetry with an average inter QD spacing of 7nm. It is also found the height fluctuation of the QDs was 1nm indicating size variation of the QDs and imperfect crystal structure of the superlattice. Scanning tunneling spectroscopy was performed to investigate the electronic structure of the PdSe QDs using a variable z-mode with an external lock-in amplifier in the bias range of -2 to 2V. Single site STS showed resonant peaks from molecular orbitals of QDs before the ligand exchange process; however, the peaks were not observed after the ligand exchange due to necking between the QDs in the superlattice. In addition, the size of band gap was decreased as increasing the number of nearest neighboring QDs due to necking between QDs. Layer 2 QDs showed more p-type behavior than layer 1 QDs possibly due to the band bending effect at the interface of HOPG and QD superlattice.

Processing and Characterization of Air-Liquid, Solid-Liquid and Air-Solid Interfaces Focus Topic
Room 202A - Session PC+AS+BI+EM+NS+PB+SS-TuA

Progress in Industrial Processes and Characterization of Interfaces and Gas-Solid Interfacial Processes and Characterization

Moderators: Jeffrey Fenton, Medtronic, Xiao-Ying Yu, Pacific Northwest National Laboratory

2:20pm **PC+AS+BI+EM+NS+PB+SS-TuA1 Near Ambient Pressure XPS as a Standard Tool for True Non-destructive High-throughput Surface Chemical Analysis in Industrial Applications***, Andreas Thissen, P. Dietrich,* SPECS Surface Nano Analysis GmbH, Germany*; M. Kjaervik, W.E.S. Unger,* Bundesanstalt für Materialforschung und -prüfung (BAM), Germany **INVITED**

Since many decades X-ray excited Photoelectron Spectroscopy (XPS) or Electron Spectroscopy for Chemical Analysis (ESCA) is a well-accepted standard method for non-destructive chemical analysis of solid surfaces. Over the last years it has been possible to develop XPS instrumentation, that can work far beyond the standard conditions of high or ultrahigh vacuum: Near Ambient Pressure (NAP)-XPS, or ESCA under environmental conditions has become a method, that enters the field of standard surface chemical analysis and thus also the industrial sector. The main reason for this is the extremely fast solid surface analysis of any (degassing or non-degassing) material. Furthermore the environmental conditions around the sample avoid strong surface degradation due to vacuum or photon stimulated desorption. Even during the analysis the sample stays under its equilibrium conditions. Last, but not least the surrounding gas pressures of a couple of mbar acts as built-in charge neutralization on any type of material. This Environmental Charge Compensation (ECC) also decreases the negative influences of the characterization on the sample constitution. All this considered, NAP-XPS is capable of true non-destructive high throughput analysis of sample surfaces. The influence of the ambient conditions on quantification in XPS will be demonstrated and discussed.

After a short summary of the relevant development steps in NAP-XPS instrumentation over the last forty years, this presentation summarizes results of surface chemical analysis on insulating polymer samples, showing the spectroscopic resolution for C1s, F1s and O1s emission lines as a comparison for PET and PTFE. Using this, the application of ECC to bulk insulators (polymeric materials, ceramics), food samples, pharmaceuticals, and different biological materials is demonstrated. The unique ability to measure liquids, like water or aqueous solutions allow for studies of drying processes of liquid containing materials, like paper or absorber materials and finally also opens the field to medical applications, especially to studies of drug uptake into gram-negative bacteria embedded in biofilms.

The last part summarizes methods to analyze materials and device under working conditions. As examples reduction and reoxidation of catalytically active compounds and operando electrochemistry will be presented. An outlook to future industrial applications will be given.

ACKNOWLEDGEMENTS: This project has received funding from the EMPIR programme co-financed by the Participating States and from the European Union's Horizon 2020 research and innovation programme.

3:00pm **PC+AS+BI+EM+NS+PB+SS-TuA3 Surface Modifications in the Medical Device Field – Understanding of Methods to Control Adhesion and Reactions That Materials Undergo***, **Jeffrey Fenton**, B. Theilacker, A. Belu, B. Tischendorf,* Medtronic **INVITED**

Advances in materials chemistry have increased the need for deep understanding of process-material interactions and their role in device or component longevity. In the medical device industry advances are due in part to operating in a federally regulated environment where it may be necessary to understand not only what is the surface chemistry, but how various chemistries interact with the body, what is clean, or where does a foreign material originate. This presentation will highlight case studies where microscopy and surface characterization techniques were successfully applied to help further understand materials performance and interactions with the body.

Polymers used in the medical industry often undergo numerous clinical trials, laboratory testing, and development to understand the body and polymer interactions. The interactions these materials often undergo may potentially be at odds with the bulk material properties. For example, it may be desirable to modify surface properties of PTFE for polymer adhesion or modify a surface chemistry to improve bio compatibility. Methods of polymer surface modification will be presented that either enable or hinder the adhesion of a material to the surface.

Lithium ions generated during battery discharge may undergo interactions with components in or near the battery forming chemistries that may degrade battery performance or material stability. For example, lithium ions are known to interact with silica containing glass to form lithium silicide. The formation of these silicides can degrade the hermetic seal of feedthroughs. One method of studying these interactions is in-situ interfacial reactions characterization. This facile method of generating ions in-situ can be leveraged to understand what reactions may occur at a substrate surface.

The application of surface characterization techniques such as X-ray photoelectron spectroscopy (XPS), Time of Flight-Secondary Ion Mass Spectrometry (TOF-SIMS), and Scanning Electron Microscopy (SEM) provide unique insights into surface modifications and can help ensure the reliability of medical devices. These techniques support the development and manufacturing of Medtronic products such as packing and perfusion devices to improve processing conditions, understand failure modes, and surface-tissue interactions.

4:20pm **PC+AS+BI+EM+NS+PB+SS-TuA7 Ambient Pressure X-Ray Photoelectron Spectroscopy Studies of Catalytically Active Interfaces using Electron Transparent Graphene Membranes***, R. Mom, L. Frevel,* Fritz-Haber Institute of the Max Planck Society, Germany*; J.J. Velasco-Velez,* MPI CEC Mülheim, Germany*; T.E. Jones, M. Plodinec,* Fritz-Haber Institute of the Max Planck Society, Germany*; R. Schlögl,* MPI CEC Mülheim, Germany*; **Axel Knop-Gericke**,* Fritz Haber Institute of the Max Planck Society, Germany **INVITED**

Green production of hydrogen will be an important building block in the transition to a carbon-balanced economy and could be realized by electrolytic water splitting powered by cheap renewable energy sources. Water electrolysis is currently limited by the oxygen evolution reaction (OER) and development of the associated catalysts is proceeding slowly, mainly due to missing descriptors for activity and stability of working OER catalysts. Herein, we contribute to that emerging field with in situ XPS and NEXAFS on iridium anodes. In our in situ cell the catalyst is probed through a graphene layer, which traps an electrolyte layer around the catalyst and provides electrical contact for separated iridium nanoparticles. In this way we enhance spectroscopic signal from the active surface relative to the bulk of the catalyst and reduce mass transport problems. In taking advantage of these benefits, we found that the two well-known oxidation waves occurring before the OER onset are connected to the development of two different types of electron deficient oxygen species, which are bound to one (μ_1) or two (μ_2) iridium atoms. It appears that oxygen is not only a "non-innocent ligand", but rather a protagonist in the catalysis of the OER.

During the electrochemical reduction of oxygen, platinum catalysts are often (partially) oxidized. While these platinum oxides are thought to play a crucial role in fuel cell degradation, their nature remains unclear. We studied the electrochemical oxidation of Pt nanoparticles using in situ XPS. By sandwiching the particles between a graphene sheet and a proton exchange membrane that is wetted from the rear, a confined electrolyte layer was formed, allowing us to probe the catalyst under wet electrochemical conditions. We show that the behavior at the onset of Pt oxidation is influenced by the choice of proton exchange membrane, yet universally involves PtO_2 formation. The oxidation process is fast: even bulk oxide growth occurs on the sub-minute timescale. Thus, our observations indicate that PtO_2 may take part in the transient processes that dominate Pt electrode degradation.

5:00pm **PC+AS+BI+EM+NS+PB+SS-TuA9 The Influence of Density and Chemical Bonding on Atomic and Molecular Structures of Alcohols, Water and Oxides***, **Gabor A. Somorjai**,* University of California at Berkeley **INVITED**

Alcohol oxidation reaction over platinum nanoparticles with size ranging from 2 to 8 nm deposited on mesoporous silica MCF-17 was studied in the gas and liquid phases. Among methanol, ethanol, 2-propanol, and 2-butanol oxidations, the turnover frequency increased as the nanoparticle size became large in both reaction phases. The activation energy in the gas phase was higher than that in the liquid phase. Water co-adsorption decreased the turnover rate of all the gas and liquid phase oxidations except for the gas-phase 2-butanol case, while certain amount of water promoted 2-propanol oxidation in the liquid phase. Sum frequency generation vibrational spectroscopy (SFG) study and DFT calculation revealed that the alcohol molecules pack horizontally on the metal surface in low concentration and stand up in high concentration, which affects the dissociation of b-hydrogen of the alcohol as the critical step in alcohol oxidation.

Ice surfaces have water layers with thickness ranging from one monolayer at 100K to 30 layers of 273K. At the interfaces of two ice cubes, ice layers grow at the disappearing water interfaces (regelation). SFG studies of water surfaces show three peaks in the vibrational spectrum; "free OH^-", liquid like hydrogen bonded water, with half bilayer termination, and ice-like water, with bilayer termination, with more hydrogen bonds.

Most nanocatalysts are composed of highly dispersed transition metal nanoparticles on oxides. The interface between the metal nanoparticles and the oxides plays a crucial role in determining the catalytic performance of nanocatalysts. Due to non-adiabatic electronic excitation, energetic electrons in metals can be generated during exothermic chemical processes. The energy barrier formed at the metal-oxide interfaces leads to the irreversible transport of energetic, or hot, electrons. The dopants and impurities present on the oxides can generate additional charge carriers or oxygen vacancies that affect the catalytic activity. The accumulations or depletion of hot electrons on the metal nanoparticles, in turn, can also influence the catalytic reactions. In this talk, we outline recent studies of the role of metal oxide interfaces and characteristics of fast charge transfer between metals and oxides that lead to ionization of molecules at the interface. The molecular ions produce so-called acid-base reactions. The electronic configuration of metal-oxide nanocatalysts during catalytic reactions will be introduced and its influence on heterogeneous catalysis will be outlined.

5:40pm **PC+AS+BI+EM+NS+PB+SS-TuA11 Atomic Scale Observation of Oxidation and Reduction of Palladium Surface***, **Takehiro Tamaoka**, H. Yoshida, S. Takeda,* Osaka University, Japan

Reaction processes on metal surfaces under gas environment have been investigated in various research fields such as catalysis, gas sensing, and many more. Palladium is a well–known material which is used for hydrogen storage, hydrogen sensing, and exhaust catalysis. Therefore, the phase transition of palladium in hydrogen or oxygen has been extensively investigated by means of environmental transmission electron microscopy (ETEM). However, the oxidation and reduction process of palladium surface at the atomic scale remain poorly understood.

Here, we investigated the surface structure of a wedge–shaped palladium specimen in both hydrogen and oxygen by means of in-situ atomic resolution ETEM. Under ambient condition the surface of palladium is oxidized by several nanometers. After introducing hydrogen (100 Pa) in ETEM, the native oxide layer (PdO) was reduced to metallic fcc palladium even at room temperature. After exposure and exhaustion of hydrogen, we introduced oxygen (100 Pa) in ETEM. The palladium oxide was reproduced and the ETEM results show that the oxidation started from step edges and terraces and proceeded until the palladium surface was completely covered by the palladium oxide.

We also show that oxidation of palladium is dependent on the history of hydrogen exposure. When the duration of hydrogen exposure was over 90 min., we found that the surface was not oxidized. This was not due to bulk hydrogenation as demonstrated by our electron energy loss spectroscopy (EELS) results. We performed similar studies for the surface of platinum in oxygen after prolonged hydrogen exposure. However in platinum, the oxidation of the surface was not suppressed. This suggests that the process

for suppression of oxidation, after prolonged hydrogen exposure, exists for palladium and not for platinum.

From these results, we hypothesize possible processes that explain how the prolonged hydrogen exposure suppresses the oxidation of palladium surface. We will also present atomic-scale in-situ movies on the surface dynamics in palladium and platinum in various processing.

6:00pm **PC+AS+BI+EM+NS+PB+SS-TuA12 Polymorphism of Hydrogen-Bonded Clusters at the Vacuum-Solid Interface***, **Angela Silski**, J. Petersen,* University of Notre Dame*; R.D. Brown,* Clarkson University*; S. Corcelli, S.A. Kandel,* University of Notre Dame

Molecular self-assembly is an attractive bottom-up approach to nanostructure fabrication. Using molecules as building blocks and carefully tuning the non-covalent intermolecular interactions, unique nanostructured architectures can be designed. Given the structure/function relationship on the nano- and meso-scale, this bottom-up approach to designing new architectures is critical in the careful design of novel materials with desired chemical properties. In this study, the role of hydrogen bond donor/acceptor position in metastable cluster formation is explored using scanning tunneling microscopy (STM) with complementary density functional theory (DFT) calculations. We observe a metastable cyclic pentamer for isatin (1H-indole-2,3-dione) with DFT providing support for a cyclic structure stabilized by both NH...O and CH...O hydrogen bonds between neighboring molecules. The CH...O hydrogen bond is made between the 7-position proton acting as the hydrogen bond donor and the 3-position carbonyl as the hydrogen bond acceptor, and calculations indicate that the isatin pentamer structure is 12 kJ/mol more stable than the dimer on the per molecule basis. To probe the importance of the CH...O hydrogen bond in stabilizing the isatin pentamer, we compare to isatin derivatives: we replace the 3-position carbonyl with a methyl group (3-methyl 2-oxindole), the 7-position proton with a fluorine (7-fluoroisatin), systematically move the location of the hydrogen bond donor/acceptor by one position, (phthalimide), and remove of the primary hydrogen bond donor (1,2-indandione and 1,3-indandione). We show that cyclic pentamer formation is either altered or precluded as a result of these substitutions. Additionally, the importance of CH...O bonding in forming isatin pentamers is supported by electrospray ionization mass spectrometry (ESI-MS) measurements, which include a magic-number isatin pentamer peak, whereas the derivative molecules show little clustering under the same conditions. This work is significant in understanding the role that the position of the hydrogen bond donor/acceptor groups has on the resulting 2D supramolecular assemblies.

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-TuA1 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-TuA3 Electrostatic Charge of Solution-droplet in Plasma-coupled Micro Reactor***, **Tae Hwan Kim**, SW. 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.

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3:20pm **PS+EM+NS+SS-TuA4 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-TuA7 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.-J. Pireaux,* Université de Namur, Belgium*; N. Job,* Université de Liège, Belgium*; M.J. Gordon,* University of California at Santa Barbara*; R.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.

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4:40pm **PS+EM+NS+SS-TuA8 Synthesis of Hydrogenated Amorphous Carbon Nanoparticles using High-Pressure CH_4+Ar Plasmas and Their Deposition***,* ***Kazunori Koga****, S.H. 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.

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5:00pm **PS+EM+NS+SS-TuA9 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-TuA10 Femtosecond Laser Texturing of Plasma-immersed Ti to Create TiN***,* ***Chisung Ahn****, E. Barlaz, D.N. 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-TuA11 Modeling Chemical Reactions in Contact Glow Discharge Electrolysis***,* ***Bocong Zheng****, M. Shrestha, K.L. Wang, T. Schuelke, Q.H. 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-TuA12 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.

Reconfigurable Materials and Devices for Neuromorphic Computing Focus Topic
Room 203A - Session RM+EM+NS-TuA

IoT Session: Reconfigurable Materials and Devices for Neuromorphic Computing

Moderator: Brian Hoskins, National Institute of Standards and Technology (NIST)

2:20pm **RM+EM+NS-TuA1 Non-volatile Memories for Neuromorphic Computing***,* ***Alec Talin,*** Sandia National Laboratories **INVITED**

Inspired by the efficiency of the brain, CMOS-based neural architectures and memristors are being developed for pattern recognition and machine learning. However, the volatility, design complexity and high supply voltages for CMOS architectures, and the stochastic and energy-costly switching of memristors complicate the path to achieve the interconnectivity, information density, and energy efficiency of the brain using either approach. In my talk, I will review the latest advances in neuromorphic computing architectures based on deep neural networks implemented using CMOS and memristors and describe the challenges in achieving both high accuracy and energy efficiency using these devices. I will then discuss an alternative approach based on the non-volatile redox memory (NVRM): a device with a resistance switching mechanism fundamentally different from existing memristors, involving the reversible, electrochemical reduction/oxidation of a material to tune its electronic conductivity. The first type of NVRM that I will describe is based upon the intercalation of Li-ion dopants into a channel of $Li_{1-x}CoO_2$. This Li-ion synaptic transistor for analog computing (LISTA) switches at low voltage (mVs) and energy, displays hundreds of distinct, non-volatile conductance states within a 1V range, and achieves high classification accuracy when implemented in neural network simulations[1]. The second type of NVRM I will describe operates on a similar principle but is based on the polymer system PEDOT:PSS, and which we call the electrochemical neuromorphic organic device (ENODe) [2]. Plastic ENODes are fabricated on flexible substrates enabling the integration of neuromorphic functionality in stretchable electronic systems. Mechanical flexibility makes ENODes compatible with three-dimensional architectures, opening a path towards extreme interconnectivity comparable to the human brain.

1) E. J. Fuller et al., Advanced Materials 29, 1604310 2017.

(2) Y. B. van de Burgt et al., Nature Materials 16, 414 2017.

(3) S. Agarwal et al., IEEE 2017 Symposium on VLSI Technology Digest of Technical Papers, DOI: 10.23919/VLSIT.2017.7998164.

4:20pm **RM+EM+NS-TuA7 Memristor Neural Networks for Brain-Inspired Computing***,* ***Qiangfei Xia,*** University of Massachusetts Amherst **INVITED**

As CMOS scaling approaches its limits, it becomes more difficult to keep improving the speed-energy efficiency of traditional digital processors. To address this issue, computing systems augmented with emerging devices particularly memristors, offer an attractive solution. Memristors use conductance to represent analog or digital information. The dynamic nature of memristor with both long-term and short-term memories, together with its small effective size contributes to the energy efficiency in weight updating (training). The in-memory computing scheme in a crossbar breaks the 'von Neumann bottleneck' as the weights are stored locally in each device during computing. The read out (inference) is finished in one clock cycle regardless of the array size, offering massive parallelism and hence high throughput. The capability of using physical laws for computing in a crossbar enables direct interfacing with analog signals from sensors without energy- hungry analog/digital conversions.

We developed a Ta/hafnium oxide memristor with stable multilevel resistance, linear current voltage characteristics in chosen conductance ranges, in addition to high endurance and long retention. We further integrated the memristors with foundry-made transistors into large arrays. We demonstrated that the reconfigurable memristor networks are capable of analog vector matrix multiplication, and successfully implemented a number of important applications including signal processing, image compression and convolutional filtering. We also built a multilayer memristor neural network, with which we demonstrated in-situ and self-adaptive learning capability with the MNIST handwritten digit dataset. The successful demonstration of analog computing and in-situ online training suggests that the memristor neural network is a promising hardware technology for future computing.

5:00pm **RM+EM+NS-TuA9 Indium Phosphide Synaptic Device on Silicon for Scalable Neuromorphic Computing***,* ***Jun Tao****, D. Sarkar, R. Kapadia,* University of Southern California

Inspired by the superior capability of the brain, neuronal spiking, and synaptic behavior have been mimicked by the CMOS-based neuronal cell in hardware, which contains 6-12 transistors depending on specific functionality and the robustness of the design. However, the higher energy consumption and physical area have led researchers to look for architectures based on single device and novel materials.

In our work, utilizing thin-film vapor-liquid-solid growth method, we fabricated scalable Indium phosphide (InP) channel transistors directly on Si/SiO_2 wafer, which can emulate significant synaptic characteristics such as elasticity, short- and long-term plasticity, metaplasticity, spike number dependent plasticity and spike timing dependent plasticity, by modeling gate electrode as the pre-synaptic axon terminal, the drain electrode as the post-synaptic dendrite, and the gate oxide-semiconductor channel as the synapse junction, in which we also interpreted the FET channel conductance as the synaptic weight.

We also demonstrated that by controlling the charging and discharging of interfacial traps at the gate oxide-semiconductor stack, we can essentially engineer hysteresis of the synaptic device to customize the synapse behavior and modify the synapse weight non-linearly. It underpins optimal

selectivity of signal transduction and satisfies the key neuromorphic architecture characteristic—training and learn. Tuning hysteresis in a family of transfer characteristics in spike timing dependent plasticity (STDP) emulation, we attain maximum potentiation (depression) for the minimum positive (negative) interval time, which gradually decays down to elasticity, as we expected, indicating the scalable InP channel transistors on silicon as promising devices and platform for neuromorphic computation.

5:20pm **RM+EM+NS-TuA10 Ultra-low Power Microwave Oscillators based on Phase Change Oxides as Solid-State Neurons***, **Boyang Zhao**, J. Ravichandran,* University of Southern California

Voltage or current controlled oscillators are well-established candidates for solid-state implementations of neurons. Metal to insulator transition (MIT) based phase change electrical oscillators are one of the many candidates for solid-state neurons, but current implementations are far from the ideal performance limits of energy and time necessary to induce the transition. We propose the use of nanoscale, epitaxial heterostructures of phase change oxides such as VO_2, NbO_2 and oxides with metallic conductivity as a fundamental unit of a low power electrical oscillator, capable of operating as neurons for neuromorphic computing architectures. Our simulations such that such oscillators can operate in the microwave regime and overcome many of the power consumption issues plagued by phase change electrical oscillators.

5:40pm **RM+EM+NS-TuA11 Leveraging Nanodevice Volatility for Low Energy Computing Inspired from Nature***, **Alice Mizrahi**,* NIST/University of Maryland*; T. Hirtzlin,* Centre de Nanosciences et Nanotechnologies*; B. Hoskins,* NIST Center for Nanoscale Science and Technology*; A. Fukushima,* AIST*; A. Madhavan,* NIST Center for Nanoscale Science and Technology*; H. Kubota, S. Yuasa,* AIST*; N.B. Zhitenev, J. McClelland, M.D. Stiles,* NIST Center for Nanoscale Science and Technology*; D. Querlioz,* Centre de Nanosciences et Nanotechnologies, France*; J. Grollier,* UMR CNRS/Thales **INVITED**

Artificial neural networks are performing tasks, such as image recognition and classification, that were thought only accessible to the brain. However, these algorithms run on traditional computers and consume orders of magnitude more energy more than the brain does at the same task. One promising path to reduce the energy consumption is to build dedicated hardware to perform cognitive tasks. Nanodevices are particularly interesting because they allow for complex functionality with low energy consumption and small size. I discuss two nanodevices. First, I focus on stochastic magnetic tunnel junctions, which can emulate the spike trains emitted by neurons with a switching rate that can be controlled by an input. Networks of these tunnel junctions can be combined with CMOS circuitry to implement population coding to build low power computing systems capable of processing sensory input and controlling output behavior. Second, I turn to different nanodevices, memristors, to implement a different type of computation occurring in nature: swarm intelligence. A broad class of algorithms inspired by the behavior of swarms have been proven successful at solving optimization problems (for example an ant colony can solve a maze). Networks of memristors combined with CMOS circuitry can perform swarm intelligence and find the shortest paths in mazes. These results are striking illustrations of how matching the functionalities of nanodevices with relevant properties of natural systems open the way to low power hardware implementations of difficult computing problems.

Processing and Characterization of Air-Liquid, Solid-Liquid and Air-Solid Interfaces Focus Topic
Room Hall B - Session PC+AS+BI+EM+NS+PB+SS-TuP

Processing and Characterization of Gas-Liquid, Solid-Liquid, and Gas-Solid Interfaces

PC+AS+BI+EM+NS+PB+SS-TuP1 Operando Photoelectron Spectroscopic Study of Copper-based Oxide Semiconductor Interface with Water*, **Pitambar Sapkota**, S. Ptasinska,* University of Notre Dame*; A. Cabrera,* Instituto de Física, Pontificia Universidad Católica de Chile

The quest for suitable semiconductor photoelectrodes to build efficient and stable photoelectrochemical (PEC) cells for solar water splitting is continually growing in the material sciences and solar energy community. Along with good stability in aqueous media, such photoelectrodes should have suitable band-edges and band-gap energies properly matching both the water oxidation-reduction potential and the solar spectrum, respectively. Copper-based oxide semiconductors are promising candidates fulfilling these criteria, but little is known about the interfacial properties of these compounds with H_2O under operational conditions. Therefore, knowledge of their surface dynamics and interfacial reactions under realistic conditions is essential to improve our understanding of water-splitting mechanism, as well as to increase the stability and efficacy of PEC devices. Ambient pressure X-ray photoelectron spectroscopy was used to characterize the semiconductor surface and study the chemical reactions occurring at the interface under the reaction conditions. In this study, thin films of $CuFeO_2$ and $CuFe_{1-x}Ga_xO_2$ composites were exposed to various H_2O pressures and temperatures. Water interactions with the Cu-based oxide surface and the electronic structures of the surface atoms were evaluated from the Cu 2p, Fe 2p, C 1s and O 1s photoemission spectra to identify surface species newly formed.

PC+AS+BI+EM+NS+PB+SS-TuP2 Interfacial Water in Silicon-based Catalytic Motors*, **Jordi Fraxedas**, K. Zhang, B. Sepulveda, M.J. Esplandiu,* Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Spain*; X. Garcia, J. Llorca,* Institute of Energy Technologies, Department of Chemical Engineering and Barcelona Research Center in Multiscale Science and Engineering. Universitat Politècnica de Catalunya, Spain*; V. Perez-Dieste, C. Escudero,* Alba Synchrotron Light Source, Spain

Self-propelled motors that can harvest chemical energy from their surroundings to convert it in mechanical energy are at the cutting edge of nanotechnology for their appealing applications in e.g., environmental remediation and nanobiomedicine. A full understanding of the propulsion mechanism is crucial to improve their performance and controllability. Recently, a simple motor made of silicon and a noble metal that can operate with visible light has been developed [1]. The photoactivation mechanism and consequent motion is essentially based on the formation of electron/hole pairs. The holes are strong oxidizing agents for the species in the fluid producing protons and the electrons can diffuse towards the metal surface and participate in the counterpart reduction reaction. As a result, a gradient of proton concentration is formed in the fluid which builds-up an electric field driving the motion of the fluid through electro-osmosis. A mechanism that competes with the electro-osmotic process is based on diffusion-osmosis and is triggered by the redox decomposition exclusively at the metal surface and is not light responsive. We have recently shown that it is possible to enhance/suppress one mechanism over the other by tuning the surface roughness of the micromotor metal. Thus, the actuation mechanism can be switched from light-controlled electrokinetics to light-insensitive diffusio-osmosis by only increasing the metal surface roughness [2].

We have recently performed near ambient pressure photoemission studies of Pt/Si micromotor surfaces activated by oxygen plasma in water atmosphere at the NAPP endstation of the CIRCE beamline at the ALBA synchrotron near Barcelona. We have used p-type silicon substrates with one half covered with a Pt film with a thickness of about 50 nm grown by both e-beam and sputtering deposition. The results reveal a chemical gradient at the Si/Pt edge with a reduction of the Pt species. The analysis has to carefully consider the photochemical reactions induced by the combined action of the impinging beam and the water condensed at the surfaces. The beam induced damage evolves in two regimes: an initial preferential reduction of Pt4+ species and then the reduction of Pt2+ species, which increases the metallic character of the surface.

[1] M.J. Esplandiu, A. Afshar Farniya, A. Bachtold, ACS Nano, 9, 11234 (2015).

[2] K. Zhang, J. Fraxedas, B. Sepulveda, M. J. Esplandiu, ACS Appl. Mater. Interfaces 9, 44948 (2017).

PC+AS+BI+EM+NS+PB+SS-TuP3 Chiral Modification of Oxide-Supported Pt Surfaces: An in-situ ATR-IR Study*, **Yufei Ni**,* University of California, Riverside*; F. Zaera,* University of California, Riverside

The synthesis of enantiopure compounds is of great significance to the designing of pharmaceuticals and agro products. Possible methods for the manufacture of enantiopure chemicals include the separation of racemic product mixtures and reactions with other chiral chemicals, but perhaps the most promising procedure is the use of enantioselective heterogeneous catalysis. Chiral modification of catalytically active metals such as Pt and Ni is believed to be the most feasible approach to produce chiral heterogeneous catalysts. In this context, the use of cinchona alkaloids-modified Pt for the hydrogenation of activated ketones has drawn particular attention in the past few decades. A better understanding of how these chiral modifiers work to bestow enantioselectivity is still a prerequisite for the design of such catalysts.

In this project, we have used attenuated total reflection infrared absorption spectroscopy (ATR-IR) to investigate the details of the adsorption of such cinchona-alkaloid chiral modifiers on the Pt surfaces of supported catalysts in situ at the liquid-solid interface. It was determined that adsorption can be only observed after H_2 pretreatment of the catalyst. A comparison study in terms of adsorption strength was carried out using not only cinchona alkaloids such as cinchonidine and cinchonine but also simpler alternatives such as (R)- or (S)-(−)-1-(1-naphthyl) ethylamine (NEA), naphthylmethyl amine, and dimethyl naphthyl ethylamine.The adsorption strength of the different modifier molecules was found to be quite different among those compounds. This is illustrated by the fact that quinoline can displace s-NEA from Pt but not vice versa, for instance, and by the observation that when Pt is exposed to a solution containing both quinoline and s-NEA only the quinoline's signature peaks can be detected by ATR-IR spectroscopy. The ordering of the modifiers studied in terms of adsorption strength was found to correlate with their ability to chirally modify the Pt catalyst during the hydrogenation of unsaturated aldehydes.

Finally, it was found that NEA bonds to the metal through the nitrogen atom of its anime moiety, and not through the aromatic ring as commonly believed.

PC+AS+BI+EM+NS+PB+SS-TuP4 Wettability Behaviour of Synthesized Carbon Nanospheres and its Application as a Photocatalyst*, **Sonal Singhal**, A.K. Shukla,* IIT Delhi, India

Superhydrophobic and superhydrophilic surfaces have been widely investigated due to their diverse range of applications such as self-cleaning, microfluidic application in biotechnology, corrosion, Anti-reflecting coatings and microelectronic mechanical system etc. Here, a facile chemical vapour deposition method is reported for the synthesis of carbon nanospheres (CNSs). Henceforth, the morphology of as-synthesized sample is characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). X-ray diffraction (XRD), Raman spectroscopy and FTIR spectroscopy are used to determine the phase purity, chemical composition and presence of chemical bonds on the surface of synthesized CNSs. TEM and SEM results reveal the presence of CNSs with a diameter ranging from 50 nm to 400 nm. Raman spectroscopy confirms the presence of disordered carbon and low graphitization, which are also confirmed by TEM and XRD results. Optical properties of as-synthesized CNSs is investigated by UV-Vis spectroscopy and photoluminescence. Wettability behaviour of as-synthesized carbon nanospheres is investigated by contact angle measurements. CNSs shows a water contact angle of 152^0, which confirms the fabrication of superhydrophobic carbon nanosphere surface. After the proper explanation of wettability behaviour, it also discusses the application of as-synthesized CNSs as a photocatalyst. As it is well known, catalyst enhances the chemical reaction rate without changing its properties. Therefore, various kind of catalysts has been developed for the purpose to enhance the catalysis for environmental applications. Among different materials, carbon-based materials are widely used as a catalyst support due to their excellent properties. Considering these facts, the degradation of an organic pollutant under UV light is discussed here using CNSs.

PC+AS+BI+EM+NS+PB+SS-TuP5 Thermally Driven Solid-solid Li^+ Transfer into Nanostructured TiO_2, ***Tiffany Kaspar**, T. Varga,* Pacific Northwest National Laboratory*; D.A. Shapiro,* Advanced Light Source, Lawrence Berkeley National Laboratory*; A. Martinez, Y. Shin, K.S. Han, M.-S. Lee, S. Thevuthasan, V. Murugesan,* Pacific Northwest National Laboratory

Due to their good chemical stability, strong oxidation capability, and desirable lithium electrochemical activity, nanostructured titanium dioxide (TiO_2) anode materials have received considerable attention recently. Decreasing the particle size to 10-20 nm can increase the electrochemical capacity to 200-300 $mAhg^{-1}$. Furthermore, nanostructured TiO_2 anodes are non-toxic and would be suitable for cost effective mass production. Among the rutile, anatase, and brookite polymorphs of TiO_2, anatase nanoparticles have shown the best Li ion insertion properties and maximum reduction, indicating increased Li ion intercalation into the material. Here, we have synthesized 10-20 nm anatase TiO_2 nanoparticles and contacted them with solid Li- bis(trifluoromethanesulfonyl)imide (LiTFSI) as a function of temperature to understand the chemical and structural effects associated with thermally driven solid-solid Li^+ transfer to, and intercalation in, TiO_2 nanoparticles. We have used a combination of x-ray photoelectron spectroscopy (XPS), Ti L-edge scanning transmission x-ray microscopy (STXM), Raman spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy to gain a fundamental understanding of the structural evolution of TiO_2 nanoparticles during Li^+ intercalation. Our results indicate that thermally driven solid-solid Li^+ transfer to TiO_2 has occurred, and altered the TiO_2 structure at the edges of the agglomerated nanoparticles.

2D Materials Focus Topic
Room 201B - Session 2D+AM+EM+NS-WeM
Dopants, Defects, and Interfaces in 2D Materials

Moderator: Eric Pop, Stanford University

8:00am **2D+AM+EM+NS-WeM1 Carbon Doping of 2D Transition Metal Dichalcogenides by Plasma Enhanced CVD**, ***Yanfu Lu***, *F. Zhang, S. Sinnott, M. Terrones,* The Pennsylvania State University

Doping of 2D transition metal dichalcogenides has been discovered to be an effective way to tune the electronic structure and modify the lattice structure at the surface. The n-type and p-type doping of monolayer MoS_2/WS_2 heterostructures may enable the fabrication of field-effect transistors of ultra-low thickness. Plasma enhanced chemical vapor deposition provides a stable and controllable approach for introducing carbon dopants to monolayer WS_2. Photoluminescence measurement indicates that the band gap of C-doped WS_2 decreases by 0.17 eV. Corresponding first principles calculations provide the correlation between the position and chemical saturation of the carbon dopants and the electronic structure of the system. To verify covalently bonded dopants, we use Raman spectroscopy, X-ray photoelectron spectroscopy, and scanning transmission electron microscopy to examine the pristine sample and carbon-doped samples. Subsequent I-V characteristics measurements prove p-type doping and the energy band diagram. Finally, the mechanism associated with and, more importantly, the structure-property relationship of chalcogen doping are analyzed. The resulting new insights of transition metal dichalcogenide-based heterostructures and alloys are discussed.

8:20am **2D+AM+EM+NS-WeM2 Methoxy Formation Induced Defects on MoS_2***, ***Duy Le***, University of Central Florida*; P. Evans,* University of Nebraska - Lincoln*; Z. Hooshmand,* University of Central Florida*; T.B. Rawal,* Oak Ridge National Laboratory*; L. Bartels,* University of California, Riverside*; P.A. Dowben,* University of Nebraska-Lincoln*; T.S. Rahman,* University of Central Florida

Defects are known to play an important role in determining the chemical properties of otherwise inert MoS_2 basal plane. Here we report our joint experimental and theoretical study of the adsorption and reaction of methanol on the MoS_2 basal plane to determine the factors that control system reactivity. We find that exposure of the MoS_2 basal plane to methanol leads to the formation of adsorbed methoxy and coincides with sulfur vacancy generation and that the methoxy moieties bind to molybdenum, not sulfur, while some adsorbed methanol is readily desorbed near or slightly above room temperature. Our calculations also suggest that the dissociation of methanol via O–H bond scission occurs at the defect site (sulfur vacancy), followed subsequently by formation of a weakly bound H_2S species that promptly desorbs from the surface with creation of a new sulfur vacancy, in great agreement with photoluminescence and scanning tunneling microscopy data that show clear evidence of the sulfur vacancy creation on the MoS_2 surface, after exposure to methanol [1].

[1] P. Evans et al, J. Phys. Chem. C (2018). DOI: 10.1021/acs.jpcc.8b02053

* Work supported in part by DOE grant DE-FG02-07ER15842

8:40am **2D+AM+EM+NS-WeM3 Defect Engineering of 2D Materials for Advanced Electronic Devices**, ***Gwan-Hyoung Lee,*** Yonsei University, Republic of Korea **INVITED**

Two-dimensional (2D) materials have brought a great deal of excitement to nanoscience community with their attractive and unique properties. Such excellent characteristics have triggered highly active researches on 2D material-based electronic devices. New physics observed only in 2D semiconductors allow for development of new-concept devices. Assembly of 2D blocks for van der Waals heterostructures also provide a big playground for engineers and physicists to investigate unprecedented properties of 2D materials and fabricate multi-functional electronic devices. However, atomically thin 2D materials, such as graphene and transition metal dichalcogenides (TMDs), have only two surfaces at top and bottom without a bulk so that they are very sensitive to environment. In other words, properties of 2D materials can be altered easily by surface modification. In this talk, I will show novel approach to fabricate high performance 2D electronic devices by utilizing various surface treatments, such as fluorination and hydrogenation of graphene and layer-by-layer oxidation of MoS_2. When different types of defects, such as sp^3 bonds and vacancies, are induced on the surface of graphene, the electrical properties of graphene can be tuned. With mild plasma treatment, MoS_2 can be oxidized layer-by-layer and monolayer MoS_2 can be fabricated from the multilayer MoS_2. These surface treatment techniques can be used for fabrication of high performance graphene devices and MoS_2 optoelectronic devices. Defect engineering of 2D materials holds a great promise in engineering the 2D materials and fabricating advanced electronic devices of 2D materials.

9:20am **2D+AM+EM+NS-WeM5 Modeling Defects and Electron-electron Interactions in Low-dimensional Materials**, ***Daniel Gunlycke***, *C.E. Ekuma,* U.S. Naval Research Laboratory

While each nanoscale structure in a low-dimensional material can exhibit a variety of properties, the odds are that it will be (1) sensitive to defects and (2) strongly influenced by electron-electron interactions. The ratio of defect sites to pristine sites naturally increases, as structures become smaller. Electron localization can furthermore dramatically magnify the role of defects. In low-dimensional materials, dielectric screening is generally less effective, reducing the tendency for electronic interactions to become uniform across the sites in the materials. Despite the importance of both defects and electron-electron interactions, the properties of low-dimensional materials are often investigated in the absence of one or the other. This not only creates uncertainty over the predictions but could entirely miss certain physical phenomena, including insulator-to-metal transitions. In this presentation, we will discuss a general first-principles-based approach to explore realistic low-dimensional structures that explicitly accounts for both defects and electron-electron interactions [1]. It is based around a generalized Anderson Hamiltonian and applies density functional theory, as well as dynamical mean-field theory. We will also present electronic and optical properties of two-dimensional materials obtained using our method and discuss the potential for using defect engineering for improved solar cell performance.

[1] C. E. Ekuma, V. Dobrosavljevic, and D. Gunlycke, *Physical Review Letters* **118**, 106404 (2017)

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9:40am **2D+AM+EM+NS-WeM6 Post-Synthesis Modifications of Two-Dimensional $MoSe_2$ or $MoTe_2$ by Incorporation of Excess Metal Atoms into the Crystal Structure**, ***Paula Mariel Coelho,*** University of South Florida*; H. Komsa,* Aalto University, Finland*; H. Coy Diaz, Y. Ma,* University of South Florida*; A.V. Krasheninnikov,* Institute of Ion Beam Physics and Materials Research, Germany*; M. Batzill,* University of South Florida

Modifications of $MoSe_2$ and $MoTe_2$ with metallic mirror twin grain boundaries (MTB) in films grown by molecular beam epitaxy have been previously reported [1,2]. The goal of the study presented here has been to understand the formation-mechanism of MTB networks and apply this gained knowledge for controlled modifications of these 2D materials. In a combined scanning tunneling microscopy and density functional theory approach we demonstrate that excess Mo can easily diffuse into the pristine $MoSe_2$ or $MoTe_2$ (but not into MoS_2) layer and cause crystal modifications into Mo-rich twin grain boundaries. Vapor deposited Mo atoms are first incorporated by diffusing into interstitial (or split-interstitial) sites. Then, further Mo-atoms incorporate into the crystal structure to form triangular, Mo-rich grain boundary loops. Only after a critical density of MTBs is reached, Mo is no-longer absorbed by the 2D-crystal sheet and Mo-clusters start to form at the surface. The energetics and barriers for Mo-incorporation is calculated by DFT and shows that the formation of twin grain boundaries in the presence of excess Mo is favorable for $MoTe_2$ and $MoSe_2$, but not for MoS_2 - in agreement with the experiment. The achievable dense networks of MTBs constitute a new Mo-rich metallic phase that may be used for controlled electric contacts or creation of active sites in electro-catalysis [4] and thus adding new functionalities into transition metal dichalcogenide-based materials and devices. Moreover, DFT simulations suggest that this mechanism for incorporation of transition metals is not limited to Mo. This enables modification of the materials properties by heteroatom dopants and initial experimental work demonstrates the incorporation of both Ti and V. V-interstitials in $MoTe_2$ are predicted to have a magnetic moment and magnetic hysteresis curves indicate the induction of ferromagnetism in $MoTe_2$ by doping the material with less than 1% of V interstitials.

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11:00am **2D+AM+EM+NS-WeM10 Dry Cleaning and Doping of MX_2 for Contact Engineering**, ***Daniil Marinov**,* IMEC, Belgium*; J. Ludwig,* IMEC & KU Leuven, Belgium*; D. Chiappe,* IMEC, Belgium*; E. Voronina, T. Rakhimova,* Skobeltsyn Institute of Nuclear Physics, Lomonosov Moscow State University*; J.-F. de Marneffe, I. Asselberghs,* IMEC, Belgium*; S. De Gendt,* IMEC, KU Leuven, Belgium

Two-dimensional transition metal dichalcogenides (e.g. MoS_2, WS_2) are promising materials for a number of electronic and optoelectronic applications. Wafer-scale integration of these materials into sophisticated devices requires atomic-scale control of the processing steps such as deposition, etch, clean and doping. Reduction of the contact resistance is a major roadblock towards demonstration of high-performance devices. Significant Schottky barrier at the metal-MX_2 interface as well as surface contamination (e.g. by polymer residues) are the main factors contributing to the high contact resistance in fabricated MX_2 devices. In this study, a fully dry cleaning and doping technique is developed with a particular focus on contact engineering.

We demonstrate that a remote H_2 plasma is efficient for removal of organic residues from MX_2 surfaces. However, sulfur can be also stripped from the topmost layer by reactive H atoms. The main challenge is thus to precisely control the sulfur loss while maintaining the cleaning efficiency. At high substrate temperature, a 200 nm PMMA layer can be fully removed selectively to a single layer of WS_2 without damaging the 2D material (as confirmed by photoluminescence measurements). At low substrate temperatures significant S-vacancy formation was observed. Surface temperature is therefore the key parameter for controlling the reactivity of H atoms on WS_2.

Controllable formation of sulfur vacancies opens routes for substitutional doping. After H_2 plasma strip, WS_2 and MoS_2 samples were exposed to a flow of molecular gases (Cl_2, CO, OCS) without igniting the plasma. It is shown that Cl_2 and OCS can react with H_2 plasma treated MX_2 forming stable surface groups. Ex-situ conductive AFM measurements confirm that molecular doping prevents the loss of conductivity (that is observed after H_2 plasma alone). Moreover, OCS and Cl_2 exposure enhances electrical current injection in the material through grain boundaries and edges. The latter effect is beneficial for contact resistance reduction on MX_2.

To gain a deeper insight in the observed surface phenomena, DFT simulation of the interaction of atomic (H, Cl, F) and molecular (OCS, Cl_2) species with MX_2 surface was performed. S-vacancy creation by atomic hydrogen via formation of gas phase H_2S was observed in simulations, in qualitative agreement with the experiments. Moreover, dissociative adsorption of Cl_2 and OCS in S-vacancy sites is predicted by the DFT model.

Dr D. Marinov has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No 752164.

11:20am **2D+AM+EM+NS-WeM11 Deep Learning for Atomically-Resolved Scanning Transmission Electron Microscopy Experiments on 2D Materials**, ***Maxim Ziatdinov**, S.V. Kalinin,* Oak Ridge National Laboratory

Understanding fundamental atomic-scale mechanisms behind solid state reactions and phase transformations is critical for optimizing functional properties of technologically relevant materials. Recent advances in scanning transmission electron microscopy (STEM) have allowed to visualize dynamic processes in solid state systems, induced by thermal or chemical stimuli or electron beam, on the level of individual atoms and single atomic defects. However, while there have been multiple STEM studies on materials structure evolution, the materials-specific knowledge on the kinetics and thermodynamics of these processes and atomic potentials is almost non-existent, which is mainly due to the inherent limitations of the current (semi-)manual image analysis techniques. Here we demonstrate an approach based on deep convolutional neural networks for automated analysis of dynamic STEM data from 2-dimensional materials, such as monolayer WS_2, under e-beam irradiation. Our approach allows to create a library of atomic defects, explore subtle atomic distortions around the defects of interest and map chemical transformation pathways on the atomic level. We specifically show how the developed framework can be used for extracting diffusion parameters of sulfur vacancies in WS_2 and for studying transformation pathways for Mo-S complexes, including detailed transition probabilities.

11:40am **2D+AM+EM+NS-WeM12 Magnetic Doping in 2D MBE-grown-$MoSe_2$/graphene Heterostructures Studied by Photoelectron Spectroscopy and Band Structure Imaging**, ***Maxime Gay**, O.J. Renault,* CEA-LETI, France*; MT. Dau, C. Vergnaud, M. Jamet,* CEA-INAC-SPINTEC, France

2D TMDCs present a unique combination of electronic and mechanical properties such as a direct bandgap, strong spin-orbit coupling and K-valley inequivalence, with an atomic-scale thickness [1]. Introducing magnetic phases into these materials opens exciting perspectives towards spin control in magnetic tunnel junctions. To date, magnetism in 2D systems was mostly studied by theoretical calculations. Within the diluted magnetic semiconductors model, transition metal atoms from the monolayer are substituted by a few Mn, Fe or Co atoms [2-4].

Our study focuses on Mn-doped-$MoSe_2$ monolayers, grown by molecular beam epitaxy on graphene, and characterized by photoemission techniques (XPS, kPEEM) coupled with observations at different scales (DRX, TEM). Before doping, we found that the in-plane lattices of graphene and $MoSe_2$ are aligned with each other and that a bandgap opens in the graphene around the Fermi level [5-6]. After Mn doping, the obtained Mn insertion is measured up to 15% by XPS. The influence of Mn doping on the band structure of $MoSe_2$/graphene heterostructure will be presented and discussed.

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Electronic Materials and Photonics Division
Room 101A - Session EM+AN+MI+SS-WeM

Surface and Interface Challenges in Electronics and Photonics

Moderators: Andy Antonelli, Nanometrics, Michael Filler, Georgia Institute of Technology

8:00am **EM+AN+MI+SS-WeM1 Few Monolayer Atomic Layer Deposition (ALD) to Engineer New Surfaces and Interfaces**, ***Parag Banerjee**,* Washington University in St. Louis **INVITED**

Atomically precise modification of surfaces and interfaces with few monolayer material leads to improved understanding and significant enhancements in properties, performance and reliability of heterogeneous materials and devices. This talk highlights the impact of few monolayer insulators, wide bandgap semiconductors and metals, deposited using atomic layer deposition (ALD) on a variety of surfaces and interfaces with direct relevance to electronic and photonic devices.

The first part of this talk deep dives into the process science of ALD in its early cycles. The nature and structure of few monolayer ALD films is highlighted. In particular, configurational state and entropy of adlayers during every half-cycle of ALD[1] is exploited to exquisitely manipulate nucleation and growth of metallic Ru thin films.[2]

In the second part of this talk, applied aspects of few monolayer engineering of surfaces and interfaces is discussed. Case studies included are the non-linear optical phenomena on Au-Al_2O_3 and Au-ZnO surfaces,[3] high performance photocatalysts for CO_2 photoreduction,[4] improved optoelectronic responses from surface passivated CuO nanowires[5] and few monolayer Ta_2O_5 to improve reliability of electrochromic windows.[6]

Regardless of the application, ALD at its ultimate thickness limit holds true potential for surface and interface engineering. The control of this process appears to be remarkably simple and yet, has hidden complexities that continue to push the boundaries of discovery of new materials and concept devices.

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8:40am **EM+AN+MI+SS-WeM3 Lattice-alignment mechanism of SiGe on Sapphire***, **HyunJung Kim**, National Institute of Aerospace; S. Choi,* NASA Langley Research Center

In the conventional heteroepitaxy processes, the deposition of dissimilar materials has been made with the same or similar crystal structure and perfect or nearly matching lattice constants, such as Ge/Si (diamond cubic), InAs/GaAs (zinc-blende), and GaN/Al_2O_3 (hexagonal/trigonal). On the other hand, the super-heteroepitaxy of two semiconductors with dissimilar crystal structures such as SiGe (diamond cubic)/Al_2O_3 (trigonal) is not readily achievable but requires scrupulous manipulation of growth conditions for single crystal formation. Epitaxial growth patterns of SiGe on *r*-plane and *c*-plane of sapphire substrates show 90°-rotated and 60°-rotated twin defects, respectively [1,2].

A team at NASA Langley Research Center developed a technique for super-hetero-epitaxy of single crystal SiGe growth; diamond-cubic structure of SiGe on trigonal structure of the *c*-plane sapphire substrate by a transformed lattice structure under a new lattice-alignment model [2]. Although the growth conditions were effective for the formation of single crystal film, how the mechanism or physics of single crystal formation of SiGe at the interface of sapphire was not theoretically and experimentally defined with the order of atomic scale level in arrangement. This work presents the interfacial image of SiGe/Al_2O_3 using high-resolution transmission electron microscope (HRTEM) to show the SiGe/Al_2O_3 interfacial bonding for superheteroepitaxy mechanism. The first two atomic layers of the SiGe are Si-rich where Si atoms match with the surface oxygen lattice of the Al_2O_3 substrate. After the Ge composition increases, the monolayer spacing is also increased due largely to the dominance of Ge composition since the lattice constant of Ge is bigger than that of Si. These results highlight the importance of a cleanliness of sapphire substrate, the Si-affinity to oxygen that ties up Si- of SiGe with the oxygen of sapphire, and eventually causing the deformation of SiGe cubic structure for super-heteroepitaxy [3]. From the essential understanding of the SiGe/Al_2O_3 interface mechanism, both low temperature SiGe super-heteroepitaxy and the III-V or II-VI semiconductor epitaxy are possible.

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9:00am **EM+AN+MI+SS-WeM4 An Effort to Resolve Band Offset Anomalies in ZnO/GaN Heterostructures***, **Monu Mishra**[1], A. Gundimeda, V. Vandana, G. Gupta,* CSIR-National Physical Laboratory, India

Gallium Nitride (GaN) and Zinc Oxide (ZnO) are well established wide band gap (WBG) semiconductors facilitating potential application in futuristic energy-efficient opto/micro-electronics technology. Despite of owing the merits of both semiconductors, the understanding of ZnO/GaN heterostructures is still posing challenges. The available reports display anomalies amongst calculated valence band offset (VBO) and defect state of ZnO/GaN interface. The influence of surface and interfacial properties perturbs the electronic structure, localized charge density and defect states at the interface, yet the impact of these properties on VBO requires more scientific attention. Hence, sharp interfaces of ZnO/GaN heterostructures (ZnO thickness = 2, 5 and 8 nm) were fabricated via atomic layer deposition (ALD) of ZnO on MOCVD grown highly crystalline GaN epilayer and further investigated by HR-XPS, UPS and PL spectroscopy. The impact of ZnO thickness on band bending (upwards & downwards), surface/interface dipole strength and defects states (vacancies, interstitials, donor/acceptors etc.) on valence & conduction band offsets (VBO/CBO) were thoroughly analysed. It was observed that the VBO at the interface was reduced via 0.6 eV as the ZnO thickness was increased from 2 nm to 8 nm which was ascribed to interface dipole strength along with dramatic change in localized BB (downwards-flatband-upwards). A type-II band alignment was perceived at all ZnO/GaN interfaces though the nature & contribution of defects states (especially oxygen vacancies and zinc interstitials) varied incommensurately. The defect band spectra revealed a blue shift (~502 eV) which correspond to the conversion of yellow-green emission in ultrathin ZnO/GaN heterostructure (2 nm ZnO) to characteristic green emission in bulk ZnO. The analysis revealed that the thickness of ZnO overlayer in ZnO/GaN heterostructure significantly alters the electronic structure and defect states at the interface and thus the resolution of anomalies in the present analysis would be useful for the fabrication of ZnO/GaN heterostructure based efficient optoelectronic devices.

9:20am **EM+AN+MI+SS-WeM5 Stress Relaxation in the Si-SiO2 System and its Influence on the Interface Properties***, **Daniel Kropman**, T. Laas,* Tallinn University, Estonia*; A. Medvids,* Riga Technical University, Latvia

It is known that internal mechanical stresses (IMS) due to the differences in the thermal expansion coefficients between films and substrates and lattice mismatch appear in the Si-SiO_2 system during the process of its formation and that point defects (PD) generation and redistribution could be used to reduce partially the surface stress. However, this process on the atomic scale is till not studied. The goal of the present report is to investigate the stress relaxation mechanism in the Si-SiO_2 system using EPR, IR absorption spectroscopy, scanning elektron microscopy (SEM) and samples deflection measurements. PD density and stresses in the Si-SiO_2 system were varied by oxidation condition (temperature, time, cooling rate, ambient) and by Si_3N_4 deposition on SiO_2. Different sign of the thermal expansion coefficient of the SiO_2 and Si_3N_4 on Si allow to modifay the IMS at the interface. It has been found that samples deflection decreases or increases simultaneously with EPR signal intensity depending on the oxidation condition (temperature).

At oxidation temperature 1100^{0}C the deflection of the samples(h) decreases with the increase of EPR signal intensity (vacancies),while at a oxidation temperature 1200^{0}C EPR signal (I) and deflection increase simultaneously. Those allows to suggest that at lower oxidation temperature PD (vacancies) reduce the tensil IMS in Si, while at higher oxidation temperature compressive IMS created PD in SiO_2 (E' centers).At an intermediate oxidation temperature tensil stresses in Si and compressive stresses in SiO_2 may bee equal and compensate each others. It has been find that at oxidation temperature 1130^{0}C IMS at the Si-SiO_2. interface are lower than at 1100^{0}C and 1200^{0}C. Lower defect dencity on samples crossection microphotos obtained by SEM and PD dencity diminishing.in samples oxidized at 1130^{0}C confirmed thise suggestion.In Fig,2 the EPR signal and IR absorbtion line-width dependence on the oxidation time is shown. It can bee seen ,that EPR signal and IR absorbtion line-width at 1100 cm^{-1} dependence on the oxidation time (oxide thickness) is nonmonotonous and depended on the cooling rate .In slowly cooled samples the increase of the EPR signal is accompanied by the decrease of $\Delta\nu$ but,in fast cooled samples EPR signal and $\Delta\nu$ increase simultaneously with increase oxidation time.

Absent of the cooling rate influence on the PD density and $\Delta\nu$ dependence on the oxidation time at I(t) and $\Delta\nu$(t) dependence intersection points show, that IMS by an appropriate choice of the SiO_2 film thickness dissapear.

9:40am **EM+AN+MI+SS-WeM6 Unique Sensitivity to Deep Trap States Demonstrated by CREM of Broad Bandgap Dielectric Layers***, **Hagai Cohen**,* Weizmann Institute of Science, Israel*; K.X. Steirer,* Colorado School of Mines

Chemically resolved electrical measurements (CREM) present an efficient and sensitive means for studies of structural-electrical inter-relationships in heterostructures. Operated in-situ to x-ray photoelectron spectroscopy (XPS), the technique is yet far from being fully exploited. Recent progress in our CREM instrumentation has, however, opened new opportunities to which this report is dedicated. Using broad-bandgap dielectric layers, such as SiO_2, SiON and ZnOS, we tested the CREM resolving power and sensitivity to charge trap states. These experiments yielded band diagrams with fine details on charge traps, which typically require the application of

[1] **National Student Award Finalist**

advanced optical techniques combined with the electrical characterization tools.

In addition, an intriguing process of doubly triggered conductance in ZnOS was observed. The ZnOS layers exhibited very poor conductance under either electrical or optical input signals, whereas simultaneous application of the two yielded extremely high sample currents. Based on the in-situ derived band diagram, a comprehensive explanation of the effect is provided. Moreover, we show how the CREM analytical tool can also provide a potential activator of future related devices.

11:00am **EM+AN+MI+SS-WeM10 Fabrication of Multilayered Optically Active Nanocrystal Solids by Surface Passivation using Metal Oxides: ALD vs CVD***, **Riya Bose**, A.D. Dangerfield,* University of Texas at Dallas*; S.M. Rupich,* University of Texas*; Y.J. Chabal, A.V. Malko,* University of Texas at Dallas

Semiconductor nanocrystal quantum dots (NQDs) provide a powerful platform for optoelectronic applications with their size/shape/composition tunable properties and inexpensive solution based synthesis techniques. Integration into solid state devices requires deposition of NQD films, and often a controlled assembly of multilayered NQD structures to ensure maximum light absorption and optimum efficiency of the devices. However, thin film fabrication is found to degrade its properties compared to NQDs in solution, especially a decrease in the photoluminescence (PL) quantum yield (QY) is frequently observed. Also, the bottleneck for fabrication of multilayer NQD films remains the use of solution phase deposition methods, where the solvent in the subsequent step of deposition dissolves the initial layer until each NQD layer is rendered insoluble by means of any surface passivation technique. Surface passivation techniques also play a critical role to protect the deposited layers from oxidation and deterioration. An attractive method to passivate NQD films during the deposition as well as from environmental exposure is to overcoat them with various metal oxides grown using atomic layer deposition (ALD). Though there are few reports of ALD encapsulation of NQD films, they mostly attend to charge transfer-based devices and aim to improve carrier moblities. Typically, such studies report a significant quenching of the PL intensity after encapsulation. In this study, we aim to investigate the exact growth mechanism of metal oxide layers by ALD on the surface of NQD films and how it, along with the ALD parameters, affects their PL properties. With the aid of in-situ FTIR and ex-situ XPS measurements during Al_2O_3 deposition on oleic acid capped CdSe-ZnS core-shell nanocrystals, it is observed that the interaction of the metal precursor trimethyl aluminium (TMA) with the surface of the NQDs leads to the reorganization of the ligands as well as replaces Zn, leading to PL intensity quenching. In order to prevent this, we opted for a pulsed chemical vapour deposition (CVD) like approach for metal oxide deposition where simultaneous purging of both the metal and oxygen precursors leads to formation of metal oxide in a gas phase in the immediate vicinity of the NQD surface. We found that minimization of TMA interaction with the NQDs' surface indeed leads to enhancement of the PL intensity and elongation of carrier PL lifetime. These measurements provide clear indication of defect-free surface passivation proving that CVD-like Al_2O_3 encapsulation is a suitable technique for controlled deposition of multilayered NQD structures that preserves its optoelectronic properties.

11:20am **EM+AN+MI+SS-WeM11 The Role of Surface Oxides for the Optoelectronic Performance of III-V Semiconductor Nanowires***, J. Colvin, A. Troian, O. Persson, A. Mikkelsen, **Rainer Timm**,* Lund University, Sweden

III-V semiconductor nanowires (NWs) have a large technological potential within electronics, optoelectronics, and energy harvesting [1,2], mainly due to their flexibility in creating heterostructures by axial stacking during epitaxial growth. Because of their small diameter and their very large surface-to-volume-ratio, the performance of NW devices is strongly determined by surface properties. We have previously studied surfaces and surface oxides of semiconductor NWs by scanning tunneling microscopy and spectroscopy (STM/S) [3] as well as X-ray photoemission spectroscopy [4]. Here, we will correlate the surface properties of InAs and InP NW heterostructures with their electrical and photovoltaic behavior, which has been measured for individual upright-standing NWs using the STM tip as local nanoprobe [5].

InP and GaInP pin-junction NWs have been cleaned from their native oxide by annealing under atomic hydrogen background and re-oxidized by exposure to ambient conditions. By illuminating the InP NWs that were contacted by the STM nanoprobe, we observed a decrease of the open-circuit voltage from 0.75 V to 0.70 V upon native oxide removal and an increase back to 0.76 V upon re-oxidation, confirming the need of surface passivation for improving InP solar cells. However, the ideality factor of the NW pin-diodes remained constant at n = 1.82 upon oxide removal, but improved to n = 1.67 upon re-oxidation. Furthermore, our XPS results indicate the outdiffusion of Zn dopants from the p-doped NW segments, forming a Zn-rich shell around the NW.

A more significant effect of the presence of native surface oxide was found for InAs NWs which consist of one segment of wurtzite and one segment of zincblende crystal structure. Upon removal of the native surface oxide, we obtained an increase in conductivity of these NWs by two orders of magnitude, while reference NWs with pure wurtzite structure showed a slight decrease in conductivity with the same surface treatment. This effect can be explained by a staggered type-II surface band alignment at the wurtzite/zincblende interface of oxidized NWs, which turned into flat-band conditions upon oxide removal, as confirmed by nano-focus XPS measurements.

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11:40am **EM+AN+MI+SS-WeM12 Photonic Annealing of 2D Transition Metal Dichalcogenides for Tailored Optical Properties***, **Rachel Rai**, K. Gliebe,* University of Dayton; Air Force Research Laboratory*; N.R. Glavin, R. Kim, A. Jawaid, R. Wheeler, L. Bissell,* Air Force Research Laboratory*; C. Muratore,* University of Dayton

Thin layers of transition metal dichalcogenides (TMD) have attracted significant interest in the field of optoelectronics due to their unique light absorption and emission properties in the visible frequency range. Development of bright, flexible, large area emission sources based on 2D materials using photonic annealing represents an exciting opportunity for future quantum systems. Here we introduce new correlations relating the optical properties of WSe_2, a well-known single photon emitter, to post-processing annealing techniques to include lasers, broadband radiation, and nanoscale electron beams. Modulation of the total energy flux during growth of amorphous TMD material to develop purely amorphous materials or materials with nanoscale nuclei was employed by the authors to examine effects of pre-existing nuclei on crystallization kinetics (i.e., activation energy) and the resulting optical properties. We correlate the wavelength and intensity of photoluminescence from WSe_2 deposited on plasma treated and as-received flexible substrates and present techniques to control film continuity and the areal density of free edges from islands on discontinuous films for tuning the intensity of optical emission. A significant increase in photoluminescence intensity is accompanied by a change in domain boundary density, correlating well to theory. Furthermore, examination of quantum confinement effects by producing nanoscale crystalline areas (between 5-50 nm) with precisely controlled volumes via electron beam radiation provides insight on light emission mechanisms.

12:00pm **EM+AN+MI+SS-WeM13 Polarity Control of GaN Nanowires on Diamond: Experiment and Theory***, **Karin Larsson**,* Uppsala University, Sweden*; M. Hetzl, M. Kraut, T. Hoffmann, M. Stutzmann,* Technical University Munich, Germany

III-nitride nanowires on diamond substrates are of current interest for two different potential applications: (i) selectively grown n-type AlGaN nanowires on p/i – diamond are promising for the electrical control and the efficient optical and electrical readout of individual NV-centers in diamond as qubits and (ii) AlGaN/diamond n/p-heterodiodes are an interesting option for future ultraviolet LEDs and laser diodes. For both applications, the polarity of AlGaN nanowires grown on diamond has a strong influence on the optoelectronic properties of the heterojunctions, because the polarization-induced interface charge strongly influences the details of the diamond/III-nitride band alignment. Thus, the growth of nanowire arrays with randomly fluctuating polarity will have a negative influence on the electronic properties of the heterojunctions.

In this presentation, we will discuss recent experimental results concerning the control of GaN nanowire polarity on diamond (111) substrates via different surface termination treatments (hydrogenation, oxygen termination, nitrogen radical exposure [1]). Systematic experimental investigations have shown that even very well ordered periodic nanowire arrays deposited by Selective Area Growth exhibit a high degree of polarity disorder. Diamond is a well-suited substrate for these investigations, since

it supports several different types of stable surface structures which only differ by about one monolayer and have a strong influence on the preferred nanowire polarity. The effect of different surface terminations on nanowire polarity will be recapitulated. Furthermore, we complement these experimental investigations by theoretically studying the effect of diamond surface termination on the energetically preferred GaN polarity. First principle DFT-calculations are used to calculate the interface energies and the corresponding atomic configurations of the different diamond/GaN interfaces. Strong variations observed in the interface chemistry between diamond and GaN nanowires will be discussed based on the available experimental and simulation data.

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Processing and Characterization of Air-Liquid, Solid-Liquid and Air-Solid Interfaces Focus Topic
Room 202A - Session PC+AS+BI+EM+PB+SS-WeM

Novel Approaches and Challenges of Interfaces

Moderators: Andrei Kolmakov, National Institute of Standards and Technology (NIST), Xiao-Ying Yu, Pacific Northwest National Laboratory

8:00am **PC+AS+BI+EM+PB+SS-WeM1 Probing Chemical Species and Potential Profiles of Electrified Interfaces***, **Ethan J. Crumlin,*** Advanced Light Source, Lawrence Berkeley National Laboratory **INVITED**

Interfaces play an important role in nearly all aspects of life, and are essential for electrochemistry. Electrochemical systems ranging from high temperature solid oxide fuel cells (SOFC) to batteries to capacitors have a wide range of important interfaces between solids, liquids, and gases which play a pivotal role in how energy is stored, transferred, and/or converted. This talk will focus on our use of ambient pressure XPS (APXPS) to directly probe the solid/liquid electrochemical interface. In particular, I will discuss how we were able to probe the potential drop within the electrochemical double layer (EDL) as well as the potential of zero charge under polarization conditions. This unique approach was accomplished by measuring spectral changes observed in both the electrolyte (water) and a neutral spectator probing molecule (pyrazine). By combining these experiments with numerical simulations provided the ability to discern the shape of the electrochemical double layer profile as a function of both electrolyte concentration and applied potentials. Extending beyond the EDL, I will highlight some of our recent investigations into both the oxygen evolution reaction on a platinum electrode as well as a magnesium electrode in a non-aqueous electrolyte. Information gained from these studies will aid in the guided design and control of future electrochemical interfaces.

8:40am **PC+AS+BI+EM+PB+SS-WeM3 Observation of Electron Transfer in Riboflavin Reduction by In Situ Liquid SIMS***, **Rachel Komorek**, X.F. Yu, Z.H. Zhu, X-Y. Yu,* Pacific Northwest National Laboratory

Riboflavin is of vital significance in living processes as a precursor of the two important coenzymes flavin mononucleotide (FMN) and flavin adenine dinucleotide (FAD).[1] The isoalloxazine ring in riboflavin plays an important role in energy supplementation and cellular respiration, since it has the capability to accept electrons in some redox reactions.[2] Understanding riboflavin reduction could potentially bring insight into the electron transfer process between cell surfaces and conductive materials. Thus, the electrochemical reduction process of riboflavin has drawn increasing attention. In this study, the riboflavin reduction mechanism in an aqueous solution has been investigated using time-of-flight secondary ion mass spectrometry (ToF-SIMS) with the electrochemical cell.[3, 4] Positive and negative ion mode mass spectra were used to depict the molecular information of species dissolved in the electrolyte. The distribution of key reduction intermediates were mapped at the electrode-electrolyte interface using dynamic depth profiling. To examine product formation as a function of applied potentials, measurements were made by holding the potential at 0, -0.3, 0.3, and 0.6 V respectively, once interesting electrochemistry was determined using the cyclic voltammogram. Furthermore, gold and graphite electrodes were both used in our experiment to investigate if the electrode surface plays a role in in the electrochemical reaction mechanism. Preliminary spectral principal component analysis (PCA) results have shown key chemical distinctions in the electrolyte at 0, -0.3, 0.3, and 0.6 V. Selected peak spectral PCA is required to gain a better understanding of this observation, which will allow for a more comprehensive chemical profile of the electron transfer process in riboflavin redox reactions.

Key words: in situ liquid SIMS, SALVI, riboflavin reduction, electrochemistry, electron transfer

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9:00am **PC+AS+BI+EM+PB+SS-WeM4 Electrowetting of Liquid Drops Revisited by XPS***, **Sefik Suzer**, P. Gokturk, B. Ulgut,* Bilkent University, Turkey

Electrowetting behavior of liquid drops has been followed in-situ and in-vacuum using XPS in a chemically resolved fashion, under both dc and ac excitations. Various Liquid drops, compatible with the UHV conditions, consisted of an Ionic Liquid (DEME-TFSI), Poly-ethylene-glycol (M.W. ~600 amu) and their mixtures. For the dielectric substrate, a ~300 nm thick silicon oxide (SiO_2/Si) without and with a thin hydrophobic coating (CYTOP) has been employed. XPS data have been recorded both in the conventional scan- and also in the fast (<1s) snap-shot modes. Intensity and position of the peaks, representing the liquid drops (F1s in the case of the IL, or C1s/O1s of the PEG) as well as those of the substrates (Si2p for the oxide only and F1s for the hydrophobic coated one) have been recorded under various electrical excitations. Under ac excitation at a fixed frequency, intensity modulations in the XPS peaks reveal geometrical changes of the drops, while the peak position modulations reveal electrical potentials developed. Monitoring position modulations as a function of the changes in the ac frequency (10^{-2} – 10^5 Hz) allows us to tap into ionic, dipolar and electrical contributions of the dielectric susceptibility of both the liquid drops and the substrates. Experimental details and various application will be presented and discussed.

*This work is partially supported by TUBITAK through Grant No. 215Z534

9:20am **PC+AS+BI+EM+PB+SS-WeM5 Probing Interfaces in Heterogeneous Catalysts at Atomic Scale: Current and Emerging STEM Techniques***, M. Chi, **Wenpei Gao**,* Oak Ridge National Laboratory **INVITED**

Chemical reactions take place on the surfaces and interfaces of heterogeneous catalyst systems. Depending on the phase of the reactant, the reactive interfaces include those between solid-gas, solid-liquid, and triple-phase interfaces of solid-gas-liquid. At these interfaces, the catalyst provides active sites where the reactants are adsorbed, activated, and converted to new chemical species that are eventually released from the catalyst surface. The ability of catalysts in promoting these reactions is determined by the surface binding energy, which can be modified by tuning the interfacial atomic arrangements or by forming new interfaces, e.g., forming core-shell structures. Understanding the formation of these interfaces during synthesis and their structural and chemical evolution during operation are important to the rational design of future high-performance catalysts. Probing these dynamically evolving interfaces at a sufficient spatial resolution, however, presents many challenging. Recent work on elucidating the formation and the operation mechanisms of interfaces in precious metal-based heterogeneous catalysts using *in situ* atomic-scale scanning transmission electron microscopy (STEM) techniques will be discussed. Several emerging STEM-based methods, such as vibration spectroscopy and atomic-scale differential phase contrast imaging that are currently under development within the microscopy community will be introduced, and their prospective influence on future studies to design functional interfaces in heterogeneous catalysts will be discussed.

Acknowledgements: Research supported by the Center for Nanophase Materials Sciences, which is a U.S. Department of Energy (DOE) Office of Science User Facility.

11:00am **PC+AS+BI+EM+PB+SS-WeM10 From 2D to Advanced 3D Surface Functionalization using Self-limiting Reactions in the Fluidized Bed Reactor Technology**, ***Didier Arl***, *T. Da Cunha, N. Adjeroud, K. Menguelti, M. Gerard, D. Lenoble,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

The integration of novel functional nanomaterials like high specific surface powders in polymeric or inorganic matrices requires a fine control of their properties. The design of these nanoscopic agents is linked to the development of nanotechnology processes which can be transferred from planar substrates to complex 3D surfaces. In this framework we showed how self-limiting reactions inspired by Atomic Layer Deposition can be applied to functionalize powder by using a specifically designed Fluidized Bed Reactor. A specific interest has been given to work in non-saturated regime with nickel or Cobalt acetylacetonate to obtain well controlled metal nanocatalysts of 5-10nm diameter. Depending on the process window, some interesting properties have been demonstrated such as ferromagnetic behavior or the systematic recover of the Metal-Carbide phase that increase the throughput of Carbon Nanotubes growth. These activated nanostructures can expressly improve the electrical, the thermal or the mechanical properties of some related composites depending on how some processing parameters such as exposure time, pressure or local temperature can be tailored.

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-WeM2 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-WeM3 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.T. DeJarld,* US Naval Research Laboratory*; K. Qiao, Y. Kim,* Massachusetts Institute of Technology*; S.P. Pavunny, D.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.

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9:00am **PS+AS+EL+EM+SE-WeM4 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

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

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

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

Research Corporation (SRC) program sponsored by NIST through award number 70NANB17H041.

9:20am **PS+AS+EL+EM+SE-WeM5 Invited Talk-Future Stars of AVS Session: Engineering the Properties at Heusler Interfaces**, ***Jason Kawasaki*** [1], 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, 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-WeM6 Invited Talk-Future Star of AVS Session: Atom Probe Tomography for 3D Semiconductor Devices Applications**, ***Ajay Kumar Kambham*** [2], 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-WeM10 Invited Talk-Future Stars of AVS Session: Three-Dimensional Imaging of Complex Oxide Interfaces**, ***Divine P. Kumah*** [3], 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-WeM11 Invited Talk-Future Stars of AVS Session: lluminating Physics of Magnetron Sputtering Discharges**, ***Matjaz Panjan*** [4], 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.

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11:40am **PS+AS+EL+EM+SE-WeM12 Peter Mark Memorial Award: Plasma-bio Interactions: Investigating Mechanisms to Enable New Applications**, ***Peter Bruggeman*** [5], 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.

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

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Acknowledgements

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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-WeM1 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-WeM2 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.

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8:40am **PS+EM-WeM3 DSA Patterning for and Beyond CMOS***, Patricia Pimenta Barros,* CEA-LETI, France*; N. Posseme,* CEA, LETI, France*; S. Barnola,* CEA-LETI, France*; R. Tiron,* CEA-LETI, MINATEC, France*; A. Gharbi, MA. Argoud, Z. Chalupa, M.-G. Gusmao-Cacho,* CEA-LETI, France*; A. Paquet,* Arkema, France*; F. Delachat,* CEA-LETI, France*; C. Nicolet, C. 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.

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9:20am **PS+EM-WeM5 Composition Modulation of SiGe for Si/SiGe Dual Channel Fin Application***, **Yohei Ishii,*** Hitachi High Technologies America Inc.*; Y.-J. Lee,* National Nano Divice Laboratories*; W.-F. 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.

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9:40am **PS+EM-WeM6 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.-P. 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-WeM10 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.

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11:20am **PS+EM-WeM11 A Study on the Distortion of Poly Si Nano Hole Profile with High Aspect Ratio in sub X nm***, **Jin Won Lee**, J.Y. Lee, K.J. Seong, T.S. Kwon, H.H. Jeong, S.S. Hong, D.W. Han, B.R. Lim, A.R. Ji, Y.M. Oh, J.C. 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-WeM12 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).

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Thin Films Division
Room 102A - Session TF+EM+MI-WeM

Thin Film Processes for Electronics and Optics I

Moderators: Virginia Wheeler, U.S. Naval Research Laboratory, Mark Losego, Georgia Institute of Technology

8:00am **TF+EM+MI-WeM1 Crystalline Conductors: Transition Metal Nitride Materials and Device Applications*, David Meyer*,** *D.S. Katzer, N. Nepal, B.P. Downey, M.T. Hardy, D.F. Storm,* U.S. Naval Research Laboratory **INVITED**

Development of gallium nitride and related III-N materials thin film growth technology has been instrumental in realizing high performance light-emitting, RF, and power electronic devices for both commercial and military applications. To continue pushing the frontiers of nitride materials research, we have recently incorporated a multi-pocket electron-beam evaporator into our nitride molecular beam epitaxy growth system to enable the evaporation of refractory transition metals. In spite of the complexity of the equilibrium phase diagrams of transition metal nitide (TMN) compounds, we have found that it is possible to grow single-phase TMN thin films epitaxially on SiC and AlN by carefully managing growth kinetics. This talk will discuss our latest results involving TMNs, such as NbN_x and TaN_x, which can be nearly lattice-matched and integrated within III-N heterostructures. Cross-sectional transmission electron microscopy indicates that TMN/III-N interfaces are atomically abrupt with no evidence of interdiffusion of the host elements. We anticipate that the device applications of these metallic films are quite broad ranging from selective etching of sacrificial layers for epitaxial lift-off of processed devices, to buried metallic or superconducting electrodes for quantum computation circuit elements, to optical mirrors and waveguides for improved optoelectronics.

8:40am **TF+EM+MI-WeM3 Growth Mechanism and Characteristics of Hf-Si-O Film by PE-ALD using TDMAS and TDMAH Precursors and Oxygen Plasma Gas*, Toshihide Nabatame,*** National Institute for Materials Science (NIMS), Japan*; M. Inoue,* National Institute for Materials Science (NIMS)*; E. Maeda, K. Yuge, M. Hirose,* Shibaura Institute of Technology, Japan*; M. Takahashi, K. Ito,* Joining and Welding Research Institute, Osaka University, Japan*; N. Ikeda,* National Institute for Materials Science (NIMS), Japan*; T. Ohishi,* Shibaura Institute of Technology, Japan*; A. Ohi,* National Institute for Materials Science (NIMS), Japan

GaN-based power devices with metal-oxide-semiconductor (MOS) structure have been widely investigated for next-generation power devices. To reduce the leakage current, Hf-Si-O has one candidate material among various gate insulators. To fabricate Hf-Si-O film, a HfO_2/SiO_2 laminate film was generally deposited by ALD. The growth mechanism of SiO_2 films was greatly changed by the oxidant gas when Tris(dimethylamino)silane (TDMAS) was as precursor [1]. By using ozone gas, the stable growth rate and high quality SiO_2 films could be obtained while no growth using H_2O gas. We expect that similar data can be also obtained by using oxygen plasma gas. However, the growth mechanism of the SiO_2 film during HfO_2/SiO_2 laminate film deposition and its characteristics have not been fully understood.

In this study, we systematically investigate growth rate of HfO_2/SiO_2 laminate film by plasma-enhanced ALD (PE-ALD) using TDMAS and Tetrakis(dimethylamino)hafnium (TDMAH) precursors and oxygen plasma gas, and also examine characteristics of the Hf-Si-O films.

The HfO_2/SiO_2 laminate films were deposited on SiO_2/Si substrates by PE-ALD at 300 °C with TDMAH and TDMAS precursors and oxygen plasma gas. The composition Hf/Si ratio of the HfO_2/SiO_2 laminate films were varied by changing each number of ALD cycle. The SiO_2 film was also deposited on SiO_2/Si and HfO_2/Si substrates by the same PE-ALD condition. The Hf-Si-O films were formed by post-deposition annealing (PDA) at 700 – 900 °C in a N_2 atmosphere. The growth per cycle (GPC) of the HfO_2/SiO_2 laminate, HfO_2, and SiO_2 films was estimated by spectroscopic ellipsometry, XPS, and cross-sectional TEM measurements. The structure of Hf-Si-O films was identified by XRD analysis, and electrical characteristics of capacitors with Hf-Si-O films were examined using capacitance – voltage measurement.

The GPC of the HfO_2/SiO_2 laminate, HfO_2, and SiO_2 films on SiO_2/Si substrates were found to be 0.08, 0.08, and 0.04 nm/cycle, respectively, regardless of Hf/Si composition ratio. Considering to the GPC of the HfO_2 (0.08 nm/cycle), the estimated GPC of a SiO_2 layer during HfO_2/SiO_2 laminate film deposition was 0.08 nm/cycle, which was unexpected, but increased by about 2 times compared to that of SiO_2 film on SiO_2/Si substrate. This suggest that an initial adsorption of TDMAS precursor on

the SiO_2 and HfO_2 films must be different and strongly affects to the GPC. The Hf-Si-O films (Hf/Si=2/1) maintains amorphous structure even after PDA temperature at 900 °C. The Hf-Si-O films (Hf/Si=2/1) exhibited high dielectric constant of around 14 as expected.

Reference

[1] L. Han, and Z. Chen, ECS J. of Solid Sate Sci. and Technol., 2 N228 (2013).

9:00am **TF+EM+MI-WeM4 Atomic Layer Epitaxy of Ultra-wide Bandgap Ga_2O_3 Films**, ***Virginia Wheeler**, N. Nepal,* U.S. Naval Research Laboratory*; L.O. Nyakiti,* Texas A&M University*; D.R. Boris, S.G. Walton, B.P. Downey, D.J. Meyer,* U.S. Naval Research Laboratory*; C.R. Eddy, Jr.,* U. S. Naval Research Laboratory

Ga_2O_3 has emerged as a promising material for next generation power electronics and UV photodetectors applications due to its large bandgap (4.9 eV) and the availability of affordable native substrates from melt-grown bulk crystals. While β-Ga_2O_3 (monoclinic) is the most stable and studied of five polymorphs, the slightly less energetically favorable α- and ε-Ga_2O_3 phases have unique characteristics that can be exploited. The α-Ga_2O_3 (rhombohedral corundum) has the largest bandgap of 5.3 eV and can be alloyed with α-Al_2O_3 and α-In_2O_3 for bandgap engineering. T he ε-Ga_2O_3 phase (hexagonal wurtzite) is a polar phase, with a calculated polarization strength that is 10 and 3 times larger than that of GaN and AlN, respectively. Like the III-N system, polarization induced charges can lead to higher charge densities and mobilities in two-dimensional electron gases formed at heterojunctions, which would improve the viability of Ga_2O_3 electronic devices. In this work, we use atomic layer epitaxy (ALEp) to produce high-quality homo- and heteroepitaxial Ga_2O_3 films and investigate phase selectivity as a function of substrate type and orientation, growth temperature (T_g), plasma gas phase chemistry and gas pressure.

All ALE Ga_2O_3 films were deposited in a Veeco Fiji G2 reactor equipped with a load lock and turbo pump using trimethygallium and O_2 plasma precursors. Initial studies on c-plane sapphire substrates showed that decreasing chamber pressure an order of magnitude during the plasma step resulted in a shift from pure β-Ga_2O_3 to pure α-Ga_2O_3. Additionally, at 350°C and 8 mTorr, the phase could be altered by a varying the O_2 plasma flow from 5-100 sccm. Optical emission spectroscopy indicate that the ratio of O*/O2 is critical for phase selectivity while the high ion flux to the surface can contribute to the crystallinity at low T_g. By varying T_g from 300 to 500°C at 8 mTorr, films went from mixed β/ε phase at <350°C, to pure α-Ga_2O_3 at 350°C, to pure β-Ga_2O_3 at 500°C. Using the optimum growth conditions for α-Ga_2O_3 on c-sapphire, the influence of substrate was explored using a variety of substrates including AlN, GaN (bulk and epilayers), SiC, diamond, and Si. Deposition on III-N and β-Ga_2O_3 substrates all resulted in crystalline β- Ga_2O_3 films, while amorphous films were deposited on both SiC and Si. This suggests that a clean crystalline substrate interface is critical to obtaining high quality films and promoting metastable phases is more dependent on growth parameters than underlying crystal symmetry. Finally, we will discuss simple electrical properties of optimum films of each phase to validate feasibility of the process in device applications.

9:20am **TF+EM+MI-WeM5 Effects of Process Gases and Gate TiN Electrode during the Post Deposition Anneal to ALD-Al_2O_3 Dielectric Film**, ***Masaya Saito**, A. Teramoto, T. Suwa, K. Nagumo, Y. Shiba, R. Kuroda, S. Sugawa,* Tohoku University, Japan

We investigated effects of a post deposition anneal(PDA) to Al_2O_3 film which was formed by the low temperature atomic layer deposition(ALD)(1). Al_2O_3 films were formed at 75°C by the ALD process using $Al(CH_3)_3$ as a precursor and H_2O as an oxidant, and these thicknesses were 40 nm. TiN films were formed as gate electrodes of MIS capacitors. We applied three kinds of PDAs. N_2 and O_2 annealing at 400°C were applied just after the ALD(PDA Ⅰ(a), (b)), and N_2 annealing at 400°C was applied after the gate electrode formation (PDA Ⅱ). We measured C-V and I-V characteristics.

The negative V_{FB} compared to the ideal one(+0.54 V) was observed in the C-V curve without PDAs, and the fixed charge density calculated from V_{FB} was ~10^{13} cm^{-2}. In contrast, positive V_{FB} compared to the ideal one was observed in the C-V curve with PDA Ⅰ(b), and the fixed charge density was ~10^{11} cm^{-2}. These results indicate that PDA Ⅰ(b) is effective to decrease the fixed charges. Moreover, the hysteresis in the C-V curve decreased by PDA Ⅰ(b), and the leakage current also decreased within the voltage range of C-V measurement. It is considered that the decrease of hysteresis was caused by decreasing the electrons that were trapped in the Al_2O_3 film(2). However, a few samples broke down at low voltage after PDA Ⅰ(b). In contrast, we couldn't measure the C-V characteristics of almost capacitors with PDA Ⅰ(a) because the capacitors broke down at low voltage. In the case of PDA Ⅱ, which means N_2 annealing after the gate electrode formation, the leakage current decreased same as PDA Ⅰ(b) and the production yield was still good even after PDA Ⅱ This was different tendency from PDA Ⅰ(a) even as the same annealing. However, V_{FB} shifted to the positive voltage by the PDA Ⅱ and the fixed charge density was ~10^{12} cm^{-2}. This was the same phenomenon as the PDA Ⅰ(b).

We considered these phenomena as follows; the oxidizing species were desorbed by PDA just after the ALD, and then the film quality was bad after the N_2 annealing. The oxygen for improving the film was supplied by the O_2 annealing with the desorption. When PDA was carried out after the gate electrode formation, the desorption did not occur because of capping by the gate electrode, and then the oxidizing species were sufficient for improving the film by the annealing.

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Acknowledgement:

This work was carried out at fluctuation free facility of New Industry Creation Hatchery Center, Tohoku University.

9:40am **TF+EM+MI-WeM6 Controlling the NbO_xMaterials System for Neuromorphic Computing**, ***Alexander C. Kozen**,* U.S. Naval Research Laboratory*; Z.R. Robinson, A.H. Rowley,* The College at Brockport - SUNY*; T.J. Larrabee, M.E. Twigg, H.S. Cho, S.M. Prokes,* U.S. Naval Research Laboratory

The niobium oxide system has seen recent interest, particularly due to its potential use as both a non-volatile, in the case of Nb_2O_5, or volatile, in the case of NbO_2, memristor material. Nb_2O_5 is a high k dielectric (k~41) with a high refractive index (n~2.2) and a wide bandgap (3.5 eV), while NbO_2 is a thermochromic material with a lower bandgap (1.2 eV) that undergoes a first order crystalline phase transition at a critical temperature (T_c) of 800˚C. Both of these phases, along with their intermediate sub-oxides, can serve as material components of memristors to facilitate low-power neural computing hardware.

We will examine the impact of annealing temperature, duration, and atmospheric chemistry on the phase selectivity of the NbO_x thin films fabricated using atomic layer deposition. Anneals of stoichiometric amorphous Nb_2O_5 films are kinetically limited by both Nb^{5+} to Nb^{4+} reduction and crystallization steps, and we find that the addition of H_2 during annealing is critical for the Nb^{5+} to Nb^{4+} reduction. To remove this kinetic-limiting step, we instead deposit reduced amorphous NbO_2 films, which crystallize at lower temperatures. We investigate the optical and electrical properties of both amorphous and crystalline NbO_x films and discuss the utility of the NbO_x materials system to the fabrication of memristor materials.

11:00am **TF+EM+MI-WeM10 Sputtering Power Dependent on Switching Characteristics of ZnO-based Transparent Resistive Memory Devices**, ***Firman Mangasa Simanjuntak**,* Tohoku University, Japan*; T. Ohno,* Oita University, Japan*; S. Samukawa,* Tohoku University, Japan

Transparent resistive random access memory (T-RRAM) devices have great potential as data storage for invisible electronics.[1] ZnO material is one of the promising candidates for T-RRAM application due to its high transparency to the visible light.[2] However, ZnO is an *n*-type semiconducting material which the intrinsic donor defects exist abundantly; consequently, the ZnO-based switching devices require high current compliance to operate as compared to another oxide system .[1,3] The employment of the high current compliance is to facilitate the formation of conducting filament. Various efforts have been made to improve the ZnO-based switching memories, such as: by controlling the thickness, introducing a dopant(s), adjusting the gas ambient during deposition, stacking with various material(s) and structure(s).[1] However, modulating the switching characteristics by controlling the sputtering power is still less overlooked. In this work, we investigated the influence of sputtering power in resistive switching characteristics of ZnO-based T-RRAM devices.

An approximately 50 nm thickness of ZnO films were deposited onto Indium Tin Oxide (ITO)-coated transparent substrates using conventional RF sputtering. Various sputtering power was used for the deposition while Ar/O_2 ambient is maintained at 2/1 ratio. The deposition rate was measured using a surface profilometer. In order to fabricate sandwich device structure, circular gallium-doped ZnO (GZO) top electrodes were deposited onto the ZnO/ITO structure; patterned using a metal shadow

mask with 150 µm in diameter. X-ray diffraction and X-ray photoelectron spectroscopy were used to investigate the crystal structure and the defect concentration of the ZnO films, respectively. A semiconductor device analyzer was used to measure the electrical characteristics of the devices.

XRD pattern indicated that all ZnO films show (002) oriented crystals. The devices made with higher sputtering power showed lower leakage current for OFF state and lowered current compliance to form the conducting filament (for ON state). We also found that the donor defects (oxygen vacancies and zinc interstitials) decrease as the sputtering power increases. These findings indicate that the sputtering power parameter cannot be simply overlooked in the T-RRAM fabrication.

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[3] T. Ohno and S. Samukawa, Appl. Phys. Lett. **106**, (2015).

11:20am **TF+EM+MI-WeM11 Influence of Iintrinsic and Extrinsic Dopants in HfO_x Films for Resistive Switching Memory***, **SungYeon Ryu**, Y. Kim,* Seoul National University of Science and Technology, Republic of Korea*; W.Y. Park, S.G. Kim,* SK Hynix Inc., Republic of Korea*; B.J. Choi,* Seoul National University of Science and Technology, Republic of Korea

Bipolar type resistive switching random access memories (RRAMs) utilized by TaO_x and HfO_x as switching materials, have been demonstrated superior to unipolar type RRAMs owing to the low switching current and better reliability. Bias-polarity-dependent valence change mechanism in HfO_x is attributed to the repeated generation and rupture of conducting filaments (CF), which could be the clusters of oxygen vacancies (V_o). As the device size scales down to 2x nm, the dimension of CF and the whole device area become comparable, and thus the involvement of oxygen loss or unintended V_O incorporation, that is, intrinsic defects may significantly degrade the device reliability. On the other hand, extrinsic defects by doping metallic elements may also change the switching characteristics and device variability depending on the fabrication methods, such as, co-sputtering, implantation, thermal and photo-assisted diffusion, etc.

In this study, influence of both intrinsic and extrinsic defects was investigated systematically. The device having TiN contact-plug with 28 to 2000-nm-diamenter formed in SiO_2 inter-layer was fabricated. 1.2-nm-thick HfO_x layer was deposited by atomic layer deposition (ALD). At first, for the control of intrinsic defect, the fabricated RRAM devices were post-annealed in both air and vacuum (~10mTorr) at a wafer temperature of 150 to 250 ^oC for 20 min, respectively. Electrical property is measured by semiconductor parameter analyzer (HP-4155) and function generator (AFG-3102) for DC and AC measurements. More reliable switching and free-from abnormal switching behavior, such as reset-failure, were observed in the vacuum-annealed device.

Secondly, Al- and Ga-doped HfO_x films are grown by using thermal ALD to change the structural and chemical properties of HfO_2 film via incorporating extrinsic defects. Dopant concentration and location were controlled by the ALD cycle ratio and sequence. Through Al doping, pristine resistance and forming voltage of the device were increased with increasing Al cycle ratio. On the other hand, Ga-doped HfO_2 device showed reverse switching polarity. The resistive switching characteristics caused by intrinsic and extrinsic defects in HfO_x films will be presented in detail.

Acknowledgment

This paper was result of the research project supported by SK hynix Inc.

11:40am **TF+EM+MI-WeM12 Scaling up of an Electrochemical Atomic Layer Deposition of Copper***, D. Dictus,* Lam Research Corporation, Belgium*; **Aniruddha Joi**,* Lam Research Corporation*; G. Alessio Verni,* Lam Research Corporation, Belgium*; K. Vandersmissen,* Imec, Belgium*; B. Frees,* Lam Research Corporation, Belgium*; Y. Yezdi,* Lam Research Corporation

Just like atomic layer deposition in the gas phase, electrochemical atomic layer deposition in the liquid phase holds the promise of delivering very good conformality and uniformity for nm-thick film deposition by using surface limited reactions. Up to today however, there is no industry in which such process has been scaled up from cm-size coupons to industrial-scale substrates. In this paper, the scale up of electrochemical ALD of Cu is reported and it is demonstrated that this process can be used to fill <20 nm Cu interconnect lines as required for future microchip technology nodes.

The e-ALD process is a cyclic process that consists of a step in which a monolayer of Zn is deposited at a potential below the one, at which, Zn would grow multilayers (underpotential deposition), followed by a step in which the zinc is spontaneously displaced by Cu when the substrate is allowed to drift to the open circuit potential (surface limited replacement reaction, SLRR). By cycling between potentiostatic Zn deposition and open-circuit steps, Cu films can be grown in layer-by-layer fashion.

In contrast to classical electroplating processes, e-ALD processes do not require significant overpotential to create uniform nucleation. Also, current densities are small since the deposited amount of material per cycle is low. Therefore, the e-ALD process can be used to deposit Cu with atomic layer thickness control on substrates with high resistivity which gives the advantage of being able to plate on very thin (sub-20 A) liner materials.

Development of the e-ALD process is done on a Sabre electroplating tool from Lam Research on 300 mm substrates. These substrates contain a thin layer of Ru or Co on which the copper is deposited. The e-ALD process forms the seed layer for further metallization of the interconnect or can by itself fill the narrow interconnect lines.

We will demonstrate that good thickness uniformity can be achieved on 300 mm substrates with initial sheet resistance up to 1000 Ohm/sq and that filling of interconnect lines with dimensions smaller than 14 nm is achieved. Test chips containing our new Cu deposition process show high yield and the Cu interconnect lines have low resistance. This demonstrates the potential use of this new production method in future technology nodes.

12:00pm **TF+EM+MI-WeM13 A Novel High-deposition-rate PECVD Process based on Hollow Cathode Plasma Technique***, S. Shayestehaminzadeh, N. Rivolta,* AGC Glass Europe, Belgium*; M. Datz,* Interpane E&B GmbH*; **John Chambers**,* AGC North America*; H. Wiame,* AGC Glass Europe, Belgium

AGC Plasma has recently developed a hollow cathode plasma device as part of its activity as the industrial vacuum equipment manufacturing segment of AGC. This device has been successfully scaled up in order to perform the Plasma Enhanced Chemical Vapor Deposition (PECVD) processes for the coatings on the glass sizes ranging from a few square-centimeters up to a few square-meters (jumbo-sized glass plates 3.2 x 6.0 m^2). Plasma generation is undergone between multiple linear hollow cathode cavities, alternately driven by commercially available mid-frequency AC or pulsed power. This enables the generation of a dense and uniform plasma inside the cavities as well as outside of the cavities through the linearly located holes where a less dense plasma (as compared to inside the cavity) but still dense enough, can be utilized in order to activate the reaction between precursor and reactive gases in the depositing chambers. This geometry and condition allow the system to be scalable to relevant sizes for any typical vacuum processes.

The selected plasma generation method does not require magnets incorporated into the source. This will allow a simplified cooling system within the plasma source, as well as the possibility for adding other magnets to be positioned within the process chamber for modifying the plasma geometry. Based on plasma and vacuum simulations, the electrode-cavity design has been dramatically improved and can be driven by various gases, such as oxygen, nitrogen, argon, helium, and hydrogen. Plasma operation is also possible in an extremely wide range of pressures from 1 mTorr to 1 Torr, while the most useful process pressures for PECVD are generally in the 1 mTorr to 30 mTorr range. The wide hollow cathode pressure operation range allows for the deposition of multilayer coating stacks by magnetron sputtering and PECVD in the same vacuum coating lines.

Electrode faces have also been enhanced using surface coatings to avoid erosion during high power operation, also reducing subsequent debris and extending source lifetime. Depending on the choice of precursor materials, the desired film properties, and in-chamber magnetic field geometries, dynamic deposition rates for inline PECVD coatings of 200-500 nm*m/min have been demonstrated for SiO_2 on flat glass products however by selecting different gases and precursors various materials can be deposited using the same source line. This unique process opens a new range of possibilities to be investigated for a variety of substrates. These plasma sources are now commercially available in either lab or industrial sizes to explore new applications.

Electronic Materials and Photonics Division
Room 101A - Session EM+2D+SS-WeA

Wide and Ultra-Wide Bandgap Materials for Electronic Devices: Growth, Modeling and Properties

Moderators: Erica Douglas, Sandia National Laboratories, Rachael Myers-Ward, U.S. Naval Research Laboratory

2:40pm **EM+2D+SS-WeA2 2300 V Reverse Breakdown Voltage Ga_2O_3 Schottky Rectifiers**, ***Jiancheng Yang***[1], *F.R. Ren,* University of Florida; *M.J. Tadjer,* U.S. Naval Research Laboratory; *S.J. Pearton,* University of Florida; *A. Kuramata,* Tamura Corporation and Novel Crystal Technology, Inc., Japan

A reverse breakdown voltage of 2300 V with corresponding breakdown field of 1.15 MV/cm was demonstrated for 20 µm epi-β-Ga_2O_3 edge-terminated vertical Schottky rectifiers. This breakdown voltage is the highest ever reported for Ga_2O_3 rectifiers. Ga_2O_3 has an energy band gap of range 4.5 – 4.9 eV, which correlates to the theoretical breakdown electric field of ~8 MV/cm. The theoretical Baliga figure of merit (defined as V_B^2/R_{ON}, where V_B is the reverse breakdown voltage and R_{ON} is the on-state resistance) of Ga_2O_3 estimated to be 400% higher than GaN.[1] Previously reported, an unterminated Ga_2O_3 rectifier shown a breakdown voltage of 1600 V, and a field-plated Schottky diode has a breakdown voltage of 1076 V with the epi thickness 7 µm [2,3] This work has shown the improvement of the Ga_2O_3 vertical rectifiers breakdown voltage using a field-plate terminated approach with a lightly doped 20 µm Ga_2O_3 epitaxial layer . The edge-terminated Schottky rectifiers of various dimensions (circular geometry with diameter of 50-200 µm and square diodes with areas 4 × 10^{-3}- 10^{-2} cm^2) fabricated on 20µm lightly doped (n=2.10 × 10^{15} cm^{-3}) β-Ga_2O_3 epitaxial layers grown by hydride vapor phase epitaxy on conducting (n=3.6 × 10^{18} cm^{-3}) Ga_2O_3 substrates grown by edge-defined, film-fed growth. The R_{ON} for these devices was 0.25 Ω-cm^2, leading to a figure of merit (V_B^2/R_{ON}) of 21.2 MW/cm^2. The Schottky barrier height with the Ni/Au based metallization was 1.03 eV, with an ideality factor of 1.1 at room temperature. The Richardson's constant of 43.35 A/cm-K^2 was extracted from the temperature dependent forward IV. The breakdown voltages for the different size devices ranged from 1400-2300V, with a general, but not a linear trend of decreasing breakdown voltage for larger area rectifiers. The diode reverse recovery time of ~22 ns was measured by switching the diode from +2V to -2V.

1. J. Green, K. D. Chabak, E. R. Heller, R. C. Fitch, M. Baldini, A. Fiedler, K. Irmscher, G. Wagner, Z. Galazka, S. E. Tetlak, A. Crespo, K. Leedy, and G. H. Jessen, IEEE Electron Device Lett., vol. 37, no. 7, pp. 902–905, Jul. (2016)

2. J. Yang, S. Ahn, F. Ren, S. J. Pearton, S. Jang, and A. Kuramata, IEEE Electron Device Lett,. 38(7), 906 (2017).

3. K. Konishi, K. Goto, H. Murakami, Y. Kumagai, A. Kuramata, S. Yamakoshi, and M. Higashiwaki, Appl. Phys. Lett. 110, 103506 (2017).

3:00pm **EM+2D+SS-WeA3 Characterization of β-$(Al,Ga,In)_2O_3$ Epitaxial Films for UV Photodetector Applications**, ***Luke Lyle***, *L.M. Porter, R. Davis,* Carnegie Mellon University; *S. Okur, G.S. Tompa,* Structured Materials Industries, Inc.; *M. Chandrashekhar, V. Chava, J. Letton,* University of South Carolina

β-Ga_2O_3 has garnered increased attention over the last few years due to its ultra-wide bandgap of ~5.0 eV and the ability to grow Ga_2O_3 single crystals from the melt. In addition to its desirability for high power electronics, Ga_2O_3 is well suited for solar-blind UV photodetectors. These detectors are coveted by numerous industries and the military for applications ranging from flame- and missile-plume detection to ozone hole monitoring. In this study we have grown $(Al,Ga,In)_2O_3$-based alloy epitaxial films on sapphire via metalorganic chemical vapor deposition (MOCVD) to investigate their potential application for wavelength-tunable UV photodetectors. The films were characterized structurally, optically, and chemically using x-ray diffraction (XRD), optical transmittance, and energy dispersive x-ray spectroscopy (EDX). Based on XRD and EDX results, β-$(Al_xGa_{1-x})_2O_3$, β-$(In_xGa_{1-x})_2O_3$, and β-Ga_2O_3 epitaxial films with compositions through x = 0.29 (for Al) and x = 0.13 (for In) were grown. The optical bandgap was found to correspondingly vary between 5.5±0.1 and 4.3±0.3 eV, as a function of composition. MSM- and Schottky-based solar-blind UV photodetectors were also fabricated on selected films. The devices showed responsivities up to 1E5 A/W and quantum efficiencies up to 6E5 at 220 nm from a deuterium lamp. The wavelength tunability of the photodetectors is currently being investigated and will be discussed in this presentation.

3:20pm **EM+2D+SS-WeA4 High Three-terminal Breakdown Voltage Quasi-two-dimensional β -Ga_2O_3 Field-effect Transistors with a Dual Field Plate Structure**, ***Jinho Bae,*** Korea University, Republic of Korea; *H.W. Kim, I.H. Kang,* Korea Electrotechnology Research Institute (KERI), Republic of Korea; *G.S. Yang, S.Y. Oh, J.H. Kim,* Korea University, Republic of Korea

β-Ga_2O_3 is an intriguing material because of its large direct bandgap (4.85 eV), high breakdown field (~8 MV/cm) and excellent thermal and chemical stability. Baliga's figure of merit of β-Ga_2O_3 is 3214.1, superior to those of other materials such as GaN (846.0) or SiC (317.1). Although β-Ga_2O_3 is not a van der Waals material, β-Ga_2O_3 can be mechanically exfoliated from single crystal substrate into thin layer due to the large anisotropy of the unit cell. Quasi-2D β-Ga_2O_3 devices shows superior electrical properties and robustness in harsh environment, which shows potential of β-Ga_2O_3 as nanoscale power devices. However, quasi-2D β-Ga_2O_3 power devices show premature breakdown due to the electric field concentration. Adopting multiple field plates to relieve the electric field concentration and prevent premature breakdown greatly enhance the performance of power devices, which can be applied to β-Ga_2O_3 nanoelectronic power devices.

H-BN has been used as a dielectric material of 2D devices due to its excellent thermal conductivity and high dielectric constant, as well as atomically flat surface, which can be obtained through mechanical exfoliation. In our work, we used h-BN as a gate field plate dielectric layer by selective transfer on β-Ga_2O_3 channel using PDMS film. SiO_2 dielectric layer was deposited on devices followed by metal deposition for source field plate structure. By applying dual field plate structure, β-Ga_2O_3 devices can show excellent performance in high voltage condition.

β-Ga_2O_3 MESFETs with h-BN gate field plate were fabricated by using the β-Ga_2O_3 and h-BN flakes obtained from respective crystals. Ohmic metal was deposited on mechanically exfoliated β-Ga_2O_3 flakes, followed by precise positioning of exfoliated h-BN flakes on the channel. Gate field plate was fabricated with a part of the electrode overlapped with h-BN. Dual field plate structure was fabricated after deposition of SiO_2 and source field plate metal. Fabricated devices showed excellent output and transfer characteristics even after one month storage, which shows excellent air-stability. Three-terminal off-state breakdown voltage of fabricated device was measured, which shows improvement in breakdown voltage. The electric field distribution was calculated by Silvaco Atlas framework to study the effect of dual field plate on electric field, which explains the improvement of breakdown voltage in those structure. In this study, we present that the performance of β-Ga_2O_3 MESFET as a power device can be improved by adopting dual field plate structure, paving a way to the high-power nanoelectronic β-Ga_2O_3 devices. The details of our work will be discussed in the conference.

4:20pm **EM+2D+SS-WeA7 GaN Vertical Device Technology and its Future**, *S.C. Chowdhury,* ***Dong Ji,*** UC Davis **INVITED**

Vertical GaN devices are ideal for high power applications owing to their wide bandgap-originated material properties, similar to SiC. What makes GaN vertical devices more attractive than SiC, is the capability to offer bulk regions with electron mobility over 1200cm^2/V·sec. Due to higher carrier mobility made possible by superior growth techniques, the figure of merit offered by GaN diodes or FETs is higher compared to SiC counterparts. From TCAD drift diffusion simulation we have shown the advantage of GaN devices become rapidly significant over SiC diodes at higher voltages. In our experimental studies we have successfully demonstrated transistors blocking over 1.4kV.

In this presentation, we will go over various types of vertical devices for power conversion that we are pursuing in our group and go over the achievements and challenges in each.

CAVETs were the first vertical devices[1] that demonstrated the potential of GaN in these technology. CAVETs are realized with Mg-ion implanted [2] current blocking layers (CBLs) with regrown channel. Alternatively they can have Mg-doped CBLs with a regrown channel layer on a trench. In our trench CAVETs we have successfully blocked up to 880V with an R_{on} less than 2.7milli-ohm cm^2.

To date, most successful results in GaN vertical devices have come out of MOSFETs, which traditionally rely on inversion channels. MOSFETs with an un-doped GaN interlayer as a channel and in-situ MOCVD oxide, called OG-FET have demonstrated superior performance with low specific on-state resistance (R_{on}) Over 1.4kV blocking with an R_{on} less than 2.2milli-ohm cm^2

[1] **National Student Award Finalist**

was recently demonstrated by our group where the role of channel mobility got highlighted[3].

One of common issue in all these devices is the realization of a robust buried p-n junction, which we will also go over along with other challenges faced by each of these device types and discuss paths to overcome those.

1. S. Chowdhury, M. H. Wong, B. L. Swenson, and U. K. Mishra, IEEE Electron Device Letters **33**, 41 (2012).

2. S. Mandal, A. Agarwal, E. Ahmadi, K. M. Bhat, D. Ji, M. A. Laurent, S. Keller, and S. Chowdhury, IEEE Electron Device Letters, **38**, 7 (2017)

3.D. Ji, C. Gupta, S. H. Chan, A. Agarwal, W. Li, S. Keller, U. K. Mishra, and S. Chowdhury, *International Electron Devices Meeting, IEDM*, 2017

5:00pm **EM+2D+SS-WeA9 Effects of Proton Irradiation Energy on SiN_x/AlGaN/GaN Metal-insulator-semiconductor High Electron Mobility Transistors**, ***Chaker Fares**, F.R. Ren,* University of Florida*; J.H. Kim,* Korea University, Republic of Korea*; S.J. Pearton,* University of Florida*; C.F. Lo, J.W. Johnson,* IQE*; G.S. Yang,* Korea University, Republic of Korea

The effects of proton irradiation energy ranging from 5 to 15 MeV on the electrical properties of SiNx/AlGaN/GaN metal-insulator-semiconductor high electron mobility transistors (MISHEMTs) using in-situ grown silicon nitride as the gate dielectric were studied. In applications such as satellite-based communication, remote sensing, radar technology, and nuclear energy production, microelectronics that are resistant to radiation must be utilized. Of the many materials and device architectures previously investigated, AlGaN/GaN high electron mobility transistors (HEMTs) show significant potential for environments where radiation hardness, elevated temperature, and high-power operation are required. Although several studies have been performed to analyze how HEMTs respond to irradiation damage, data on the effects of proton irradiation energy on MISHEMTs are scarce. In this study, AlGaN/GaN MISHEMT samples were irradiated at various proton irradiation energies at a fixed dose of 2.5×10^{14} cm^{-2} to determine the effects on device performance. After proton irradiation, all devices were functional and showed minimal degradation compared to previous reports of HEMTs irradiated at similar conditions.The dc saturation current was reduced by 10.4, 3.2 and 0.5% for MISHEMTs irradiated with proton energies of 5, 10, and 15 MeV, respectively. Device performance degradations were more pronounced in the irradiated samples under high-frequency operation. At a frequency of 100 KHz, the saturation drain current reduction at a gate voltage of 3 V was 40%, 19% and 17% after proton irradiation at 5, 10, and 15 MeV, respectively. At higher duty cycles, the drain current reduction is less severe. The results of this study demonstrated the device reliability of AlGaN/GaN MISHEMTs in environments where a resilience to radiation is required.

5:20pm **EM+2D+SS-WeA10 Cesium-Free III-Nitride Photocathodes Based on Control of Polarization Charge**, ***Douglas Bell**,* Jet Propulsion Laboratory, California Institute of Technology*; E. Rocco, F. Shahedipour-Sandvik,* SUNY Polytechnic Institute*; S. Nikzad,* Jet Propulsion Laboratory, California Institute of Technology

III-nitride photocathodes are well-suited for ultraviolet (UV) detection, with commercial, defense, and astronomical applications. Photocathodes detect light by absorbing photons which create electron-hole pairs, and emitting those electrons into vacuum, where they are detected and amplified by a gain-producing device such as a microchannel plate. This type of device is capable of ultra-low dark current and enables photon counting. The wide bandgaps available in the AlGaN family provide intrinsic solar blindness, and the long-wavelength cutoff may be tuned by control of composition.

Among other properties, negative electron affinity (NEA) is desirable for these structures in order to maximize quantum efficiency (QE), or the number of electrons emitted per incident photon. Normally surface cesiation is used to create low or negative electron affinity of the GaN photocathode surface; however, the resulting highly reactive surface must be protected from air during fabrication and use, necessitating a sealed-tube configuration. Even so, the reactive surfaces of these devices cause degraded performance over time. Cesium-free photocathodes would offer lower cost, smaller size and mass, improved robustness, and greater chemical stability, in addition to the major advantages of higher QE and longer lifetimes.

We will report on the use of polarization engineering in order to achieve high QE without the use of Cs. We will discuss progress in design, fabrication, and characterization of polarization-engineered III-nitride photocathodes. An important component of these designs is the use of N-polar GaN and AlGaN. The nitride polarity affects the interface and surface polarization charge, and the ability to achieve low electron affinity depends critically on control of this charge. Designs using polarization charge engineering also enable optimization of the near-surface potential to further increase QE. We will describe the growth challenges of N-polar GaN and AlGaN and its implementation in photocathode devices. We will present results demonstrating high (>15%) QE for non-cesiated N-polar GaN photocathodes, with a clear path toward higher efficiency devices.

5:40pm **EM+2D+SS-WeA11 Current Enhancement for Ultra-Wide Bandgap AlGaN High Electron Mobility Transistors by Regrowth Contact Design**, ***Erica Douglas**, B. Klein, S. Reza, A.A. Allerman, R.J. Kaplar, A.M. Armstrong, A.G. Baca,* Sandia National Laboratories

Recently, ultra-wide bandgap (UWBG) materials, such as Al-rich AlGaN with bandgaps approaching 6 eV, are being investigated to drive high-power electronic applications to even higher voltages, due to increased critical electric field compared to wide bandgap materials, such as GaN.[1] However, challenges have been encountered with Al-rich AlGaN, and in particular an increase in contact resistance as the bandgap for heterostructures increases.[2] High contact resistance ultimately limits the performance that can be achieved for these novel heterostructure-based devices, as source and drain resistances can be dominated by Ohmic contacts. While planar metal stacks with a rapid thermal anneal have shown some level of success, a complimentary approach using doped regrowth for the Ohmic contact regions with materials of lower bandgap has also shown a potential path for lowering contact resistance.[2] Our work explores regrown Ohmic contacts composed of lower bandgap Si-doped GaN to $Al_{0.85}Ga_{0.15}N/Al_{0.7}Ga_{0.3}N$ heterostructures , achieving a maximum saturated drain current of ~ 45mA/mm. Additionally, we demonstrate the ability to increase the saturated drain current almost 3X (from ~45 mA/mm to ~130 mA/mm) for UWBG HEMTs through a circular perforation design as well as a comb-type structure by means of regrowth contact design engineering.

[1] R. J. Kaplar, *et. al*, “Review—Ultra-Wide-Bandgap AlGaN Power Electronic Devices,” ECS J. Solid State Sci. Technol., vol. 6, no. 2, pp. Q3061-Q3066, Jan. 2017.

[2] B. A. Klein, *et. al*, “Planar Ohmic Contacts to $Al_{0.45}Ga_{0.55}N/Al_{0.3}Ga_{0.7}N$ High Electron Mobility Transistors,” ECS J. Solid State Sci. Technol., vol. 6, no. 11, pp. S3067-S3071, Aug. 2017.

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6:00pm **EM+2D+SS-WeA12 Understanding Homoepitaxial GaN Growth**, ***Jennifer Hite**, T.J. Anderson, M.A. Mastro, L.E. Luna, J.C. Gallagher, J.A. Freitas,* U.S. Naval Research Laboratory*; C.R. Eddy, Jr.,* U. S. Naval Research Laboratory

The availability of high quality, free-standing GaN substrates opens windows for new device applications in III-nitrides, especially in vertical structures. With the introduction of these native substrates, the properties of nitrides are no longer dominated by defects introduced by heteroepitaxial growth. However, additional materials challenges are coming to the forefront that need to be understood and surmounted in order to allow homoepitaxial devices to achieve their full potential.

In order to enable device-quality epitaxial layers, a deeper understanding of substrate preparation and the effects of the substrate and growth initiation on the characteristics of the epitaxial layers is required for metal organic chemical vapor deposition (MOCVD) growth of homoepitaxial films. We investigate these effects on epi morphology, uniformity, and impurity incorporation at the interface and in the films. Although the initial substrate factors influencing the epi can be subtle, they can have far reaching impact on device performance. Additionally, the interface between substrate and epitaxy is examined to enable reduction of unintentional impurity incorporation, especially Si, at this surface. By studying these effects using wafers from several different vendors, with substrates from both hydride vapor phase epitaxy (HVPE) and ammonothermal techniques, an understanding of the requirements for device quality MOCVD homoepitaxy can be determined.

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-WeA1 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-WeA2 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.M. Paquette,* University of Missouri-Kansas City*; S.W. 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-WeA3 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-WeA7 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-WeA9 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-WeA10 ALD-Sequential Etch to Address Advanced BEOL Etch/Integration Challenges***, **Xinghua Sun**, Y.-T. 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-WeA11 The Underlying Role of Mechanical Rigidity and Topological Constraints in Reactive Ion Etching of Amorphous Materials***, **Gyanendra Bhattarai**, S. Dhungana, B.J. Nordell, A.N. Caruso, M.M. Paquette,* University of Missouri-Kansas City*; W. Lanford,* University at Albany*; S.W. 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 ($\langle r \rangle$) 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 $\langle r \rangle$. 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-WeA12 Plasma Processing of Phase Change Materials for PCRAM***, N.D. Altieri, **Ernest Chen**, J.P. Chang,* University of California, Los Angeles*; S.W. Fong, C.M. Neumann, H.-S. Wong,* Stanford University*; M. Shen, T.B. 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.

Surface Science Division
Room 203C - Session SS+AS+EM-WeA

Semiconducting Surfaces

Moderators: Melissa Hines, Cornell University, Ludo Juurlink, Leiden University

2:20pm **SS+AS+EM-WeA1 Functionalizing Semiconductor Surfaces and Interfaces*, Stacey Bent,*** Stanford University **INVITED**

Semiconductor surface and interface science serves as the foundation for applications ranging from microelectronics to optoelectronics to bio-sensing. Given the importance of semiconductor surface chemistry in important technologies of today, understanding the fundamental chemistry at a molecular level is key to future advances. This talk will describe studies on the adsorption of organic molecules at semiconductor surfaces, aimed at the ultimate goal of controlling the chemical and electrical properties of these hybrid systems. The presentation will examine model systems of molecular adsorption on the Ge(100)-2×1 surface using a combination of experimental and theoretical methods. The reactivity of different functional groups will be described, with particular focus on reactions of bi- and trifunctional molecules. The results help elucidate the way in which the molecular structure as well as the identity of the reactive moieties affect the product distribution of the molecules upon adsorption. Monolayer surface chemistry is also extended to the formation of covalently-bound organic multilayers through the process of molecular layer deposition (MLD). Results will be presented of our studies to understand MLD mechanisms and bonding. We show that chain termination events during MLD can be counteracted by absorption of precursors into the MLD film, which reintroduces reactive sites that lead to continuation of film growth. We will also describe new MLD chemistries, including photo-initiated MLD that forms new carbon-carbon bonds at the surface.

3:00pm **SS+AS+EM-WeA3 Atomic Structure of UHV-prepared GaP(111)A Surface and its Reactivity Towards Simple Molecules*, Denis Potapenko,*** *X. Yang, B.E. Koel,* Princeton University

Effective pyridine-catalyzed photo-reduction of CO_2 to methanol has been demonstrated on p-type GaP(111)A photocathode. Despite the considerable effort there is still no consensus about either the molecular mechanisms of this process or the role of electrode's surface. As a part of larger effort aimed at elucidation of the mechanisms of CO_2 photoreduction we have conducted a UHV study of the atomic-scale structure and reactivity of the single-crystal GaP(111)A surface. Atomic-resolution STM images supported by LEED data show that ion sputtered and annealed surface exhibit both 2 x 2 Ga-vacancy reconstruction and relatively disordered P-trimer formations. The stoichiometric excess of Ga leads to formation of large droplets on the surface. TPD experiments and IR spectroscopy with water and methanol demonstrate dissociative adsorption of these molecules that leads to recombinative desorption around 300 K.

3:20pm **SS+AS+EM-WeA4 Stabilization Mechanism of the Se- or S-treated GaAs(111)B Surface*, Shunji Goto,*** The University of Electro-Communications (UEC-Tokyo), Japan*; A. Ohtake,* National Institute for Materials Science (NIMS), Japan*; J.N. Nakamura,* The University of Electro-Communications (UEC-Tokyo), Japan

GaAs surfaces are stabilized by surface treatments with S or Se because of the reduction of the dangling bond density [1,2]. Recently, it has been reported that when the GaAs(111)B-(2 x 2) As trimer surface is treated with Se, the diffraction pattern changes from (2 x 2) to (1 x 1) [3]. The Se-treated GaAs(111)B-(1 x 1) surface was considered to have a simple structure; all As atoms of the ideal (111)B surface are replaced by Se atoms. However, a scanning tunneling microscope (STM) image shows highly disordered array of bright features with a density of 0.25 per (2 x 2) unit [4,5]. This is incompatible with the simple structure model for (1 x 1). Very recently, another structure model has been proposed for the Se-treated surface, where three As atoms on the topmost surface are replaced by Se atoms per (2 x 2) unit. This As / Se terminated model is electronically stable because the so-called electron counting rule is satisfied and the STM simulations for this model reproduces the most of features of STM experiments. In this study, we discuss the structural stability of the As / Se termination model from the viewpoint of the formation energy. We depict a phase diagram as functions of chemical potentials of Se (μ(Se)) and As (μ(As)) using the first-principles calculations within the density functional theory.

Under the As-rich and Se-poor conditions, the (2 x 2) As-trimer surface is the most stable phase. The As / Se terminated surface appears in the phase diagram under more As (Se) poor (rich) conditions, being consistent with the recent experiment [5]. It is noted that the fully-Se-terminated (1 x 1) surface can exist as a stable phase in the limit of Se-rich condition, whereas this surface does not satisfy the electron counting rule and has a metallic surface state attributed to surplus electrons of Se. At the fully-Se-terminated surface, a lone pair forms at each Se site and resultant excess electrons occupy the anti-bonding orbital of the outermost bilayer. As a result, the surface Se atoms hardly leave any dangling bond. We have also found that the S-treated surface is passivated by a similar mechanism.

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4:20pm **SS+AS+EM-WeA7 Novel Pathways in Reaching Buried Interfaces of Organic/Inorganic Hybrid Systems: A Mechanistic Understanding of Polymer Adsorption on Passivated Metal Oxide Surfaces*, Tom Hauffman,*** *S. Pletincx, K. Marcoen, F. Cavezza,* Vrije Universiteit Brussel, Belgium*; L.-L. Fockaert, J.M.C. Mol,* Technical University Delft, Netherlands*; H. Terryn,* Vrije Universiteit Brussel, Belgium

The interface between a metal oxide and its coating is of great importance for the durability and efficiency of the entire organic/inorganic hybrid system. However, the analysis of such solid/solid interfaces is challenging, as they are masked by a µm-thick polymer layer on one side and a thick metal oxide matrix on the other side. The main difficulty will be to investigate buried interfaces non-destructively with conventional surface analysis techniques.[1,2]

In this work, we characterize interfacial interactions of several ultrathin polymeric films with aluminum and zinc oxides by utilizing novel methodologies, leading to the characterization of a realistic model interface. The adsorption mechanisms are established by using XPS for chemical state information and ToF-SIMS for direct molecular information of these ultrathin organic overlayers.

The use of these nanometer thin films opens up the possibility of an in situ characterization of environmental influences such as water ingress. The use of Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) is employed to describe the adsorption mechanism in the presence of water vapor. Furthermore, ATR-FTIR Kretschmann is utilized to obtain a near-interface infrared spectrum while simultaneously, the influence of an above-the-polymer electrolyte (such as water) on the interface is characterized.[3]

The homogeneity of these interfacial interactions is characterized on the nanoscale using nano-infrared spectroscopy. This novel technique allows to conduct infrared spectroscopy on the nanoscale by using an AFM tip, which probes the expansion of the material due to IR absorbance. This results in a local vibrational spectrum.

This work comprises novel synthesis routes and methodologies, which enable to probe interfacial changes in hybrid systems non-destructively and in situ. As such, coatings systems can be optimized with respect to the bare substrate.

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4:40pm **SS+AS+EM-WeA8 Surface Modification of Metal Oxide Surfaces with Gas-Phase Propiolic Acid for Dye Sensitization by Click Reaction*, Chuan He,*** *A.V. Teplyakov, B. Abraham, M. Konh, Z. Li, L. Gundlach, S. Bai,* University of Delaware*; E. Galoppini, H. Fan, R. Harmer,* Rutgers, the State University of New Jersey

The dye sensitization on metal oxide (ZnO, TiO_2, Fe_2O_3, CuO) surfaces has attracted plenteous attention due to their numerous applications in solar

energy conversion, photo-catalysis, sensing, etc. Substantial research efforts focused on designing different dyes and surface nanostructuring. However, the actual chemical attachment schemes still heavily rely on the use of sensitizer molecules functionalized with carboxylic (COOH) or phosphonic ($P(O)(OH)_2$) anchor groups. Despite consequential progress in chemical modification schemes, the very nature of these functional groups may cause very pronounced surface morphology change of the nanomaterials designed because of etching process in liquid phase. In addition, these acidic groups often lead to the formation of multiple binding configurations (such as monodentate or bidentate miixtures) on the surface. To address both issues, we developed a two-step preparation procedure to achieve the morphology preservation of metal oxide surfaces and well-defined covalent binding of the intersurface functionality. The first step requires exposing clean metal oxide nanostructures to a gas-phase prop-2-ynoic acid (propiolic acid) in medium or high vacuum, which results in the formation of a robust and stable surface-bound carboxylate with ethynyl groups available for further modification. For the second step, we applied copper catalyzed click reaction on this preserved surface to covalently bind dye molecules functionalized with azido groups to these pre-functionalized surfaces. For example, a suitable organic dye (9-(4-azidophenyl)-2,5-di-tert-butylperylene (DTBPe-Ph-N_3)) was used to investigate a distinct signature of covalently-bound dye molecules on ZnO nanorods surface. In this study, we have confirmed the morphology preservation and selective covalent attachment of the carboxylic acid onto the metal oxide surface by the combination of measurements including scanning electron microscopy (SEM), infrared, X-ray absorption photoelectron spectroscopy (XPS), solid-state 13C NMR, transient absorption spectroscopy (TA) and density functional theory (DFT) calculations.

5:00pm **SS+AS+EM-WeA9 Solar Energy Storage in the Norbornadiene-quadricyclane System: From Surface Science to In-situ Photochemistry and photospectroelectrochemistry**, *M. Schwarz, F. Waidhas, C. Schuschke,* Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany*; S. Mohr,* Friedrich-Alexander-Universität Erlangen-Nürnberg*; O. Brummel, T. Döpper, C. Weiss, K. Civale,* Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany*; M. Jevric,* Chalmers University of Technology, Gothenburg, Sweden*; J. Bachmann,* Friedrich-Alexander-Universität Erlangen-Nürnberg. Germany*; A. Görling, A. Hirsch,* Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany*; K. Moth-Poulsen,* Chalmers University of Technology, Gothenburg, Sweden*; **Jörg Libuda**,* Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany

Photochemical isomerization of small organic molecules enables chemical energy storage via a single-photon-single-molecule process. A prototypical example is the conversion of norbornadiene (NBD) to its strained metastable valence isomer quadricyclane (QC), which releases up to 100 kJ/mol upon cycloreversion. This makes the NBD-QC system a solar fuel with an energy density comparable to state-of-the-art batteries.

In order to obtain a better understanding of NBD-based energy storage systems, we studied both the photochemical conversion and the catalytically and electrochemically triggered back-conversion at atomically defined interfaces. We combined vibrational spectroscopy with in-situ photochemistry in ultrahigh vacuum (UHV) and in electrochemical (EC) environments. In UHV, NBD and QC films were grown by physical vapor deposition (PVD) on Pt(111). By infrared refection absorption spectroscopy (IRAS), we observe spontaneous cycloreversion in QC monolayers even at 130 K, while QC multilayers are stable. Adsorbed NBD adopts a η_2:η_1 geometry which involves an agostic C-H-Pt interaction. At 300 K, this species undergoes dehydrogenation by splitting off the agostic H.

In UHV environments, the conversion from NBD to QC can be triggered in-situ by UV light and a co-deposited photosensitizer (PS). In electrochemical environments, back-conversion can be triggered by the electrode. On Pt(111) electrodes, we monitored the back-conversion in-situ by electrochemical infrared reflection absorption spectroscopy (EC-IRRAS). The corresponding spectra were analyzed based on simulated spectra from density functional theory (DFT). Using a new photoelectrochemical IRRAS setup (PEC-IRRAS), we monitored the complete storage and release cycle by in-situ vibrational spectroscopy. Selectivities were determined both for the conversion and the back-conversion, showing that the stability of the PS is a critical step in the storage cycle. Much higher reversibility could be obtained using new NBD derivatives which avoid an additional PS.

To better control the energy transfer via the electrode interface, we investigated NBD derivatives anchored via a carboxylic-acid function to atomically defined oxide surfaces. In UHV, dense monolayers of surface-anchored NBD derivatives were prepared by PVD onto Co_3O_4(111) films on Ir(100). The molecules adopt an upright-standing orientation with the NBD units pointing away from the interface. Finally, we explored the behavior of these films in (photo)electrochemical environments.

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5:20pm **SS+AS+EM-WeA10 In-situ Characterization of Photon induced Chemistries in Organotin Clusters with Ambient Pressure XPS**, ***J. Trey Diulus***[1]*, R.T. Frederick,* Oregon State University*; M. Li,* Rutgers, the State University of New Jersey*; D.C. Hutchison, I. Lyubinetsky, L. Árnadóttir, M.R. Olsen,* Oregon State University*; E.L. Garfunkel,* Rutgers, the State University of New Jersey*; M. Nyman,* Oregon State University*; H. Ogasawara,* SLAC National Accelerator Laboratory*; G.S. Herman,* Oregon State University

Solution-based organometallic nanoclusters are unique nanoscale material precursors due to the precise control over their size, shape, and structure. The interaction of photons with these clusters can result in the preferential removal of organic ligands at room temperature. This process leads to a change in solubility, which makes these materials prime candidates for next-generation photoresists for extreme ultraviolet (EUV) nanolithography. In this study, we are investigating the interaction of soft X-ray radiation with organotin based clusters to better understand the transition from organometallic to metal oxide nanoclusters. As a model system we are studying the charge neutral, sodium templated, butyl-tin Keggin (β-$NaSn_{13}$) cluster [$NaO_4(BuSn)_{12}(OH)_3(O)_9(OCH_3)_{12}(Sn(H_2O)_2)$]. For analysis, the β-$NaSn_{13}$ clusters were dissolved in 2-heptanone and spin-coated to form uniform thin films (~20 nm thick). Ambient pressure X-ray photoelectron spectroscopy (AP-XPS) was used to measure the Sn 3d, O 1s, and C 1s core-levels, using photon energies above and below key absorption edges. These measurements allowed us to characterize changes in the both the atomic concentrations and chemical states of β-$NaSn_{13}$ under a range of ambient conditions, including ultrahigh vacuum and multiple partial pressures (between 0.01 to 1 Torr) of oxygen, water, methanol, nitrogen, and hydrogen. Successive C 1s scans were collected during exposure to measure the change in intensity with respect to exposure time, ambient, and photon energy. A significant reduction in the C 1s signal was observed for oxygen ambients, suggesting the oxygen partial pressure was able to increase the rate of butyl group desorption from the β-$NaSn_{13}$ clusters. Furthermore, a photon dose array was collected in each condition to determine whether ambient conditions have an effect on the photon induced chemistries leading to a solubility transition. The dose array was plotted as contrast curves, which indicate that an oxygen ambient significantly lowers the required photon dose relative to UHV. We also found that a water ambient significantly increases the required photon dose compared to an oxygen or UHV ambient. These studies ultimately improve the understanding of photon induced chemistries in the β-$NaSn_{13}$ based thin films and provide mechanistic insights for the formation of tin oxide nanomaterials at surfaces.

5:40pm **SS+AS+EM-WeA11 Integrated Photonics Driven Electron Emission from LaB_6 Nanoparticles**, ***Fatemeh Rezaeifar****, R. Kapadia,* University of Southern California

In this report, we demonstrate the novel approach of integrated photonics waveguide driven electron emission from Lanthanum hexaboride (LaB_6) nanoparticles drop-casted over the surface of an optical waveguide. We use integrated waveguide under LaB_6 electron emitter as a mean to transport photons and evanescently couple them to emitter. This evanescent coupling occurs through longer interaction length and photons can be absorbed efficiently compared to free space laser illumination from top on a metallic emitter. Furthermore, nanoparticles with the average diameter of 4 nm are at the order of electron mean free path and electron emission occurs with fewer scattering compared to electron emission from conventional bulky metallic emitters. As such, in our proposed device, the higher optical absorption along with fewer scattering inside nanoparticles enable us with larger quantum efficiency electron emitters beyond the available photon driven emitters.

We experimentally studied the photon driven electron emission characteristics obtained by coupling of CW laser (wavelength = 405 nm) to LaB_6 nanoparticle emitters drop-casted on top surface of the silicon nitride (Si_3N_4) integrated waveguide with height of 5 µm and width of 50 µm. Optical V-groove was fabricated for coupling 405 nm laser from 200 µm optical fiber in to Si_3N_4 waveguide. The work function of the LaB_6 is only 2.69 eV and it requires very small E-field to collect the photon driven

[1] **Morton S. Traum Award Finalist**

emitted electrons. We observed photocurrent at E-field as small as 0.3 V/μm while the dark current detection from LaB_6 nanoparticles begins at higher E-field, 3.5 V/μm. In addition, we present the photocurrent dependency on the laser power. At small E-field in which no tunneling is possible, we observed a linear relation between the photocurrent and laser power indicating single photon ability for this emission process. This matches to the expected slope of 1 for single photon absorption process, given that the work function of LaB_6 is only 2.69 eV, and our photon energy at 405 nm is 3.1 eV. Finally, we present the comparative results for the emission properties from LaB_6 nanoparticles illuminated with free space laser to evaluate the performance of the proposed integrated photonics driven emitters. While free space illuminated method results in emission current as small as 1 pA with 390 mW of laser power, the integrated photonics driven emitter emits above 50 pA with much smaller laser power transporting inside the optical waveguide, 100 μW. As such, we conclude integrated photonics driven emitter as a potential solution for increasing the quantum efficiency of the future electron emitters.

6:00pm **SS+AS+EM-WeA12 Photon Stimulated Desorption and Diffusion of CO on TiO_2(110)**, ***Nikolay Petrik**, R. Mu, A. Dahal, Z.-T. Wang, Z. Dohnalek, I. Lyubinetsky, G.A. Kimmel,* Pacific Northwest National Laboratory

Thermal diffusion of CO adsorbed on rutile TiO_2(110) was studied in the 20 - 110 K range using photon-stimulated desorption (PSD), temperature programmed desorption (TPD) and scanning tunneling microscopy. During UV irradiation, CO desorbs from certain photoactive sites (e.g. oxygen vacancies). This phenomenon was exploited to study CO thermal diffusion in three steps: first empty these sites during a first irradiation cycle, then replenish them with CO during annealing, and finally probe the active site occupancy in the second PSD cycle. The PSD and TPD experiments show that the CO diffusion rate correlates with the CO adsorption energy – stronger binding corresponds to slower diffusion. Increasing the CO coverage or hydroxylation of the surface decreases the CO binding and increases the CO diffusion rate. Relative to the reduced surface, the CO adsorption energy increases and the diffusion decreases on the oxidized surface. The CO diffusion kinetics can be modeled satisfactorily as an Arrhenius process with a "normal" prefactor (i.e. $\nu = 10^{12}\ s^{-1}$) and a Gaussian distribution of activation energies where the peak of the distribution is ~0.28 eV and the full width at half maximum (FWHM) is ~0.1 eV at the lowest coverages. The observations are consistent with a significant electrostatic component of the CO binding energy on the TiO_2(110) surface which is affected by changes in the surface dipole and dipole-dipole interactions.

Thin Films Division
Room 102A - Session TF+EM+MI-WeA

Thin Film Processes for Electronics and Optics II

Moderators: Hilal Cansizoglu, University of California, Davis, John F. Conley, Jr., Oregon State University

2:20pm **TF+EM+MI-WeA1 What can we Benefit from Nanochemistry of Crystalline Silicon?**, ***Naoto Shirahata**,* National Institute for Materials Science, Tsukuba, Japan **INVITED**

The richly tunable optical properties of colloidal silicon nanoparticles, in conjunction with flexible functionalization of their surfaces, makes them important class of materials with various potential applications in the ranging from medicine to optoelectronics. Bulk crystal of silicon is an indirect bandgap semiconductor, resulting in poor light emission and a weak absorption onset – major technological barrier for their use in photonics. The successful approaches in transforming silicon into efficient light emitters are appearance of the quantum confinement effect and reformation in atomic structure and periodicity from diamond cubic lattice to nanoclusters having a direct gap structure. The improved optical properties including photoluminescence quantum yields, require the efficient radiation recombination between photogenerated electron-hole pairs across the gaps. To achieve this, the surface chemistry plays an important role. In particular, the formation of carbon-silicon linkage at the surface of the nanoclusters results in the enhanced radiative recombination probability.

Today's talk starts by describing a brief overview of light emitting silicon nanoparticles to understand their place in the world of colloidal semiconductor nanocrystals. Next, the talk focuses on the reliable approaches to give a fine tuning of photoluminescence spectra with high spectral symmetries and impressively narrow spectral linewidths. Recent progress of chemical synthesis and surface functionalization of silicon nanoparticles is then demonstrated, in conjunction with their applications including efficient light emitting diodes and non-toxic biomarkers adapted for two-photon excitation fluorescence cell imaging. The performance of silicon-based light emitters are influenced significantly by surface moiety.

Since the finding of porous silicon in 1990, the free-standing, strongly luminescent silicon nanoparticles have become a masterpiece of nanoscience and nanochemistry. Such thermodynamically-stable colloidal nanoparticles will continue to lead to novel concepts of medical and device applications in near future.

3:00pm **TF+EM+MI-WeA3 Low-temperature Homoepitaxial Growth of Two-dimensional Antimony Superlattices in Silicon**, ***April Jewell**, M.E. Hoenk, A.G. Carver, S. Nikzad,* Jet Propulsion Laboratory

Our group has previously reported on the growth of antimony delta-doped silicon by low-temperature molecular beam epitaxy. In this presentation we will discuss the extension of our antimony delta doping capabilities to the growth of n-type superlattices (i.e. films that incorporate multiple delta layers). We will discuss details related to growth optimization, and show results from in situ monitoring by Auger electron spectroscopy and electron diffraction. We will also report on electrical characterization of our films and preliminary device measurements.

JPL's delta doping and superlattice doping (i.e., two-dimensional "2D" doping) processes have been developed primarily for use with silicon-based scientific imagers. A key performance metric for these detectors is photometric stability, a parameter that depends largely on passivation at the detector interface. Our approach uses an atomically thin (2D), highly concentrated layer of dopant atoms embedded within nanometers of the surface. This allows for dopant concentrations in the range of 10^{13}-10^{14} cm^{-2} (10^{20}-10^{21} cm^{-3}); higher than can be achieved with 3D doping techniques. Resulting quantum effects within the highly-doped 2D layers result in exceptional stability in 2D-doped devices.

N-type 2D-doping with antimony is challenging primarily because it tends to segregate to the surface. Segregation is suppressed at low temperatures; however, this may compromise epitaxial growth and lead to poor dopant incorporation and activation. Even so, it has been shown that at sufficiently slow silicon deposition rates it is possible to maintain epitaxial growth even at low temperatures for finite thicknesses. In our previous work with single n-type delta layers, we demonstrated activated dose concentrations as high as 2×10^{14} cm^{-2} and sharp dopant profiles (~35 Å FWHM). Under the current effort we have further optimized our growth processes to achieve even sharper dopant profiles and multiple delta layers. This is enabled by switching from a standard effusion cell to a valved cracker cell for antimony evaporation, which allows for high atom and carrier densities on the order of ~10^{21} cm^{-3} with peak distribution at ~10 Å FWHM.

The performance of our low-temperature 2D-doping processes has been validated by applying both p-type and n-type superlattice-doping to fully depleted photodiodes. The superlattice-doped devices show significantly higher responsivity than the equivalent ion-implanted devices. Additionally, when exposed to pulsed X-rays the superlattice-doped devices exhibit fast response and recovery times required for use in pulsed power experiments.

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4:40pm **TF+EM+MI-WeA8 Epitaxial Growth and Electrical Properties of VO_2Thin Films**, ***Yang Liu**, S. Niu, T. Orvis, H. Zhang, H. Wang, J. Ravichandran,* University of Southern California

We report the epitaxial growth and the electrical properties, especially the metal-to-insulator transition (MIT) of vanadium dioxide (VO_2) thin films synthesized on lanthanum strontium aluminate tantalate (LSAT) (111) substrates by a pulsed laser deposition method. X-ray diffraction study shows that the epitaxial relation between the VO_2 thin films and LSAT substrate is given as VO_2(020)||LSAT(111) and VO_2[001]||LSAT[11-2]. We observed a sharp change of four orders of magnitude in resistance at the MIT temperature of 345K. We measured distinctive Raman spectra below and above the transition point indicating a structural transition between the insulator and metallic phases, as observed in past investigations.

5:00pm **TF+EM+MI-WeA9 A Novel Technique for the Growth of Gallium Oxide Nanowires for UV Detection***, **Badriyah Alhalaili,*** UC, Davis*; R.J. Bunk, H. Mao,* UC Davis*; R. Vidu,* UC, Davis*; H. Cansizoglu,* UC Davis*; M.S. Islam,* UC, Davis

Recently, high interest in wide bandgap semiconductors for a variety of applications has grown. Due to the unique thermal, optical, and electrical properties of Ga_2O_3, the scientists attract to the assessment of Ga_2O_3 nanowires (NWs) as a valuable material in semiconductor research fields, especially for applications in harsh environments and power electronics. Compared to thin films, nanowires exhibit a higher surface-to-volume ratio, increasing their sensitivity for detection. Additionally, nanowire devices exhibit quantum effects not seen in bulk materials and allow for crystalline materials to be grown on arbitrary substrates in spite of lattice mismatch due to lattice strain relaxation at the interface. In this work, we explore a simple and inexpensive method of growing high-density gallium oxide NWs at high temperatures. The gallium oxide NWs growth mechanism can be obtained by heating and oxidizing the gallium metal into high temperatures above 900 °C. This process can be optimized for large-scale production with high-quality, dense and long-length of gallium oxide NWs. We show the results of the characterization of the materials including the optical band gap, Schottky barrier height with metal contacts, and photoconductance of β-Ga_2O_3 nanowires. The influence of density on these Ga_2O_3 nanowires will be examined in order to determine the optimum configuration for the detection of UV light.

5:20pm **TF+EM+MI-WeA10 Enhanced Efficiency in Photon-trapping Ge-on-Si Photodiodes for Optical Data Communication***, **Hilal Cansizoglu**, C. Bartolo Perez, Y. Gao, E. Ponizovskaya Devine, S. Ghandiparsi, K.G. Polat, H.H. Mamtaz, M.F. Cansizoglu,* University of California, Davis*; T. Yamada,* University of California, Santa Cruz*; A.F. ElRefaie, S.Y. Wang,* W&WSens Devices, Inc.*; M.S. Islam,* University of California, Davis

High speed, surface illuminated Ge-on-Si *pin* photodiodes with improved efficiency are fabricated and characterized. External quantum efficiency (EQE) of the Ge-on-Si *pin* diode is enhanced to >80% at 1300 nm and 73% at 1550 nm with only 2 µm thick intrinsic Ge layer, which is required to maintain high speed operation. Improved EQE is achieved by guiding incident light into the device structure with the help of microholes arranged in a lattice with a periodicity at the scale of wavelength. Vertically propagating light is coupled to the lateral modes in the material with periodic holes and absorbed efficiently despite a thin layer. More than 350% of EQE is enhanced by hole arrays compared to the case without holes up to 1700 nm wavelength. Such promising results enable Ge-on-Si photodiodes potentially cover both existing C band (1530 nm-1560 nm) and L band (1560 nm-1620 nm) and a new data transmission window (1620 nm-1700 nm), which can be a solution to capacity crunch of conventional standard single mode fiber (SSMF) cables. CMOS/BiCMOS compatible fabrication of photon-trapping Ge-on-Si photodiodes can lead to integrated transceiver circuits with electronics for cost-effective solutions in various near-infrared sensing applications such as metro and long haul dense wavelength division multiplexing (DWDM) systems, laser radar (LIDAR) systems, quantum communications and near-infrared imaging.

5:40pm **TF+EM+MI-WeA11 Correlating Composition and Structure with Optical Properties of Combinatorial Sputtered Thin Film Au_xAl_{1-x} Alloys***, **Robyn Collette**,* University of Tennessee Knoxville*; Y. Wu, J.P. Camden,* University of Notre Dame*; P.D. Rack,* University of Tennessee Knoxville

Surface plasmon resonances can be sustained by metallic nanostructures and have been explored for potential optoelectronic device applications. Superior plasmonic properties may be realized by alloying and consequently tuning the LSPR, however, there has been limited work done on alloys for use in plasmonic devices. The alloy behavior greatly depends on the ordering of the structure; thus, it is crucial to explore how the optical properties are related to the structure of the alloy.

In this work, the structure and optical properties of Au-Al thin film alloys were investigated as both individual metals have strong plasmon resonances. Initially, 350 nm thick Au_xAl_{1-x} (0.15<x<0.72) was co-sputtered on 100mm x 15mm silicon substrates. Subsequently samples of 0.9<x<1 and 0<x<0.2 were investigated. Energy dispersive spectroscopy (EDS) was used to measure the composition as a function of position on the substrate for the combinatorial samples. The crystal structure at various compositions were subsequently determined using grazing incidence x-ray diffraction (GIXRD) and the dielectric constants, ε_1 and ε_2, were determined via spectroscopic ellipsometry. The evolution of phases was studied by annealing various compositions under vacuum and the optical properties were correlated to observed phases on the equilibrium phase diagram.

Lastly, we explore the plasmonic properties of lithographically patterned Au_xAl_{1-x} (0 <x<0.2). The optical transmission and reflection is measured and compared with electron energy loss spectroscopy results. The phase evolution is studied using a (scanning) transmission electron microscope with an *in situ* laser heating system and the low loss electron energy loss spectra are correlated to the structural changes. Interestingly, we found in the mixed phase region containing Al and $AuAl_2$ that as the concentration of $AuAl_2$ increased, an increase of ε_1 and a decrease of ε_2 around 1.5 eV.

6:00pm **TF+EM+MI-WeA12 The Multifunctional TiO2 Thin Films Sensor***, **Awais Ali**, M. Alam, S. Nasser, N. Akbar, A. Saeed, A.S. Bhatti,* COMSATS Institute of Information Technology, Islamabad Pakistan

In the present work, multifunctional/hybrid UV and IR sensing was performed by Nd doped TiO_2 thin films. Thin films were sputter deposited and concentrations of dopants was varied in targets. The results suggested that the incorporation of Nd produced compressional stresses in lattice, which resulted in textured growth and asymmetry of bonds as confirmed by XRD and Raman spectroscopy. The dopant driven non-stoichiometry and presence of O vacancies was evident from XPS measurements. The defects and dopant mediated luminescence was obtained in visible and IR regions, respectively. The sensing of UV light was attributed to the host (titania), whereas successful incorporation of dopant helped in sensing IR source.

2D Materials Focus Topic
Room 201B - Session 2D+EM+MI+MN+NS+SS-ThM

Novel 2D Materials

Moderator: Han Wang, University of Southern California

8:20am **2D+EM+MI+MN+NS+SS-ThM2 Controlled Growth of 2D Ni-Silicate and Silica Films on Ni_xPd_{1-x} (111) Substrates**, ***Chao Zhou***, *X. Liang, G.S. Hutchings, Z. Fishman, J.-H. Jhang, S. Hu, S. Ismail-Beigi, U.D. Schwarz, E.I. Altman,* Yale University

The discrete lattice constants and distinct chemical properties of different transition metal substrates hamper the systematic study of how the substrates can influence two-dimensional (2D) materials growth. The recent report of single-crystal epitaxial Ni-Pd alloy films with continuously tunable lattice constants open the possibilities to tackle this issue. Two-dimensional silica and transition-metal-doped silicate films prepared on metal substrates can be 2D analogues of porous bulk zeolites. In this research, 2D silica and Ni-silicate films were prepared on Ni_xPd_{1-x} (111) substrates under different growth conditions. After annealing in 2×10^{-6} Torr oxygen, Ni from the alloy substrates incorporates into the silica structure to form a crystalline 2D Ni-silicate structure, while an amorphous 2D silica bilayer can be observed after being annealed in 4×10^{-8} Torr oxygen. Density functional theory (DFT) was employed to model various silica and silicate phases on Ni_xPd_{1-x} (111) substrates. The results show that the 2D Ni-silicate films are thermodynamically stable on the substrates when the oxygen chemical potential is in the oxygen-rich range. In oxygen-deficient environments, 2D silica tends to form a stable Ni-free phase. With continuous control over the composition of NiPd alloy films, the surface strain applied on the Ni-silicate films through the lattice mismatch between the substrate and overlayer could also be continuously tuned. Only single-domain commensurate crystalline 2D Ni-silicate can be observed in zero or low-strain systems, while a second incommensurate crystalline domain which is rotated by 30° with respect to the commensurate domain can be observed when the lattice mismatch is over 1.85%.

8:40am **2D+EM+MI+MN+NS+SS-ThM3 Topological Materials**, ***Hsin Lin,*** Institute of Physics, Academia Sinica **INVITED**

Topological materials host various novel quantum phases of electrons which are characterized by band topology and topologically protected surface/edge states. Despite recent progress, intense world-wide research activity in search of new classes of topological materials is continuing unabated. This interest is driven by the need for materials with greater structural flexibility and tunability to enable viable applications in spintronics and quantum computing. We have used first-principles band theory computations to successfully predict many new classes of topologically interesting materials, including Bi_2Se_3 series, the ternary half-Heusler compounds, $TlBiSe_2$ family, Li_2AgSb-class, and $GeBi_2Te_4$ family as well as topological crystalline insulator (TCI) SnTe family and Weyl semimetals TaAs, $SrSi_2$, $(Mo,W)Te_2$, Ta_3S_2, and LaAlGe family. I will also highlight our recent work on unconventional chiral fermions in RhSi and several material candidates for new TCI.

9:20am **2D+EM+MI+MN+NS+SS-ThM5 Few-Layer Rhenium Disulfide Synthesized Via Chemical Vapor Deposition**, ***Michael Valentin,*** Army Research Laboratory*; A. Guan, A.E. Nguyen, I. Lu, C.S. Merida, M.J. Gomez,* University of California, Riverside*; R.A. Burke, M. Dubey,* Army Research Laboratory*; L. Bartels,* University of California, Riverside

Transition metal dichalcogenides (TMDs) are exciting new materials that have received much attention due to their semiconducting properties in the direct bandgap. Well-studied TMDs, such as molybdenum disulfide (MoS_2) and tungsten diselenide (WSe_2), exhibit a direct bandgap in the monolayer form, but an indirect bandgap in the bulk form. Rhenium disulfide (ReS_2), on the other hand, is a new TMD that is unique in its ability to retain a direct bandgap independent of thickness. By using chemical vapor deposition (CVD), few-layer ReS_2 is synthesized and characterized by optical methods such as Raman spectroscopy and photoluminescence. We also show characterization results for atomic force microscopy (AFM), x-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), transmission electron microscope (TEM), and electrical transport to determine thickness, crystallinity, homogeneity, and electrical characteristics for use in future flexible electronics.

9:40am **2D+EM+MI+MN+NS+SS-ThM6 Dipolar Disorder of a van-der-Waals Surface Revealed by Direct Atomic Imaging**, *M.A. Susner,* Air Force Research Laboratory*; M.A. McGuire*, ***Petro Maksymovych,*** Oak Ridge National Laboratory

Recently, the family of transition metal thiophosphates –exhibiting ferroelecric, antiferromagnetic and correlated electron ground states – have gained attention as possible control dielectrics for the rapidly growing family of 2D and quasi-2D electronic materials [1]. Being van-der-Waals crystals, the surfaces of these materials can be created without dangling bonds, unlike those of complex oxides. Yet, because of robust insulating properties, the structure of their surfaces, the role of disorder, the structure of the topological defects in the order parameter and many other properties directly relevant to their prospective interfaces is almost entirely unknown.

Here we present the first atomically resolved imaging of $CuScP_2S_6$ s carried out using cryogenic non-contact atomic force microscopy. The surface exhibits good crystalline ordering at the atomic scale, revealing contrast on sub-unit cell level. The most remarkable property is long-range commensurate modulation of the surface morphology, with a topographic amplitude of only 2-3 pm. Combined with XRD analysis of the bulk and Monte-Carlo simulation of the Ising model on triangular lattice, we propose that the modulation arises from antiferroelectric polarization domains, albeit with frustrated long-range order. The key structural ingredient for this state is centrosymmetric position of Sc^{3+} within the layer, which forces the surrounding displacing Cu+1 ions to adopt a frustrated antiferroelectric state - in direct analogy frustrated magnetic systems. We will further discuss the peculiarities of nc-AFM imaging of this materials from the statistical analysis of the variation of images between scan, as well as the force-distance curve arrays. The possibility to directly visualize polar order opens broad opportunities to understand the atomistic aspect of ferroelectric, glassy and incommensurate phases in this material class, beginning with $CuInP_2S_6$ – which exhibits Curie temperature ~315K and giant negative electrostriction [2]. Research was sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U. S. Department of Energy. Microscopy experiments were conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

[1] Susner Michael A., Chyasnavichyus Marius, McGuire Michael A., Ganesh Panchapakesan, and Maksymovych Petro, Advanced Materials **29**, 1602852 (2017).

[2] S. M. Neumayer, E. A. Eliseev, M. A. Susner, A. Tselev, B. J. Rodriguez, S. Jesse, S. V. Kalinin, M. A. McGuire, A. N. Morozovska, P. Maksymovych, and N. Balke, ArXiv:1803.08142 [Cond-Mat] (2018).

11:00am **2D+EM+MI+MN+NS+SS-ThM10 Advanced ARPES Analyzer and Momentum Microscope KREIOS 150 – Concepts and first results on layered materials and topological insulators**, ***Paul Dietrich,*** *M. Wietstruk, T.U. Kampen, A. Thissen,* SPECS Surface Nano Analysis GmbH, Germany

Modern ARPES analyzers provide a high degree of parallelization in data acquisition, recording hundreds of energy and angle channels simultaneously. Additionally, integrated deflectors enable users to perform angle scanning perpendicular to the analyzer's entrance slit to record (k_x, k_y, E) data sets without sample rotation. However, the design of conventional analyzers implies a limited acceptance angle and corresponding accessible momentum space volume. Due to the trade-off between acceptance angle and angle resolution multiple changes in sample position and lens modes are necessary during a typical high resolution ARPES experiment. The new KREIOS 150 Energy Analyzer uses an extractor zoom lens design to overcome these limitations.

This new lens provides a full solid acceptance angle with highest angular resolution. In contrast to standard ARPES measurements with conventional hemispherical analyzers, electronic structure data from and beyond the 1st Brillouin zone is recorded without any sample movement. In addition the lens of such an instrument can work in a lateral imaging mode for microscopy as well. This enables navigation on the sample and reduces the size of the area under investigation in ARPES down to a few micrometers in diameter. This combination of large acceptance angle, high angular resolution and small acceptance area, makes this instrument the ideal tool for electronic structure studies on small samples or sample areas. The design is compact with a straight optical axis.

The capabilities of this instrument were tested at the UE 56/2 at the Bessy II synchrotron in Berlin. Specification tests show excellent angle and lateral resolution as well as small spot capability down to 2µm FOV. Subsequently

real live samples like Graphene on Germanium were measured. Even on macroscopically rough surfaces like Graphene on $NbSe_2$ excellent ARPES and X-PEEM results could be obtained. By taking advantage of the small spot capability of the KREIOS 150 meaningful band structure data has been recorded on such patchy samples.

Acknowledgements: We thank Yu. Dedkov (University of Shanghai, China) and M. Fonin (University Konstanz) for providing beamtime and samples for the measurements with KREIOS 150 at BESSY II.

11:20am **2D+EM+MI+MN+NS+SS-ThM11 Carbon Nanomembranes with Sub-nanometer Channels: 2D Materials for Water Purification with High Selectivity and Highest Permeance***, Y. Yang, P. Dementyev, N. Biere, D. Emmrich, P. Stohmann, R. Korzetz, X.H. Zhang, A. Beyer, S. Koch, D. Anselmetti,* ***Armin Gölzhäuser,*** Bielefeld University, Germany

Clean water is a global challenge, and membrane filtration is a key technology to achieve it. Here, we report on carbon nanomembranes (CNMs) with sub-nanometer channels that prove to be excellent water filters, combining a high selectivity with an exceptionally high water permeance. The CNMs are fabricated via the cross-linking of terphenyl self-assembled monolayers [1], resulting in a ~1.2 nm thick membrane perforated by channels with diameters below ~0.7 nm and areal densities of $\sim 10^{18} m^{-2}$. When tested as filter membranes, it was found that the CNMs efficiently block the passage of most gases and liquids [2]. However, water passes through, and it does this with a record-breaking permeance of $\sim 1.1\times 10^{-4}$ $mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$. This suggests that water molecules translocate fast and cooperatively through the sub-nanometer channels.Assuming all channels in a TPT-CNMs are active in mass transport, we find a single-channel permeation of ~66 water molecules$\cdot s^{-1} \cdot Pa^{-1}$.We compare this with molecular transport through other carbon nanoconduits, such as carbon nanotubes or membrane proteins (aquaporins). As the fabrication of CNMs is scalable, their utilization opens a path towards the application of 2D-materials in energy-efficient water purification.

[1] A. Turchanin and A. Gölzhäuser: Carbon Nanomembranes, *Adv. Mater*. **2016,**28, 6075.

[2] Y. Yang, P. Dementyev, N. Biere, D. Emmrich, P. Stohmann, R. Korzetz, X. Zhang, A. Beyer, S. Koch, D. Anselmetti, A. Gölzhäuser, *ACS Nano*, in press.

11:40am **2D+EM+MI+MN+NS+SS-ThM12 Discovery of Dirac Monolayers and Elucidation of Functonalites by Advanced Soft X-ray Spectroscopy***,* ***Iwao Matsuda,*** University of Tokyo, Japan **INVITED**

Vapor deposition of three-dimensional (3-D) crystal on a substrate often results in formation of the novel 2-D materials with intriguing electronic states. The approach has been well-known in the field of "Surface Science", which has attracted our attentions over the past decades. Triggered by fabrication of the graphene layers, researches on such monatomic sheets have extended to various kinds such as silicene, germanene and so on. Soft X-ray spectroscopies, such as photoemission spectroscopy, have been used to directly probe electronic states of monatomic layers and also to examine carrier dynamics under the *operando* condition. We recently observed Dirac Fermions in a 2-D boron sheet, borophene, that forms spontaneously on the Ag(111) surface. Furthermore, we found pairing of the Dirac cones due to Moire-periodic perturbations of the overlayer-substrate interactions. In the Cu_2Si monolayer, we also discovered the 2-D Dirac nodal line fermions that are protected by the mirror reflection symmetry. In the presentation. I will describe details of our research on the novel 2-D Dirac materials and introduce the advanced soft X-ray techniques that reveal their functionalities for developing devices.

[1] B. Feng, IM *et al*.,Phys. Rev. Lett., **118**, 096401 (2017) .

[2] B. Feng, IM *et al*.,Adv. Mater. **30**, 1704025 (2018) .

[3] B. Feng, IM *et al*.,Nature Comm., **8**, 1007 (2017) .

Electronic Materials and Photonics Division
Room 101A - Session EM+MI+MN+NS-ThM

Nanostructures for Electronic and Photonic Devices

Moderators: Sang M. Han, University of New Mexico, Jason Kawasaki, University of Wisconsin - Madison

8:00am **EM+MI+MN+NS-ThM1 Extreme Nanophotonics from Ultrathin Metallic Junctions***,* ***Maiken Mikkelsen,*** Duke University **INVITED**

New optical nanomaterials hold the potential for breakthroughs in a wide range of areas from ultrafast optoelectronics such as modulators, light sources and hyperspectral detectors, to efficient upconversion for energy applications, bio-sensing and on-chip components for quantum information science; they also serve as inspiration for entirely new devices and technologies. An exciting opportunity to realize such new nanomaterials lies in controlling the local electromagnetic environment on the atomic- and molecular-scale, (~1-10 nm) which enables extreme field enhancements, but represents a largely unexplored length scale. We use creative nanofabrication techniques at the interface between chemistry and physics to realize this new regime, together with advanced, ultrafast optical techniques to probe the emerging phenomena. Here, I will provide an overview of our recent research demonstrating tailored light-matter interactions by leveraging ultra-small plasmonic cavities fabricated using bottom-up techniques. Examples of our demonstrations include perfect absorbers and combinational colors [*Adv. Mat. 27, 7897 (2015)*, *Adv. Mat. 29, 1602971 (2017)*], actively tunable nanostructures [*Nano Lett., 18, 853 (2018)*], tailored emission from two-dimensional semiconductor materials [*Nano Lett. 15, 3578 (2015)*, *ACS Phot. 5, 552 (2018)*] and strong coupling.

8:40am **EM+MI+MN+NS-ThM3 The Geode Process: A Route to the Large-Scale Manufacturing of Functionally-Encoded Semiconductor Nanostructures***, M. Mujica, G. Tutuncuoglu, V. Breedveld, S.H. Behrens,* ***Michael Filler,*** Georgia Institute of Technology

Future large-area electronic and photonic technologies will require the manufacturing of materials and devices at very high rates without sacrificing nanoscale control of structure and composition. Semiconductor nanowires, for example, can be produced with exquisite spatial control of composition and morphology using the vapor-liquid-solid (VLS) mechanism that, however, remains limited to very small manufacturing rates. Here, we introduce the Geode process to synthesize functionally-encoded semiconductor nanowires at throughputs orders of magnitude beyond the state-of-the-art. Central to the Geode process are sacrificial, porous-walled, seed particle-lined silica microcapsules, whose interior surface serves as a high-surface area growth substrate. Microcapsules protect the growing nanostructures, are produced with a scalable emulsion templating technique, and are compatible with large-scale chemical reactors. We will show how microcapsule structure and drying is influenced by silica nanoparticle type and concentration, emulsification parameters, and nanoparticle cross-linking agent. We will also demonstrate the synthesis of Si nanowires with programmable dopant profiles on the microcapsule interior, which not only shows the versatility of the process, but also allows the impact of precursor gas transport limitations to be characterized.

9:00am **EM+MI+MN+NS-ThM4 Disordered Microsphere-Based Coatings for Effective Radiative Cooling under Direct Sunlight***, S. Atiganyanun, J. Plumley, K. Hsu,* University of New Mexico*; T.L. Peng,* Air Force Research Laboratory*;* ***Sang M. Han****, S.E. Han,* University of New Mexico

Radiative cooling is a process where a material loses heat due to strong emission of photons in the mid-infrared spectrum and enhanced light scattering in the solar region. This process would allow cooling of materials below the ambient temperature under the sun without the use of electricity and therefore would significantly reduce energy consumption. In this work, we have demonstrated a passive radiative cooling of disordered silica microsphere coatings below the ambient temperature while exposed to direct sunlight. To fabricate the coatings, silica microspheres are deposited by colloidal sedimentation method and spray coating method. In the first method, silica colloidal stability is disrupted by addition of KCl solution. The instability causes the colloids to agglomerate and sediment, creating a disordered uniform coating. In the second method, much like commercial painting, the colloidal solution is forced through a spray nozzle and deposited onto a substrate. Scanning electron microscopy show that the resulting structures are disordered without short- or long-range order. Optical measurements also indicate that the coatings produced under optimal conditions have a short transport photon mean free path of approximately 4-8 µm in the solar spectral region. These coatings also exhibit high emissivity above 95% in the atmospheric transparency window. These results suggest strong photon scattering properties in the visible region, while providing a strong thermal emission. Such films would enable effective radiative cooling. To test the cooling performance, we apply this film on top of a black substrate and expose the material to a direct sunlight during the summer in New Mexico. Temperature measurement of the samples shows that our coating reduces the substrate temperature below that of the ambient air by as much as 12 °C during daytime. Similar testing with a commercial solar-rejection paint indicates that the silica coating performs better than the commercial paint by 4.7 °C on average. Additionally the similar technique is used to fabricate disordered coatings made of polystyrene-polymethyl methacrylate microspheres. Outdoor experiments have shown that the polymer coatings

perform better than the commercial paint by 5.5 °C on average. Disordered coatings made of microspheres in a paint format will also be discussed.

9:20am **EM+MI+MN+NS-ThM5 Assessing Strain Relaxation in Nanostructured InGaN Multiple Quantum Wells Using X-Ray Diffraction Reciprocal Space Mapping and Photoluminescence Spectroscopy**, ***Ryan Ley**, C.D. Pynn, M. Wong, S.P. DenBaars, M.J. Gordon,* University of California at Santa Barbara

The III-Nitrides are excellent materials for LEDs, lasers and power electronics due to their tunable bandgap and high defect tolerance. These materials are increasingly important for displays in mobile and portable electronic devices, which currently suffer from short battery lives because displays based on liquid crystals or organic LEDs are inefficient. Producing high quality III-Nitride material with the indium compositions needed for efficient green and red emission is presently very challenging, due in large part to strain effects resulting from the large lattice mismatch between InGaN and GaN. However, there are some indications that nanostructuring can reduce or eliminate some of these strain issues.

This talk will highlight our recent work using colloidal and templated lithography and Cl2 /N2 plasma etching to fabricate nanoscale InGaN/GaN LED structures (diameter = 150-600nm), and how sub micron scale patterning affects the strain state and optical behavior of MQW emitters. InGaN/GaN LED structures were grown by MOCVD on c-plane sapphire substrates and characterized before and after nanopatterning using on-axis (0002) and off-axis (10-15 and 11-24) XRD reciprocal space maps (RSM), rocking curves and photoluminescence (PL) spectroscopy at 14K. RSM analysis found degrees of relaxation of 30% and 20% for the smallest and largest structures, respectively, and rocking curves revealed a 0.7nm decrease in the InGaN quantum well thickness. These relaxation effects also correlate well with spectral blue shifts (~10-15nm) in the PL, which are supported by 1D quantum mechanical and electrostatic simulations. Overall, this work shows that nanopatterning of InGaN/GaN active emitters at sub-micron length scales can reduce strain related issues in the III-Nitrides and potentially allow higher incorporation of indium for green and red emission.

9:40am **EM+MI+MN+NS-ThM6 Scalable, Tunable, and Polarization-Independent High Contrast Grating Reflectors for Integration into Resonant-Cavity micro-LEDs**, ***Pavel Shapturenka**, S.P. DenBaars, M.J. Gordon,* University of California at Santa Barbara

III-nitride blue and green micro-LEDs have exhibited quantum efficiencies of over 40%, which is a nearly fivefold efficiency boost over current OLED and LCD digital display technologies. In order to realistically continue LED miniaturization below 10 microns for high-resolution and near-eye pixel displays, it is necessary to maintain emission directionality and output power. One method to accomplish this is to make a resonant-cavity micro-LED device with a high-reflectance mirror and an output coupler.

We demonstrate a low-cost, tunable, and scalable colloidal lithography method to fabricate suspended TiO_2 high-contrast grating (HCG) reflectors across the visible wavelength range for eventual integration as an output coupler in a resonant-cavity LED. Silica spheres (310-960 nm diameter), deposited via Langmuir-Blodgett dip-coating, were used as a mask to define a quasi-ordered, hexagonal pattern on a 200 nm thick TiO_2 film. Subsequent pattern transfer with SF_6 reactive ion and XeF_2 chemical etching of sacrificial Si layers beneath the TiO_2 layer yielded a periodic, high index contrast between the suspended array structure and the surrounding air medium. Near-normal-incidence reflectance measurements on structures of increasing hole pitch (310-960 nm) showed an increase in maximum reflected wavelength from 370 to >1000 nm, while maintaining a high-%R bandwidth of 40-100 nm. The reflectance was also observed to be polarization-independent. Finite-difference time domain (FDTD) simulations of structural imperfection stemming from the colloidal lithography process, e.g., deviations in hole diameter, pitch, and hexagonal symmetry, indicate that absolute reflectance is most affected by hole offset from hexagonal lattice positions. The talk will highlight processing methods, optical characterization of HCGs, and underlying trends in the effect of HCG geometry on optical response as predicted by FDTD simulations. This work suggests that scalable fabrication of visible-wavelength HCGs is feasible and holds promise for integration into resonant-cavity LEDs.

11:00am **EM+MI+MN+NS-ThM10 Nano-optical Activation of Defect-bound Excitons in Monolayer WSe_2: Towards Room-temperature 2D Single-photon Optoelectronics**, ***Jim Schuck***, Columbia University **INVITED**

The emergence of two-dimensional (2D) monolayer transition metal dichalcogenides (1L-TMDC) as direct bandgap semiconductors has rapidly accelerated the advancement of room temperature, 2D optoelectronic devices. Optical excitations on the TMDCs manifest from a hierarchy of electrically tunable, Coulombic free-carrier and excitonic many-body phenomena. In our most recent nano-optical investigations of these materials, we have demonstrated that a model hybrid architecture, a nano-optical antenna and a 1L-WSe_2 nanobubble, activates the optical activity of BX states at room temperature and under ambient conditions. These results show that engineered bound-exciton functionality as, in this case, localized nanoscale light sources, can be enabled by an architectural motif that combines localized strain and a nano-optical antenna, laying out a possible path for realizing room-temperature single-photon sources in high-quality 2D semiconductors.

11:40am **EM+MI+MN+NS-ThM12 Light Scattering Properties of Silver Nanoprisms in Different Environments**, ***Yuri Strzhemechny***, Texas Christian University*; S. Requena,* Harris Night Vision*; H. Doan,* Texas Christian University*; S. Raut,* University of North Texas Health Science Center*; Z. Gryczynski,* Texas Christian University*; I. Gryczynski,* University of North Texas Health Science Center

Embedding nanostructures into different environments, such as polymer matrices, organic and biological solutions oftentimes produces unique optoelectronic properties of the resulting compound system that are distinct from those of the host and nano-filler. Such strong modifications can be caused by the interface phenomena, the change in the spatial distribution and orientation of the nanostructures or a combination thereof. In this work, we report on optical properties of silver triangular prism nanoparticles embedded in water, lipid solutions, and polyvinyl alcohol (PVA) polymer thin films. For our studies, using a common chemical reduction routine, we synthesized, batches of silver nanoparticles with different size distributions and distinct size-dependent dipole resonance spectra. Silver nanoprisms suspended in water yielded a noticeable wavelength-dependent depolarization of scattered light associated with different surface plasmon modes. Consequently, the same nanostructures were placed into lipid environments to estimate the rejection of a polarized background scattering during depolarization measurements. After that, the composite thin films were fabricated via incorporation of silver nanoparticles into PVA. We studied linear dichroism in those Ag/PVA films, as-prepared and subjected to controllable stretching. Re-orientation of the nanoprisms upon stretching leads to a significant increase of the linear dichroism for the plasmonic modes associated with the in-plane dipole oscillations and a decrease of the linear dichroism corresponding to the out-of-plane plasmonic modes. These observations are in good agreement with the assumption that stretching of the nanocomposite films leads to an anisotropic realignment of the nanoprisms.

12:00pm **EM+MI+MN+NS-ThM13 Core-Shell Processing of BTO Nanocomposites for Optimal Dielectric Properties**, ***Kimberly Cook-Chennault***, Rutgers University

High permittivity polymer-ceramic nanocomposite dielectric films leverage the ease of flexibility and processing of polymers and functional properties of ceramic fillers. Physical characteristics of these materials can be tuned for application to a variety of applications, such as, advanced embedded energy storage devices for printed wired electrical boards and battery seperators. In some cases, the incompatibility of the two constituent materials; hydrophilic ceramic filler and hydrophobic epoxy can limit the filler concentration and therefore, dielectric properties of these materials. Use of surfactants and core-shell processing of composite fillers is traditionally used to achieve electrostatic and steric stabilization for adequate ceramic particle distribution. This work aims to understand the role of surfactant concentration in establishing meaningful interfacial layers between the epoxy and ceramic filler particles by observing particle surface morphology, dielectric permittivity and device dissipation factors. A comprehensive study of nanocomposites that were comprised of non-treated and surface treated barium titanate (BT) embedded within an epoxy matrix was performed. The surface treatments were performed with ethanol and 3-glycidyloxypropyltrimethoxysilan, where the best distribution, highest value of permittivity (~ 48.03) and the lowest value of loss (~0.136) were observed for the samples that were fabricated using 0.5 volume fraction of $BaTiO3$ and 0.02 volume fraction of silane coupling agent.

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-ThM1 Femtosecond Laser Processing of Ceria-Based Micro Actuators***, J. 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,* ***Erez Benjamin****,* 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-ThM2 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-ThM3 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-ThM5 Polymer Templated Annealing of DNA Patterned Gold Nanowires***,* ***Tyler Westover****, B. Aryal, R.C. 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-ThM10 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-ThM12 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-ThM13 Enhancing Light Extraction from Free-standing InGaN/GaN light Emitters Using Bio-inspired Backside Surface Structuring*,*** *L. Chan, C.D. Pynn, S.P. 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-ThM1 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-ThM3 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-ThM4 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-ThM5 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-ThM10 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.

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11:40am **PS+EM+TF-ThM12 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.U. Engelmann, R.L. Bruce, E.A. Joseph,* IBM Research Division, T.J. Watson Research Center*; D. Metzler,* IBM Research Division, Albany, NY*; G.S. 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-ThM13 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.-P. 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.

Surface Science Division
Room 203C - Session SS+EM+NS-ThM

Defects in and Functionalization of 2D Materials

Moderators: Lars Grabow, University of Houston, Greg Kimmel, Pacific Northwest National Laboratory

8:00am **SS+EM+NS-ThM1 Holes, Pinning Sites and Metallic Wires in Monolayers of 2D Materials**, ***Thomas Michely***, University of Cologne, Germany **INVITED**

The moiré formed by a monolayer of hexagonal boron nitride with Ir(111) provides through a chemisorbed valley region within a physisorbed mesa a unique site for its functionalization. Through gentle ion irradiation and mild annealing a regular array of vacancy clusters is created with the clusters positioned at the valleys where their edges bind to the substrates. Such a nanomesh with a regular array of holes with sizes below 1 nm holds promise for filter applications. Through vapor phase deposition of a variety of materials (e.g. Au or C) arrays of clusters with of tunable size and high thermal stability are formed at valley regions. Compared to the graphene moiré the templating effect of the hexagonal boron nitride moiré is superior due to the uniqueness of the valley pinning site in the unit cell.

Monolayers of hexagonal boron nitride or graphene are also excellent substrates for the on-surface synthesis of new compounds ranging from metal-organic nanowires to transition metal disulfides created by reactive molecular beam epitaxy with elemental sulfur. This synthesis method provides clean, well-decoupled layers with only well-defined defects.

The most exciting defects we observed so far are two types of mirror twin boundaries in MoS_2 islands. In these boundaries we observe for the first time spin-charge separation in real space making use of the unique local spectroscopic capabilities of low temperature STM and STS to identify the position and energy of quantum mechanical states in a one dimensional box. We critically discuss these results in the light of previous related research.

Contributions to this work by Wouter Jolie, Joshua Hall, Clifford Murray, Moritz Will, Phil Valerius, Charlotte Herbig, Carsten Speckmann, Tobias Wekking, Carsten Busse, Fabian Portner, Philipp Weiß, Achim Rosch, Arkady Krasheninnikov, Hannu-Pekka Komsa, Borna Pielić, Marko Kralj, Vasile Caciuc and Nicolae Atodiresei as well as financial support through CRC1238 within projects A01 and B06 of DFG are gratefully acknowledged.

8:40am **SS+EM+NS-ThM3 CO Chemisorption at Pristine, Doped and Defect Sites on Graphene/Ni(111)**, ***Mario Rocca***, *G. Carraro,* University of Genova, Italy*; M. Smerieri, L. Savio,* IMEM-CNR, UOS Genova, Italy*; E. Celasco, L. Vattuone,* University of Genova, Italy

Due to its electrical properties graphene (G) has been successfully used as a sensing element for the detection of different gases reaching ppm sensitivities which are ascribed to the doping induced by adsorption. The sensitivity depends indeed critically on the chemical nature of the gas and is lower for CO than for other poisoning species. The nature of the active sites is, however, still unclear. If it were due to physisorption, the values of the adsorption energy cannot explain the need for high temperature re-generation of the sensing element. Chemisorption must thus be involved, either at defects or by doping, determining the magnitude of the heat of adsorption and consequently the sensitivity and the range of temperatures at which the sensor can operate. In order to clarify these issues we investigated experimentally adsorption of CO on G supported on polycrystalline Cu and Ni(111) by HREELS and XPS.

No adsorbed CO was found at RT while at 100 K chemisorbed CO forms on G supported on Ni(111). G on Cu is on the contrary inert. This result indicates that the nature of the substrate plays an essential role in the adsorption process. The heat of adsorption q is estimated to be about 0.58 eV/molecule at low coverage, so that an equilibrium coverage of 0.1 ML is expected at RT under a CO partial pressure of only 10 mbar. We identify top-bridge graphene as the most reactive configuration.

Doping G/Ni(111) by N_2^+ ion bombardment allows for the formation of a second, more strongly bound moiety, characterized by a CO stretch frequency of 236 meV and by an initial heat of adsorption (0.85 eV/molecule). The presence of N (in pyridinic or substitutional sites) enhances therefore significantly the chemical reactivity of G/Ni(111) towards CO.

Finally in presence of isolated defects, created by low energy Ne^+ ions bombardment on single layer graphene supported on different substrates (polycrystalline Cu and Ni(111)), no CO adsorption occurs for defected G/Cu, while HREELS peaks form promptly for G/Ni(111). Two moieties, desorbing just above 350 K, are present under vacuum conditions after exposure at RT. The CO stretch frequencies and the ratio of their intensities indicate that they are due to chemisorbed CO at the G/Ni(111) interface close to the vacancies rather than at the defected G layer. The red-shift of the C1s binding energy indicates that in such regions detachment of the G layer from the substrate occurs.

Amending of vacancies occurs for subsequent exposures, as demonstrated by the reduction of the adsorbed coverage in subsequent CO doses followed by annealing at 380 K, indicating that a Bouduard-like reaction takes place under the graphene cover.

9:00am **SS+EM+NS-ThM4 Geometry of Cu Islands Buried Beneath the Surface of Graphite***, A. Lii-Rosales,* Ames Laboratory and Iowa State University*; S. Julien,* Northeastern University*; Y. Han, J.W. Evans,* Ames Laboratory and Iowa State University*; K.-T. Wan,* Northeastern University*; **Patricia A. Thiel,*** Ames Laboratory and Iowa State University

Deposition of Cu on a sputtered graphite surface, in ultrahigh vacuum, can be manipulated to produce buried islands of metallic, multilayer Cu. The Cu islands are covered by a graphitic layer consisting of several graphene sheets. This layer drapes like a tarpaulin over the Cu islands. We have observed flat-topped islands as tall as 40 nm and as wide as 600 nm. One of the most striking features of island geometry is the fact that the slope of the tarpaulin at the sides of the islands is invariant over a wide range of island volumes. The variation of the ratio of island diameter to height as a function of island volume is far less regular in the experimental data, suggesting that kinetic limitations may play a role in determining this parameter. To investigate the physical forces responsible for the island geometries, we develop a model for island shape that incorporates the distortion energy of graphene, adhesion of Cu with graphitic surfaces, adhesion of graphene with graphite, and other parameters. The energy parameters involving Cu surfaces and Cu-carbon interfaces are derived from DFT calculations. The values and trends predicted by the model are discussed and compared with experiment. In particular, the model indicates that the slope of the island sides should be invariant, consistent with experiment.

9:20am **SS+EM+NS-ThM5 Intercalation of O_2 and CO between Graphene and Ru(0001) and the Role of Defects***, **Jory Yarmoff**, T. Li,* University of California, Riverside

Graphene (Gr) is a fascinating 2D material that is being widely being considered for applications in electronic devices due to its unique electronic and materials properties. Also, because of its high thermal stability and inertness, it is a promising candidate for use as a protection layer for metal substrates. Here, graphene films grown on Ru(0001) are exposed to O_2 and ^{13}CO and investigated with helium low energy ion scattering (LEIS). LEIS spectra collected at different scattering angles can distinguish between adsorbed and intercalated molecules. It is found that O_2 and CO do not adsorb to the graphene surface but instead intercalate between Gr and the substrate. It is shown that a much lower annealing temperature is needed to remove intercalated oxygen than chemisorbed oxygen on bare Ru. During the thermal desorption, some of the graphene is etched away via chemical reaction forming gaseous CO or CO_2. In addition, carbon vacancy defects are produced in the Gr films via 50 eV Ar^+ bombardment. Isolated single carbon vacancy defects enable molecular adsorption at the defect sites and ease the overall intercalation of oxygen. The defects also improve the thermal etching efficiency of Gr by intercalated oxygen. When the defects are large enough to consist of open areas of bare substrate, oxygen dissociatively chemisorbs to Ru. Intercalated ^{13}CO molecules sit upright with the O end on top, as on clean Ru. The CO molecules tilt, however, when the temperature is raised. This is likely due to increased vibrational amplitudes combined with the confining effect of the Gr film.

9:40am **SS+EM+NS-ThM6 Organic-2D Transition Metal Dichalcogenide van der Waals Heterostructures***, **Yu Li Huang**,* Institute of Materials Research & Engineering (IMRE), A*STAR, Singapore*; Z. Song,* National University of Singapore*; D. Chi,* Institute of Materials Research & Engineering (IMRE), A*STAR, Singapore*; A.T.S. Wee,* National University of Singapore

The recent emergence of two-dimensional transition metal dichalcogenides (2D TMDs) has led to a rapid burgeoning of the field due to their novel electronic and optical properties with potential electronics/photonics applications. Organic materials, on the other hand, have exhibited great success in the field of flexible electronics, with an extensive number of available molecules with tunable properties. Marrying the fields of organics and 2D TMDs will bring benefits that are not present in either material alone, enabling even better, multifunctional flexible devices. In parallel, the integration of 2D TMDs with selected organics is also a promising and controllable approach to modulate the properties of the TMDs without structural damage, thereby optimizing or even enhancing their desired properties for specific device applications. Central to the realization of all those applications is a fundamental understanding of the organic-2D TMD interface.[1]

Here, we will present our recent studies on hybrid organic/2D TMD heterostructures.[2-4] With combined experiments and theoretical modeling, the interfacial interactions between the organic layers and the TMDs as well as the energy level alignment at the interface are explored. The comprehensive understanding of the underlying physical mechanisms that govern the properties of organic-2D TMD interfaces at the atomic scale is of fundamental importance for developing this technique further for device applications.

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11:00am **SS+EM+NS-ThM10 Influence of Surface Functionalization on Surface Topography and Growth of Metal Oxide Structures on HOPG***, **Kathryn Perrine**, M. Trought, I. Wentworth, C. de Alwis, T.R. Leftwich,* Michigan Technological University

Growth of heterogeneous catalysts, plasmonic and other nanostructured materials requires atomic level control and molecular level understanding of the growth of metals and metal oxides on surfaces. Surface functionalization of 2D materials can be used to promote selective nucleation of metal oxides with control over the deposition and growth. However, this requires an understanding of surface functionalization. This surface chemical functionalization can be combined with the atomic-level control of atomic layer deposition (ALD). ALD is a vapor deposition technique that utilizes self-limiting surface reactions to grow metal oxides, where the surface functional group initiates the first step in the deposition process.

2D materials are ideal for selective functionalization that may not require lithography steps due to the fact that their sheets are in a stable configuration making them chemically unreactive. Highly oriented pyrolytic graphite (HOPG) is an ideal model of the graphene surface, a well-known 2D material, which is comprised of sp^2 hybridized aromatic hydrocarbon sheets. HOPG consists of stacked graphene sheets where the terraces of the carbon sheets are chemically unreactive in ambient conditions and their defects are highly reactive. Oxidation methods are used to produce an assortment of different functional groups on HOPG and can lead to different types of functionalities on the surface and its defects.

We investigate how surface oxidative etching and functionalization influences the growth of metal oxide structures at tailored defects and functional sites on HOPG. Two different acids were used to etch the HOPG surface to produce functional groups resulting in different surface topographies. The functionalized HOPG was then exposed to trimethylaluminum and water, a well-known ALD reaction, to produce Al_2O_3 as a proof-of-concept to observe the growth of Al_2O_3 on both functional and defect sites. Vibrational spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) were used to measure surface functionalization and Al_2O_3 growth on HOPG. Field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM) and Raman spectral imaging were used to image the changes in surface topography after etching and ALD deposition. Results indicate that the Al_2O_3 deposition and growth is dictated by the surface functionalization and topography. This suggests that understanding the effects of surface functionalization of 2D materials is necessary for controlling the growth of metal oxide structures.

11:20am **SS+EM+NS-ThM11 Impurity Induced Chemical Properties of BN on Rh(111) Studied by First Principle Calculations: A New Phase**, ***Zahra Hooshmand***[1], *D. Le, T.S. Rahman,* University of Central Florida

Hexagonal boron nitride (h-BN), an insulating layer of sp^2 hybridized structure between B and N, grown on Rh(111) forms a Moiré pattern with elevated (rim) and depression (valley) areas. The valleys are circular dipole rings which act as trapping centers for the adsorption of nanoparticles and molecules [1]. The presence of the native carbon impurities in Rh potentially gives rise to the formation of hexagonal carbon rings under every other rim area as suggested by recent experiments [2] and could lead to new structures and novel chemistry. Here, on the basis of Density Functional Theory (DFT) simulations with dispersion corrections, we show that these rings tend to grow in a manner in which the center of each ring is placed on top of the Rh atom. These rings grow next to each other and form islands which are separated from each other by an equal distance while the BN monolayer remains untouched, i.e. there is no C-B or C-N bond formed. Our calculations show that while no broken bonds between B and N were observed, the increase in the concentration of carbon impurities will enhance the height modulations among different regions of BN Moiré pattern leaving the former valleys unchanged while decreasing their area. The new higher elevated regions show strong accumulation of charge and the lower elevated regions display depletion of charge. This gives rise to modification of dipole rings and results in altered adsorption of pentacene on BN. Our simulations of Scanning Tunneling Microscope (STM) images from this structure, are in good agreement with experimental data for number of rings from 3 to 5. However spatial density of states analysis shows that in the presence of 5 rings islands the gap in BN on the higher elevated regions vanishes and the band gap on these areas for 3 and 4 rings islands reduces. The calculations of local variations in work function also show that these variations become more pronounced by growth of islands and reduces the work function of lower elevated regions in new phase. This results show that by control of the concentration of local impurities underneath the rim areas in BN, the chemical properties are modified and the monolayer could be engineered for interesting chemical reactions. [1] H. Dil et al., *Science*, 2008, 319, 1824-1826. [2] Koslowski et al. Private communication.

This work was supported by National Science Foundation, Grant #NSF CHE-1465105"

11:40am **SS+EM+NS-ThM12 Texture of Atomic-layer Deposited MoS: A polarized Raman Study**, ***Vincent Vandalon***, *A. Sharma, W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands; *A.A. Bol,* Eindhoven University of Technology, Netherlands

Advances in optical characterization techniques for 2D transition metal dichalcogenides (2D-TMDs) such as MoS2 are essential in the context of tailoring the texture and surface functionalization of these materials. Tailoring of the texture of *synthesized* MoS2 results in uniquely different material characteristics: out-of-plane fins of MoS2 have been demonstrated to possess excellent catalytic performance, most likely due to exposed catalytically active edge sites, whereas basal plane oriented MoS2 shows excellent electronic properties. The large impact of texture on the exhibited properties underlines the need for rapid and facile characterization of the texture and especially the angular grain orientation. So far, cross section high-resolution transmission electron microscopy (HR-TEM) is widely employed to obtain insight into texture but it suffers from a limited throughput. On the other hand, Raman spectroscopy has been established as the *go-to* technique for the determination of e.g. film thickness of these TMDs. Here we will show that the angular grain distribution can also be determined using *polarized* Raman spectroscopy

We have found that plasma-enhanced atomic-layer deposition (PE-ALD) of MoS2 allows control over the texture and results in out-of-plane fins or basal plane oriented material depending on the processing conditions using HR-TEM. To study the texture of the PE-ALD synthesized films with Raman spectroscopy, we have investigated the so far unknown impact of the angular grain distribution on the Raman response. The Raman response of nanocrystalline MoS2 was modeled for a range of different textures. This allowed us to determine the angular grain distribution from the peak ratio of the two dominant Raman peaks (i.e. the A1g and E2g modes). Furthermore, the modeling also showed that performing *polarized* variant of Raman spectroscopy is essential for the accurate determination of the angular grain distribution because of the additional information it provides. A systematic polarized Raman study into the evolution of the fraction of out-of-plane material with film thickness allowed us to gain insight into the growth process. Moreover, the influence of a post-deposition high-temperature anneal in a H2S atmosphere on the texture, known to yield improved material properties, was also investigated. To conclude, polarized Raman spectroscopy offers a rapid method to gain insight into the angular grain distribution of synthesized MoS2 and this approach can be readily extended to other MX2 materials.

[1] **National Student Award Finalist**

2D Materials Focus Topic
Room 201B - Session 2D+EM+MN+NS-ThA
Novel Quantum Phenomena in 2D Materials

Moderator: Hsin Lin, Institute of Physics, Academia Sinica

2:20pm **2D+EM+MN+NS-ThA1 Double Indirect Interlayer Exciton in a $MoSe_2$/WSe_2 van der Waals Heterostructure**, ***Aubrey Hanbicki***, *H.-J. Chuang, M. Rosenberger, C.S. Hellberg, S.V. Sivaram, K.M. McCreary, I. Mazin, B.T. Jonker,* Naval Research Laboratory

Tailoring semiconductor heterostructures for specific functionalities has led to varied opto-electronic devices including solar cells, photodetectors, light-emitting diodes and lasers. An emerging class of heterostructures involves monolayer semiconductors such as many of the transition metal dichalcogenides (TMDs) which can be combined to form van der Waals heterostructures (vdWHs). vdWHs offer novel functionalities making them promising hosts for future devices. One unique new heterostructure property is an interlayer exciton (ILE), a spatially indirect, bound electron-hole pair with the electron in one TMD layer and the hole in the other. Here, using state-of-the-art preparation techniques, we are able to resolve emission from the ILE in a $MoSe_2$/WSe_2 heterostructure into two distinct peaks separated by 24 meV at zero field. These peaks have nearly equal intensity, indicating they are of common character, and have *opposite* circular polarizations when excited with circularly polarized light. *Ab initio* calculations successfully account for these observations – they show that both emission features originate from excitonic transitions that are indirect in momentum space and are split by spin-orbit coupling. Also, the electron is strongly hybridized between both the $MoSe_2$ and WSe_2 layers, with significant weight in both layers, contrary to the commonly assumed model. Thus, the transitions are not purely interlayer in character. This work represents a significant advance in our understanding of the static and dynamic properties of TMD heterostructures.

This research was performed while H.-J.C. held an American Society for Engineering Education fellowship and M.R.R and S.V.S held a National Research Council fellowship at NRL. This work was supported by core programs at NRL and the NRL Nanoscience Institute. This work was also supported in part by a grant of computer time from the DoD High Performance Computing Modernization Program at the U.S. Army Research Laboratory Supercomputing Resource Center.

2:40pm **2D+EM+MN+NS-ThA2 Comparison of A- and B-exciton Intensity and Polarization in Transition Metal Dichalcogenide Monolayers and Heterostructures**, ***Kathleen McCreary***, *A.T. Hanbicki, S.V. Sivaram, B.T. Jonker,* U.S. Naval Research Laboratory

We survey a large number of monolayer TMDs to better understand the conditions responsible for various emission characteristics that have been reported in literature. We find that the intensities for both A- and B- peak emission vary widely as a result of sample-to-sample variations. However, a measurable B-peak intensity is evident in all samples. There is a clear linear relationship between the two peak intensities. The emission from the dominant A-peak is commonly several orders of magnitude higher than B-peak emission, resulting in B/A-intensity ratios well below 1%. Yet, as the A-peak intensity decreases, the ratio of B/A monotonically increases, and we observe a B/A ratio up to 30% in monolayer MoS_2. The A-excitonic emission is further quenched when $MoS_2$is incorporated into an MoS_2/$MoSe_2$heterostructure, where we observe comparable A- and B-peak intensities. We attribute these variations to differences in exciton recombination times, clarifying contradictory reports regarding the accessibility and significance of B-peak emission. Furthermore, we observe a high degree of valley polarization in both B-exciton emission in isolated monolayers and A-exciton emission in heterostructures, consistent with our model detailing the rapid exciton lifetimes in B-emission and van der Waals heterostructures.

Supported by core programs at NRL and the NRL Nanoscience Institute

3:00pm **2D+EM+MN+NS-ThA3 Optospintronics and Magnetism with 2D Materials and Heterostructures**, ***Roland Kawakami,*** The Ohio State University **INVITED**

I will review our latest developments in spintronics, optospintronics and magnetism in two-dimensional (2D) materials and heterostructures. Graphene continues to exhibit improved properties for spin transport and demonstrates additional functionality through the use of vertically stacked heterostructures. One of the interesting new directions is optospintronics enabled by heterostructures of graphene and transition metal dichalcogenides (TMD) [1]. Due to the valley optical selection rules of TMDs and the large spin-orbit coupling, the helicity of the photon is coupled to the valley spin polarization of electrons. Thus, circularly polarized optical excitation into a TMD/graphene heterostructure generates spin polarization in the TMD that subsequently transfers to the graphene. This optical spin injection into graphene is an example of new functionality for the expanding field of 2D spintronics. In the area of 2D magnets, we have used molecular beam epitaxy (MBE) to deposit monolayer $MnSe_2$, which exhibits ferromagnetism at room temperature [2]. These results open the door for new possibilities for magnetoelectronic applications with low dimensional materials.

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4:00pm **2D+EM+MN+NS-ThA6 Giant Electromechanical Response in Van-der-Waals Layered Crystals**, ***Sabine Neumayer***, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory*; E.A. Eliseev,* National Academy of Sciences of Ukraine*; A. Tselev,* CICECO and Department of Physics, University of Aveiro, Portugal*; A.N. Morozovska,* National Academy of Sciences of Ukraine*; M.A. Susner, M.A. McGuire,* Oak Ridge National Laboratory*; J. Brehm, S. Pantelides,* Vanderbilt University*; N. Balke, P. Maksymovych,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

Obtaining ultrathin electromechanically active materials for memory and energy applications encounters numerous challenges as significant downscaling of classical ferroelectrics such as perovskite oxides is severely constrained by size and screening effects. Moreover, interfacing pseudo-cubic ferroelectrics with 2D electronic materials faces challenges related to defect and impurities, which limit performance. Van der Waals ferroelectrics, especially transition metal thiophosphates such as copper indium thiophosphate (CIPS) yield promising prospects for applications as ultrathin piezoelectric structures and interface materials due to their stable surfaces, layered structure and transition temperatures near room temperature. Here, we use scanning probe microscopy to explore the remarkable functional properties of CIPS across the transition temperature. At low temperatures, strong electromechanical response is measured despite the small polarization values and the material contracts in electric fields rather than expanding. These findings point to giant negative electrostrictive coefficients, which were quantified using Landau-Ginzburg-Devonshire analysis. Above the transition temperature, CIPS shows dielectric tunability comparable to BST at low frequencies. In addition, electromechanical strain exceeding 10 nm displacement was measured upon fully reversible field induced formation of particles on the surface. Complimentary DFT calculations provide further insight into the role of ionic displacement in electromechanical behavior.

Research conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility . Research was sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U. S. Department of Energy.

4:20pm **2D+EM+MN+NS-ThA7 A Universal Method for Measuring Valleytronic Quality of 2D Materials using Conventional Raman Spectroscopy**, ***Steven Vitale***, *J.O. Varghese, D.A. Nezich, M. Rothschild,* MIT Lincoln Laboratory

Valleytronics offers a new information processing paradigm based on the momentum index of real or quasi-particles in 2D materials as the fundamental unit of information storage instead of charge. A major challenge to realize valleytronic computing is the development of deterministic material growth processes which yield valleytronic-quality material with the requisite valley relaxation lifetime (T1) and valley dephasing time (T2). Unfortunately direct measurement of T1 and T2 requires complex instrumentation to perform ultrafast spectroscopic measurements and thus is not practical for routine material analysis. In this paper, we demonstrate that an accurate and reproducible measurement of $T1/T_{exc}$ (where T_{exc} is the exciton recombination lifetime) can be performed a simple Raman microscope. By simultaneously measuring the photoluminescence of the 2D material and the Raman transition of the underlying silicon substrate as a function of the incident laser polarization angle, one can remove sources of error and equipment-to-equipment variability. This technique is completely general and can be applied to any

valleytronic material which can be grown-on or transferred-to a Raman-active crystalline substrate, such as silicon. Using this technique we show that valley relaxation in a sample of CVD-grown MoS_2 is an order of magnitude slower at 4 K than at 100 K. Oxidation of MoS_2 left exposed to the ambient environment severely decreases the valleytronic quality of the material. Two-dimensional mapping of the valley relaxation time of CVD MoS_2 domains at 4 K shows a three-fold spatial symmetry which is suggestive of new valley physics phenomena which arise in 2D crystals of finite size. MoS_2 domain size also affects the valley relaxation time, which has significant material-growth implications for real valleytronic applications. Finally we compare these measurements to our calculated requirements for valley relaxation time in a practical information processing device and quantify the challenges for future valleytronic material growth.

4:40pm **2D+EM+MN+NS-ThA8 Discovery of Intrinsic Ferromagnetism in 2D van der Waals Crystals***, **Xiang Zhang**, C. Gong,* University of California, Berkeley **INVITED**

In this talk, I will present our discovery of the intrinsic ferromagnetism in 2D van der Waals (vdW) crystals, including the prominent dimensionality effect and unprecedented magnetic field control of the Curie temperature in the nearly-ideal 2D Heisenberg ferromagnet. Significant fundamental physics in 2D magnetism and the corresponding exotic phenomena we observed will be expounded. Updated research on the complex magnon scatterings, material level engineering of 2D magnetism, and the development of novel concept of spintronic devices will be further discussed. Finally, I will envision the possible directions towards advancing 2D magnets for practical spintronic applications.

5:20pm **2D+EM+MN+NS-ThA10 Spectroscopic Evidence of Pair-mediated Bosonic Modes in Superconductor FeSe/SrTiO3(100) Film***, **Minjun Lee**,* Seoul National University, Republic of Korea*; M. Oh, H. Jeon, S. Yi, I. Zoh,* Seoul National University, Republic of Korea*; C. Zhang,* Seoul National University, Republic of Korea*; J. Chae, Y. Kuk,* Center for Quantum Nanoscience, Institute for Basic Science, Republic of Korea

Single layer FeSe on $SrTiO_3$(100) is atypical but noticed system in superconductivity. This has unique properties due to the substrate phonon. Unlike other bulk systems, the presence of the interface allows the substrate phonons to affect the superconducting layer. We have investigated substrate phonon effects on superconducting FeSe layer by using scanning tunneling spectroscopy and Eliashberg theory. We were able to measure acoustic, optical and substrate phonons in d^2I/dV^2 spectroscopy. We found these phonon modes attribute to the paring of electrons in this superconducting layer. These results are analyzed by Eliashberg model and we will discuss the coupling strength of these bosonic features. We have found that the substrate phonon has major contribution to increase the transition temperature of this system.

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-ThA1 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-ThA3 Flexible Electronic Devices Based on Two Dimensional Materials***, R. Kim, N.R. Glavin,* Air Force Research Laboratory*; R.H. Rai, K. Gliebe, M. Beebe,* University of Dayton; Air Force Research Laboratory*; J. Leem, S. Nam,* University of Illinois at Urbana-Champaign*; R. Rao,* Air Force Research Laboratory*; **Christopher Muratore**,* University of Dayton*; K.M. Burzynski,* University of Dayton and Air Force Research Laboratory, Materials and Manufacturing Directorate

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-ThA4 Contact Resistances and Schottky Barrier Heights of Metal-SnS Interfaces***, **Jenifer Hajzus**, L.M. 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, U.S. Naval Research Laboratory

2:20pm **PS+EM+TF-ThA1 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-ThA2 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-ThA3 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-ThA4 The Smoothing Effect in Atomic Layer Etching (ALE)**, ***Keren Kanarik***, *S. Tan, W. Yang, I.L. Berry, T.B. Lill, Y. Pan, R.A. 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-ThA6 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-ThA8 Low Temperature Surface Preparation of GaN Substrates for Plasma Assisted-Atomic Layer Epitaxial Growth*, Samantha G. Rosenberg,*** U.S. Naval Research Laboratory*; D.J. Pennachio,* University of California, Santa Barbara*; M. Munger,* SUNY Brockport*; C. Wagenbach,* Boston University*; V.R. Anderson,* U.S. Naval Research Laboratory*; S.D. Johnson,* U. S. Naval Research Laboratory*; N. Nepal, A.C. Kozen, J.M. Woodward,* U.S. Naval Research Laboratory*; Z.R. Robinson,* SUNY Brockport*; K.F. Ludwig,* Boston University*; C.J. Palmstrøm,* University of California, Santa Barbara*; C.R. 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-ThA9 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-ThA10 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.L.G. 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.

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-ThA1 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-ThA3 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.V. 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-ThA4 Redox-Active Ligands for Single-Site Metal-Organic Complexes on Surfaces as Heterogeneous Catalysts***, **Tobias Morris**,* Indiana University*; D.L. Wisman,* Indiana University, NAVSEA Crane*; I.J. Huerfano, N.A. Maciullis, K.G. Caulton, S.L. 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-ThA6 Oxidation and Ablation of HOPG Using Supersonic Beams of Molecular Oxygen Combined with STM Visualization***, **Ross Edel**, T. Grabnic, B. Wiggins, S.J. 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.

5:00pm **SS+EM+PS+TF-ThA9 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.E. 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-ThA10 Adsorption and Reactions on Topological Insulators Surfaces Probed by Low Energy Ion Scattering**, ***Haoshan Zhu***[1], *W. Zhou, J.A. 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-ThA11 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-ThA1 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

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[2] G. Schwartz et al., Nature Commun. **4**, 1859 (2013).

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3:00pm **TF+AS+EL+EM+NS+PS+SS-ThA3 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-ThA4 Investigation of Low Temperature ALD-deposited SnO_2 Films Stability in a Microfabrication Environment**, ***Tony Maindron,*** *S.M. Sandrez, N.V. 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

[1] **Morton S. Traum Award Finalist**

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-ThA6 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*; A.D. Giddings, T.J. Prosa, D.J. Larson,* CAMECA Instruments Inc.*; S. Kölling, P.M. Koenraad, F. Roozeboom,* ***Erwin Kessels****, M.A. 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 ºC. 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 ºC. This material provides a record optoelectronic quality after post-deposition crystallization of the films at 200 ºC. 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).

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4:20pm **TF+AS+EL+EM+NS+PS+SS-ThA7 Roll-to-Roll Processable OTFT Sensors and Amplifier***,* ***Kai Zhang****,* University of Oxford, Department of Materials, UK*; C.-M. Chen, B. Choubey, H.E. 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:

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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-ThA8 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-ThA9 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-ThA10 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-ThA11 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.A.R. Watt, H.E. 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

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Electronic Materials and Photonics Division
Room Hall B - Session EM-ThP
Electronic Materials and Photonics Division Poster Session

EM-ThP3 Thermal Engineering for High-Power, Flexible Electronics*, Katherine Burzynski,* University of Dayton and Air Force Research Laboratory, Materials and Manufacturing Directorate*; E.W. Blanton, N.R. Glavin, E.R. Heller, M. Snure, E.M. Heckman,* Air Force Research Laboratory*; C. Muratore,* University of Dayton

Consumers and military personnel are demanding faster data speeds only available through fifth generation (5G) wireless communication technology. Furthermore, as wearable sensors and other devices become more ubiquitous, devices demonstrating enhanced flexibility and conformality are necessary. A fundamental challenge for flexible electronics is thermal management. Even on rigid substrates with significantly higher thermal conductivity than polymeric and other flexible substrates, the full potential of semiconducting materials is often thermally limited. The flexible gallium nitride (GaN) high electron mobility transistors (HEMTs) employed in this work are grown on a two-dimensional boron nitride (BN) release layer that allows the conventionally processed devices on sapphire wafers to be transferred using a polymeric stamp and placed onto a variety of rigid and flexible substrates. Characterization of the GaN device behavior on the as-grown sapphire wafers (prior to transfer) provide a baseline for evaluation of the thermal performance of engineered interfaces and substrates. With conventional substrates, device performance (specifically, the saturation current) is reduced when the device is transferred to polymeric substrates. The thermal dissipation is further restricted due to the addition of an adhesive layer to the substrate. Thermal imaging of devices in operation reveals that the current passing through an as-grown GaN transistor on a sapphire wafer reaches the target operating temperature at approximately five times the power of the same device transferred to a flexible substrate. Printable, thermally conductive nanocomposites integrating 1D, 2D, and 3D forms of carbon in a flexible, photocurable polymer matrix, as well as metal nanoparticles, were developed to maximize heat transfer from GaN devices. The thermal conductivity of the candidate substrate materials was measured experimentally, and the performance of devices transferred to these novel flexible composite substrates was characterized. The measured thermal data was used in computational simulations to predict flexible substrate architectures effectively promoting point-to-volume heat transfer to improve device performance. Additive manufacturing for engineered architectures of the flexible, thermally conductive substrate materials was demonstrated to substantially reduce the thermal limitation of high-power flexible electronics.

EM-ThP4 Growth and Magneto-optical Properties of ZnO/$Zn_{1-x}Mn_xO$ Thin Films on Si Substrates*, Da-Ren Liu,* ITRC,NARL,Taiwan, Republic of Korea*; C.-J. Weng,* ITRC,NARL, Taiwan, Republic of Korea

ZnMnO is one of the most promising diluted magnetic semiconductors (DMS) materials due to its predicted above room temperature ferromagnetism. In this study, ZnO layer was conformally deposited on the Si substrates by atomic layer deposition (ALD). Then the $Zn_{1-x}Mn_xO$ ($0.01 < x < 0.10$) coatings were grown on ZnO layer by Nd:YAG pulsed laser deposition (PLD). The thickness and roughness of the films were characterized by grazing-incidence x-ray reflectivity (GIXR). According to the results of high-resolution x-ray diffraction, the ZnO/ $Zn_{1-x}Mn_xO$ thin films are polycrystalline with a preferential growth direction of (002). The surface and cross-section morphologies of films were analyzed by the field-emission scanning electron microscope (FE-SEM). Photoluminescence spectra demonstrate ultraviolet emission peaks which have shift with the increase of Mn ion concentration. The temperature-dependent magnetization (M-T) curves of the ZnO/ $Zn_{1-x}Mn_xO$ thin films were measured by a superconducting quantum interference device (SQUID) magnetometer and the magneto-optical properties were measured by micro-MOKE spectroscopy. The results show the room temperature ferromagnetism of the ZnO/ $Zn_{1-x}Mn_xO$ thin films suggested that the possibility for the application to diluted magnetic semiconductors.

EM-ThP5 The Formation of Stable GeO_2 Oxide on Germanium Epitaxial Layer using the High Pressure Oxidation*, Nakjun Choi, J.H. Bae,* Sungkyunkwan University, Republic of Korea

Thermal oxidized of Ge films under high pressure have been investigated to examine the possibility for the gate oxide. Ge oxides were grown either Ge wafers or Ge epitaxial films grown on Si wafer. The temperature range was from 450 °C to 550 °C, and three different pressures such 10, 30, and 50 atm were chosen for a high pressure dry oxidation. The physical property of GeO_2 films were analyzed using the transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy(XPS). Additionally, Au/GeO_2/Ge MOS capacitors were characterized using C-V and I-V measurement. The hysteresis behavior in C-V characteristics and the interface trap density (D_{it}) are significantly reduced through the high pressure oxidation. Consequently, the properties of both GeO_2 film and GeO_2/Ge interface are successfully improved by suppressing GeO volatilization utilizing high pressure.

EM-ThP6 NH_4OH Solution Wet Etching for Silicon Channel Thinning of Junctionless-FET*, Lucas Stucchi-Zucchi, A.R. Silva, J.A. Diniz,* University of Campinas, Brazil

Junctionless-FET (JL-FET) devices were fabricated on SOI substrate using NH_4OH solution silicon etching as means to thin the channel substrate. The devices gate dielectric was silicon oxynitride grown using O_2/N_2 ECR (Electron-Cyclotron-Resonance) plasma, and its gate metal was TiN defined through lift-off and deposited using reactive sputtering. The electric contacts were fabricated with sputtered aluminum defined through lift-off and annealed on a conventional oven. Samples were characterized during the fabrication processes using optical microscopy and scanning electron microscopy (SEM). The device electrical performance was measured using a probestation and then cross-section SEM images were extracted using Ga+ Focused Ion Beam milling.

The final channel thickness was 65nm measured in the cross-section images, which also showed the angled sidewalls characteristic of the NH_4OH solution wet etching. The channel dopant concentration was estimated at approximately 10^{17} atoms/cm^3 through Pseudo-MOS electrical measurements, this was the doping concentration that was planned according to the simulation steps to ensure transistor behavior by sacrificing electrical contact quality. Electrical measurements showed transistor behavior and low leakage currents, despite the negative threshold voltage and poor electrical contacts, which distorted the I-V measurements due to their Schottky-like behavior. These results are as expected due to the measured channel thickness and the estimated channel dopant concentration and point favorably towards the silicon etching in NH_4OH solution being a viable technique to fabricate JL-FET devices.

In the future, Atomic Force Microscopy (AFM) measurements will be used to measure the surface roughness after the silicon wet etching in NH_4OH solution. With a more accurate etching rate, new samples will be fabricated with thinner channel thicknesses and higher dopant concentration. The enhanced fabrication process is expected to result in JL-FET devices that rival the performance of state-of-the-art MOSFET devices.

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EM-ThP7 Fabrication of Highly-Efficient Nanoscale Multilayered Thin-Film Thermoelectric Devices*, Alandria Henderson, J. Kimbrough, Z. Duncan, K. Davis, M. Howard, J. Elike, T. Wimbley, M. Glenn, Z. Xiao,* Alabama A&M University

We report the growth of nanoscale multilayered thermoelectric thin films and fabrication of integrated thermoelectric devices for high-efficiency energy conversion and solid-state cooling. Nanoscale multilayered thin films such as Sb/Sb_2Te_3 and Te/Bi_2Te_3 thin films were grown using the e-beam evaporation. Integrated thermoelectric devices were fabricated with the nanoscale multilayered thin films using the clean room-based microfabrication techniques such as UV lithography. X-ray diffraction and reflection and high-resolution tunneling electron micrograph (HR-TEM) were used to analyzed the e-beam-grown nanoscale multilayered thin films. SEM was used to image and analyze the fabricated devices. The thermoelectric characteristics of the fabricated devices were measured and analyzed, and highly-efficient thermoelectric thin-film materials and integrated devices will be demonstrated and reported.

EM-ThP9 Control of Randomness in Microsphere-Based Photonic Crystals Assembled by Langmuir-Blodgett Process*, **Sarun Atiganyanun**, O.K. Abudayyeh, S.M. Han, S.E. Han,* University of New Mexico

Photonic structures in biological systems typically exhibit an appreciable degree of disorder within their periodic structures. Such disorder contributes to unique optical properties but has not been fully understood. Towards the goal of improving this understanding, we have investigated Langmuir-Blodgett (LB) assembly of silica microspheres to controllably introduce randomness to photonic structures. We theoretically modeled the LB assembly process and determined a condition for surface pressure and substrate pulling speed that results in maximum structural order. For each surface pressure, there is an optimum pulling speed, and vice versa. Photonic structures fabricated at various conditions were characterized by scanning electron microscopy and light scattering analysis, which confirms the modeled optimum condition. However, along the trajectory defined by the optimum condition, the structural order decreases moderately as the pulling speed increases. This moderate decrease in structural order would be useful for controlled introduction of randomness into the periodic structures. Departing from the trajectory, our experiment reveals that a small change in pulling speed at a given surface pressure can significantly disrupt the structural order. According to these observations, mechanism of forming structural order in LB assembly is proposed. Additionally we also find that, for multilayer LB assembly at a fixed pulling speed, the surface pressure should increase as the number of layers increases to achieve maximum structural order. In summary, this work quantitatively presents the optimum trajectories for n^{th} layer assembly relating surface pressure and pulling speed.

EM-ThP10 Incorporation of Ferroelectric HfO_2 into Magnetoelectric Random-Access Memory (MeRAM) Devices*, K. Fitzell, **Jeffrey Chang**, A. Acosta, H. Ma, X. Li, K.L. Wang, J.P. Chang,* University of California, Los Angeles

In contrast to manipulating magnetization with applied current, using an applied electric field can significantly reduce the required energy and result in less heat generation, leading to increased ene rgy density. This can be accomplished using the voltage-controlled magnetic anisotropy (VCMA) effect, which forms the basis of next-generation magnetoelectric MRAM devices. Specifically, applying an electric field across a CoFeB/MgO interface can decrease the perpendicular magnetic anisotropy field as a result of the altered electron density at the interface, thus destabilizing the magnetization state and allowing for its efficient and deterministic reorientation with a small applied magnetic field. This op eration principle stands in contrast to that of STT-RAM, which uses upwards of 100 fJ to write a single bit (300,000 times more energy than the actual energy barrier to switching).

Previous research on CoFeB/oxide interfaces has shown that increasing the dielectric constant of the oxide layer also increases the sensitivity of the interfacial magnetic anisotropy energy to an applied electric field (Kita et al., 2012). Our previous work involving MgO/PZT/MgO composite tunneling barriers showed a 40% increase in the VCMA effect upon addition of PZT to the tunneling barrier. However, the ferroelectric order of PZT is very weak at such small dimensions, and the leakage current and high annealing temperatures required of PZT prevent this technology from being industrially relevant. On the other hand, the orthorhombic phase of HfO_2 has been shown to possess desirable ferroelectric properties even in ultrathin films. In addition, ferroelectric HfO_2 boasts superior compatibility with CMOS technology as well as desirable electrical properties for device integration.

In this work, a method for depositing orthorhombic phase HfO_2 (FE-HfO_2)-based thin films via a radical-enhanced atomic layer deposition process is described. These ferroelectric thin films were subsequently incorporated into the tunneling junctions of CoFeB/MgO-based magnetic tunnel junction in an effort to enhance the VCMA effect and introduce ferroelectric functionality into magnetoelectric random-access memory devices.

EM-ThP11 Extreme Environment Operation of $Al_{0.85}Ga_{0.15}N/Al_{0.7}Ga_{0.3}N$ High Electron Mobility Transistors*, **Patrick Carey**, F.R. Ren,* University of Florida*; A.G. Baca, B. Klein, A.A. Allerman, A.M. Armstrong, E.A. Douglas, R.J. Kaplar,* Sandia National Laboratories*; S.J. Pearton,* University of Florida

$Al_{0.85}Ga_{0.15}N/Al_{0.7}Ga_{0.3}N$ high electron mobility transistors (HEMT) underwent DC characterization across the temperature ranging from room temperature to 500°C. Due to a high Schottky barrier height and low gate leakage current achieved on Al0.85Ga0.15N barrier layer, drain current modulation up to a gate voltage of 10 V was demonstrated at 500°C. The high aluminum content in these devices enables stability at high temperature due to the ultra-wide bandgap of ~ 5.7 eV. Conventional low Al content HEMT devices have previously shown improved elevated temperature operation as compared to their Si or GaAs counterparts, but are unable to operate under extreme temperature tested herein and suffer from high gate leakage current with heating. The drain current on/off ratio of 1011 were obtained with low gate leakage currents. The drain current degraded by ~50% from room temp to 500°C. The subthreshold slope of 80 mV/dec and 230 mV/dec were obtained at room temperature and 500°C, respectively. From the subthreshold slopes, trap densities were calculated to be 2.3×10^{11} cm^{-2} at room temperature and 3.3×10^{12} cm^{-2} at 500°C. These novel devices show great promise for application in the power, space, and defense industry where extreme performance is necessary.

EM-ThP12 Electrical Characterization of the Reduced Effective Schottky Barrier Height by Nanoscale Ge bi-layer of CZTSe Solar Cells*, **Sanghyun Lee**,* Indiana State University

In the past ten years, there have been constant attempts to develop high efficient thin film solar cells, which are cost-effective, environmentally benign, and reliable. The most strongest candidate of emerging alternatives is $Cu_2ZnSn(S,Se)_4$ (or kesterite) solar cells, herein CZT(S,Se). With abundant elements in earth's crust, CZT(S,Se) shows high absorptions coefficient (>10^4 cm^{-1}) and a tunable direct band gap energy, ranging from 1 to 1.4 eV, which makes it an ideal platform for future renewable energy devices . However, the efficiency improvement and understanding of emerging CZT(S,Se) is still in early stage compared to the counterparts such as $Cu(In,Ga)Se_2$ (CIGS) and CdTe. In recent progress, Germanium (Ge) incorporation into CZT(S,Se) solar cells has received extensive attention to deepen the understanding of this types of devices as Ge-alloyed CZT(S,Se) solar cells have demonstrated improvements in device performance. However, several challenges still remain such as a large Voc-deficit, sever heterojunction interface recombination, and a Schottky-type back contact barrier.

The presence of Schottky barrier near back contact limits the hole movement which influences the current-voltage characteristics and deteriorates the Voc-deficit as well. To investigate the impact of this back contact barrier height, we fabricated and characterized a set of CZTSe solar cells by utilizing DC magnetron sputtering by applying ultra thin Ge nanolayers. We investigated the back contact interface between CZTSe/$MoSe_2$ and Mo metal contact in an effort to improve a back contact barrier. By incorporating nanoscale Ge bi-layers below and below the absorber, a barrier height is considerably improved. The results indicate that nanoscale Ge bi-layers improves the back contact barrier height by 27 % as compared to CZTSe:Ge monolayer devices (see a supporting document device A). The back contact improvement is possibly caused underlying Ge nanolayer (<2.5 nm) between the absorber and Mo metal contact. The improvement of the efficiency loss caused by the series resistance component is reduced by 50%, which is attributed to the improved Schottky-type back contact barrier. This allows the improved efficiency up to 8.3% by incorporating nanoscale CZTSe: Ge bi-layers.

EM-ThP13 Optimal Contact Photolithography Techniques For HEMT Substrates using I-line Photoresist*, **Whitney Ingram**, A. Jones, B. Klein, A.G. Baca, A.M. Armstrong, A.A. Allerman, E.A. Douglas,* Sandia National Laboratories

Gallium nitride-based high electron mobility transistors (HEMTs) utilize a variety of substrates, including those that are optically transparent in the visible and ultraviolet wavelength spectrum such as sapphire and silicon carbide(SiC). Compared to silicon substrates, SiC and sapphire substrates can exhibit a distinct set of photolithography patterning challenges such as backscattering (from the underlying chuck and other areas of the substrate) which can influence the critical dimension (CDs), pattern integrity, and pattern resolution. In this study, computational photolithography and rigorous coupled wave guide analysis are used to calculate the optical reflectivity, the transmission and absorption of a multilayered stack comprised of i-line photoresist and an antireflective coating on sapphire substrates with $Al_xGa_{1-x}N$ epitaxial layers (with x ranging from 0 to 1). These simulations are used to target optimal resist and arc thickness, and exposure energy needed to reach the target feature with high fidelity. As a proof of concept, fully resolved patterns down to 0.5 µm are experimentally obtained on sapphire substrates using conventional contact photolithography driven by simulated for optimal conditions. Due to the lack of experimental information on photolithography on optically transparent substrates with ultra-wide bandgap heterostructures, this method can provide relevant insight into determining optimal process window for optically transparent substrates.

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.

EM-ThP14 High-mobility Helical Tellurium Field Effect Transistors Enabled by Transfer-free, Low-temperature Direct Growth*, **Guanyu Zhou**, R. Addou, Q. Wang, S. Honari, C.R. Cormier, L. Cheng, R. Yue, C.M. Smyth, A. Laturia, J. Kim, W.G. Vandenberghe, M.J. Kim, R.M. Wallace, C.L. Hinkle,* University of Texas at Dallas

The transfer-free direct growth of high performance materials and devices could enable transformative new technologies. Here we report room temperature field-effect hole mobilities as high as 707 $cm^2V^{-1}s^{-1}$, achieved using transfer-free, low-temperature (≤120°C) direct growth of helical tellurium (Te) nanostructure devices on SiO_2/Si. The Te nanostructures exhibit significantly higher device performance than other low-temperature grown semiconductors, and we demonstrate that through careful control of the growth process, high-performance Te can be grown on other technologically relevant substrates including flexible plastics like polyethylene terephthalate (PET) and graphene in addition to amorphous oxides like SiO_2/Si and HfO_2. The morphology of the Te films can be tailored by the growth temperature, and we identify different carrier scattering mechanisms for films with different morphologies. The transfer-free direct growth of high-mobility Te devices could enable major technological breakthroughs, as the low-temperature growth and fabrication is compatible with the severe thermal budget constraints of emerging applications. For example, the vertical integration of novel devices atop a silicon complementary metal oxide semiconductor (CMOS) platform (thermal budget <450 °C) has been theoretically shown to provide a 10x systems level performance improvement, while flexible and wearable electronics (thermal budget <200 °C) could revolutionize defense and medical applications.

EM-ThP18 100 keV Proton Irradiation Effects on AlGaN/GaN Epistructures*, **Min Khanal**, S. Uprety, K. Yapabandara, V. Mirkhani, S. Wang, B. Schoeneck, T. Isaacs-Smith, A. Ahyi, M.J. Bozack, M. Park,* Auburn University

The electronics that are used in spacecraft are subject to space radiation hazards. The space radiation environment includes trapped electrons and protons of the Van Allen radiation belts, and non-trapped transient solar and galactic cosmic rays and solar flare particles. The protons with the cut-off energy of 100 keV are present above the upstream of the Earth's bow shock. Since gallium nitride and its alloys are proven to be relatively radiation tolerant, these materials are considered as promising candidates for space electronic applications. Therefore, it is consequential to study the effect of 100 keV protons on the AlGaN/GaN HEMTs if the devices are to be used for space applications. In this research, the effect of 100 keV protons with the fluences 1×10^{10}, 1×10^{12}, and 1×10^{14} cm^{-2} on materials/device characteristics of AlGaN/GaN HEMTs constructed on Si wafers were studied by means of optical and electrical characterization. The electrical characteristics of the devices were analyzed by using conventional transistor I-V and C-V measurements in order to relate the material's fundamental properties to the device performance. The slight degradation on the electrical characteristics and the shift in the threshold voltage was observed in the irradiated samples. The crystal quality of the epilayer was examined *via* micro-Raman spectroscopy and no substantial degradation in the crystal quality was observed.The possible introduction and/or the alternation of the defects were probed using the photoluminescence (PL) spectroscopy and spectroscopic photocurrent-voltage techniques. The surface morphology of the samples was studied by atomic force microscopy (AFM) and scanning electron microscopy (SEM), and a slight increase in the surface roughness was observed. The surface analysis was performed using X-ray photoelectron spectroscopy, and the surface elemental composition was not altered after irradiation. It is concluded that the crystal quality of the AlGaN/GaN HEMT layers and the electrical characteristics of the AlGaN/GaN HEMTs were not severely degraded in spite of the exposure to a high fluence of protons with the energy 100 keV.

EM-ThP19 Properties of WSe_2 Thin Films Grown by Molecular Beam Epitaxy*, P. Litwin, K.M. Freedy, T. Zhu, M. Zebarjadi, **Stephen McDonnell**,* University of Virginia

The synthesis of high quality transition metal dichalcogenide (TMD) films is of significant interest for potential applications in nanoelectronic and thermoelectric devices. Molecular beam epitaxy (MBE) is a promising route, providing fine control over growth conditions. To further understand the growth conditions on film quality, we study the effect of processing conditions on the resultant material quality. MBE is used to synthesize bilayer $WSe_2$and it is shown using in-vacuo x-ray photoelectron spectroscopy (XPS) that the process conditions can directly influence the resultant chemistry and electronic structure. Specifically, we show that the initial nucleation conditions are critical to achieving repeatable and high-quality WSe_2. Our combination of MBE and in-situ XPS studies show that WSe_2chemistry can be controlled through processing conditions. We also use ex-situ characterization to determine properties such as cross-plane resistance and Seebeck coefficient. It is shown that Ni and Au contacts result in negative and positive Seeback coefficients respectively. Furthermore, Ni contacts are found to degrade over time.Presented will be our results showing the process control of WSe_2chemistry. Also shown will be the impact of these changes on device relevant properties, such as resistance and Seebeck coefficient.

EM-ThP20 Effects of O_2 Partial Pressure on Ga_2O_3 Thin-films*, **Seth King**,* University of Wisconsin - La Crosse

Gallium oxide (Ga2O3) has recently become recently become a material of great interest due as it is a stable, wide bandgap oxide which is capable of being used as a transparent conducting oxide or dielectric layer in the next generation of electronic devices [2]. While the majority of work has focused on single crystal materials, few results exist regarding the growth and nucleation of polycrystalline Ga2O3 materials [2,3].

The present study utilizes spectroscopic ellipsometery, x-ray diffraction, and four-point resistivity measurements to investigate how the physical properties of Ga2O3 thin-films may be altered by changing the partial pressure of O2 during reactive RF sputter deposition. The results will yield important information regarding how material properties are related to deposition conditions using an industrially applicable fabrication process.

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2D Materials Focus Topic
Room 201B - Session 2D+EM+MN+NS-FrM
Nanostructures including Heterostructures and Patterning of 2D Materials

Moderator: Xiang Zhang, University of California, Berkeley

8:20am **2D+EM+MN+NS-FrM1 Interfacial Strength and Surface Damage Characteristics of Two-dimensional h-BN, MoS_2 and Graphene***, **Frank DelRio**,* National Institute of Standards and Technology*; B.C. Tran Khac, K.H. Chung,* University of Ulsan, South Korea

Two-dimensional (2D) materials such as single- and multi-layer hexagonal boron nitride (h-BN), molybdenum disulfide (MoS_2), and graphene have attracted intensive interest due to their remarkable material properties. In this study, the film-to-substrate interfacial strengths and surface damage characteristics of atomically-thin h-BN, MoS_2 and graphene were systematically investigated via atomic force microscopy (AFM)-based progressive-force and constant-force scratch tests and Raman spectroscopy. The film-to-substrate interfacial strengths of these atomically-thin films were assessed based on their critical forces (*i.e.*, normal force where the film was delaminated from the substrate) as determined from progressive-force scratch tests. The evolution of surface damage with respect to normal force was further investigated using constant-force tests. The results suggested three different steps in the evolution of surface damage. At relatively low normal force, no significant change in topography and friction force was observed, which points to elastic deformation in the scratched area. As normal force increased, the formation of defects in the film and plastic deformation in the substrate were noted. At this stage, although the films have not yet failed, their topography, friction force, crystalline quality, and mechanical strengths were affected, which notably degraded their tribological performance. At normal forces above the critical force, delamination of the film from the substrate occurred. The compressive strain-induced buckling in front of the AFM tip was the primary source of mechanical instability. As the compressive strain increased, the atomic bonds were compressed, and eventually ruptured. As the number of layers increased, the tribological performance of h-BN, MoS_2, and graphene were found to significantly improve due to an increase in the interfacial strengths and a decrease in the surface damage and friction force. In all, the findings on the distinctive surface damage characteristics and general failure mechanisms are useful for the design of reliable nanoscale protective and solid-lubricant coating layers based on these 2D materials.

9:00am **2D+EM+MN+NS-FrM3 Sequential Edge-epitaxy: Towards Two-dimensional Multi-junctions Heterostructures and Superlattices***, **Humberto Rodriguez Gutierrez**,* University of South Florida **INVITED**

Atomically thin layers are known as two-dimensional (2D) materials and have attracted a growing attention due to their great potential as building blocks for a future generation of low-power and flexible 2D optoelectronic devices. Similar to the well-established 3D electronics, the development of functional 2D devices will depend on our ability to fabricate heterostructures and junctions where the optical and electronic properties of different compounds are brought together to create new functionalities. Vertical heterostructures can be produced by selective van der Waals stacking of different monolayers with distinct chemical composition. However, in-plane lateral heterostructures, where different materials are combined within a single 2D layer, have proven to be more challenging. During the formation of the hetero-junction, it is important to minimize the incorporation of undesired impurities and the formation of crystal defects at the junction that will impact the functionality of the 2D device. When fabricating periodic structures it is equally important to develop the ability to control the domain size of each material. In this talk, we will review different techniques that have been used to create 2D lateral heterostructures of transition metal dichalcogenide compounds. Emphasis will be made in our recently reported one-pot synthesis approach, using a single heterogeneous solid source, for the continuous fabrication of lateral multi-junction heterostructures of TMD monolayers. In this method, the heterojunctions are sequentially created by only changing the composition of the reactive gas environment in the presence of water vapor. This allows to selectively control the water-induced oxidation and volatilization of each transition metal precursors, as well as its nucleation on the substrate, leading to sequential edge-epitaxy of distinct TMDs. This simple method have proven to be effective for continuous growth of TMD-based multi-junction lateral heterostructures, including selenides, sulfides and ternary alloys. Basic devices with field effect transistor configuration were fabricated to study the electrical behavior of these heterojunctions, their diode-like response, photo-response as a function of laser power as well as photovoltaic behavior of the heterojunctions will be discussed.

9:40am **2D+EM+MN+NS-FrM5 Interpretation of π-band Replicas Observed for Mono- and Multi-layer Graphene Grown on 4H SiC(0001)***, T.B. Balasubramanian, M. Leandersson, J. Adell, C. Polley,* Lund University, Sweden*; **Leif Johansson**, R. Yakimova, C. Jacobi,* Linkoping University, Sweden

Graphene has made a major impact on physics due to its large variety of properties. The peculiar band structure of free standing graphene, showing linear dispersion and a Dirac point at the Fermi energy, makes it attractive for various applications. Large-scale epitaxial films have been grown on Si-terminated SiC substrates. However, the electronic structure is influenced when the graphene is laid upon a substrate whose lattice symmetry does not match that of graphene [1,2]. Six replicas oriented around each Dirac cone were observed already in the first ARPES experiments [1] of graphene grown on SiC(0001), and later reported [2] to have around 40 times lower intensity than a main Dirac cone. They were found to have the same relative separation and orientation as the rosette spots observed around the 0;th and 1x1 SiC and Graphene spots in the low energy electron diffraction (LEED) pattern and were explained [2] to have similar origin, i.e. to originate from photoelectron diffraction.

In two later ARPES investigations [3,4] additional weaker replicas were reported to exist along the Γ-K direction in the Brillouin zone of Graphene. One of them showed the existence [3] only for 1 ML but not 2 ML samples while the other reported [4] the existence in both 1 ML and 3 ML graphene samples. The origin of these replicas were in both cases attributed to a modulation of the ionic potential in the graphene layer/layers induced by the charge modulation of the carbon layer at the interface, i.e. the carbon buffer layer. Thus to an initial state effect instead of the earlier proposed final state effect. In both those experiments un-polarized HeI radiation was utilized, so the symmetry of the π-band replicas was not determined. We therefore investigated monolayer and multilayer graphene samples using linearly polarized synchrotron radiation, which allowed us to exploit the so called dark corridor [5] to directly determine the symmetry of the replica cones. Our ARPES data therefore clearly show the origin of these additional replicas observed using He-I radiation and moreover reveal the existence of some weaker replicas not earlier reported. An interpretation of our ARPES data in terms of final state photoelectron diffraction effects is shown to account for the location and symmetry of the π-band replicas observed.

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10:00am **2D+EM+MN+NS-FrM6 Effect of SiC(0001) Substrate Morphology and Termination on Multilayer Hexagonal Boron Nitride Epitaxy by Plasma-Enhanced CBE***, **Daniel J. Pennachio**, N.S. Wilson, E.C. Young, A.P. McFadden, T.L. Brown-Heft,* University of California at Santa Barbara*; K.M. Daniels, R.L. Myers-Ward, D.K. Gaskill, C.R. Eddy, Jr.,* U.S. Naval Research Laboratory*; C.J. Palmstrøm,* University of California at Santa Barbara

Despite the prevalent use of hexagonal boron nitride (hBN) in 2D devices as a gate dielectric, tunnel barrier, or substrate, the quality of hBN thin films are typically lacking relative to flakes exfoliated from bulk crystals. To address the challenges of hBN epitaxy, this work studies the growth of hBN on single-crystal epitaxial graphene on SiC(0001) via plasma-enhanced chemical beam epitaxy (PE-CBE). As PE-CBE is conducted in an ultra-high vacuum environment, hBN nucleation, composition, and morphology were able to be examined using a combination of *in-situ, in-vacuo,* and *ex-situ* characterization techniques to gain insight into the formation of high-quality hBN films and hBN/graphene heterostructures.

It was found that utilization of high growth temperature (>1400°C) and nitrogen plasma flux (5×10^{-6} Torr background pressure) resulted in improved multilayer hBN film morphology over lower temperature (1300°C) depositions and CBE growths without nitrogen plasma flux. PE-CBE also produced more stoichiometric films than CBE without plasma at temperatures above 1400°C, as determined by *in-vacuo* X-ray photoelectron spectroscopy (XPS). *In-situ* reflection high energy electron diffraction (RHEED) showed streaky diffraction patterns persisting throughout several nanometers of PE-CBE hBN growth, indicative of a

smooth, epitaxial film. Crystallinity and epitaxial arrangement of hBN nuclei were examined by *in-vacuo* and *ex-situ* scanning probe microscopy (SPM). Scanning probe spectroscopy provided information on the electrical properties of the hBN films relative to bulk values.

The epitaxial alignment of the hBN/graphene/SiC(0001) heterostructure was studied by RHEED and by comparing nuclei edge alignment, as measured with SPM or scanning electron microscopy, to the substrate lattice orientation. It was found that the rotational alignment of the hBN nuclei depended on the substrate surface morphology. Nuclei on the (6√3×6√3)R30° SiC surface reconstruction, a graphene-like buffer layer, aligned directly to the buffer layer, while hBN nuclei on 4° off-cut epitaxial graphene substrates showed preferential alignment to substrate macrosteps rather than the graphene lattice. These ~25nm high macrosteps were then examined by cross-sectional transmission electron microscopy (TEM), which showed that the epitaxial graphene and hBN conformally blanketed the macrostep facets despite the macrostep's effect on nuclei orientation. The macrostep-directed nucleation outlined in this work provides a potential route to controlling the hBN/graphene rotational alignment during van der Waals epitaxy, an important variable for modulating electronic properties in this 2D system.

10:20am **2D+EM+MN+NS-FrM7 Nanoelectromechanical Drumhead Resonators from 2D Material Bimorphs***, **Sun Phil Kim**, J. Yu, E. Ertekin, A.M. van der Zande,* University of Illinois at Urbana-Champaign

Atomic membranes of monolayer 2D materials represent the ultimate limit in size of nanoelectromechanical systems. Yet, new properties and new functionality emerge by looking at the interface between layers in heterostructures of 2D materials. In this talk, we demonstrate the integration of 2D heterostructures as nanoelectromechanical systems and explore the competition between the mechanics of the ultrathin membrane and the incommensurate van der Waals interface. We fabricate electrically contacted, 5-6 µm circular drumheads of suspended heterostructure membranes of monolayer graphene on monolayer molybdenum disulfide (MoS_2), which we call a 2D bimorph. We characterize the mechanical resonance through electrostatic actuation and laser interferometry detection. The 2D bimorphs have resonance frequencies of 5-20 MHz and quality factors of 50-700, comparable to resonators from monolayer or few layer 2D materials. The frequencies and eigenmode shape of the higher harmonics display split degenerate modes showing that the 2D bimorphs behave as membranes with asymmetric tension. The devices display dynamic ranges of 44 dB, but there is a strong dependence of the dissipation on the drive. Under electrostatic frequency tuning, devices display small tuning of ~ 20% compared with graphene resonators > 100%. In addition, the tuning shows a recoverable kink that deviates from the tensioned membrane model for atomic membranes, and corresponds with a changing in stress of 0.014 N/m. One model that would account for this tuning behavior is the onset of interlayer slip in the heterostructure, allowing the tension in the membrane to relax. Using density functional theory simulations, we find that the change in stress at the kink is much larger than the energy barrier for interlayer slip of 0.0001 N/m in a 2D heterostructure, but smaller than the energy barrier for an aligned bilayer of 0.034 N/m, suggesting local pinning effect at ripples or folds in the heterostructure. Finally, we observe an asymmetry in tuning of the full width half max that does not exist in monolayer materials. These findings demonstrate a new class of NEMS from 2D heterostructures and unravel the complex interaction and impact of membrane morphology, and interlayer adhesion and slip on the mechanics of incommensurate van der Waals interfaces.

10:40am **2D+EM+MN+NS-FrM8 Atomically-precise Graphene Etch Masks for 3D Integrated Systems from 2D Material Heterostructures***, **Jangyup Son**,* University of Illinois at Urbana-Champaign*; A.M. van der Zande,* University of Illinois at Urbana Champaign

Atomically-precise fabrication methods are critical for the development of next-generation technologies in which electronic, photonic, and mechanical devices approach the atomic scale. In no area is this challenge more apparent than in nanoelectronics based on two-dimensional (2D) heterostructures, in which van der Waals (vdW) materials, such as graphene, hexagonal boron nitride (hBN), and transition metal dichalcogenides (TMDs), are integrated stacked to form functional electronic devices with nanometer thicknesses. A major challenge in the assembly of vdW heterostructure devices is the difficulty of patterning and individually connecting each molecular layer.

In this presentation, we demonstrate the use of graphene as a highly selective, atomically-thin etch mask and etch stop in van der Waals heterostructures. we also show the advantages of graphene etch masks (GEM) through advanced device demonstrations. We demonstrate that most inorganic 2D materials, such as hBN, TMDs, and black phosphorus (BP), are efficiently etched away by exposing those to XeF_2 gas at room temperature. In contrast, instead of getting etched, atomically-thin monolayer graphene is chemically functionalized (*i.e.* flurographene (FG)) under XeF_2 exposure due to the formation of sp^3 bonds by the addition of fluorine atoms onto the graphene surface. Based on this, we used exfoliated (and CVD) graphene layer as etch mask for patterning other 2D layers in micro (and macro) scale vdW heterostructures. We also demonstrate the use of this selective etching and GEM in mainly two different applications: 3D-integrated heterostructure devices with interlayer vias and suspended graphene mechanical resonators. First, we fabricate an electrical device having buried contacts in a 2D material heterostructure. Holes were etched through the top layer of hBN in an encapsulated BN-G-BN heterostructure to locally expose the buried graphene layer and contacts were fabricated by evaporating metal electrodes on the exposed graphene regions. The resulting encapsulated graphene device shows a low contact resistance of ~ 80 ohm·mm ($n = -2\times10^{12}$ cm^2) at room temperature, leading to high carrier mobility of ~ 140,000 $cm^2V^{-1}s^{-1}$, which is comparable to the electrical properties of state-of-the-art edge contacted graphene devices. Second, we fabricate a suspended graphene membrane by vapor phase etching of a BP thin film supporting graphene. We show that the graphene membrane behaves as a nanomechanical resonator with a frequency of 5.24 MHz and quality factor of ~255, comparable to graphene NEMS prepared on conventional substrates.

11:00am **2D+EM+MN+NS-FrM9 Insights into the O Atom Adsorption and O_2 Dissociation on Halogenated Graphene Surfaces***, **Reynaldo Geronia**,* University of the Philippines Diliman*; A.A.B. Padama,* University of the Philippines Los Baños, Philippines*; J.D. Ocon,* University of the Philippines Diliman, Philippines*; P.-Y. A. Chuang,* University of California, Merced

Oxygen reduction reaction (ORR) usually depends on precious metal-based catalysts like platinum and its alloys to facilitate its sluggish kinetics. The high cost of these materials however limits the employment of ORR-based technologies in commercial applications like fuel cells and metal-air batteries. Interestingly, recent works have demonstrated that doped metal-free carbon catalysts, such as graphene-based materials, can facilitate adsorption of ORR intermediate species [1]. This motivates us to investigate the interaction of oxygen atom and oxygen molecule on halogenated graphene systems.

In this work, we performed density functional theory (DFT) based calculations to investigate the stability of coplanar and non-coplanar halogen (X = F, Cl, Br, I) doped monovacant graphene systems. The stability of halogenated-graphene is strongly influenced by the size of halogen dopant as well as the geometry of the vacancy [2]. The calculated adsorption properties of atomic [3] and molecular oxygen on halogenated graphene systems, on the other hand, signifies the possibility of O_2 dissociation. We note that the dissociation of the molecule results to the distortion of the geometric structure of the substrate. This leads mostly to the formation of dangling and bridging C-O bonds along the edge of the graphene monovacancy which could have facilitated the dissociation of the molecule. Depending on the halogen, adsorption of oxygen can strengthen or weaken existing C-X bonds, due to differences between the abilities of oxygen and halogens to induce charge transfer and to participate in π bonding with carbon. These findings are expected to increase our understanding of novel graphene-based materials, which are currently being developed with the aim of reducing the use of noble metals as catalysts in fuel cells.

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[2] R.M. Geronia, A.C. Serraon, A.A.B. Padama, J.D. Ocon, ECS Trans. 77 (2017) 607-620.

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Magnetic Interfaces and Nanostructures Division
Room 203A - Session MI+EM-FrM

Magnetism and Spin-Orbit Coupling at Surfaces, Interfaces and Thin Films

Moderator: Valeria Lauter, Oak Ridge National Laboratory

8:20am **MI+EM-FrM1 Interfacial Spin-orbitronics: Spin-charge Current Conversion in Topological Insulators and Rashba Interfaces***, **Juan Carlos Rojas Sánchez**,* Institut Jean Lamour, Universite de Lorraine, France **INVITED**

Materials with large efficiency of spin-charge current interconversion are highly desirable to study new physical phenomena as well as for spintronics applications. Heavy metals or alloys exhibiting large spin-orbit coupling scatter the electrons in opposite directions when they have opposite spin. Thus an injection of charge current yields a transversal spin current in such materials. The charge-spin current conversion phenomenon in those 3D materials is so-called Spin Hall Effect (SHE). We can exploit this effect to manipulate a magnetization in a heavy metal/ferromagnetic structure [1-3]. We have shown such a manipulation in Si-SiO_2//W(3 nm)/Co_xTb_{1-x}(3.5 nm)/Al(3 nm) structures. Interesting, we have found out that the temperature of the devices reach a novel characteristic temperature just before the magnetization switching takes place [3].

On the other hand, new classes of materials such as 3D topological insulator which are trivial insulator in their bulk but hold metallic states in their surfaces are also highly interesting for spintronics. The spin-orbit coupling (SOC) in the 2DEG states at Topological Insulator (TI) or Rashba Interfaces is predicted to be more efficiency that their 3D counterparts for spin-charge current conversion. Indeed, we have found the highest efficiency at room temperature using the topological insulator α-Sn [4]. The underlying physics of charge-spin current interconversion in such 2D systems is different of the SHE and is called Edelstein Effect (EE) [5-7], also known as inverse spin galvanic effect [8]. I will show results of spin-to-charge conversion by spin pumping experiments and their analysis in term of inverse Edelstein Length [4-7] . Experimental results based on ARPES and spin pumping indicate that direct contact of metallic ferromagnetic layer is detrimental for the surfaces states of topological insulators but we can keep the surfaces states of α-Sn using Ag spacer. I will use the conversion parameters obtained at room temperature with α-Sn to demonstrate the very large advantage of the SOC effects in 2D interface states with respect to the Spin Hall Effect (SHE) of 3D metals and the resulting perspective for low power spintronic devices.

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[5] J.-C. Rojas-Sánchez et al. Nat. Comm **4**, 2943 (2013)

[6] E. Lesne, J.-C. Rojas-Sánchez et al. Nat. Mat. **15**, 1261 (2016)

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9:00am **MI+EM-FrM3 Spin-orbit Coupling in Ion-surface Collisions Observed by a Polarized $^4He^+$ Ion Beam***, **Taku Suzuki**, O. Sakai,* National Institute for Materials Science, Japan

Recently, we found spin-orbit coupling (SOC) act as a mechanism of spin dependent low-energy He^+ ion scattering on solid surfaces. It is intuitively interpreted as the effect on the projectile electron spin of the magnetic field induced by the projectile angular motion around the target nucleus during the projectile–target binary collision (Biot-Savart law). Because a polarized He+ ion beam is useful for studying surface magnetism, it is important to understand the mechanism of the spin dependent He^+ ion scattering. In the present study, we further investigated SOC from both the experimental and theoretical approaches. In the experiment, electron-spin-polarized $^4He^+$ ion beam was projected onto the target surface, and the intensity of scattered He^+ ions was measured as a function of their kinetic energy (spin-polarized ion scattering spectroscopy). We found that the scattering angle θ dependence of the spin dependent scattering is remarkably different between the targets of the transition metal and the non-transition metal. This is explained from SOC in the collisional intermediate state, in which an electron of the target is virtually transferred to the He^+ ion.

9:20am **MI+EM-FrM4 Transport and Magnetic Properties of $LaAlO_3/SrTiO_3$ Heterostructure during Cooling and Warming***, **Zengming Zhang**, X.Q. Wang, M. Zhang, A. Rahman, R.C. Dai, Z.P. Wang, Z.J. Ding, L. Cheng,* University of Science and Technology of China

The $LaAlO_3$ thin films were grown on TiO_2 terminated (001) $SrTiO_3$ substrate using pulsed laser deposition technique. The transport and magnetic properties of $LaAlO_3/SrTiO_3$ (LAO/STO) heterostructure were studied during cooling and warming. The conductivity accelerated recoveries are found at around 70K and 160K for larger electrode interval of several mm, and more obvious for thicker LAO films. This indicated that the domain wall scale increases with the interface variation from fully strain state to partial strain state as the layers of LAO increase. During thermal cycling, both magnetoresistance(*xx*) and magnetization separate around the conductivity accelerated recovery temperature as seen in Fig. (c). The phenomenon is attributed to the mobile and trapping of defects such as single vacancy and divacancy by polarized domain walls due to the measuring current at the critical temperature [1-2].

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9:40am **MI+EM-FrM5 Engineering the Magnetic Properties of Complex Oxide Heterostructures***, **Yayoi Takamura**,* University of California at Davis **INVITED**

Complex oxides possess a wide range of intriguing and technologically relevant functional properties including ferromagnetism, ferroelectricity, and superconductivity. Furthermore, the interfaces of complex oxides have been shown to exhibit unexpected functional properties not found in the constituent materials. These functional properties arise due to various structural and chemical changes as well as electronic and/or magnetic interactions occurring over nanometer length scales at interfaces, and they have the potential to be harnessed to enable new, more versatile, and energy efficient devices. In this talk, I will present some of our recent work investigating the interfacial interactions which occur at ferromagnetic/antiferromagnetic (FM/AF) and FM/FM interfaces. While these interfacial interactions have been widely studied in metallic systems, fundamental differences are observed in complex oxides systems. Specifically, I will discuss FM/FM heterostructures consisting of the soft-FM $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) and hard-FM $La_{0.7}Sr_{0.3}CoO_3$ (LSCO) layers which display a unique exchange spring behavior where the chemical and magnetic interfaces no longer coexist. This phenomena is explained due to the formation of an interfacial layer characterized by magnetically active Co^{2+} ions which forms due to a robust charge transfer interaction at the LSCO/LSMO interface. In the second half of the talk, I will discuss the development of measurement protocols for angle-dependent soft x-ray absorption spectroscopy measurements which can be used to unambiguously determine the orientation of the AF spin axis in (111)-oriented heterostructures and to probe how it responds to an applied magnetic field due to exchange interactions with the adjacent FM layer. For the LSMO/$La_{0.7}Sr_{0.3}FeO_3$ (LSFO) system, the LSFO layers possess two populations of AF order: the majority of AF moments cant out-of-the-plane of the film along low-index crystallographic directions, while a minority of AF moments lie within the (111)-plane. The relative orientation of the AF and FM spins differs for each type of AF domain. These results demonstrate how the many competing interactions in complex oxide heterostructures open up new opportunities to tailor their functional properties for future spintronic devices.

10:20am **MI+EM-FrM7 Location of the Valence Band Maximum in the Band Structure of Anisotropic 1T'-$ReSe_2$***, **Markus Donath**, P. Eickholt, J. Noky,* Westfälische Wilhelms-Universität Münster, Germany*; E. Schwier, K. Shimada, K. Miyamoto, T. Okuda,* Hiroshima University, Japan*; C. Datzer, M. Drüppel, P. Krüger, M. Rohlfing,* Westfälische Wilhelms-Universität Münster, Germany

Transition-metal dichalcogenides (TMDCs) are a focus of current research due to their fascinating optical and electronic properties with possible technical applications. $ReSe_2$ is an interesting material of the TMDC family, with unique anisotropic properties originating from its distorted 1*T* structure (1*T'*). To develop a fundamental understanding of the optical and electric properties, we studied the underlying electronic structure with angle-resolved photoemission (ARPES) as well as band-structure calculations within the density functional theory (DFT)–local density

approximation (LDA) and *GdW* approximations [1]. We observe anisotropic valence-band dispersions parallel to the surface. We find that along ΓM_1, which is the direction perpendicular to the "diamond" chains, the bandwidth of the hightest valence band is significantly smaller than in any other direction. Photon-energy-dependent measurements reveal a k_z-dependent band dispersion, reflecting the interlayer coupling. Two valence band maxima are identified within experimental limits of about 50 meV: one at the high-symmetry point *Z*, and a second one at a non-high-symmetry point in the Brillouin zone. Thus, the position in **k** space of the global valence band maximum is undecided experimentally. Theoretically, an indirect band gap is predicted on a DFT-LDA level, while quasiparticle corrections lead to a direct band gap at the *Z* point.

[1] P. Eickholt *et al.*, Phys. Rev. B **97**, 165130 (2018).

10:40am **MI+EM-FrM8 Controlling Antiferromagnetic Order at the Surface of La doped $BiFeO_3$**, ***Hendrik Ohldag,*** SLAC National Accelerator Laboratory; *B.-K. Jang,* Korea Advanced Institute of Science and Technology; *J.H. Lee, K-E. Kim,* Korea Advanced Institute of Science and Technology, Republic of Korea; *H. Jang,* SLAC National Accelerator Laboratory; *K.-T. Ko,* Max Planck Institute for Chemical Physics of Solids; *M.H. Jung,* Pohang University of Science and Technology, Republic of Korea; *T.Y. Koo,* Pohang Light Source; *Y.H. Jeong,* Pohang University of Science and Technology, Republic of Korea; *J.-S. Lee,* SLAC National Accelerator Laboratory; *C-H. Yang,* Korea Advanced Institute of Science and Technology, Republic of Korea

Emergence of a triple phase point in two dimensional (*e.g*. pressure and temperature) space can offer useful opportunities for the inter-coupling of two seemingly independent order parameters because of phase proximity. To illustrate the significance of this potential capability we employ a generic concept regarding electric control of magnetic order by manipulating chemical pressure: *i.e*. lanthanum substitution into the model antiferromagnetic ferroelectric $BiFeO_3$. Our results are made possible by the remarkable finding that a multiferroic triple phase point of a single spin disordered phase and two spin ordered phases emerges near room temperature in $Bi_{0.9}La_{0.1}FeO_3$ferroelectric thin films. By using spatially resolved x-ray absorption spectroscopy, we provide direct evidence that electric poling of a particular region of the compound near the triple phase point results in an antiferromagnetic phase while adjacent un-poled regions remain magnetically disordered, opening a promising avenue for magnetoelectric applications at room temperature.

11:00am **MI+EM-FrM9 Control of Magnetism at the Antiperovskite/Perovskite Interface**, *D.-F. Shao, T.R. Paudel,* ***Evgeny Tsymbal,*** University of Nebraska-Lincoln **INVITED**

Complex oxide materials with the perovskite crystal structure (ABO_3) are known for their interesting macroscopic physical properties involving the interplay between magnetism, ferroelectricity, and conductivity. Much less explored are the *antiperovskite* compounds (AXM_3) where the atomic positions of cations and anions are inverted creating unique, wide-ranging properties different from perovskites. Due to the structural similarity, interfaces combining perovskite and antiperovskite compounds can be fabricated, forming a new playground for materials design, where the coupling across the interface may lead to new fundamental properties and functional behavior. Here, based on density-functional calculations, we explore the magnetoelectric effect at the (001) interface between antiperovskite $GaNMn_3$ and perovskite $ATiO_3$ (A = Sr and Ba). Bulk $GaNMn_3$ is an antiferromagnet with the magnetic moments of the Mn ions lying in the (111) planes, forming non-collinear Γ^{5g} spin configurations with a zero net magnetization ground state. We predict that different from the Γ^{5g} non-collinear magnetism of the bulk $GaNMn_3$, strong magnetic moment enhancement and reorientation emerge at the $GaNMn_3/ATiO_3$ (001) interface, resulting in a sizable net magnetization pointing along the [110] direction. Moreover, switching the ferroelectric polarization of $BaTiO_3$ leads to reversal of the net magnetization of $GaNMn_3$. This phenomenon occurs due to the effect of ferroelectric polarization on the magnitude of the antiferromagnetic exchange coupling between the nearest Mn atoms at the interface. Reversal of magnetization by electric means is the holy grail of voltage-controlled spintronics, and thus our results pave a new route to achieve this functionality by exploiting antiperovskite/perovskite interfaces.

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Han, Y.: SS+EM+NS-ThM4, 66
Hanbicki, A.T.: 2D+EM+MN+NS-ThA1, **68**; 2D+EM+MN+NS-ThA2, 68
Hanna, A.R.: PS+AS+EM+SS-MoM8, **10**
Hao, S.: 2D+EM+MI+NS-TuM2, 19
Harb, J.: NS+AN+EM+MI+MN+MP+PS+RM-ThM5, 62
Hardy, M.T.: TF+EM+MI-WeM1, 48
Harmer, R.: SS+AS+EM-WeA8, 55
Hartmann, G.: PS+AS+EM+SS-MoM11, 11
Hartmann, J.M.: PS+EM+SE-TuM1, 23
Hasan, N.: 2D+EM+MI+MN+NS-TuA12, **29**
Hauffman, T.: SS+AS+EM-WeA7, **55**
He, C.H.: SS+AS+EM-WeA8, **55**
Heckman, E.M.: EM-ThP3, 76
Hellberg, C.S.: 2D+EM+MN+NS-ThA1, 68
Heller, E.R.: EM-ThP3, 76
Henderson, A.: EM-ThP7, **76**
Hennessy, J.: PS+EM+TF-ThA9, **71**
Henry, M.D.: TF+EM+MI+PS-MoA8, **18**
Herman, G.S.: SS+AS+EM-WeA10, 56; TF+AS+EL+EM+NS+PS+SS-ThA8, **74**
Hertzberg, J.B.: MP+AM+EM+NS-MoA10, **17**
Herzinger, C.M.: EL+AS+EM-MoM11, 4
Hetzl, M.: EM+AN+MI+SS-WeM13, 42
Heylman, K.D.: NS+AN+EM+MN+MP+RM-TuM5, 22
Higashiwaki, M.: EL+EM-MoA1, 12
Hight Walker, A.: EM+2D+NS+PS+RM+TF-ThA4, 69
Hilfiker, M.: EL+AS+EM-MoM3, 2
Hinkle, C.L.: EM-ThP14, 78; PS+AS+EL+EM+SE-WeM4, **44**
Hirata, A.: PS+EM+NS+SS-TuA12, 35
Hirose, M.: TF+EM+MI-WeM3, 48
Hirsch, A.: SS+AS+EM-WeA9, 56
Hirtzlin, T.: RM+EM+NS-TuA11, 36
Hite, D.A.: MP+EM+MN+NS-MoM8, **6**
Hite, J.K.: EM+2D+SS-WeA12, **52**
Hiyoto, K.: NS+2D+AN+EM+MN+MP+PC+RM-MoM5, **7**
Ho,: NS+2D+AN+EM+MN+MP+PC+RM-MoM1, **7**
Ho, L.W.: EL+EM-MoA6, 13
Hobart, K.: EM+2D+AN+MI+MP+NS-TuA11, 31
Hoenk, M.E.: TF+EM+MI-WeA3, 57
Hoffmann, T.: EM+AN+MI+SS-WeM13, 42
Hofmann, S.: 2D+EM+MI+NS+TF-MoM3, **1**
Hofmann, T.: EL+AS+EM-MoM11, 4; PS+AS+EL+EM+SE-WeM2, **44**
Hogan, L.T.: NS+AN+EM+MN+MP+RM-TuM5, 22
Honari, S.: EM-ThP14, 78
Hong, S.S.: PS+EM-WeM11, 47
Hong, Y.L.: EL+AS+EM-MoM8, 3
Hooshmand, Z.: 2D+AM+EM+NS-WeM2, 39; SS+EM+NS-ThM11, **67**
Horak, E.H.: NS+AN+EM+MN+MP+RM-TuM5, **22**
Hori, M.: PS+AS+EM+SS-MoM11, 11; PS+EM+SE-TuM13, 25; PS+EM+TF-ThM3, 63
Hoskins, B.: RM+EM+NS-TuA11, 36
Hou, B.: 2D+EM+MI+MN+NS-TuA12, 29
Howard, M.: EM-ThP7, 76
Hsu, K.: EM+MI+MN+NS-ThM4, 60
Hu, S.: 2D+EM+MI+MN+NS+SS-ThM2, 59
Hu, X.: PS+EM-WeA3, **53**
Huang, S.: PS+EM+SE-TuM4, 24
Huang, Y.L.: SS+EM+NS-ThM6, **66**
Huerfano, I.J.: SS+EM+PS+TF-ThA4, 72
Hurard, C.: PS+EM+SE-TuM4, 24
Hutchings, G.S.: 2D+EM+MI+MN+NS+SS-ThM2, 59
Hutchison, D.C.: SS+AS+EM-WeA10, 56
Hwang, S.H.: PS+EM+NS+SS-TuA8, 34
— I —
Ihlefeld, J.: TF+EM+MI+PS-MoA8, 18
Ihn, T.: 2D+EM+MI+MN+NS-TuA3, 28
Ikeda, N.: TF+EM+MI-WeM3, 48
Illiberi, A.: TF+AS+EL+EM+NS+PS+SS-ThA9, 75
Ingram, W.: EM-ThP13, **77**
Inlek, I.V.: MP+EM+MN+NS-MoM9, **6**
Inoue, M.: TF+EM+MI-WeM3, 48
Isaacs-Smith, T.: EM-ThP18, 78
Isarraraz, M.: 2D+EM+MI+NS-TuM11, **20**
Ishii, Y.: PS+EM-WeM5, **47**
Ishikawa, K.: PS+AS+EM+SS-MoM11, 11; PS+EM+SE-TuM13, 25; PS+EM+TF-ThM3, 63
Ishikawa, M.: PS+EM-WeM12, 48
Ishimura, H.: PS+EM-WeM5, 47
Islam, M.S.: TF+EM+MI-WeA10, 58; TF+EM+MI-WeA9, 58
Ismail-Beigi, S.: 2D+EM+MI+MN+NS+SS-ThM2, 59
Isobe, M.: PS+AS+EM+SS-MoM1, 9; PS+EM+NS+SS-TuA12, 35; PS+EM+TF-ThA1, 70
Itagaki, N.: PS+EM+NS+SS-TuA8, 34
Ito, K.: TF+EM+MI-WeM3, 48
Ito, T.: PS+EM+NS+SS-TuA12, 35; PS+EM+TF-ThA1, 70; PS+EM+TF-ThM4, **64**
Izawa, M.: PS+EM+TF-ThA3, 70; PS+EM+TF-ThM3, 63
— J —
Jackson, T.N.: TF+AM+EM+PS-TuM6, 26
Jacobi, C.: 2D+EM+MN+NS-FrM5, 79
Jamet, M.: 2D+AM+EM+NS-WeM12, 40
Jang, B.-K.: MI+EM-FrM8, 82
Jang, H.: MI+EM-FrM8, 82

Jaouad, A.: PS+EM+SE-TuM2, 23
Jawaid, A.: EM+AN+MI+SS-WeM12, 42
Jeon, H.: 2D+EM+MN+NS-ThA10, 69
Jeong, H.H.: PS+EM-WeM11, 47
Jeong, Y.H.: MI+EM-FrM8, 82
Jevric, M.: SS+AS+EM-WeA9, 56
Jewell, A.D.: TF+EM+MI-WeA3, **57**
Jhang, J.-H.: 2D+EM+MI+MN+NS+SS-ThM2, 59
Ji, A.R.: PS+EM-WeM11, 47
Ji, D.: EM+2D+SS-WeA7, **51**
Jia, Z.: MP+EM+MN+NS-MoM9, 6
Jiang, H.: EL+EM-MoA10, 13
Jinka, O.: MP+EM+MN+NS-MoM5, 6
Job, N.: PS+EM+NS+SS-TuA7, 34
Johansson, L.I.: 2D+EM+MN+NS-FrM5, **79**
John, S.: TF+AS+EL+EM+NS+PS+SS-ThA8, 74
Johnson, E.V.: PS+AS+EM+SS-MoM2, 9
Johnson, J.W.: EM+2D+SS-WeA9, 52
Johnson, S.D.: PS+EM+TF-ThA8, 71
Joi, A.: TF+EM+MI-WeM12, **50**
Jones, A.: EM-ThP13, 77
Jones, T.E.: PC+AS+BI+EM+NS+PB+SS-TuA7, 32
Jonker, B.T.: 2D+EM+MI+MN+NS-TuA1, 28; 2D+EM+MN+NS-ThA1, 68; 2D+EM+MN+NS-ThA2, 68
Jooya, H.Z.: MP+EM+MN+NS-MoM8, 6
Joseph, E.A.: PS+EM+TF-ThM12, 65
Joubert, O.: PS+EM+TF-ThM13, 65; PS+EM-WeM6, 47
Julien, S.: SS+EM+NS-ThM4, 66
Jung Hwan, Y.: TF+EM+MI+PS-MoA3, 17
Jung, M.H.: MI+EM-FrM8, 82
Jur, J.S.: TF+AS+EL+EM+NS+PS+SS-ThA10, **75**
Jurczyk, B.E.: SS+EM+PS+TF-ThA9, 72
— K —
Kalinin, S.V.: 2D+AM+EM+NS-WeM11, 40
Kamataki, K.: PS+EM+NS+SS-TuA8, 34
Kambham, A.: PS+AS+EL+EM+SE-WeM6, **45**
Kaminsky, J.: PS+EM-WeA1, 53
Kampen, T.U.: 2D+EM+MI+MN+NS+SS-ThM10, 59
Kanarik, K.J.: PS+EM+TF-ThA4, **70**
Kanatzidis, M.: 2D+EM+MI+NS-TuM2, 19
Kandel, S.A.: PC+AS+BI+EM+NS+PB+SS-TuA12, 33
Kaneko, T.: PS+EM+SE-TuM10, 24
Kang, I.H.: EM+2D+SS-WeA4, 51
Kapadia, R.: EM+MP+PS-MoM2, 4; RM+EM+NS-TuA9, 35; SS+AS+EM-WeA11, 56
Kaplar, R.J.: EM+2D+SS-WeA11, 52; EM-ThP11, 77
Karahashi, K.: PS+EM+NS+SS-TuA12, **35**; PS+EM+TF-ThA1, 70; PS+EM+TF-ThM4, 64
Karandikar, P.: NS+AN+EM+MI+MN+MP+PS+RM-ThM2, **62**
Kaspar, T.C.: PC+AS+BI+EM+NS+PB+SS-TuP5, **38**
Kato, T.: PS+EM+SE-TuM10, **24**
Katsouras, I.: TF+AS+EL+EM+NS+PS+SS-ThA9, 75
Katz, M.: EM+MP+PS-MoM6, 5
Katzer, D.S.: TF+EM+MI-WeM1, 48
Kavrik, M.: EM+AM+NS+PS-MoA10, 15; EM+MP+PS-MoM1, 4; EM+MP+PS-MoM6, 5
Kawakami, R.: 2D+EM+MN+NS-ThA3, **68**
Kawamura, K.: PS+EM+TF-ThA3, 70; PS+EM+TF-ThM3, 63
Kawasaki, J.: PS+AS+EL+EM+SE-WeM5, **45**
Kenny, J.: PS+EM+SE-TuM3, 23
Kent, A.: MI+2D+EM+NS-MoA3, **15**
Kephart, J.: EM+2D+AN+MI+MP+NS-TuA3, 29
Kerstetter, L.: EM+AM+NS+PS-MoA8, 14
Kessels, W.M.M.: SS+EM+NS-ThM12, 67; TF+AS+EL+EM+NS+PS+SS-ThA6, **74**
Khanal, M.P.: EM-ThP18, **78**
Kikuchi, Y.: PS+EM-WeA10, 54
Kilic, U.: EL+AS+EM-MoM3, **2**
Kim, E.: MP+EM+MN+NS-MoM8, 6
Kim, H.: 2D+EM+MI+MN+NS-TuA7, 28
Kim, H.J.: EM+AN+MI+SS-WeM3, **41**
Kim, H.W.: EM+2D+SS-WeA4, 51
Kim, I.: TF+AS+EL+EM+NS+PS+SS-ThA10, 75
Kim, J.: EM+2D+AN+MI+MP+NS-TuA11, 31; EM-ThP14, 78; MP+EM+MN+NS-MoM10, **7**; MP+EM+MN+NS-MoM9, 6; PS+AS+EL+EM+SE-WeM3, 44
Kim, J.H.: EM+2D+SS-WeA4, 51; EM+2D+SS-WeA9, 52
Kim, K-E.: MI+EM-FrM8, 82
Kim, M.J.: EM-ThP14, 78
Kim, R.: EM+2D+NS+PS+RM+TF-ThA3, 69; EM+AN+MI+SS-WeM12, 42
Kim, S.: 2D+EM+MN+NS-FrM7, **80**
Kim, S.G.: TF+EM+MI-WeM11, 50
Kim, TH.: PS+EM+NS+SS-TuA3, **33**
Kim, Y.: EM+2D+AN+MI+MP+NS-TuA11, 31; PS+AS+EL+EM+SE-WeM3, 44; TF+EM+MI-WeM11, 50
Kimbrough, J.: EM-ThP7, 76
Kimmel, G.A.: SS+AS+EM-WeA12, 57
King, S.T.: EM-ThP20, **78**
King, S.W.: PS+EM-WeA11, 54; PS+EM-WeA2, 53
Kishi, Y.: PS+AS+EM+SS-MoM3, 9
Kiuchi, M.: PS+EM+TF-ThA1, 70
Kjaervik, M.: PC+AS+BI+EM+NS+PB+SS-TuA1, 31
Klein, B.: EM+2D+SS-WeA11, 52; EM-ThP11, 77; EM-ThP13, 77
Klein, P.: EM+2D+AN+MI+MP+NS-TuA10, 30
Klein, P.B.: EM+2D+AN+MI+MP+NS-TuA11, 31
Klimov, N.N.: NS+AN+EM+MN+MP+RM-TuM12, 22
Knapper, K.A.: NS+AN+EM+MN+MP+RM-TuM5, 22
Knight, S.: EL+EM-MoA1, 12
Knop-Gericke, A.: PC+AS+BI+EM+NS+PB+SS-TuA7, **32**
Ko, K.-T.: MI+EM-FrM8, 82
Ko, W.: PS+EM+SE-TuM4, 24
Kobayashi, H.: PS+EM+TF-ThA3, 70; PS+EM+TF-ThM3, 63
Koch, S.: 2D+EM+MI+MN+NS+SS-ThM11, 60
Kodambaka, S.: SS+EM+PS+TF-ThA3, 72
Koel, B.E.: SS+AS+EM-WeA3, 55
Koenraad, P.M.: TF+AS+EL+EM+NS+PS+SS-ThA6, 74
Kofuji, N.: PS+EM-WeM12, 48
Koga, K.: PS+EM+NS+SS-TuA8, **34**
Kölling, S.: TF+AS+EL+EM+NS+PS+SS-ThA6, 74
Komorek, R.: PC+AS+BI+EM+PB+SS-WeM3, **43**
Komsa, H.: 2D+AM+EM+NS-WeM6, 39
Kondo, H.: PS+AS+EM+SS-MoM11, 11; PS+EM+SE-TuM13, 25
Konh, M.: SS+AS+EM-WeA8, 55
Koo, T.Y.: MI+EM-FrM8, 82
Korde, M.: EL+EM-MoA3, 12
Korlacki, R.: EL+AS+EM-MoM3, 2; EL+EM-MoA1, 12
Korzetz, R.: 2D+EM+MI+MN+NS+SS-ThM11, 60
Kotler, Z.: NS+AN+EM+MI+MN+MP+PS+RM-ThM1, 62
Kouzuma, Y.: PS+EM+TF-ThA3, 70
Kozen, A.C.: PS+EM+TF-ThA8, 71; TF+EM+MI-WeM6, **49**
Krasheninnikov, A.V.: 2D+AM+EM+NS-WeM6, 39
Kraut, M.: EM+AN+MI+SS-WeM13, 42
Kresin, V.V.: NS+2D+AN+EM+MN+MP+PC+RM-MoM10, 8
Kropman, D.: EM+AN+MI+SS-WeM5, **41**
Krüger, P.: MI+EM-FrM7, 81
Krylov, S.: NS+AN+EM+MI+MN+MP+PS+RM-ThM1, 62
Ku, H.S.: MP+AM+EM+NS-MoA6, 16; MP+EM+NS-TuM12, 21; MP+EM+NS-TuM3, 20; MP+EM+NS-TuM6, 21
Kub, F.J.: EM+2D+AN+MI+MP+NS-TuA11, 31
Kubota, H.: RM+EM+NS-TuA11, 36
Kuk, Y.: 2D+EM+MN+NS-ThA10, 69
Kumagai, Y.: EL+EM-MoA1, 12
Kumah, D.P.: PS+AS+EL+EM+SE-WeM10, **45**
Kumar, P.: MP+EM+NS-TuM5, 21
Kummel, A.C.: EM+2D+AN+MI+MP+NS-TuA12, 31; EM+AM+NS+PS-MoA10, 15; EM+AM+NS+PS-MoA2, 14; EM+MP+PS-MoM1, 4; EM+MP+PS-MoM6, **5**
Kuo, Y.: EM+AM+NS+PS-MoA6, **14**
Kuramata, A.: EM+2D+SS-WeA2, 51
Kurihara, M.: PS+EM+TF-ThA3, 70; PS+EM-WeM12, 48
Kuroda, R.: TF+EM+MI-WeM5, 49
Kushner, M.J.: PS+EM+SE-TuM4, **24**; PS+EM+SE-TuM6, 24
Kuwahara, K.: PS+EM-WeM2, 46
Kwak, I.J.: EM+2D+AN+MI+MP+NS-TuA12, **31**
Kwon, J.: 2D+EM+MI+MN+NS-TuA2, **28**
Kwon, T.S.: PS+EM-WeM11, 47
— L —
L. Raja, L.: PS+AS+EM+SS-MoM11, 11
Laas, T.: EM+AN+MI+SS-WeM5, 41
Lagrasta, S.: PS+EM+SE-TuM12, 25; PS+EM-WeM1, 46
Lake, R.: MP+AM+EM+NS-MoA6, 16; MP+EM+MN+NS-MoM5, 6; MP+EM+NS-TuM12, **21**; MP+EM+NS-TuM3, 20; MP+EM+NS-TuM6, 21
Lane, B.: PS+AS+EM+SS-MoM11, 11
Lanford, W.: PS+EM-WeA11, 54; PS+EM-WeA2, 53
Larrabee, T.J.: TF+EM+MI-WeM6, 49
Larsen, K.G.: 2D+EM+MI+NS-TuM3, **19**
Larson, D.J.: TF+AS+EL+EM+NS+PS+SS-ThA6, 74
Larson, S.: NS+2D+AN+EM+MN+MP+PC+RM-MoM4, **7**
Larsson, K.M.E.: EM+AN+MI+SS-WeM13, **42**
Laturia, A.: EM-ThP14, 78
Law, M.: EM+2D+AN+MI+MP+NS-TuA12, 31
Lawrence, C.: EM+AM+NS+PS-MoA8, 14
Lazzarino, F.: PS+EM-WeA9, 54
Le, D.: 2D+AM+EM+NS-WeM2, **39**; SS+EM+NS-ThM11, 67
Le, S.: EM+2D+NS+PS+RM+TF-ThA4, 69
Leandersson, M.: 2D+EM+MN+NS-FrM5, 79
Lee, C.H.: 2D+EM+MI+MN+NS-TuA2, 28
Lee, G.H.: 2D+AM+EM+NS-WeM3, **39**; 2D+EM+MI+MN+NS-TuA2, 28
Lee, J.H.: MI+EM-FrM8, 82
Lee, J.-S.: MI+EM-FrM8, 82
Lee, J.W.: PS+EM-WeM11, **47**
Lee, J.Y.: 2D+EM+MI+MN+NS-TuA2, 28; PS+EM-WeM11, 47

Lee, K.: 2D+EM+MI+MN+NS-TuA7, 28
Lee, M.: 2D+EM+MN+NS-ThA10, **69**; EM+MP+PS-MoM6, 5
Lee, M.-S.: PC+AS+BI+EM+NS+PB+SS-TuP5, 38
Lee, P.: PS+EM-WeA3, 53
Lee, S.: EL+AS+EM-MoM11, 4; EM-ThP12, **77**; TF+AM+EM+PS-TuM6, 26
Lee, SW.: PS+EM+NS+SS-TuA3, 33
Lee, Y.: PS+EM+TF-ThA2, 70
Lee, Y.-J.: PS+EM-WeM5, 47
Leem, J.: EM+2D+NS+PS+RM+TF-ThA3, 69
Leftwich, T.R.: SS+EM+NS-ThM10, 66
Lehnardt, S.: 2D+EM+MI+NS-TuM3, 19
Lei, W.: NS+2D+AN+EM+MN+MP+PC+RM-MoM11, **8**
Lenoble, D.: PC+AS+BI+EM+PB+SS-WeM10, 44
Letton, J.: EM+2D+SS-WeA3, 51
Leusink, G.J.: EM+MP+PS-MoM8, 5
Lewis, R.: TF+EM+MI+PS-MoA8, 18
Ley, R.T.: EM+MI+MN+NS-ThM5, **61**
Lezec, H.J.: NS+AN+EM+MN+MP+RM-TuM3, 22
Li, C.: PS+EM+TF-ThM12, 65
Li, H.: PS+AS+EM+SS-MoM4, **9**; PS+EM+NS+SS-TuA12, 35
Li, L.: PS+EM-WeA2, 53
Li, M.: SS+AS+EM-WeA10, 56
Li, Q.: NS+2D+AN+EM+MN+MP+PC+RM-MoM11, 8
Li, T.: SS+EM+NS-ThM5, 66
Li, X.: 2D+EM+MI+NS+TF-MoM5, 1; EM-ThP10, 77
Li, Y.: EL+AS+EM-MoM11, 4
Li, Z.: SS+AS+EM-WeA8, 55
Liang, X.: 2D+EM+MI+MN+NS+SS-ThM2, 59
Liao, I.: 2D+EM+MI+MN+NS-TuA11, 29
Libuda, J.: SS+AS+EM-WeA9, **56**
Liddle, J.A.: NS+AN+EM+MI+MN+MP+PS+RM-ThM3, **62**
Lii-Rosales, A.: SS+EM+NS-ThM4, 66
Lill, T.B.: PS+EM+TF-ThA4, 70; PS+EM-WeA12, 54
Lim, B.R.: PS+EM-WeM11, 47
Lin, E.: EM+AM+NS+PS-MoA1, 13
Lin, H.: 2D+EM+MI+MN+NS+SS-ThM3, **59**
Lin, K.Y.: PS+EM+TF-ThM12, **65**
Liong, L.C.: EL+EM-MoA6, 13
Litwin, P.: EM-ThP19, 78
Liu, D.R.: EM-ThP4, **76**
Liu, J.: EL+EM-MoA10, **13**
Liu, S.Y.: EL+AS+EM-MoM8, 3; EL+EM-MoA10, 13
Liu, Y.: MP+EM+NS-TuM5, 21; TF+EM+MI-WeA8, **57**
Llorca, J.: PC+AS+BI+EM+NS+PB+SS-TuP2, 37
Lo, C.F.: EM+2D+SS-WeA9, 52
Long, J.: MP+AM+EM+NS-MoA6, 16; MP+EM+NS-TuM12, 21; MP+EM+NS-TuM3, 20; MP+EM+NS-TuM6, 21
Lou, Q.: PS+EM-WeA1, 53
Loup, V.: PS+EM+SE-TuM1, 23
Lu, I.: 2D+EM+MI+MN+NS+SS-ThM5, 59
Lu, Y.: 2D+AM+EM+NS-WeM1, **39**
Lu, Y.-T.: PS+EM-WeA10, 54
Lubomirsky, I.: NS+AN+EM+MI+MN+MP+PS+RM-ThM1, 62
Ludwig, J.: 2D+AM+EM+NS-WeM10, 40
Ludwig, K.F.: PS+EM+TF-ThA8, 71
Luna, L.E.: EM+2D+AN+MI+MP+NS-TuA11, 31; EM+2D+SS-WeA12, 52
Lutker-Lee, K.: PS+EM-WeA10, 54
Lyle, L.A.M.: EM+2D+SS-WeA3, **51**
Lyubinetsky, I.: SS+AS+EM-WeA10, 56; SS+AS+EM-WeA12, 57

— M —

Ma, H.: EM-ThP10, 77
Ma, Y.: 2D+AM+EM+NS-WeM6, 39
Maboudian, R.: 2D+EM+MI+NS+TF-MoM10, 2
Macco, B.: TF+AS+EL+EM+NS+PS+SS-ThA6, 74
Maciullis, N.A.: SS+EM+PS+TF-ThA4, 72
Mackus, A.J.M.: TF+AM+EM+PS-TuM1, **25**
Madhavan, A.: RM+EM+NS-TuA11, 36
Maeda, E.: TF+EM+MI-WeM3, 48
Maeda, K.: PS+EM-WeM5, 47
Magesan, E.: MP+AM+EM+NS-MoA10, 17
Magnozzi, M.: EL+AS+EM-MoM6, **3**
Maguire, P.: PS+EM+NS+SS-TuA4, 33
Maindron, T.: TF+AS+EL+EM+NS+PS+SS-ThA4, **73**
Maksymovych, P.: 2D+EM+MI+MN+NS+SS-ThM6, **59**; 2D+EM+MN+NS-ThA6, 68
Malko, A.V.: EM+AN+MI+SS-WeM10, 42
Mamtaz, H.H.: TF+EM+MI-WeA10, 58
Mane, A.U.: TF+EM+MI+PS-MoA9, 18
Mangolini, L.: NS+2D+AN+EM+MN+MP+PC+RM-MoM6, 8
Mao, H.: TF+EM+MI-WeA9, 58
Marcoen, K.: SS+AS+EM-WeA7, 55
Mariantoni, M.: MP+AM+EM+NS-MoA3, **16**
Marinov, D.: 2D+AM+EM+NS-WeM10, **40**
Mariotti, D.: PS+EM+NS+SS-TuA4, 33
Marques, E.: TF+AM+EM+PS-TuM10, 26
Martinez, A.: PC+AS+BI+EM+NS+PB+SS-TuP5, 38
Martinez, E.: PS+EM+SE-TuM12, 25
Martinis,: MP+EM+MN+NS-MoM3, **6**
Mastro, M.A.: EM+2D+SS-WeA12, 52
Mathur, A.: EL+EM-MoA5, 12
Matsubara, K.: PS+AS+EM+SS-MoM9, 10
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