Electronic Materials and Processing
Room: 9 - Session EM+TF+OX+GR-MoM

High-k Dielectrics for MOSFETs I
Moderator: A.C. Kummel, University of California San Diego

8:20am **EM+TF+OX+GR-MoM1 Surface Preparation and Dielectric Growth for Graphene-based Devices**, ***R.M. Wallace***, University of Texas at Dallas **INVITED**

In addition to interesting physics, numerous device applications are under investigation for graphene. Many of these devices require an interaction of graphene with dielectrics, and require a thorough understanding of the graphene/dielectric interface. As practical device applications require large area graphene, CVD methods have been employed to synthesize graphene and typically involve a wet chemical transfer process, which can leave residues that impact device behavior. This talk will review recent progress in the investigation of CVD graphene growth, transfer and dielectric growth processes with an emphasis on in-situ studies of the surfaces produced by these processes and the resultant electrical behavior. This work is supported by the NRI SWAN Center.

9:00am **EM+TF+OX+GR-MoM3 Antimonide-Based P-Channel MOSFET: Progress and Challenges**, ***S. Oktyabrsky***, *A. Greene, S. Madisetti, P. Nagaiah, M. Yakimov, R. Moore, S. Novak, H. Bakhru, V. Tokranov*, University at Albany-SUNY **INVITED**

Development of p-type MOSFETs using new materials is an important goal to provide a further scaling of CMOS circuits. Although Ge is still considered as a main candidate for novel p-channels due to its superior bulk transport properties, recent progress in strained III-Sb channels and MOS technologies makes it a good competitor in particular for deeply scaled devices. The materials parameters affecting MOSFET's figures-of-merit are reviewed with the emphasis on strain in quantum wells (QWs), effective mass, density of states and mobility.

Progress in development of materials for III-Sb channels is reported. Optimization of MBE growth of metamorphic buffers and GaSb on lattice-mismatched GaAs substrates has resulted in "step-flow" growth mode of GaSb with monolayer-high steps on the surface, ~10^7cm^{-2} dislocation density and bulk hole mobility 860cm^2/Vs. Optimization of strain in QWs provided the highest Hall mobility of 1020 cm^2/Vs at sheet hole density of 1.3x10^{12}/cm^2 obtained for $In_{0.36}Ga_{0.64}Sb$ with compressive strain of 1.8%. Hole mobility in QW channel was benchmarked against the thickness of top semiconductor AlGaSb barrier. The effect of interface-related scattering hole mobility in the channel was found to be significantly less than e.g. for n-InGaAs, that might be due to stronger localization of holes in QWs.

Two approaches to fabricate high-quality III-Sb/high-k interface were studied: all *in-situ* Al_2O_3 or HfO_2 gate oxides, and *ex-situ* atomic layer deposited (ALD) Al_2O_3 with InAs top semiconductor capping layer. Interface with *in-situ* MBE gate oxides was found to improve with *in-situ* deposited a-Si interface passivation layer (IPL). Interfaces with better thermal stability, reduced interface trap density and hysteresis were observed on both n- and p- type GaSb MOSCaps with the IPL. P-type MOSFETs with HfO_2 showed a maximum drain current of 23 mA/mm for a 3µm gate length. Use of a-Si IPL has also resulted in a significant (over an order of magnitude) reduction of the hole density in QWs and corresponding negative flat band voltage shift and drop of mobility which becomes remote Coulomb scattering-limited. An interface with ALD Al_2O_3 was improved by a thin 2nm interface layer of InAs which was treated with HCl or$(NH_4)_2S$ immediately prior to ALD process. Optimized annealing further improved the C-V characteristics, reduced interface trap density down to 10^{12} cm^{-2}eV^{-1}, leakage current and MOSFET subthreshold slope down to 200 mV/dec. Increasing annealing temperature to and above 450°C drastically degraded C-V characteristics due to low thermal budget of antimonides.

9:40am **EM+TF+OX+GR-MoM5 Interface Study of the Atomic Layer Deposited Al_2O_3 on $Al_{0.25}Ga_{0.75}N$**, ***X. Qin***, *B. Brennan, H. Dong, R.M. Wallace*, The University of Texas at Dallas

Due to the high two-dimensional electron gas (2-DEG) density, AlGaN/GaN high electron mobility transistors (HEMTS) are recognized as key devices for high power and low noise applications. However, the associated large gate leakage current degrades the performance of AlGaN HEMTs. In order to solve this problem, MOS-HEMTs have been developed, in which the incorporation of a high-k gate dielectric layer can overcome the drawbacks.

In this work, the native and treated $Al_{0.25}Ga_{0.75}N$ surface chemical states and structure of were studied by x-ray photoelectron spectroscopy (XPS), ion scattering spectroscopy (ISS) and low energy electron diffraction. Different chemical treatment processes including $(NH_4)OH$, $(NH_4)_2S$ and HF were studied, followed by atomic layer deposition (ALD) Al_2O_3 layers on $Al_{0.25}Ga_{0.75}N$. The oxidation states of the $Al_{0.25}Ga_{0.75}N$interface and Al_2O_3 deposition process were studied by in-situ XPS analysis. In addition, ex-situ atomic force microscopy (AFM) was used to observe the surface topography before and after the Al_2O_3 deposition. According to the XPS results, it is found that chemical treatments could remove the native Al_2O_3 but were not effective to eliminate the Ga oxide, and the growth rate of Al_2O_3 is low on the native and treated $Al_{0.25}Ga_{0.75}N$ samples. The AFM images show that there are many pin holes in the surface of $Al_{0.25}Ga_{0.75}N$. Studies of HfO_2 deposition will also be presented.

This work is supported by the AOARD under AFOSR Grant No. FA2386-11-1-4077

10:00am **EM+TF+OX+GR-MoM6 Ideal Monolayer Nitridation of Semiconductors using a Nitrogen Radical Generator**, ***A.T. Lucero***, *J. Kim*, University of Texas at Dallas

Thin silicon nitride films have long been desirable for various applications. Suggested uses range from surface and interface passivation to ultra-thin dielectric layers. Traditional deposition techniques are low pressure chemical vapor deposition (LPCVD) and plasma enhanced chemical vapor deposition (PECVD). High quality LPCVD films require high processing temperatures, and PECVD exposes the substrate to damaging plasma and electric potentials. While both techniques are suitable for many applications, there are some instances where both processes are too harsh.

In this paper, we report the growth of silicon nitride using a remote nitrogen radical generator system. Growth temperatures range from room temperature to 400 °C,and growth time is varied from two minutes to one hour. Film composition is analyzed using x-ray photoelectron spectroscopy (XPS) and morphology is checked using atomic force microscopy. Results indicate that surface nitrogen saturation can be reached at both low temperatures and short exposure times,and that the reaction is self limiting, terminating at one monolayer. Film thickness is approximately one Angstrom, as determined by XPS. Results for silicon and III-V passivation will be discussed.

We would like to thank Toshiba Mitsubishi-Electric Industrial Systems Corporation for providing the nitridation system used in this study.

11:00am **EM+TF+OX+GR-MoM9 Characterization of ALD Laminated Gate Dielectrics on GaN MOSCAPs**, ***D. Wei***, *T. Hossain,* Kansas State University*, N. Nepal, N.Y. Garces,* Naval Research Laboratory*, H.M. Meyer III,* Oak Ridge National Laboratory*, C.R. Eddy, Jr.,* Naval Research Laboratory*, J.H. Edgar*, Kansas State University

To improve the efficiency of GaN based power electronic devices there is tremendous and growing interest in employing metal-insulator-semiconductor (MIS) transistors. As with all compound semiconductors, there is a significant challenge in forming an electronic quality dielectric-semiconductor interface. Thus, there is a need to better understand and improve the dielectric-semiconductor interface quality in order to improve the overall performance of the device.

This research focuses on the benefits and properties of Al2O3, TiO2 and TiO2-Al2O3 nanolaminate thin films deposited on GaN and GaOx/GaN by plasma-assisted atomic layer deposition (PA-ALD) for gate dielectric development. Correlations were sought between the films' structure, composition, and electrical properties. The gate dielectrics were approximately 15nm thick as determined by spectroscopic ellipsometry. The interface carbon concentration, as measured by x-ray photoelectron spectroscopy (XPS) depth profile, was lower for Al2O3/GaN than TiO2/GaN, and the nanolaminate structure did not decrease the carbon concentration. However, carbon was not detected at the interface for the GaN samples pretreated by annealing in O2 for 30 minutes at 800°C. Also, according to XPS, the Al2O3 films had a better coverage than TiO2. The RMS roughness of TiO2 and Al2O3 top layers were ~0.53nm and ~0.20nm respectively, as determined by atomic force microscopy. The dielectric constant of Al2O3 on GaOx/GaN was greatly increased compared to that of the TiO2-Al2O3 and pure Al2O3 on GaN substrate. In addition, the Al2O3 deposited on the GaOx/GaN showing no hysteresis in capacitance-voltage (C-V) characteristics, which is corresponding with a negligible carbon concentration from the XPS depth profile. These results indicate the

promising potential of plasma ALD deposited Al2O3 serving as the gate oxide on GaOx/GaN based MOS devices.

11:20am **EM+TF+OX+GR-MoM10 Passivation of Interfacial Defects in GaAs and Other III-Vs**, ***J. Robertson***, Cambridge University, UK **INVITED**

It has always been harder to make FETs from GaAs than Si, because of 'Fermi level pinning' and the difficulty of passivating its surfaces. These issues were discussed by Spicer et al [1] in the 'unified defect model' and Hasegawa [2] is his 'Disorder Induced Gap states' model. Since 1997 it was possible to make inverted GaAs MOSFETs using the epitaxial Gadolinium gallium oxide [3]. The main impetuous now is to use atomic layer deposition (ALD) to make scalable FETs [4], as recently achieved by Intel [5]. The obvious question is why (In)GaAs is much harder to passivate than Si. The early answer was its poor native oxide. But since the advent of good ALD HfO2 or Al2O3 oxides on Si, this answer is deficient, as they should also work on GaAs [6]. The underlying reason for defects is not stress, it must be chemical. I show that it arises from the polar bonding of GaAs [7], and a driving force to keep the surface Fermi level in a gap. The electron counting rule of Pashley [8] that describes surface reconstructions is shown to be a variant of auto-compensation, and it works more generally [9]. It leads to a continuous generation of defects if it is not satisfied. So the answer is to deposit oxide layers that meet this rule, and also to break any surface reconstructions that may lead to As-As dimers [9]. Diffusion barriers are also crucial to a good passivant, on GaAs or on Ge .

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Oxide Heterostructures-Interface Form & Function Focus Topic
Room: 7 - Session OX+EM+MI+NS+TF-MoM

Structure–Property Relationships in Epitaxial Oxide Interfaces
Moderator: E.I. Altman, Yale University

8:20am **OX+EM+MI+NS+TF-MoM1 Role of Dual-laser Ablation in Controlling Mn Oxide Precipitation during the Epitaxial Growth of Mn Doped ZnO Thin Films with Higher Doping Concentrations**, *D. Mukherjee,* ***M. Hordagoda****, R.H. Hyde, N. Bingham, H. Srikanth, P. Mukherjee, S. Witanachchi*, University of South Florida

The low solubility of Mn (equilibrium limit of 13 %) and precipitation of Mn oxides at slightly higher Mn doping (> 4 %) have remained major obstacles in the growth of Mn doped ZnO (ZnO:Mn) thin films for potential spintronic applications. In this work, epitaxial ZnO:Mn thin films were deposited on c-cut Al_2O_3 (0001) substrates, with increasing Mn concentrations from 2 to 12 %, using the dual-laser ablation process. In this process, an excimer (KrF) laser and a CO_2 laser pulses are spatially and temporally overlapped onto the target surface. Initially the target is heated by the CO_2 laser to produce a transient molten layer, from which the slightly time-delayed KrF laser initiates the ablation. Ablation for a momentary liquid target not only results in a drastic reduction of particulates in the deposited films but also overcomes the problem of non-congruent ablation of the ZnO:Mn target, leading to stoichiometric film deposition. Moreover, the optimum coupling of the laser energies produces an ablation plume that has a broader angular distribution, compared to the plume generated by KrF pulse alone, as observed from the intensified-charge-coupled-detector (ICCD) images of the ablated plumes. This allows the deposition of uniform films over larger area. Further, the higher ionization of the ablated species as seen in the optical emission spectra (OES) of the dual-laser ablated plumes leads to enhanced gas phase reaction and better film morphology and crystallinity. X-ray diffraction studies revealed that the dual-laser deposited ZnO:Mn films were single crystalline with no secondary phase formation even at 12 % doping while single-laser deposited ZnO:Mn films showed secondary Mn oxide phases. Room temperature magnetic measurements showed ferromagnetism (FM) with enhanced saturation magnetization (M_s) values from 1.3 emu/cm^3 for 2 % ZnO:Mn films to 2.9 emu/cm^3 for 12 % ZnO:Mn films. In- and out-of-plane magnetization revealed absence of magnetic anisotropy. Further, temperature dependent Hall measurements showed a strong correlation between the effective carrier densities and the observed FM. All these measurements suggested a carrier mediated mechanism of FM in ZnO:Mn thin films. Using both the experimental data and theoretical analysis the FM in less conducting ZnO:Mn films was described by a bound magnetic polaron model whereas that in highly conducting films was consistent with a carrier mediated interaction via RKKY exchange mechanism.

8:40am **OX+EM+MI+NS+TF-MoM2 Structural Characterization of Heterojunction *n*-ZnO/*p*-NiO Thin Films Epitaxially Deposited on (0002)Al_2O_3 Substrates**, ***Y.H. Kwon****,* Sungkyunkwan University, Republic of Korea*, J.H. Lee,* KAIST, Republic of Korea*, S.H. Chun,* Sungkyunkwan University, Republic of Korea*, J.Y. Lee,* KAIST, Republic of Korea*, H.K. Cho*, Sungkyunkwan University, Republic of Korea

Recently, oxide semiconductors with superior electical properties have been considered as candidates to replace Si based electronics. Furthermore, their thermally and chemically stable characteristic is preferable for devices. Especially, among a lot of oxides, ZnO based semiconductors have been extensively investigated to apply in wide application such as thin film transistor and light emitting diode. ZnO is an intrinsic *n*-type semiconductor which characteristic comes from Zn interstitials and O vacancies. And band-gap and exciton binding energy are 3.37 eV and 60 meV, respectively, which is suitable for optical application operating in ultra-violet region. Therefore, *p-n* homojunction diode structure combined with *n*-ZnO and *p*-ZnO having well matched interface had been studied by a lot of researchers.[1] However, it was not reliable since *p*-type ZnO synthesized by doping of group V elements is unstable and return to the *n*-type by self-compensation.[2]

Therefore, *p-n* heterojunction diode composed of *n*-ZnO and stable *p*-type oxide such as Cu_2O and NiO was alternatively studied.[3] Among the *p*-type oxides, NiO with wide direct band-gap (3.7 eV) have been expected to apply in optical applications. And conductivity of NiO could be significantly controlled by Li+ doping. Furthermore, according to T. Dutta et. al., (111) plane of NiO could well matched with (0002) of ZnO by domain match epitaxy.[4]

In this study, heterojunction diode structure was fabricated with *n*-type ZnO and *p*-type NiO on [0002] oriented Al_2O_3 substrates. RF magnetron sputtering method was used for deposition of NiO and ZnO films. After the deposition of NiO films at 400°C in O_2 atmosphere, ZnO films were grown at 600°C and in Ar and O_2, mixed gas atmosphere. XRD result showed the NiO films were fabricated with high crystallinity and preferred orientation of $[111]_{NiO}$. And sixfold symmtery of $(100)_{NiO}$ plane obtained by phi-scan indicates that the NiO films were bi-epitaxially grown on Al_2O_3 substrates. In addition, electrical properties of NiO showed relatively low resisitivity (1.648 Ωcm) and high mobility (14.52 cm^2/Vs) due to Li^+ doping. Sixfold symmetry of $(1\text{-}102)_{ZnO}$ observed at phi-scan result indicates that ZnO films were also epitaxially grown on [111] oriented NiO films.

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9:00am **OX+EM+MI+NS+TF-MoM3 Manipulating the Electrostatic Boundary Conditions of Polar Interfaces**, ***Y. Hikita***, SLAC National Accelerator Laboratory **INVITED**

Transition metal oxides (TMO) offer various functionalities ranging from electronic devices to environmental catalysts [1, 2]. Often, the central part of such devices is the interface between different materials. In order to improve their device performance, control of charge transport across these interfaces is essential. Originally developed in semiconductor heterostructures, interface band alignment control is based on the interface electrostatic boundary conditions and is one of the most fundamental methods to tune the carrier transport across interfaces [3]. Given their strongly ionic nature and their accessibility to multiple valence states, the TMO interface should be more suitable than covalent semiconductors for manipulating interface band alignments. Here we focus on epitaxial metal-semiconductor Schottky interfaces between perovskite oxides to demonstrate the effectiveness of this technique. I will present two $SrTiO_3$ based perovskite Schottky junctions in which the interface energy barriers were modulated by interface dipoles controlled on the atomic scale [4].

Further, I will present the application of this technique in the form of an all-oxide hot electron transistor [5].

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11:20am **OX+EM+MI+NS+TF-MoM10 Strain-induced Oxygen Vacancy Ordering at $SrTiO_3/La_{0.5}Sr_{0.5}CoO_3$ Interfaces, and its Impact on Magnetic "Dead" Layers**, *S. Bose, M. Sharma, M. Torija,* University of Minnesota*, J. Gazquez, M. Varela,* Oak Ridge National Laboratory*, J. Schmitt, C. He,* University of Minnesota*, S. El-Khatib,* American University of Sharjah, United Arab Emirates*, M. Laver, J. Borchers,* NIST Center for Neutron Research*, **C. Leighton***, University of Minnesota

The remarkable functionality and epitaxial compatibility of complex oxides provides many opportunities for new physics and applications in oxide heterostructures. Perovskite cobaltites provide an excellent example, being of interest for solid oxide fuel cells, oxygen separation membranes, catalysis, ferroelectric RAM, resistive switching memory, and oxide spintronics. However, the same delicate balance between phases that provides this diverse functionality also leads to a serious problem - the difficulty of maintaining desired properties close to the interface with other oxides. Although this problem is widespread, manifests itself in several ways, and could present a significant roadblock to the development of heterostructured devices for oxide electronics, there is no consensus as to its origin. In our work, using SrTiO3(001)/La1-xSrxCoO3 as a model system, we have combined epitaxial growth via high pressure oxygen sputtering [1] with high resolution x-ray diffraction, atomic resolution scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS), and detailed magnetic, transport, and neutron scattering measurements to determine the fundamental origin of the deterioration in interfacial transport and magnetism [2,3]. The effect is found to be due to nanoscopic magnetic phase separation in the near-interface region driven by a significant depletion in interfacial hole doping due to accumulation of O vacancies. This occurs due to a novel mechanism for accommodation of lattice mismatch with the substrate based on formation and long-range ordering of O vacancies [4]. This fundamental link between strain state and O vacancy formation and ordering is explored in detail in this presentation. We demonstrate that the O vacancy density, depth profile, and ordering vector can all be controlled via strain, leading to a potential mechanism to substantially improve interfacial properties.

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11:40am **OX+EM+MI+NS+TF-MoM11 Fabrication and Characterization of Titanium Oxide Films with Tunable Stiffness**, *K. Gotlib-Vainshtein, O. Girshevitz, C.N. Sukenik,* Bar Ilan University, Israel*, D. Barlam,* Ben Gurion University, Israel*, E. Kalfon-Cohen, **S.R. Cohen***, Weizmann Institute of Science, Israel

The design of surfaces with controlled stiffness is attractive for a variety of applications ranging from controlling cell growth to mechanical and electrical engineering design. Here, the creation of layered composites with tunable surface stiffness has been achieved by coating a soft PDMS polymer with a stiff film of amorphous titanium oxide with thickness varying from 2 to 50 nm. The oxide layer is smooth (6 nm rms roughness at 2 μm^2 image size), and crack-free. Air plasma treatment was used to form a silica surface layer on the soft polymer base to promote of adhesion of the titania overlayer. To gain insight into the mechanics of the layered structure, nanomechanical quantification has been performed using different experimental approaches, as well as modeling studies. The surface mechanical properties of the samples have been probed using both instrumented nanoindentation and atomic force microscopy—based nanomechanical characterization. These results have been compared to finite element analysis (FEA) simulations.

By fitting the FEA simulations with experimental curves it is shown that the hard titania film and softer PDMS substrate individually maintain their characteristic elastic moduli, while the stiffness of the vertical nanocomposite can be controllably modified by changing the thickness of the stiff layer. Liquid phase deposition of the oxide allows control of its thickness at the nm level. During an indentation cycle, the stiff layer transmits the stress to the underlying PDMS base by deformation of its overall shape, but only negligible compression of the film thickness.

This synthetic approach can be quite versatile, and can, in principle, be extended to different oxides and a wide range of thicknesses. It allows control of surface properties while maintaining bulk material properties. This exploratory work is a first step towards defining the range of surface stiffnesses that can be achieved in this way, as well as developing general methodologies for their characterization.

Electronic Materials and Processing
Room: 9 - Session EM+TF+OX+GR-MoA

High-k Dielectrics for MOSFETS II

Moderator: C.L. Hinkle, University of Texas at Dallas, H.J. Kim, National Institute of Aerospace (NIA)

2:00pm **EM+TF+OX+GR-MoA1 "6.1" Family: The Next Generation of III-V Semiconductors for Advanced CMOS: Epitaxial Growth and Passivation Challenges**, ***C. Merckling***, *A. Alian, A. Firrincelli, S. Jiang, M. Cantoro, J. Dekoster, M. Caymax, M. Heyns*, IMEC, Belgium **INVITED**

The integration of high carrier mobility materials into future CMOS generations is presently being studied in order to increase drive current capability and to decrease power consumption in future generation CMOS devices. If III-V materials are the candidates of choice for n-type channel devices, antimonide-based III-V semiconductors present the unique property of owning both high electrons (InSb) and holes (GaSb) mobilities, which triggered much of the interest in these III-Sb compounds for advanced CMOS. Moreover recent simulations have demonstrated that higher hole mobility could be found in strained III-antimonides compounds, suggesting the possibility of an all III-antimonide solution for full III-V based CMOS. In this work we studied the heteroepitaxy of 6.1 family semiconductors (GaSb, AlSb & InAs) on various III-V and Si substrates as well as the passivation of such semiconductors.

The relatively large lattice parameter of “6.1” semiconductors makes the growth and the integration on standard surfaces difficult. But is it possible to grow such semiconductors fully relaxed with low defect density due to the formation of a highly periodic array of 90º misfit dislocations at the III-Sb/substrate interface. In this contrbution both MBE and MOVPE growth techniques have been studied in order to propose novel integration scheme on Si substrate.

In a second part, we will focus on the passivation of these III-V semiconductors. Because III-V surfaces are very sensitive to oxygen compounds, this will generate the formation of native oxide. This undesirable interlayer will contribute aggressively to the high density of surface states within the energy band gap, resulting in Fermi level pinning which disturbs the basic III-V MOSFET-operation. In this context both ex-situ and in-situ Al_2O_3 high-κ gate dielectric deposition by standard ALD or MBD processes is reported. The interface is abrupt without any substantial interfacial layer, and is characterized by high conduction and valence band offsets. Finally, MOS capacitors showed well-behaved C-V with relatively low D_{it} along the band gap. Such a D_{it} profile is promising for the future devices and suggests possibility to attain a low subthreshold swing.

2:40pm **EM+TF+OX+GR-MoA3 Improving Nucleation and Passivation of Ge(100) via H_2O and H_2O_2 Dosing**, ***T. Kaufman-Osborn***, *K. Kiantaj, J.S. Lee, A.C. Kummel*, University of California San Diego

Germanium is a promising candidate for potential channel materials due to its higher hole and electron mobility. To minimize the oxide-semiconductor interfacial defect density, a proper passivation layer must be used before the oxide layer is deposited. In this study, a monolayer of H2O chemisorbates is shown to activate TMA chemisorption due to the Ge-OH bonds catalyzing the formation of an ultrathin passivation layer which can serve as an ideal ALD nucleation template on a Ge surface. However, since H2O chemisorption results in equal density of Ge-H and Ge-OH sites on the Ge(100), H2O can only provide a maximum of 0.5 monolayer of Ge–OH sites, limiting the TMA nucleation density. By using H2O2 dosing, the density of Ge–OH sites can be doubled thereby increasing the potential TMA nucleation density. This study compares the passivation of the Ge(100) surface via H2O and H2O2, for the application of nucleating ALD growth on the surface, using scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS).

A saturation H2O dose onto Ge(100) resulted in 0.85 ML coverage of –OH and –H species chemisorbed on the surface. The remaining unreacted atoms on the surface have half filled dangling bond states causing a large local amount of conduction band edge states in the bandgap. The Ge–OH and Ge–H sites on the surface have limited thermal stability. Annealing the H2O/Ge(100) sample to 100°C significantly reduces the H2O coverage due to the recombinative desorption of H2 or H2O.

A saturation dose of H2O2 on Ge(100) at 25oC results in a coverage of 0.95 ML of Ge–OH species chemisorbed on the surface with very few unreacted sites. Compared to a H2O dose, H2O2 provides more than double the number of reactive Ge-OH sites thereby increasing the number of potential ALD nucleation sites. In contrast to the H2O passivated surface, annealing the H2O2/Ge surface to 100°C generates no additional dangling bond sites and even eliminates the dangling bonds present from the 25oC dose and forms a highly ordered surface of Ge-OH bonds. The improved coverage of Ge–OH sites allows for increased nucleation density of O-Al bonds and also minimizes the dangling bonds which are considered as the major source of interfacial trap states (Dit). The improved thermal stability allows for an increased thermal budget during ALD cycles. STS measurements show that TMA nucleation on the H2O2 functionalized Ge(100) surface unpins the Fermi level and has a wide bandgap with no band edge states demonstrating very good interface quality.

3:00pm **EM+TF+OX+GR-MoA4 Electrical and Physical Characteristics of High-k/Metal Gate MOS Devices on MBE-Grown Germanium on Silicon Using Aspect Ratio Trapping**, ***S.R.M. Anwar***, *C. Buie, N. Lu, M.J. Kim, C.L. Hinkle*, University of Texas at Dallas

Due to its high hole mobility and relative compatibility with Si CMOS processing, Ge has long been considered as a replacement channel material for PMOS devices. Selective area growth of Ge channels on bulk Si substrates would be ideal for minimizing fabrication costs and allowing the co-implementation of other materials (III-Vs for NMOS). However, due to the 4.2% lattice mismatch between Ge and Si, unacceptably high dislocation densities ($\sim10^9$ cm^{-2}) are created during this heteroepitaxy.

In this work, we investigate the fabrication of MOS gate stacks on MBE-grown Ge on Si using Aspect Ratio Trapping (ART)[1,2] to reduce Ge defect density. ART is a growth technique that allows for the reduction of defects for lattice mismatched materials by trapping the threading dislocations into the sidewalls of patterned nanoscale trenches in which the epitaxial growth takes place. This technique has the added benefit of producing the necessary geometric structure required for highly scaled tri-gate devices while reducing defect density simultaneously. Surface roughness and defect density dependence on growth temperature and growth rate will be discussed as will be the effect of varying the trench geometry. RHEED, XRD, XPS, TEM, EPD, AFM, SEM, and IPE data are correlated with growth conditions to produce high quality heteroepitaxial growth. Data will be presented demonstrating the use of low-temperature buffer layers in conjunction with low-growth rate bulk Ge results in a reduction in threading dislocations of 2-3 orders of magnitude.

MOS devices were fabricated on the MBE-grown Ge on Si samples. A high-quality interface was obtained using a DI-H_2O surface functionalization by pre-pulsing the H_2O 50 times in the atomic layer deposition (ALD) chamber at 250 °C.[3] A thin interfacial Al_2O_3 film was deposited by ALD at 250 °C followed by forming gas anneal (FGA) performed for 30 minutes at 350 °C. This FGA step converts the surface functionalized oxide to a thin layer of GeO_2 resulting in improved electrical performance. 2.5 nm of HfO_2 was then deposited by ALD. 10 nm of RF sputtered TiN was deposited as the gate metal followed by low-temperature anneals in various ambients to tune the effective work function of the HfO_2/TiN gate stack.[4] A final FGA for 30 minutes at 350 °C completed device processing. These devices show excellent PMOS characteristics and will be discussed.

This work is supported by the SRC Global Research Corporation.

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3:40pm **EM+TF+OX+GR-MoA6 *In Situ* Infrared Spectroscopy Study on the Temperature Dependence on the Growth Mechanism of Atomic Layer Deposition of Al_2O_3 on InP(100)**, ***W. Cabrera***, The University of Texas at Dallas, *I.M. Povey*, Tyndall National Institute, *Y.J. Chabal*, The University of Texas at Dallas

One of the current challenges in fabricating III-V-based electronics is the growth of an interfacial layer during the atomic layer deposition (ALD) of high-k dielectrics on III-V substrates, which has led to poor quality electrical properties. A process that can mitigate this problem is the “clean-up” effect that occurs when trimethylaluminum (TMA) is deposited by atomic layer deposition during the formation of Al2O3. A recent theoretical study suggests that the principal pathway in the “clean-up” effect of TMA on the native oxides of GaAs and InGaAs involves oxygen gettering1. In this work, *in-situ* infrared absorption spectroscopy has been used to investigate the temperature dependence of the native oxide and the interface formation during Al2O3 deposition using TMA and deuterium oxide (D2O) on chemically-treated InP(100) surfaces. Upon annealing a degreased sample to 300°C, compositional changes are observed, as evidenced by new absorption features in the region of 900-1250 cm-1 of the infrared spectrum

prior to TMA exposure. The initial native oxide, comprised in part of In(PO3)3 is transformed into an InPO4-rich surface. Upon TMA exposure at 300°C, there is a clear loss of In(PO3)3 and gain of InPO4 (at 1007 and 1145 cm-1, respectively) along with the formation of Al-O bonds (absorption band at 800 cm-1)2. These observations are consistent with the "clean up" effect observed on GaAs3 and InGaAs4, and on InP(100)5 where TMA preferentially withdraws oxygen from the native oxide forming Al-O bonds. However, the TMA reduces In(PO3)3 and forsters the formation of InPO4. Furthermore, TMA exposure of the native oxide at lower deposition temperatures (150°C) gives rise to methoxy (CH3) formation as evidenced by the appearance of a band centered at 1475 cm-1. This indicates that TMA not only withdraws oxygen from the native oxide but also transfers a methyl group to the surface oxygen, which may lead to carbon contamination at the interface. Al2O3 oxide films are formed after 10 TMA and D2O cycles on both degreased native oxide and chemically treated (HF and (NH4)2S) InP(100) substrates, although the quality is higher on the (HF and (NH4)2S)-treated surface. A more clearly defined LO phonon mode is detected for that surface, suggesting that a denser oxide is formed.

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4:00pm **EM+TF+OX+GR-MoA7 Ultimate Scaling of High-k Gate Dielectrics: Current Status and Challenges**,
T. Ando, *M.M. Frank, E.A. Cartier, B.P. Linder, J. Rozen,* IBM T.J. Watson Research Center, *K. Choi,* GLOBALFOUNDRIES, *V. Narayanan*, IBM T.J. Watson Research Center
INVITED

Current status and challenges of aggressive equivalent-oxide-thickness (EOT) scaling of high-k gate dielectrics via higher-k (>20) materials and interfacial layer (IL) scavenging techniques are reviewed [1]. La-based higher-k materials [2, 3] and La-silicate IL with HfO_2 [4] showed aggressive EOT values (0.5–0.8 nm), but with large effective workfunction (EWF) shifts toward the Si conduction band edge, limiting their application to nFET. Further exploration for pFET-compatible higher-k materials is needed. Meanwhile, IL scavenging is a promising approach to extend Hf-based high-k dielectrics to future nodes [4, 5]. Remote-scavenging techniques enable EOT scaling below 0.5 nm. We will review IL scavenging techniques from the viewpoints of (1) IL growth condition; (2) Choice of scavenging element; (3) Location of scavenging element; (4) Choice of high-κ material and (5) Maximum process temperature. Careful choice of materials and processes based on these considerations is indispensable. Mobility-EOT trends in the literature suggest that short-channel performance improvement is attainable with aggressive EOT scaling via IL scavenging or La-silicate formation. However, extreme IL scaling is accompanied with loss of EWF control [6] and with severe penalty in reliability [7]. Therefore, highly precise IL thickness control in an ultra-thin IL regime (<0.5 nm) will be the key technology to satisfy both performance and reliability requirements for future CMOS devices.

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

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4:40pm **EM+TF+OX+GR-MoA9 AR-XPS Study of Al_2O_3/In-based III-V Interfaces after Annealing under Vacuum at Low Temperature**,
E. Martinez*, H. Grampeix, O. Desplats,* CEA, LETI, MINATEC Campus, France*, A. Herrera-Gomez, O. Ceballos-Sanchez,* CINVESTAV-Unidad Queretaro, Mexico*, J. Guerrero, K. Yckache, F. Martin*, CEA, LETI, MINATEC Campus, France

III-V semiconductor substrates are a potential solution for MOSTETs down scaling below the 16 nm technological node. Indium based semiconductors, such as InGaAs, InAs and InP are promising compounds to improve the speed of operation. The quality of the interface between these high mobility substrates and the gate oxide is of crucial importance to preserve the devices electrical properties. Aluminium oxide is used to remove the As oxide ("self-cleaning" effect). The gate-last scheme is preferred to control of the high-k/III-V since it involves low temperature post deposition annealing [1]. State-of-the-art control of this interface has been obtained with annealing at 400°C under vacuum [2].In this work we focus on the impact of low temperature annealing under vacuum on the quality of the Al_2O_3/In-based III-V interfaces. We have studied the interfacial oxides formed between alumina and III-V substrates such as InGaAs, InAs and InP. Annealing at 600°C under ultra high vacuum (UHV) is first performed and compared to thermal treatments at 600°C and 400°C at 3 10^{-4} mbar. Substrate passivation is done with NH_4OH (4 %). The 3-nm thick alumina is deposited by Atomic Layer Deposition (ALD) using TMA and H_2O as precursor and oxidant. Angle-resolved photoelectron spectroscopy (AR-XPS) has been carried out to investigate the interfacial chemical bonding states. Consistent and robust analysis of the As 3*d*, P 2*p*, Ga3*d* and In 3*d* core levels was carried out through the simultaneous fitting method [3]. At 600°C, we show that, on InGaAs, no interfacial oxides are created after annealing under UHV, whereas a thin interfacial $InGaO_x$ is observed under secondary vacuum. A clear difference between the three substrates is observed after annealing at 400°C under 3 10^{-4} mbar. In particular, the indium oxidation and the relative stability of interfacial oxides are substrate dependant. On InAs, indium hydroxide is formed after annealing, by OH release from TMA/H_2O deposited alumina. This is not the case with additional elements such as Ga and P, which react with residual species to create their respective oxides. On InGaAs, a regrowth of $InGaO_x$ is observed after anneal, as a result of preferential oxidation of Ga. On InP, the $InPO_x$ interfacial oxide seems to decrease after anneal.**Acknowledgements**This work was performed with financial support from the MOS35 project funded by the French National Research Agency. Measurements were carried out at the NanoCharacterization Centre (NCC) of MINATEC. [1] H. Zhao et al., Appl. Phys. Let. 95, 253501 (2009)[2] Y. Urabe et al., Appl. Phys. Let. 97, 253502 (2010)[3] J. Muñoz-Flores et al., J. Electron. Spec. Rel. Phen. 182, 81 (2011)

5:00pm **EM+TF+OX+GR-MoA10 Effect of a H_2 Plasma Pre-treatment on the Reduction of Native Oxides at the PEALD Al_2O_3/InAs Interface**,
E. Cleveland*, L. Ruppalt, J.B. Boos, B. Bennett, J. Champlain, S.M. Prokes*, Naval Research Laboratory

The integration of high-*k* dielectrics with high mobility III-V semiconductor materials has attracted extensive interest recently as an alternative to Si-based complementary metal-oxide semiconductor (CMOS) applications at the 16 nm node and beyond. Among the III-V semiconductors, InAs is a promising material as the channel material in metal-oxide-semiconductor field-effect transistors (MOSFETs) due to its extremely high electron mobility and high saturation velocity. However, problems arise in the fabrication of high performance channel MOSFETS due to the poor quality of the gate oxide/InAs interface. InAs has a highly reactive surface and on exposure to air will form a native oxide layer composed of In₂O₃ and As₂O₃. The complexity of these native oxides leads to the formation of a relatively high density of interface states which in turn act as charge traps thus pinning the Fermi level and degrading device performance. Wet-chemical treatments based on HCl and (NH4)2S have been found to be an effective means of removing these oxides, however, due to the rapid re-oxidation and lack of reproducibility a better means of interface cleaning is needed. Recently, there has been much interest in the field of surface cleaning combined with atomic layer deposition (ALD) in order to deposit high quality dielectrics on III-V semiconductor materials, such as InAs and GaSb. Therefore, we examined the use of a H₂ plasma as a means to obtain an oxide-free InAs interface prior to the deposition of high-*k* Al₂O₃ via plasma enhanced atomic layer deposition (PEALD). Ex-situ XPS, AFM, and C-V measurments were performed to establish the effect of the plasma exposure time, temperature and rf power on the removal of the native oxide. It will be demonstrated that by removing or reducing the native oxides on the InAs surface that the density of interface defects at the Al₂O₃/InAs interface can be reduced and enhance the electrical performance. Similar work done on GaSb will be discussed, where XPS spectra revealed a significant reduction in Sb-O features for longer H₂ plasma exposures as the peaks associated with Ga-O increased. C-V measurements of fabricated MOSCAPS also found that samples treated with longer H₂ plasma exposures exhibited better C-V characteristics.

Oxide Heterostructures-Interface Form & Function Focus Topic

Room: 7 - Session OX+SS+TF+MI-MoA

Chemistry of Oxide Surfaces and Interfaces

Moderator: M. Engelhard, EMSL, Environmental Molecular Sciences Laboratory

2:00pm **OX+SS+TF+MI-MoA1 Investigation of Al_2O_3 Nanostructure Surfaces Using Charge Optimized Many Body Potentials**, ***D.E. Yilmaz***, *T. Liang, S.B. Sinnott, S.R. Phillpot*, University of Florida

Aluminum oxide nanostructures have drawn attention due to their Interesting physical and optical properties. In particular, photoluminescence peaks for these systems are attributed to oxygen vacancies and surface effects. Here, we apply third-generation Charge Optimized Many Body (COMB) potentials for the Al-$A_{l2}O_3$ system to investigate the properties of Al_2O_3 nanoparticle surfaces. In particular, the elastic properties and local atomistic strain distribution of nanoparticles with a range of sizes are determined, and the corresponding vibrational spectra are determined. The effect of oxygen vacancies and adsorbed surface atoms on the local strain and vibrational spectra are also determined. This work is supported by the National Science Foundation (DMR-1005779).

2:20pm **OX+SS+TF+MI-MoA2 Manipulating Ferroelectric Surfaces for Direct NO_x Decomposition**, *M.W. Herdiech, A. Kakekkhani, S. Ismail-Beigi,* ***E.I. Altman***, Yale University

Current technology for removing nitrogen oxides from engine exhausts relies on nearly stoichiometric air to fuel ratios. Under these conditions, the concentrations of CO and unburned hydrocarbons in the exhaust stream are high enough to efficiently remove adsorbed oxygen from the platinum based catalysts in catalytic converters, ensuring that the catalysts do not become saturated with adsorbed oxygen. Direct catalytic decomposition of NO_x to N_2 and O_2 in the presence of excess O_2 would eliminate the need for reducing species in automobile engine exhaust streams, allowing these engines to be run more efficiently. We have been investigating the potential of ferroelectric supports to modify the behavior of supported layers to enable direct NO_x decomposition. Our approach involves first principles density functional theory and surface science techniques. Using both approaches we have investigated the interactions of N, O, and NO with bare ferroelectric lead titanate surfaces and surfaces modified to expose catalytic layers, in particular Ru oxides. Theory indicates that the behavior of the $PbTiO_3$ surface towards these species is sensitive to the polarization direction and termination of the ferroelectric and that stable RuO_2-terminated surfaces can be created by manipulating the termination of the substrate. Experiments take advantage of plasma sources that allow the behavior of O and N atoms to be studied individually and expitaxial growth to manipulate the termination of the ferroelectric support. Favored reaction pathways are assessed using theory and temperature programmed desorption and related mass spectrometry methods.

2:40pm **OX+SS+TF+MI-MoA3 Catalyst Synthesis by Atomic Layer Deposition**, ***P.C. Stair***, Northwestern University & Argonne National Laboratory **INVITED**

Atomic Layer Deposition (ALD) has enormous potential for the synthesis of advanced heterogeneous catalysts with control of composition and structure at the atomic scale. The ability of ALD to produce conformal oxide coatings on porous, high-surface area materials can provide completely new types of catalyst supports. At the same time ALD can achieve highly uniform catalytically active metal and oxide phases with (sub-) nanometer dimensions.

Vanadium oxide species supported on high surface area oxides are among the most important catalytic materials for the selective, oxidative conversion of hydrocarbons to useful chemicals. In our laboratory ALD has been used to synthesize both the catalytic vanadium oxide and the supporting oxide on both high surface powders and anodic aluminum oxide (AAO) nanoliths. These materials have been characterized by SEM, XRF, ICP, UV-Vis absorption spectroscopy, Raman spectroscopy and evaluated for the oxidative dehydrogenation (ODH) of cyclohexane.

More recently we have studied the synthesis of supported metal particles and developed what we call "ABC-type" ALD in which metal nanoparticles and support materials are grown sequentially in each ALD cycle. This method makes possible the synthesis exceptionally small particles, ca. 0.5 nm. Using additional ALD support layers at the conclusion of the growth, the metal particles can be stabilized against sintering while still remaining active at high temperatures and reaction conditions. Moreover, the catalysts resist coke formation which is a leading cause of catalyst deactivation. These properties are imparted as a result of anchoring step and edge atom sites while leaving facet sites open for catalysis.

3:40pm **OX+SS+TF+MI-MoA6 Energy Alignment at Organic/Oxide Interfaces: The Influence of Adsorption Geometry and Chemical Bond on Interface Dipole**, ***S. Rangan***, *C. Ruggieri, S. Coh, R.A. Bartynski, K. Chitre, E. Galoppini*, Rutgers University

The lack of control of the energy alignment at the interface between an organic layer and an oxide substrate remains a limitation to the performance of promising technologies such as dye sensitized solar cells, organic light emitting diodes or organic thin film transistors. The energy alignment depends not only on the choice of the starting materials, but also on more subtle parameters such as oxide surface termination or defects, and molecular layer preparation mode.

In an effort to disentangle the different aspect of the interface of an organic/oxide system, we have studied simultaneously the adsorption geometry and the energy alignment of the Zn(II) tetraphenylporphyrin (ZnTPP) molecule on the TiO2(110) and ZnO(11-20) surfaces. Two approaches have been pursued: 1) in-situ evaporation of the ZnTPP on a clean oxide surface prepared in ultra-high vacuum resulting in weakly bound multilayers or monolayers 2) ex-situ sensitization in a solution of ZnTPP derivative, modified with COOH anchoring group for chemisorption at the oxide surface.

Scanning tunnel microscopy has been used to characterize the clean oxides and the ZnTPP adsorption modes. X-ray photoemission, ultra-violet photoemission and inverse photoemission spectroscopies have allowed the exploration of both occupied and unoccupied states of the electronic structure, resulting in the full characterization of the energy alignment at the surface as a function of the molecular overlayer thickness. The electronic transport gap, obtained from the latter experimental techniques has also been compared to the optical gap obtained from reflection electron energy loss spectroscopy, thus allowing the characterization of bound excitonic states.

The effect of the ZnTPP/oxide interface preparation, as well as the effect of the oxide substrate on the energy alignment will be presented. The discussion will be extended to metallic substrates such as Ag(100) and Au(111) surfaces

4:00pm **OX+SS+TF+MI-MoA7 Energy-Level Alignment at Organic/Oxide Interfaces**, *M.T. Greiner,* ***Z.-H. Lu***, University of Toronto, Canada **INVITED**

Oxide/organic interfaces play an important role in many organic electronic device designs. Oxides are frequently used as buffer layers to tune the energy-level alignment between electrodes and organic semiconducting layers, and thus allow for efficient hole/electron injection. As per the 'integer charge-transfer' (ICT) model, energy-level alignment at electrode/organic interfaces is governed by the electrode's Fermi level and the organic molecule's oxidation/reduction potential. While the ICT model was originally proposed for organic/organic interfaces, it also applies to a broad range of transition metal oxides. In this presentation we will discuss the energy-level alignment (ELA) of several organic semiconductors with transition-metal oxides. We will show that ELA is primarily governed by an oxide's work function, and that ELA is relatively insensitive to oxide electronic structure. As transition metal oxides can exhibit a wide range of work functions (~ 2 - 7 eV), and can possess a wide range of electronic properties (p-type to n-type) they are very versatile materials for use in organic electronics. We will their properties—such as work function and electronic structure—can best be utilized for use as buffer layers in organic light-emitting diodes and organic photovoltaics.

4:40pm **OX+SS+TF+MI-MoA9 Variable Kinetic Energy XPS of the Buried P3HT/ITO Interface**, ***M.T. Brumbach***, Sandia National Laboratories, *J.C. Woicik*, National Institute of Standards and Technology

The characterization of buried interfaces is difficult and often has to be performed by post-processing methods where the interface is revealed, disturbed, and possibly altered by environmental exposure. Variable kinetic energy X-ray photoelectron spectroscopy (VKE-XPS) offers the ability to tune the depth of analysis while the use of hard X-rays allows for a deeper analysis. The combination of variable energy hard X-rays for XPS (HAXPES) allows for systematic evaluation through a buried interfacial region. An important inorganic/organic interface for use in organic photovoltaic devices is the poly(3-hexylthiophene) (P3HT) interface with indium tin oxide (ITO). In this work P3HT/ITO buried interfaces were examined using X-ray energies from 2.2-3.9 keV. The ITO surface was additionally prepared using different pretreatment conditions. The P3HT film protected the ITO surface from adventitious adsorbents and allowed for sensitivity to the buried ITO surface. Robust peak fitting parameters were obtained to model the O 1s and In 3d lineshapes. The deconvolution of these lineshapes allowed for the clear identification of a surface layer on the

ITO which is oxidized to a greater extent than the underlying bulk ITO. The surface oxide layer, composed of indium oxide and indium hydroxide, is deficient of oxygen vacancies and would therefore be expected to act as an insulating barrier on the ITO surface. Peak fitting conditions allowed for an estimation of the thickness of this insulating layer. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

5:00pm **OX+SS+TF+MI-MoA10 Organic Molecules Adsorbed on the ZnO(10-10) Surface: An Infrared Reflection Absorption Spectroscopy Study**, ***M. Buchholz,*** Karlsruhe Institute of Technology, Germany, *H. Noei, Y. Wang,* Ruhr University Bochum, Germany, *A. Nefedov, Ch. Wöll*, Karlsruhe Institute of Technology, Germany

Except for gold, every metal forms an oxide on its surface when exposed to the ambient atmosphere. The understanding of chemical processes taking place on metal oxide surfaces are thus of crucial importance. One of the most important oxides is ZnO. As a result of its semiconducting and optical properties, this material is used in many applications such as gas sensors, thin film solar cells, as well as in photocatalysis and photooxidation[1]. The important surfaces of ZnO are the polar Zn- or O-terminated ZnO(0001) and ZnO(000-1) as well as the mixed-terminated ZnO(10-10) surface. The latter is the dominating surface for ZnO powder particles and energetically most favorable.

Here we report on the adsorption of formic acid and maleic anhydride (MA) molecules on the mixed-terminated ZnO(10-10) surface. Formic acid is a good model molecule for understanding the anchoring of carboxylic dye molecules in dye-sensitized solar cells. The choice of MA is motivated by the importance of the industrial process where MA is hydrogenated using Cu/ZnO catalysts. The identification of the reaction mechanism requires the identification of intermediates using IR-spectroscopy[2].

In last decades numerous IR investigations of oxide powders have been reported. An unambiguous assignment of the features present in the complex powder IR spectra, however, is only possible on the basis of reference data recorded for well-defined systems, e.g. surfaces of single crystals with defined orientation. Unfortunately, Infrared Reflection Absorption Spectroscopy(IRRAS) studies of molecular adsorbates on oxide single crystals, and, inparticular on ZnO, are extremely scarce due to the fact that the sensitivity of IRRAS to adsorbate vibrations is two orders of magnitude lower for oxides than for metals. Whereas in case of TiO2 recently with improved experimental setups adsorbate vibrations have been observed for a number of cases[3], to our knowledge molecular vibrations on clean ZnO single crystal surfaces have not yet been reported. With our novel UHV-IRRAS setup[4] high-quality IR spectra of different molecular adsorbates on ZnO(10-10) could be recorded in a routine fashion. In this presentation the obtained results will be presented and discussed.

M. Buchholz gratefully acknowledges the financial support from the Helmholtz Research School "Energy-Related Catalysis".

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5:20pm **OX+SS+TF+MI-MoA11** ***In Situ*** **Interface Analysis of Self-Assembled Monolayers on Metal Surfaces at High Water Activities by Means of a PM-IRRAS/QCM-Setup**, ***I. Giner***, *M. Maxisch, G. Grundmeier*, University of Paderborn, Germany

Aluminum and its alloys are widely used as engineering material and in a wide range of applications ranging from the aviation industry to the automotive and construction industries. As almost all engineering metals, aluminum under ambient conditions is covered by a native oxide film which alters significantly its surface physical and chemical properties. For corrosion protection and adhesion promotion, oxide covered aluminum surfaces are coated with organic films. Ultra-thin films or even monomolecular layers of organic acids like self-assembled monolayers (SAMs) of organophosphonic and organocarboxylic acids have been investigated as new advanced interfacial layers for aluminum alloys.1 However, the stability of the self-assembled monolayers under environmental conditions is an aspect for technical applications. Different studies concerning to the stability and structure of the self-assembly monolayers under high humidity's conditions have been performed.2 These studies revealed that the organic film decreased the amount of interfacial water layer but cannot prevent the water diffusion through the monolayer.3 The aim of the present work is to establish an in-situ setup combining quartz crystal microbalance (QCM) and PM-IRRAS to study the chemistry of passive films and adsorbed organic monolayers at high humidity. The metal coated quartz was used as the reflecting substrate for the PM-IRRAS measurement. Thereby, the structure of the monolayer, the amount of adsorbed water and the chemical state of the surface layer in the presence of an adsorbed water layer could be analysed in-situ. The surface hydroxyl density prior to organic molecule adsorption was adjusted by means of low temperature Ar- and H_2O- plasma treatments. Adsorption studies of H_2O on nonadecanoic carboxylic acid (NDA) monolayer modified surfaces in comparison to bare oxide covered aluminum surfaces showed, that the NDA monolayer leads to a reduced amount of adsorbed water based on the inability of water to form hydrogen bonds to the low energy aliphatic surface chemistry. Moreover the kinetics of chemisorption of water indicated by the oxyhydroxide peak growth at SAM/metal interfaces could be significantly inhibited. Furthermore, it is noticeable that interfacial carboxylate group coordinatively bound the oxide as well as the orientation of the NDA monolayer is not affected by the adsorption of several monolayers water. *Bibliography* 1. Thissen, P et al. *Langmuir* **2010,** *26, (1), 156-164* 2. Thissen, P et al. *Surface & Coatings Technology* **2010,** *204* (21-22), 3578-3584. 3. Maxisch, M et al. *Langmuir* **2011,***27* (10), 6042-6048

Oxide Heterostructures-Interface Form & Function Focus Topic
Room: Central Hall - Session OX-TuP

Oxide Interfaces and Heterostructures Poster Session

OX-TuP1 A Kinetic Monte Carlo Study of Cu Cluster Formation on Cu and ZnO Surfaces using COMB Potentials, ***Y.-T. Cheng***, *T. Liang,* University of Florida, *X.W. Nie,* The Ohio State University, *S.R. Phillpot,* University of Florida, *A. Asthagiri,* The Ohio State University, *S.B. Sinnott*, University of Florida

Heterogeneous systems of Cu clusters on ZnO surfaces are used as catalysts and it is a challenge to maintain the stability and activity of the catalyst under reaction conditions. Processes such as sintering, alloying, and encapsulation may play an important role in the activity of the catalyst but are difficult to model directly with electronic structure calculations. In this work, we will report on the development and use of charge-optimized many-body (COMB) potentials to model the Cu/ZnO system. In particular, the diffusion of Cu atoms and the ripening of Cu clusters on Cu and ZnO surfaces are modeled using kinetic Monte Carlo simulations, which is used in conjugation with the dimer method to find possible transition paths for Cu migration. Simulations allow for a comparison of transport mechanisms on the two different surfaces (Cu and ZnO) and the predictions are compared to the results of density functional theory calculations and published experimental data. This work was supported as part of the Center for Atomic Level Catalyst Design, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under award number DE-SC0001058.

OX-TuP3 Molecular Dynamics Simulation Studies of The Toughening Mechanisms of Bio-inspired Hybrid Ceramic-based Materials, ***K. Yao***, *T. Liang, D.E. Yilmaz, S.R. Phillpot, S.B. Sinnott*, University of Florida

Bio-inspired hybrid ceramic-based materials have attracted attention due to their high yield strength and fracture toughness. In this work, the mechanisms associated with the mechanical responses of composites of poly(methyl methacrylate), or PMMA, and Al_2O_3 in two hierarchical configurations, lamellar and brick-and-mortar, are considered. In particular, classical molecular dynamics simulations using charge optimized many-body (COMB) potentials are carried out to identify these mechanisms. The influence of such factors as the arrangement of the phases in the two different configurations, interfacial composition, nanometer-scale structure, and polymer thickness are considered. The nanometer-scale responses of the composites nanoindentation, shearing, and bending are compared with experimental data. This work is supported by DARPA.

OX-TuP4 A Variable Charge Reactive Potential for Nitrogen based Hydride and Oxide Molecules to Simulate Oxide Growth on AlN and TiN, ***J. Martinez***, *S.R. Phillpot, S.B. Sinnott*, University of Florida

An empirical, variable charge potential for Nitrogen hydride and Nitrogen oxide molecular systems based on the charge optimized many body (COMB) potential framework is proposed. The potential is fitted to structure and energetic properties of certain key molecules such as NH_3 and NO_2. This potential is used in conjunction with TiN/TiO_2 and the AlN/Al_2O_3 variable charge potentials based in the same COMB framework to study the structure, energetics, and mechanics of oxide growth on TiN and AlN under varying conditions.

OX-TuP5 Effects of Nonstoichiometry on the Structure and Electronic Properties of $LaCrO_3$ Thin Films on $SrTiO_3(001)$, *K.H.L. Zhang,* ***Y.G. Du***, *L. Qiao, S.A. Chambers*, Pacific Northwest National Laboratory

The ability to precisely control the structure, stoichiometry and defect densities in epitaxial perovskite films is emerging as one of the major challenges for understanding the sometimes novel physical properties exhibited by interfaces and superlattices of these materials. Recently we have demonstrated that structurally excellent, stoichiometric $LaCrO_3$ thin films can be grown on $SrTiO_3(001)$ by molecular beam epitaxy. In this contribution, we further explore the effects of nonstoichiometry on the structure and electronic properties of $La_{1+x}Cr_{1-x}O_3$ thin films with $-0.13<x<0.05$. Interestingly, La-deficient films maintain high crystalline quality in spite of very large deviations from stoichiometry, while La -rich films exhibit significantly degraded crystalline quality. Ongoing studies of lattice parameters, film and interface microstructures, and electronic properties will be discussed in order to elucidate different mechanisms of accommodating A-site and B-site cation imbalances during the epitaxial growth of perovskites.

OX-TuP6 The Influence of Nano-Scale Interfaces and Co-Doping on the Oxygen Ionic Conductivity of Ceria and Zirconia Based Thin Film Electrolytes, ***M.I. Nandasiri***, *Q. Langfitt, M. Quintero, T. Varga, A. Devaraj, S. Manandhar, P. Nachimuthu, V. Shutthanandan, S. Thevuthasan,* EMSL, Pacific Northwest National Laboratory, *A. Kayani*, Western Michigan University

The high temperature operation of solid oxide fuel cells (SOFC) is one of the main challenges we have to overcome, especially for commercializing SOFC for portable power generating applications. Solid state electrolytes with enhanced oxygen ionic conductivity at low and intermediate temperatures are needed to lower the operating temperature of SOFC. Thus, there is an ongoing need to develop new electrolytes or modify existing electrolytes to enhance the ionic conductivity. Co-doping can be used to modify existing ceria and zirconia based electrolytes. On the other hand, new electrolytes can be developed by utilizing the engineered interfaces in multi-layer thin films. Here, we investigate the influence of nano-scale interfaces and co-doping on the ionic conductivity of ceria and zirconia based electrolytes.

In this study, we have grown (i) multilayers of high quality samaria doped ceria (SDC) and scandia stabilized zirconia (ScSZ) epitaxial thin films, and (ii) samaria and gadolinia co-doped high quality ceria thin films using oxygen plasma-assisted molecular beam epitaxy and characterized using various capabilities. The number of layers in the SDC/ScSZ multi-layer thin films was varied from 2 to 20 by keeping the total film thickness constant at 140 nm to understand the effect of nano-scale interfaces on the ionic conductivity. To understand the effect of co-doping on the ionic conductivity of optimized SDC thin films, $Ce_{0.85}Sm_{0.15-x}Gd_xO_{2-\delta}$ (SGDC) thin films were deposited by varying the Gd concentration. The film growth was monitored using in-situ reflection high energy electron diffraction (RHEED). Structural properties of these films were studied using x-ray diffraction (XRD) and the XRD patterns confirmed the growth of epitaxial thin films. The film and layer thicknesses were determined by x-ray reflectivity. X-ray photoelectron spectroscopy was used to find the composition, depth profile and chemical state of elements of the films. The SDC/ScSZ multi-layer and SGDC thin films were carefully characterized using Rutherford backscattering spectrometry, coupled scanning transmission electron microscopy and atom probe tomography to study the oxygen vacancy and dopant distributions along with the inter-diffusion and dopant segregation at the interfaces. Oxygen ionic conductivity measurements were carried out as a function of temperature on well characterized samples using four probe surface impedance spectroscopy. Detailed analysis of oxygen ionic conductivity as a function of individual layer thickness, dopant concentration, and crystalline quality of the films will be discussed.

In Situ Microscopy and Spectroscopy Focus Topic
Room: 7 - Session IS+AS+OX+ET-WeM

In Situ Characterization of Solids: Film Growth, Defects, and Interfaces
Moderator: P.W. Sutter, Brookhaven National Laboratory

8:00am **IS+AS+OX+ET-WeM1 Revealing Gas-Surface Radical Reaction Mechanisms of Self-Assembled Monolayers by Scanning Tunneling Microscopy**, ***D.Y. Lee***, *M.M. Jobbins, S.A. Kandel*, University of Notre Dame

Scanning Tunneling Microscopy (STM) in ultra-high-vacuum is used *in situ* to investigate the surface changes of the octanethiolate self-assembled monolayer (SAM) on Au(111) upon reaction with atomic hydrogen and with atomic chlorine. For both reactions, the surface structure heavily influences the rate of monolayer degradation, but the effect of surface defects on reactivity is completely opposite when comparing the two systems. Monolayer reactivity increases with increasing hydrogen-atom exposure while decreases with further reaction with atomic chlorine. The monolayer-versus-exposure data are examined by kinetic Monte Carlo simulations and reveal that, for H-atom exposure, molecules located near surface defect sites are potentially over 500 times more reactive than close-packed areas. For Cl-atom interactions, however, the opposite occurs: close-packed regions are at least 100 times more reactive than defect sites. These observations result directly from the alkyl hydrogen abstraction and sulfur-gold bond cleavage mechanisms of SAM upon gas-phase radical bombardment.

8:20am **IS+AS+OX+ET-WeM2 *In Situ* Imaging of the Nucleation and Growth of Epitaxial Anatase TiO_2(001) Films on $SrTiO_3$(001)**, ***Y.G. Du***, *D.J. Kim, T.C. Kaspar,* Pacific Northwest National Laboratory*, S.E. Chamberlin,* University of Wisconsin Milwaukee*, I. Lyubinetsky, S.A. Chambers*, Pacific Northwest National Laboratory

TiO_2 has attracted much attention because of its potential utility in hydrogen production via water splitting, environmental remediation, and dye-sensitized solar cell fabrication. Heteroepitaxial growth of anatase is a powerful and unique way to fabricate model surfaces of the less stable anatase polymorph for fundamental surface science studies. In this work, the growth of TiO_2 anatase films on Nb doped $SrTiO_3$(001) by molecular beam epitaxy has been studied *in-situ* by scanning tunneling microscopy. We show that the initial growth follows the Stranski-Krastanov mode, where islands form on top of a wetting layer consisting of two monolayers (ML) of TiO_2. Well-defined (4x1) and (1x4) terraces are observed for film thicknesses in excess of 3 nm. At larger film thicknesses, large oriented crystallites form as a result of the coalescence of smaller islands. Within a given crystallite, either (4x1) or (1x4) reconstructed terraces account for majority of the surface. The anatase grows in units of bilayers, resulting in a step height of 2 ML. This result explains the fact that the measured period of the RHEED specular-beam intensity oscillations corresponds to the time required for deposition of 2 ML. Ar ion sputtering and UHV annealing results in a transformation to coexisting (4x1) and (1x4) reconstructed terraces on individual crystallites, as commonly observed by *ex-situ* STM studies. In addition, we show that the nucleation and growth of anatase films are influenced by Nb doping in the $SrTiO_3$ substrates by comparing with similar growth occurring on pure $SrTiO_3$ substrates.

8:40am **IS+AS+OX+ET-WeM3 *In Situ* Synchrotron X-Ray Studies of Epitaxial Oxide Thin Film Synthesis Behavior**, ***J.A. Eastman***, *M.J. Highland, P.H. Fuoss,* Argonne National Laboratory*, T.M. McCleskey,* Los Alamos National Laboratory*, D.D. Fong, C.M. Folkman, S.K. Keun, E. Perret, P.M. Baldo,* Argonne National Laboratory*, E. Bauer, Q. Jia*, Los Alamos National Laboratory **INVITED**

Intense interest is focused on the growth science of epitaxial oxide thin films because of continuing discoveries of new interesting and important properties. The key to achieving desired maximum functionality of oxide heterostructures is the ability to synthesize high-quality films with full control of factors such as composition, crystallographic orientation, surface termination, and strain state. Many of the most promising thin film synthesis techniques involve non-vacuum, high-temperature environmental conditions that are difficult or impossible to probe using standard spectroscopic or structural probes. However, the use of high-energy x-rays available at synchrotron sources such as the Advanced Photon Source (APS) provides an opportunity to obtain real-time atomic-level structural and chemical information during synthesis. This talk will describe results from recent studies at APS Sector 12ID-D using an in-situ x-ray approach to understand and control the synthesis behavior of complex oxide epitaxial thin films prepared by two very different techniques: sputter deposition or polymer assisted deposition (PAD).

We recently built a new RF magnetron sputter deposition system at the APS, which brings to bear state-of-the-art real-time in-situ x-ray scattering and spectroscopy techniques to provide insight into the growth behavior of epitaxial oxide thin film heterostructures. Initial studies of the growth behavior of epitaxial films such as (001) LaGaO3, SrZrO4, and LaGaO3/SrZrO3 multilayer heterostructures during off-axis sputtering will be described, focusing on the effects of epitaxial strain and electrical compensation (e.g., surface polarity) on growth behavior.

PAD is a solution technique capable of synthesizing dense epitaxial thin films. Past work at Los Alamos has demonstrated that PAD can be used to prepare aligned epitaxial films of many different materials. We recently performed initial in-situ synchrotron x-ray experiments aimed at obtaining a fundamental understanding of the nucleation and growth processes associated with epitaxial film formation. Studies of the synthesis behavior of (001) BaTiO3 epitaxial films will be described in this talk, focusing on the effects of thermal history and choice of substrate material on crystallization behavior and the development of epitaxy.

Argonne researchers were supported by the U. S. Department of Energy (DOE), Basic Energy Sciences (BES), Materials Sciences and Engineering Division. Los Alamos researchers were supported by the DOE through the LANL/LDRD Program. Use of the APS was supported by BES, under Contract DE-AC02-06CH11357 between UChicago Argonne LLC and the Department of Energy.

9:40am **IS+AS+OX+ET-WeM6 Understanding the Dynamic Electronic Properties of Electrode Materials by *In Situ* X-ray Absorption Spectroscopy**, ***M. Bagge-Hansen***, *J.R.I. Lee, A. Wittstock, M.D. Merrill, M.A. Worsley, T. Ogitsu, B.C. Wood, T. Baumann, M. Stadermann, M. Biener, J. Biener, T. van Buuren*, Lawrence Livermore National Laboratory

In situ characterization of the evolution in electronic structure of electrode materials during repeated charge-discharge cycling is fundamentally important for more fully understanding the processes of charge storage and degradation, which, in turn, is essential for the development of new electrical energy storage (EES) materials with tailored properties and improved performance. X-ray spectroscopies provide ideal tools with which to obtain enhanced insight into the origins of electrode behavior in EES systems due to their capabilities for direct, element specific, characterization of the electronic densities of states. To date, in situ studies of EES materials have primarily focused on hard x-ray experiments due to the challenges associated with UHV compatibility and high photon attenuation of cells for soft x-ray measurements. Nonetheless, the use of soft x-ray spectroscopies to EES systems is vital since they provide complementary information that cannot be obtained via hard x-ray studies. We report the development of a cell for in situ soft x-ray emission spectroscopy and x-ray absorption spectroscopy studies of EES materials and will discuss experiments focused upon the x-ray spectroscopy characterization of a series of novel electrode materials. Prepared by LLNL under Contract DE-AC52-07NA27344.

10:40am **IS+AS+OX+ET-WeM9 *In Situ* Studies of Al_2O_3 ALD Growth and Self-cleaning on III-V Surfaces by STM and XPS**, ***L.N.J. Rodriguez***, *A. De Clercq,* IMEC, Belgium*, M. Tallarida,* BTU Cottbus, Germany*, D. Cuypers,* IMEC, Belgium*, J.P. Locquet,* KU Leuven, Belgium*, S. Van Elshocht, C. Adelmann, M. Caymax*, IMEC, Belgium

A custom built ALD UHV-compatible reactor has been used to study the growth of TMA on InP and InAlAs by STM in conjunction with additional studies performed in a reactor attached to a synchrotron XPS. The effects of selected ex-situ cleans has been measured along with the subsequent cycles of ALD growth from TMA and water. The STM data shows morphological differences between the ex-situ cleans on InP, with sulphuric acid cleans yielding plateaus but ammonium sulphide cleans yielding rough surfaces. In-situ measurements of these surfaces after TMA dosing shows the growth of islands which converge to film closure after ten cycles of ALD growth. In-situ measurements of the I-V curves by STS allowed the creation of bandgap maps of the III-V interfaces after TMA dosing. These bandgap maps showed a non-uniform distribution with regions of either higher or lower bandgap. The mean bandgap was seen to decrease with increasing numbers of ALD cycles. In-situ XPS data on similar systems showed a reduction in surface oxides for InAlAs but not for InP. The reduction of arsenic oxides with a creation of metallic arsenic, along partial reduction of indium oxides and a conversion of aluminium sub-oxides to aluminium oxide was seen in the former case. In the latter case, a formal oxidation of

the phosphorus was seen with increased TMA dosing instead of a self-cleaning effect.

11:00am **IS+AS+OX+ET-WeM10** ***In Situ*** **Transport Measurement of Kinetically Controlled Bi Atomic Layers**, ***Y. Fujikawa***, *E. Saitoh*, Tohoku University, Japan

Thin film growth of Bi and related compounds has been attracted much attention because of their exotic properties originating in the large spin-orbit interaction of Bi. Growth of its simple substance is known to result in the formation of a thin-film phase in the initial stage, which is taken over by the bulk growth when the coverage exceeds several monolayers (ML). [1] With typical growth conditions, this transition takes place before the completion of the thin-film layer, which tends to agglomerate to form 4-ML thick islands, making it difficult to measure the intrinsic property of the thin-film phase. In this work, Bi growth on Si(111)-7x7 has been performed in a multi-probe VT-STM system, which provides wide-ranging opportunity of kinetic control and *in-situ* transport measurement during the thin film growth. By tuning the kinetic condition of the growth, it becomes possible to grow the thin-film phase uniformly covering the substrate. Its conductivity, monotonically increasing with the increase of the temperature, would suggest the variable-range hopping conduction rather than the carrier excitation of semiconductors. *In-situ* transport measurement has been performed during the layer-by-layer growth of the Bi thin-film phase, distinguishing the conductivity of each growth unit. It fluctuates with periods of 2 and 4 ML, which may reflect the atomic structure of the thin-film phase.

[1] Nagao *et al*., Phys. Rev. Lett. **93**, 105501 (2004).

11:20am **IS+AS+OX+ET-WeM11 CAMECA IMS Series Advanced Ion Microscopy: High Throughput, Repeatability & Automation**, *P. Peres, F. Desse, F. HIllion, M. Schuhmacher,* Cameca, S.a., France, ***A.N. Davis***, CAMECA Instruments, Inc.

The advantage of CAMECA IMS Series high performance secondary ion mass spectrometers are well established: extreme sensitivity, high mass resolution, and high dynamic range, providing low detection limits while keeping high analysis throughput. This instrument delivers high analytical performance for a wide range of applications: Si based devices, III-V and II-VI devices, both bulk materials and thin-film technology, as well as for different material science applications.

In order to meet the growing demand in terms of reproducibility and throughput performance as well as ease of use, CAMECA has developed a new IMS series, 7f-Auto.

The primary column has been redesigned in order to provide an easier and faster primary beam tuning. For high efficiency operation, automated routines for tuning the instrument are added for both primary and secondary columns, nominally: aperture adjustment, secondary ion beam centering, detector adjustement, among others. These routines not only increase the ease of use, but also enhance the reproducibility of the instruments by minimizing operator-related biases.

A motorized storage chamber has also been developed allowing to keep, under UHV environment, up to six sample holders. The holder exchange between the storage chamber and analysis chamber is fully motorized and computer controlled, allowing a set of analyses to be performed in automated, unattended mode on multiple sample holders. This significantly improves the throughput of the tool, since up to 24 samples (assuming 4 samples per holder) can be analysed in chained mode, possibly overnight. These developments will be presented and discussed in detail.

Surface Science
Room: 22 - Session SS+OX-WeM

Synthesis and Characterization of Oxides
Moderator: J.M. Millunchick, University of Michigan

8:00am **SS+OX-WeM1 Structure and Dynamics of Oxide Surfaces and Interfaces**, ***X. Pan***, University of Michigan **INVITED**

Ferroelectric materials are characterized by a spontaneous electric polarization that can be reoriented between different orientations by an applied electric field. The ability to form and manipulate domains with different polarization orientations at the nanometer scale is key to the utility of ferroelectric materials for devices such as nonvolatile memories. The ferroelectric switching occurs through the nucleation and growth of favorably oriented domains and is strongly mediated by defects and interfaces. Thus, it is critical to understand how the ferroelectric domain forms, grows, and interacts with defects. In this talk I will present the nanoscale ferroelectric switching of $BiFeO_3$ and $PbZr_{0.2}Ti_{0.8}O_3$ thin films under an applied electric field using *in situ* transmission electron microscopy with atomic resolution. We follow the kinetics and dynamics of ferroelectric switching at millisecond temporal and subangstrom spatial resolution. We observed localized nucleation events at the electrode interface, domain wall pinning on point defects, the formation of ferroelectric domains localized to the ferroelectric/electrode interface, and domain wall pinning by dislocations. We also find that in writing nanosized domains the domain wall itself can drive backswitching. It was observed that the localized 180° polarization switching in $PbZr_{0.2}Ti_{0.8}O_3$ thin films initially forms domain walls along unstable planes. After removal of the external field, they tend to relax to low energy orientations. In sufficiently small domains this process results in complete backswitching. Our results suggest that even thermodynamically favored domain orientations are still subject to retention loss, which must be mitigated by overcoming a critical domain size.

8:40am **SS+OX-WeM3 Capturing Ion-Solid Interactions with MOS Structures**, ***R. Shyam***, *E.S. Srinadhu, S. Chambers, J.E. Harriss, W.R. Harrell, C.E. Sosolik*, Clemson University

We have fabricated metal-oxide-semiconductor (MOS) devices for a study of implantation rates and damage resulting from low energy ion-solid impacts. Specifically, we seek to capture ion irradiation effects on oxides by exposing as-grown SiO_2 layers (50 nm to 200 nm) to incident beams of singly-charged alkali ions with energies in the range of 100 eV to 5 keV. The oxide is analyzed post exposure by encapsulating the irradiated region under a top metallic contact or within a finished MOS device. Characterization of the resulting ion-modified MOS device involves the standard techniques of room temperature and bias-temperature stress capacitance-voltage (C-V) measurements. The C-V results reveal alkali ion-induced changes in the flatband voltage and slope of C-V of irradiated devices which can be used to extract and delineate between implantation probabilities and irradiation effects of the ions. Biased C-V measurements are utilized to confirm the concentration or dosage of ions in the oxide. A triangular voltage sweep (TVS) measurement at elevated temperatures also reveals the total ionic space charge in the oxide and is used to extract mobility for the ions as they pass through the damaged oxide. Our C-V data show changes in flatband voltage which are greater than those expected for mobile charges present at the range calculated by SRIM which implies that stoichiometry, morphological and chemical changes in the SiO_2 layer are introduced by the ion impacts.

9:00am **SS+OX-WeM4 Synthesis and Characterization of Yttrium Aluminum Garnet and Lanthanum Zirconate Particles**, ***R.R. Harl********, *S.L. Gollub, G. Walker, B.R. Rogers*, Vanderbilt University

Rare-earth doped yttrium aluminum garnet (YAG) and lanthanum zirconate (LZO) are luminescent ceramics that have been used in TV's, LED's, metal oxide transistors, and as laser sources. These materials are thermally and chemically stable. Recent work at Vanderbilt by the Walker and Rogers research groups has shown that the emitted spectrum of proton irradiated LZO particles differs from that of non-irradiated particles, suggesting these materials may be used as passive radiation exposure indicators.

We will discuss the combustion synthesis and characterization of YAG and LZO particles. Combustion synthesis involves heating a mixture of metal nitrates and a fuel until the mixture ignites. If the proper conditions are used, the energy released by the combustion is sufficient to form polycrystalline material. The type and amount of fuel used in the synthesis affect the amount of gaseous by-products produced and flame temperature achieved during a reaction, both of affect the crystallite size formed. The organic fuels included in this study are urea and glycine with adiabatic flame temperatures 1780ºC and 1210ºC, respectively. Urea's higher flame temperature makes this fuel attractive for combustion syntheses. However, urea shows signs of degradation beginning around 120 °C, well below its ignition temperature. Glycine does not appear to degrade until approximately 230ºC much closer to its ignition temperature. The trade-off between degradation and adiabatic flame temperature suggests the temperature ramp rate used will significantly affect the performance of combustion syntheses carried out with these fuels.

We will present results of detailed thermogravimetric analysis and differential scanning calorimetry (TGA/DSC) experiments used to study the affects of heating rate on the combustion process and on the characteristics of the material formed. TGA/DSC-determined heats of combustion and heat capacities of the reactants and products will also be presented.

Characterization results of powders made using conditions determined by the TGA/DSC experiments will also be presented. X-ray photoelectron spectroscopy (XPS) was used to determine chemical bonding information. Rutherford backscattering spectroscopy (RBS) was used to provide

* Morton S. Traum Award Finalist

quantitative elemental composition of the material. X-ray diffraction (XRD) was used to determine the crystallinity of the material and to estimate crystallite sizes. Photoluminescence spectroscopy (PL) was used to characterize the materials' emission spectra.

9:20am **SS+OX-WeM5 X-ray Linear Dichroism of Epitaxial (Fe,N) Co-Doped Rutile TiO_2 Thin Films**, ***T.C. Kaspar***, Pacific Northwest National Lab, *A. Ney,* Univ. of Duisburg-Essen, Germany, *A.N. Mangham,* Pacific Northwest National Lab, *S.M. Heald,* Advanced Photon Source, Argonne National Lab, *Y. Joly,* Institut Néel, CNRS et Univ. Joseph Fourier, France, *V. Ney,* Univ. of Duisburg-Essen, Germany, *F. Wilhelm, A. Rogalev, F. Yakou,* European Synchrotron Radiation Facility, *S.A. Chambers*, Pacific Northwest National Lab

Efficient visible light photocatalysis could revolutionize hydrogen production, chemical synthesis, and pollution mitigation. Binary oxides such as TiO_2 have received much attention for these applications since they are stable under aqueous and oxidizing conditions, and show promise as ultraviolet-light photocatalysts. However, to operate in the visible portion of the solar spectrum, the wide bandgap of these oxides (~3 eV for rutile TiO_2) must be reduced. Anion doping of anatase TiO_2 has been widely explored, and shows some promise. However, in nanoparticles and fine powders, it can be difficult to determine the structural and electronic behavior of N dopants. Homoepitaxial Fe:TiO_2 and (Fe,N):TiO_2 thin films deposited on rutile TiO_2(110) were investigated by x-ray absorption spectroscopy (XAS) and associated theoretical simulations to elucidate the detailed structure of the doped materials. Co-doping with N was found to increase the extent of Fe incorporation into the rutile lattice. X-ray absorption near edge spectroscopy (XANES) spectra were collected at the Ti L-edge, Fe L-edge, O K-edge, N K-edge, and Ti K-edge. No evidence of structural disorder associated with a high concentration of oxygen vacancies was observed. Substitution of Fe for Ti could not be confirmed, although secondary phases such as Fe_2O_3 and metallic Fe could be ruled out. The similarity of the N K-edge spectra to O, and the presence of a strong x-ray linear dichroism (XLD) signal for the N K-edge, indicates that N is substitutional for O in the rutile lattice, and is not present as a secondary phase such as TiN. Simulations of the XANES spectra qualitatively confirm substitution, although N appears to be present in more than one local environment. Although optical absorption spectra confirm that substitutional N redshifts optical bandgap of Fe-doped rutile into the visible region, the film surfaces are photochemically inert with respect to hole-mediated decomposition of adsorbed trimethyl acetate.

9:40am **SS+OX-WeM6 Unified Picture of the Excess Electron Distribution at the TiO_2(110) Surface**, *P. Krueger,* Institut Carnot de Bourgogne, France, ***J. Jupille***, Institut des Nanosciences de Paris, France, *S. Bourgeois, B. Domenichini,* Institut Carnot de Bourgogne, France, *A. Verdini, L. Floreano, A. Morgante*, Laboratorio TASC, Italy

Titanium dioxide, an inert insulator in stoichiometric form, can be easily reduced into an n-type semiconductor TiO_{2-x} with the many electronic, photocatalytic and chemical properties that make the material of huge technological relevance. Formally associated with $Ti^{4+} + e^- \rightarrow Ti^{3+}$, the reduction of titania results in excess electrons (EE) that populate localized Ti 3d band gap states. Puzzling issues are the surface or subsurface distribution of EE and the lattice or interstitial nature (Ti_{int}) of the Ti^{3+} ions. Despite a number of experimental and theoretical studies, the reduced archetypal TiO_2(110) has not been unambiguously pictured yet. Regarding the location of Ti^{3+} ions, density functional theory (DFT), DFT + U scheme and DFT-Hartree-Fock hybrid functionals (the two latter including a better account of self interaction corrections) are far from consensus. EE that are suggested to be trapped either on sixfold (Ti1) and fivefold (Ti2) coordinated surface Ti, or on subsurface beneath Ti1 or beneath Ti2. In such context, the unique capability of resonant photoelectron diffraction (RPED) to map out the spatial distribution of Ti 3d gap states was previously demonstrated in the study of a TiO_2(110) surface involving vacancies in bridging oxygen rows (O_b-vac) [1]. However, our conclusion that EE mostly occupy subsurface Ti sites was later challenged by the suggestion that Ti_{int} atoms play a key role in the formation of EE [2,3]. This has prompted us to analyse the Na-covered TiO_2(110) surface on which Na adatoms are predicted to produce similar EE as by direct injection of electrons [4], while the formation of Ti_{int} is not expected.

The pivotal observation was that the Na/TiO_2 RPED pattern [4] was almost perfectly similar to the O_b-vac RPED pattern [1]. Data were fitted on the basis of the location of the Ti^{3+} ions on the Ti lattice sites. Indeed, attempts to model EE on Ti_{int} failed. A unified model of the reduced TiO_2(110) surface emerges, with EE located on subsurface beneath Ti2 > second subsurface beneath Ti1 > Ti1 [4] (See supplemental document). As shown by the qualitative agreement of the present findings with DFT approaches [5,6], the charge distribution of the Ti 3d states is dictated by electrostatics. It is essentially an intrinsic property of the titania surface that is independent on the way EE are created.

[1] Krueger et al. Phys. Rev. Lett. 100 (2008) 055501.

[2] Wendt et al., Science 320 (2008) 1755.

[3] Papageorgiou et al., Proc. Natl. Acad. Sci. U.S.A. 107 (2010) 2391.

[4] Krueger et al. Phys. Rev. Lett. 108 (2012) 126803.

[5] Albaret et al., Phys. Rev. B 65 (2001) 035402.

[6] Deskins et al., J. Phys. Chem. C 113 (2009) 14583.

10:40am **SS+OX-WeM9 XPS Satellite Structure and Covalent Bonding**, ***P.S. Bagus***, University of North Texas, *E.S. Ilton,* Pacific Northwest National Laboratory, *C.J. Nelin*, Consultant

The satellites in X-Ray photoemission spectroscopy, XPS, especially for ionic compounds, are an important part of the spectra [1, 2] and may provide information about the electronic structure. For uranium oxides, they allow the oxidation state of the U cations to be determined. [2] It would be useful to establish and to understand how the satellite intensity may be related to the extent of covalent bonding in an oxide or other ionic material. It is often believed that the intensity lost from the main XPS peaks to satellites is directly related to the covalent bonding, with greater covalent bonding leading to greater losses to satellites. We show that this relationship is not rigorously correct. A more correct relationship is between satellite intensity and the difference of the degrees of covalency in the initial, unionized, state and the final, core-hole states with larger differences leading to larger losses to satellites.. Furthermore, the final state covalency is less sensitive to the environment than is the initial state covalency since the bonding in the final state is more appropriate to that for an equivalent, Z+1, impurity atom representing the core-ionized atom. [3] We investigate the extent to which the effects of covalency can be tuned by comparing the Ni 2p XPS between NiO and Ni impurities in MgO.

1. P. S. Bagus, et al., Chem. Phys. Lett. **487**, 237 (2010).

2. E. S. Ilton and P. S. Bagus, Surf. Interface Anal. **43**, 1549 (2011).

3. W. L. Jolly and D. N. Hendrickson, J. Am. Chem. Soc. **92**, 1863 (1970).

11:00am **SS+OX-WeM10 Surface of $BaTiO_3$ (001): STM and STS Study**, ***E. Morales***, *J. Martirez, A.M. Rappe, D.A. Bonnell*, University of Pennsylvania

BaTiO3 is a versatile material that finds applications in sensors and electrooptical devices. Interactions start at the very surface, thus it is necessary to understand at a fundamental level its geometrical and electronic structure. Ferroelectricity is a key property that provides unique opportunities to explore molecular adsorption at a surface and allows investigation of chemical interactions as well. Interaction with gaseous species can be performed in-situ in "as-received" and poled crystals by controlling the poling voltage at the surface. Recent studies with macroscopic measurements show that polarization indeed affects molecular adsorption but mechanisms are not yet understood. Here we present scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) of atomically resolved reconstructions on BaTiO3 (001) surfaces, (√5x√5)R26.6^o. A comparison of electronic structure determined by STS with theoretical calculations shows that the surface that is Ti terminated. In this and other reconstructions Ti-ad atoms create filled and empty states that are imaged in STM. The interactions of reconstructed surfaces with H2O is examined with atomic resolution. This is the first atomic scale observation of molecular adsorption on a ferroelectric surface.

11:20am **SS+OX-WeM11 Synthesis and Characterization of White Light Emitting $Ca_xSr_{1-x}Al_2O_4$:Tb^{3+},Eu^{3+} Phosphor**, *S.K. Shaat, H.C. Swart,* ***O.M. Ntwaeaborwa***, University of the Free State, South Africa

Today, many researchers are making efforts to develop white light emitting phosphors that can be used in solid state lighting applications such as phosphor lamps and light emitting diodes. Aluminates with a general formula MAl_2O_4 (M = Ba, Ca, Mg, Sr) have emerged as preferred hosts for divalent (Mn^{2+} and Eu^{2+}) and trivalent (Ce^{3+},Tb^{3+}, Dy^{3+}) ions to prepare such phosphors. We have prepared a potential white light emitting $Ca_xSr_{1-x}Al_2O_4$:Tb^{3+},Eu^{3+} (x = 0, 0.3, 0.7, 1) phosphor by combustion method and we are evaluating it for application in solid state lighting. Depending on the concentration of Ca^{2+} or Sr^{2+}, the X-ray diffraction data showed that monoclinic structures of either $CaAl_2O_4$ or $SrAl_2O_4$ were crystallized and the stretching modes of Sr-Al-O and Ca-Al-O bonds were confirmed from the Fourier transform infrared spectroscopy data. The chemical compositions and electronic states of each elements of the $Ca_xSr_{1-x}Al_2O_4$:Tb^{3+},Eu^{3+} phosphor were determined using X-ray photoelectron spectroscopy. White photoluminescent was observed when $Ca_xSr_{1-x}Al_2O_4$:Tb^{3+},Eu^{3+} was excited at 227 nm using a monochromatized xenon lamp. This was a result of the combination of blue and green emissions from Tb^{3+} and red emission from Eu^{3+}. It is likely that Tb^{3+} and Eu^{3+} ions were simultaneously excited by a single photon of sufficiently high energy absorbed in $Ca_xSr_{1-x}Al_2O_4$ host.

11:40am **SS+OX-WeM12 A Novel 2-D Cu-Tungstate ($CuWO_x$) Phase on Cu(110)**, ***F.P. Netzer***, *M. Denk, D. Kuhness, M. Wagner, S. Surnev,* University of Graz, Austria, *F.R. Negreiros, L. Sementa, G. Barcaro, A. Fortunelli*, CNR-IPCF Pisa, Italy

We explore the feasibility to fabricate W-oxide nanostructures on metal surfaces via self-assembly and condensation of $(WO_3)_3$ clusters, deposited directly from the gas phase: here we report the formation of a novel two-dimensional Cu-tungstate $CuWO_x$ phase on Cu(110). A beam of $(WO_3)_3$ cluster molecules, formed by sublimation of WO_3 powder at ~900-1000°C in a thermal evaporator, has been directed onto a Cu(110)2x1-O surface oxide at low temperature and the surface has been annealed subsequently at 600 K. At low temperature (< 15 K) the $(WO_3)_3$ clusters adsorb in intact molecular form , albeit in a somewhat distorted cluster geometry [1]. Upon heating to 600K, the $(WO_3)_3$ molecules dissociate and react with the Cu-O(2x1) surface oxide, forming a wetting monolayer with a well ordered incommensurate structure. The latter has been structurally characterized by high-resolution STM imaging and LEED. The chemical nature and electronic structure of this novel 2-D W-O-Cu layer has been investigated by high-resolution XPS core level spectroscopy, NEXAFS, and valence band spectra. The unusually sharp W 4f core level spectra, the specific NEXAFS fingerprint and the evolution of the valence band all suggest that this 2-D W surface oxide is of a Cu-tungstate $CuWO_x$ type. Density functional calculations are in progress to help elucidating the physical and chemical nature of this unusual surface oxide phase.

Work supported by the ERC Advanced Grant SEPON

[1] M. Wagner, S. Surnev, M.G. Ramsey, G. Barcaro, L. Sementa, F.R. Negreiros, A. Fortunelli, Z. Dohnalek, F.P. Netzer, J. Phys. Chem. C115 (2011) 23480

Electronic Materials and Processing
Room: 9 - Session EM+OX-WeA

Oxides and Dielectrics for Novel Devices and Ultra-dense Memory
Moderator: J.F. Conley, Oregon State University, J. Kim, The University of Texas at Dallas

2:00pm **EM+OX-WeA1 Dielectric Requirements for a Novel Tunnel-FET Based on Room-Temperature Superfluidity in Graphene Double Layers**, ***L.F. Register***, *X. Mau, D. Reddy, D. Basu, W. Jung, I. Sodeman, D. Pesin, A. Hassibi, A.H. MacDonald, S.K. Banerjee*, University of Texas at Austin **INVITED**

The Bilayer pseudo-spin Field Effect Transistor (BiSFET) is a novel transistor concept based on possible room temperature superfluidity in two graphene layers separated by a thin dielectric. In principle, the switching energy per device could be on the scale of 10 zJ, over two orders of magnitude below estimates for "end-of the roadmap" CMOS transistors. However, at the time of writing, neither a BiSFET nor just such room temperature superfluidity have been demonstrated, and doing so poses substantial challenges both theoretical and experimental. Most significant among these challenge for this novel device concept now appear to be those associated with its novel dielectric requirements. In this presentation I will cover the basic concepts behind graphene superfluidity and BiSFET concepts, our current understanding—and limits to that understanding—of the requirements for condensate formation, and how these requirements could impact BiSFET design. In particular, I will compare and contrast the dielectric needs for the proposed BiSFET to those of conventional transistors.

2:40pm **EM+OX-WeA3 Interfaces and Surfaces in Tunnel Field-effect Transistors**, ***G. Xing***, University of Notre Dame **INVITED**

Abstract: It is now recognized that compound semiconductor tunnel field-effect transistors (TFETs) can retain MOSFET-like speed at low supply voltages given that on-current and voltage can be lowered in proportion. To achieve high on-current at low Vdd, the staggered-gap and broken-gap AlGaSb/InAs heterojunctions and graphene are being developed. In this talk I will first outline the recent experimental progress in the development of interband tunnel transistors with sub-60 mV/decade subthrehold swing at Notre Dame. Subsequent discussions will be then focused on the impact of interfaces and surfaces of the transistor on the TFET performance, in particular, the interface between the gate dielectric and semiconductor as well as the semiconductor surface after transistor isolation etch.

4:00pm **EM+OX-WeA7 Resistive Switching Characteristics of Al_2O_3/TiO_2 Bilayer ReRAM dependent on Al_2O_3 Thickness**, ***H.Y. Jeon***, *J.S. Lee, J.G. Park, W.C. Jang, H.T. Jeon*, Hanyang University, Korea

The next generation nonvolatile memory (NGNVM) devices should satisfy the device properties such as high density, fast operation speed, low power consumption, and high reliability. Recently, many type-NGNVM candidates are extensively considered to replace the conventional nonvolatile memory devices; polymer random access memory (PoRAM), phase change random access memory (PRAM), spin transfer torque random access memory (STT-RAM), and resistive switching random access memory (ReRAM). Among the many type-NGNVMs, ReRAM has attracted a great deal of attention in semiconductor industry mainly due to its high density integration, long retention time, small cell size, and fast switching speed. Also, the ReRAM has the simple structure like metal/insulator/metal (MIM) structure allowing the fabrication of 3 dimensional stack and nano cross-bar structure. There are two types of resistive switching for ReRAM. One is unipolar resistive switching (URS) and the other is bipolar resistive switching (BRS). The URS means the operation of set (program) and reset (erase) are under the same polarity of bias, whereas the polarity of bias for set operation is opposite to that of bias for reset operation in the BRS. The URS type ReRAM needs current compliance to prevent hard breakdown of transition metal oxide (TMO) when measuring the resistive switching. The URS is usually observed in ReRAM using binary transition metal oxides such as NiO, TiO_2, and Al_2O_3, while the BRS appeared in ReRAM using perovskite materials like $Cr:SrZrO_3$, $Pr_{0.7}Ca_{0.3}MnO_3$. Among many deposition methods for metal oxide, atomic layer deposition (ALD) has recently received a great interest for manufacture of ReRAM. Especially, remote plasma ALD is expected to enhance the reactivity between metal-organic precursor and reactant gas with minimal plasma damage on substrate, allowing the low impurity content and high density of the deposited films. In RPALD, plasma is generated remotely outside of chamber. And the radicals and ions generated in plasma region enter into the chamber by a downstream flow for chemical reaction of deposition. In this study, we investigated URS switching behaviors of ReRAM using Al_2O_3/TiO_2 bilayer deposited by remote plasma atomic layer deposition (RPALD) method. The thickness of Al_2O_3 layers was varied to observe the discrepancy of set/reset voltage and operation current level. The deposited Al_2O_3 and TiO_2 films are perfectly amorphous structures and their binding states have nearly stoichiometric composition. When operating the ReRAM with different thickness ratio, the dependence of operation voltage and current level on the thickness of Al_2O_3 layers was observed.

4:20pm **EM+OX-WeA8 High- k $SrTiO_3$ Dielectric by Plasma-Assisted Atomic Layer Deposition**, ***N.Y. Garces***, *D.J. Meyer, B.P. Downey, V.D. Wheeler, D.W. Zapotok, C.R. Eddy, Jr.*, U.S. Naval Research Laboratory

Strontium titanate (STO) is a promising material that offers the possibility of achieving large dielectric permittivity (k) constants for gate dielectric and other applications. Thin (~28 nm) STO films were deposited by remote plasma-assisted atomic layer deposition on the native oxide of n-type Si substrates in an Oxford Instruments FlexAL reactor at ~250°C using Bis(Tris-IsopropylCyclopentadienyl) Strontium, Tetrakis(dimethylamido)titanium as metal precursors, and a remote oxygen plasma as oxidizer. The general approach to deposit the ternary perovskite SrTiO3 is by alternating the ALD of the constituents TiO2 and SrO in a specific ratio to control such properties as the stoichiometric composition and dielectric constant [1,2]. The deposition temperature was chosen to give optimum growth uniformity for both SrO and TiO2 and to avoid decomposition of the precursors. The growth rate of the STO films was ~ 0.14 nm/cycle, which is slightly higher than the combined growth rate of the individual components. Also, the STO growth rate and stoichiometry are highly dependent on the temperature of the strontium precursor.

Initial capacitance-voltage (C-V) and current-voltage (I-V) results on 50-250 µm diameter circular capacitors patterned on ALD SrO:TiO2 (1:1) films were obtained. These dielectrics exhibited a moderate (~ 20) dielectric constant with reduced reverse-biased leakage current of ~1.6x10-5 A/cm2but larger forward bias leakage current ~ 1.2x10-3 A/cm2at 1V. Hysteresis in forward and reverse C-V sweeps was not observed, suggesting that these films are high-quality with limited or no slow time-constant charge trapping. After annealing the STO films at 550ºC in N2 for 5 min, a reduction in the oxide thickness by ~ 9% was measured, as well as a small increase in the dielectric constant to ~ 28 as a result of crystallization [3].

During this study, the overall thickness of the dielectric was held relatively constant, while the relative ratio of SrO:TiO2 was varied to tune the stoichiometry of the films and to monitor changes in the dielectric constant, optical band gap, Eg, and the electrical performance of the resulting oxides. The thickness, g rowth rates, and ALD mode behavior of STO, SrO, and TiO2 oxides were evaluated by spectroscopic ellipsometry measurements. We will p resent electrical measurements of STO oxides of various compositions with optimized deposition conditions for the chosen precursors, as well as stoichiometry assessments by x-ray photoelectron spectroscopy.

1. Vehkamäki,et.al. Chem. Vap. Deposition, **7**, 75 (2001)

2. Popovici,et.al. *J. Electrochem. Soc., **157**, G1* (2009)

3. Langereis,et.al. *J. Electrochem. Soc., **158**, G34-G38* (2011)

4:40pm **EM+OX-WeA9 Micro-Antenna Coupled Nano-MIM Diodes: Modeling, Design, Processing and Application**, ***N. Goldsman***, Univ. of Maryland, CoolCAD Electronics LLC, *F. Yesilkoya,* Univ. of Maryland, *S. Potbhare,* CoolCAD Electronics, LLC, *M. Peckerar,* Univ. of Maryland, *A. Akturk,* CoolCAD Electronics, LLC, *K. Choi,* Univ. of Maryland, *W. Churaman,* U.S. Army Research Lab, *N.K. Dhar*, DARPA/MTO **INVITED**

An antenna coupled to a diode can convert electromagnetic power into DC power, which can be integrated over time and stored on a capacitor or used to charge a battery. The combination of the antenna and diode is typically called a “Rectenna”. We are interested in developing a rectenna that operates in the infrared region of the electromagnetic spectrum. The applications of interest for IR rectennas include self-powering circuits and infrared imagers.

The rectenna structure we focus on consists of a micro-antenna and a rectifying metal-insulator-metal (MIM) diode for converting electromagnetic wave induced alternating current on the antenna to a direct current. The antenna couples to ambient or directed electromagnetic (EM) radiation, and the diode rectifies the AC signal for DC current and power generation. The frequency or the wavelength of the EM signal dictates the physical dimensions of the antenna, and the operating frequency of the

diode. Here one of the main challenges in achieving DC output upon IR radiation is to fabricate a diode capable of operating in the infrared range of frequencies, and more specifically at 30 Terahertz corresponding to 10 micrometer infrared radiation or approximately 300oK. To meet this challenge, we are fabricating metal-insulator-metal diode structures with oxide thicknesses of on the order a couple of nanometers or less.

An application of significant interest is a high resolution, high speed IR imager that can operate at room temperatures. Expanding from a single pixel to a complete large array is a challenge because the added complexity may give rise to electromagnetic coupling between adjacent elements, which needs to be accounted for. In addition, IR imaging, which corresponds to 30 terahertz region of operation, is special because it represents an 'in-between' region between radio and optical frequencies. At 10 micron wavelengths, the photons are typically too small in energy to economically convert their AC power into DC using semiconductor or quantum based photodetectors. At the same time, their frequency is too high to utilize standard PN or Schottky barrier diode based rectification. We thus explore the use of a micro-antenna coupled to a MIM diode for AC to DC conversion. A major difficulty here is to develop a diode that responds quickly enough to be forward biased during one part of the AC cycle and reverse biased to the other half of the cycle, without having the parasitic capacitance of the diode short out the signal. The rectenna we are developing uses a Nickel/Nickel-Oxide/Nickel (Ni-NiO-Ni) MIM structure, fabricated and designed using unique modeling and processing techniques.

5:20pm **EM+OX-WeA11 High-Electron-Mobility SiGe on Sapphire Substrate for Next Generation Ultrafast Chipsets**, ***H.J. Kim***, *Y. Park,* National Institute of Aerospace (NIA)*, H.-B. Bae,* Korea Advanced Institute of Science and Technology*, S.H. Choi*, NASA Langley Research Center (NASA LaRC)

In the conventional silicon-on-sapphire (SOS) technology with the epitaxy of Si on *r*-plane (1-102) sapphire, typical device region do not need reverse bias between the substrate and device area for electrical separation, because SOS wafer is separated by the sapphire itself, a best insulator. The advantage is that the sapphire insulator is very thick, which engenders an ultra-small capacitance and therefore it can reduce parasitic capacitance and leakage current at a high operating frequency. However, SOS wafer has a limitation in carrier mobilities due to the silicon material. The mobilities of SiGe can be a few times higher than those of silicon due to the high carrier mobilities of germanium (p-type Si: 430 $cm^2/V{\cdot}s$, p-type Ge: 2200 $cm^2/V{\cdot}s$, n-type Si: 1300 $cm^2/V{\cdot}s$, n-type Ge: 3000 $cm^2/V{\cdot}s$ at 10^{16} per cm^3 doping density). Therefore, RF devices which are made with rhombohedral SiGe on c-plane sapphire can potentially run a few times faster than RF devices on SOS wafers.

NASA Langley's rhombohedral epitaxy uses an atomic alignment of the [111] direction of cubic SiGe on top of the [0001] direction of the sapphire basal plane (*c*-plane). It shows a sample of rhombohedrally grown SiGe on *c*-plane sapphire with a single crystalline percentage of 95%. Twin defects exist only at the edge of the wafer. The electron mobilities of the tested samples are between those of single crystal Si and Ge. For instance, the electron mobility of 95% single crystal SiGe is 1538 $cm^2/V{\cdot}s$ which is between 350 $cm^2/V{\cdot}s$ (Si) and 1550 $cm^2/V{\cdot}s$ (Ge) at $6x10^{17}$ /cm^3 doping concentration. Typically, a rhombohedral single crystal SiGe has 2 or 3 times higher carrier mobility than monocrystalline silicon. If the defects in SiGe can be removed, transistors with higher operational frequencies can be fabricated for a new generation of ultrafast chipsets.

5:40pm **EM+OX-WeA12 Fabrication and Characterization of Metal-Insulator-Insulator-Metal (MIIM) Tunnel Diodes**, ***A.N. Nasir***, *J.F. Conley*, Oregon State University

MIM tunnel diodes have been proposed for high speed applications such as hot electron transistors, IR detectors, and optical rectennas for IR energy harvesting as well as backplanes for LCDs. The majority of these applications require highly asymmetric and non-linear I-V behavior at low applied voltages. The standard approach to achieving asymmetric operation in MIM devices is through the use of metal electrodes with different workfunctions (Φ_M). However, the amount of asymmetry achievable using this method is limited by the Φ_M difference that can be obtained using practical metals. In this work, we use an alternative approach to achieving asymmetric and non-linear operation – engineering of the insulating tunnel barrier using nanolaminate pairs of insulators with different bandgaps and band-offsets to produce asymmetric tunnel barriers. Electrons tunneling from one metal electrode to the other will see a different shape barrier depending on the direction of tunneling and the bias applied.

Recently, we found that atomic scale roughness at the bottom metal-insulator interface can dominate the I-V characteristics of MIM diodes, even overwhelming the influence of Φ_M difference. By using the amorphous metal ZrCuAlNi (ZCAN) as an ultra-smooth bottom electrode in combination with high quality dielectrics deposited via ALD, we were able to fabricate MIM diodes dominated by FN tunneling. In this work, nanolaminate insulator stacks consisting of either HfO_2/Al_2O_3, Ta_2O_5/Al_2O_3,ZrO_2/Al_2O_3, or HfO_2/ZrO_2 are deposited on sputtered ZCAN bottom electrodes via ALD. Al dots form the top gate electrode.

MIIM I-V characteristics were found to be sensitive to the relative thickness as well as the arrangement of the individual dielectric layers. In the ZCAN / Al_2O_3 / HfO_2 / Al orientation, the asymmetric tunnel barrier opposes the effect of the asymmetric Φ_M, a larger current is measured at positive bias, and asymmetry is lower than for a neat Al_2O_3 insulator device. However, in the ZCAN / HfO_2 / Al_2O_3 / Al orientation, the asymmetric tunnel barrier enhances the asymmetric Φ_M, a larger current is measured at negative bias, and asymmetry is greater than for neat Al_2O_3 or HfO_2 insulator devices. High asymmetry is seen when conduction in both dielectric layers is dominated by FN tunneling rather than bulk limited mechanisms. Ta_2O_5/Al_2O_3, e.g., did not show an enhancement in asymmetry.

In conclusion, we have fabricated dual insulator MIIM diodes that exhibit improved asymmetry over single layer MIM diodes. These results represent an advancement of the understanding necessary to engineer thin film based MIM tunnel devices for microelectronics applications.

Magnetic Interfaces and Nanostructures
Room: 6 - Session MI+OX-WeA

Spintronics, Magnetoelectrics, Multiferroics
Moderator: G.J. Mankey, University of Alabama

2:00pm **MI+OX-WeA1 Imaging of Temperature-Driven Nucleation of Ferromagnetic Domains in FeRh Thin Films**, ***C. Baldasseroni***, *C. Bordel,* Univ. of California Berkeley*, A.X. Gray,* SLAC National Accelerator Lab*, A.M. Kaiser,* Peter-Grünberg-Institut, Germany*, F. Kronast,* Helmholtz-Zentrum Berlin für Materialien und Energie, Germany*, J. Herrero-Albillos,* Centro Univ. de la Defensa, Spain*, C.M. Schneider,* Peter-Grünberg-Institut, Germany*, C.S. Fadley,* Lawrence Berkeley National Lab*, F. Hellman*, Univ. of California Berkeley

Equiatomic FeRh is a unique material that undergoes a first order antiferromagnetic (AF) to ferromagnetic (FM) transition just above room temperature (near 350 K). This phase transition can be driven by temperature or magnetic field and is coupled to a lattice expansion. Current investigations of this unique transition range from the fundamental understanding of the origin and nature of the transition to applications associated with the transition such as a giant magnetocaloric effect.

FeRh has been studied in the bulk for over 50 years and most recently in thin film form, where the transition temperature has been shown to be sensitive to changes in composition and substrate-induced strain as well as structural and chemical order. FeRh thin films are also a promising candidate for heat-assisted magnetic recording in an exchange-spring system with a hard magnetic layer (for example FePt). Understanding the magnetic domain structure of FeRh and the mechanisms of the transition at the microscopic level involving nucleation and growth of magnetic domains as a function of temperature is vital for its further application to magnetic storage technology. Although many experimental studies of the transition have been recently performed on FeRh thin films, most of them focus on macroscopic measurements. Only a few studies have attempted at imaging domains through the transition but these have been limited to magnetic force microscopy (MFM) on bulk samples and were limited by lack of temperature control which prevented a study of the nucleation and growth across the full transition.

We used x-ray magnetic circular dichroism and photoemission electron microscopy to study the evolution of ferromagnetic domains across the temperature-driven AF to FM phase transition in uncapped and capped epitaxial FeRh thin films. The coexistence of the AF and FM phases was evidenced across the broad transition and the different stages of nucleation, growth and coalescence were observed. We also found that the FM phase nucleates into single domain islands and the width of the transition of the individual nuclei is sharper than that of the macroscopic transition.

2:20pm **MI+OX-WeA2 Magnetic Properties of Cobalt and Permalloy Thin Films Grown on Self-Assembled Monolayers by Physical Vapor Deposition**, ***G.J. Szulczewski***, *S. Schafer, B. Khodadadi, T. Mewes, J. Kreil, E. Ellingsworth, K. Anderson*, The University of Alabama

In this talk we will present results from a study to understand how terminal functional groups in self-assembled monolayers (SAMs) influence the growth and subsequent magnetic properties of Co and NiFe (permalloy) thin films. Self-assembled monolayers were made from both aryl and alkyl carboxylic acids adsorbed onto oxidized aluminum surfaces. The SAMs were characterized by contact angle measurements and x-ray photoelectron

spectroscopy. The magnetic properties of the thin films were characterized by ferromagnetic resonance spectroscopy. In general we find that reactive functional groups, for example thiols, cause the metals to grow as continuous films. In contrast, deposition of the metals onto non-reactive functional groups, for example methyl, leads to penetration of metal atoms through the SAM and cluster formation. The permalloy films are superparamagnetic below ~ 4 nm, while Co films are ferromagnetic at room temperature. The coercivity of the films is also found to vary with functional group. In the case of halide substituents, for example, flouro, chloro, bromo, and iodo on the aryl carboxylic SAMs, there is also a correlation between the magnetic properties of cobalt thin films and the strength of the carbon-halogen bond energy. Cobalt deposited onto SAMs with terminal C-F bonds tends to be non-reactive, while reactive toward C-I bonds. Not only do these reactivity patterns influence the magnetic properties of the thin film, but also they result in a measurable change in the resistance of tunnel junctions bearing these SAMs.

2:40pm **MI+OX-WeA3 Synthesis and Fundamental Properties of Fe16N2 Films - New Excitements of Fe16N2 Research and a 40-year Mystery**, ***J.-P. Wang***, University of Minnesota **INVITED**

Pursuing magnetic materials with giant saturation magnetization (Ms) has huge impacts both scientifically and technologically. However, this effort has been fundamentally shadowed for decades by the classical itinerant magnetism theory. So far, the highest 4piMs value that can be predicted by first principles calculation is 2.45 T for Fe65Co35 alloy.

In 1972, Kim and Takahashi firstly reported a material with a giant saturation magnetization (4piMs ~ 2.9 T), Fe16N2, that surpasses Fe65Co35 alloy. Thereafter, various groups in the world have investigated the formation of Fe16N2 samples including films and particles by a variety of means. Unfortunately, experimentally reported 4piMs values are largely inconsistent ranging from 2.2 T up to 2.9 T. Investigators, including theoreticians, weighted in on one side of this question or the other. In particular, at the annual conference on Magnetism and Magnetic Materials in 1996, a symposium was held on the topic Fe16N2. Key research teams on this topic presented apparently conflicting views on the synthesis and understanding of this material. No decisive conclusion was drawn on whether Fe16N2 has giant saturation magnetization at the moment. Since then, this research topic has been dropped by most of magnetic researchers since year 2000.

In 2010, Wang's group has reported the theory and fundamental experimental evidence of the origin of giant saturation magnetization and produced the Fe16N2 thin films with both giant Ms and high anisotropy. In this talk, Dr. Wang will review the history and analyze the previous inconsistencies and obstacles of the Fe16N2 topic in the past 40 years. Then he will present recent progress from his group and his collaborators on this topic. From X-ray magnetic circular Dichorism (XMCD) experiment, polarization-dependent x-ray absorption near edge spectroscopy (EXANE), polarized neutron reflectivity (PNR) and first-principle calculation, it has been both experimentally and theoretically justified that the origin of giant saturation magnetization and large magnetocrystalline anisotropy is correlated with the formation of highly localized 3d electron states in this Fe-N system. Thirdly, high magnetic anisotropy and high spin polarization ratio of Fe16N2 will be reported and discussed, which may lead to many new applications, such as in spintronic device and rare-earth free magnet. Finally remaining fundamental questions and possible approaches to address them will be reviewed and discussed.

This talk is a joint effort with five research teams at ORNL, Argonne National Lab, Brookheaven National Lab and one lab from Netherland.

4:00pm **MI+OX-WeA7 Spin Transfer Torque MRAM - Modeling, Experiments and Future Prospects**, ***D. Apalkov***, *A. Khvalkovskiy, V. Nikitin, S. Watts, A. Driskill-Smith, D. Lottis, R. Chepulskyy, V. Voznyuk, X. Tang, K. Moon, E. Chen, C.M. Park, M. Krounbi*, Grandis, Inc. **INVITED**

Spin transfer torque magnetic random access memory (STT-MRAM) is a new and promising memory technology that features fast read and write times, small cell sizes of < 6F2, nonvolatility, radiation hardness and low power consumption.

In this work, we will go over the fundamental physics of magnetoresistance and spin transfer torque effects – key scientific phenomena required for STT-MRAM memory operation. The precursor technology – conventional MRAM – is now successfully used in commercial applications; however it cannot be scaled down to compete with DRAM or Flash technologies. We will go over the *Write-Store-Read* (WSR) trilemma, which is the challenge to achieve fast and reliable writing, reading and storing information at the same time in STT-MRAM. For a successful product, the desired probability of a switching error at the current deliverable by the transistor should be less than 10-3 for storage-class memory and 10-9-10-18 for working-class memory. Depending on the switching time, two regimes of switching, thermal and precessional, can be identified, and the switching error can dramatically depend not only on the switching regime but also on the switching time within the regime. For the reading process, one critical parameter is read disturb – probability of inadvertent switching of the element during reading operation. For memory applications, this probability has to be smaller than ~10-20 (with some dependence on particular design and array size). For storing the recorded information, the thermal stability parameter, defined as the ratio of energy barrier to kBT is important and typically has to be larger than 60-80 depending on specific application.

STT-MRAM can be implemented in two major realizations: in-plane and perpendicular. For each of them, single and dual MgO designs can be implemented, with the dual MgO design having up to 50% reduction of the switching current and providing much better switching symmetry than a single one. Special attention will be paid to our recent developments to of in-plane Dual MTJ design. By building special structure with modified reference layers, we were able to extract contributions from each barrier. Even though STT switching current is reduced in Dual design, the quality of the two barriers in currently built structures is deteriorated as compared to single MTJ. Respectively further improvement from Dual designs is expected if the quality of the two barriers is improved.

4:40pm **MI+OX-WeA9 Epitaxial Growth of Multiferroic Heterostructures of Magnetic and Ferroelectric Oxides using the Dual-laser Ablation Technique**, ***D. Mukherjee***, *M. Hordagoda, R.H. Hyde, N. Bingham, H. Srikanth, P. Mukherjee, S. Witanachchi*, University of South Florida

Epitaxial multiferroic $PbZr_{0.52}Ti_{0.48}O_3$ (PZT)/ $CoFe_2O_4$ (CFO)/ $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) composite thin films were fabricated on single-crystal $SrTiO_3$ substrates using the dual-laser ablation process. In this process, the target was initially heated by a pulsed CO_2 laser to produce a transient molten layer, from which a spatially-overlapped and slightly time-delayed pulsed KrF laser initiated the ablation. This not only resulted in a drastic reduction of particulates in the deposited films but also overcame the problem of non-congruent ablation of PZT, due to the high volatility of Pb, leading to stoichiometric PZT film deposition [1]. Moreover, the optimum coupling of the laser energies led to higher ionization of the ablated species particularly atomic oxygen (O) as seen in the optical emission spectra of the plumes. The higher excitation of O led to enhanced gas phase reaction and consequently reduced the oxygen vacancy-related point defects inherent in oxide films. X-ray diffraction (XRD) studies revealed the single crystalline nature and the cube-on-cube epitaxial relationship in the PZT/CFO/LSMO films. Atomic force microscopy revealed surface roughness values as low as 1.6 nm for the top PZT layers. Cross-sectional high resolution transmission electron microscope (HRTEM) images not only evidenced the epitaxial growth but also atomically sharp and flat interfaces with no structural defects (Suppl. PDF). The lattice parameters calculated from the HRTEM images matched well with the values obtained from XRD. Selected area electron diffraction (SAED) patterns showed linear square arrays confirming the single crystalline nature of the interfaces. Magnetization measurements exhibited perpendicular magnetic anisotropy with the easy axis along the film plane for the PZT/CFO/LSMO films, similar to PZT/LSMO bilayer thin films. PZT/CFO/LSMO films showed enhanced in-plane saturation magnetization (M_s) values of 360 emu/cm^3 as compared to 280 emu/cm^3 for PZT/LSMO and larger coercive field of 2.5 kOe as compared to 0.1 kOe for PZT/LSMO thin films. For ferroelectric measurements, top LSMO dot electrodes with 100 µm diameter were deposited using laser ablation to make LSMO/PZT/CFO/LSMO capacitors. Polarization measurements showed well saturated and square hysteresis loops at low nominal switching voltages of 5 V and with higher remnant polarization (P_r) values of 120 µC/cm^2 as compared to 90 µC/cm^2 for PZT/LSMO thin films.

[1]. D. Mukherjee et al, "Role of dual-laser ablation in controlling the Pb depletion in epitaxial growth of $Pb(Zr_{0.52}Ti_{0.48})O_3$ thin films with enhanced surface quality and ferroelectric properties", Journal of Applied Physics 111, 064102 (2012).

5:00pm **MI+OX-WeA10 The Highly Polarized Surface of Magnetoelectric Antiferromagnet**, ***N. Wu***, *X. He, J. Santana, J. Wang,* University of Nebraska-Lincoln, *E. Vescovo,* Brookhaven National Laboratory, *C. Binek, P.A. Dowben*, University of Nebraska-Lincoln

Manipulation of magnetically ordered states by electrical means is among the most promising approaches towards novel spintronic devices. Electric control of the exchange bias can be realized when the passive antiferromagnetic pinning layer is replaced by a magneto-electric antiferromagnet, like the prototypical magneto-electric Cr_2O_3(0001). Chromia works well in this case so long as there is also a finite remanent spin polarization at the surface or boundary, which can be achieved by cooling the thin film in the presence of both magnetic and electrics fields.

We have demonstrated that a very unusual high polarization can exist at the surface of the Cr_2O_3 (0001) from spin-polarized photoemission [1] and is robust against surface roughness. Both magnetic single domain and multi-domains were imaged by magnetic force microscopy and X-ray magnetic circular dichroism – photoemission electron microscopy (XMCD-PEEM) [2] as achieved by field cooling in the presence of electrics fields. The similar boundary magnetization has also been observed on the (110) surface of Fe_2TeO_6 by the XMCD-PEEM, which suggests this possible interface spin polarization to be a more universal phenomenon for magnetoelectric antiferromagnets.

References:

[1] Xi He, Yi Wang, Ning Wu, Anthony N. Caruso, Elio Vescovo, Kirill D. Belashchenko, Peter A. Dowben and Christian Binek, Nature Materials 9, 579 (2010).

[2] Ning Wu, Xi He, Aleksander L. Wysocki, Uday Lanke, Takashi Komesu, Kirill D. Belashchenko, Christian Binek, and Peter A. Dowben, Physical Review Letters 106, 087202 (2011).

5:20pm **MI+OX-WeA11 Sub-monolayer Spin Rotation of Photoelectrons from FePc on Fe(110)**, ***J.E. Rowe***, *D.B. Dougherty, A.A. Sandin,* North Carolina State University, *E. Vescovo*, Brookhaven National Laboratory

Spin-resolved photoemission at the National Synchrotron Light Source, Brookhaven National Laboratory has been used to study the occupied electronic states of sub-monolayers to multi-layers of iron phthalocyanine (FePc) adsorbed on ~10-20 monolayer epitaxial films on Fe(110) on W(110). We find that the spin-resolved photoemission changes rapidly as a function of coverage and the initial (majority spin axis along [110] rotates by ~ 30 degrees for sub-monolayer coverage and then becomes unpolarized at ~1 monolayer (ML). The coverage is determined by work function measurements which show that the initial work function of clean Fe(110) of 5.0 eV decreases monotonically to a value of ~3.8 eV at a coverage that we assign as ~1 monolayer of FePc. These values were determined from the measurements of the photoelectron spectrum using the low-energy vacuum-level cutoff of a biased sample. We used low intensity light at 41.4 eV photon energy to provide accurate intensity data and a well-defined vacuum-level threshold.

Our spin-resolved data for clean Fe(110) show highly spin-polarized photoelectrons from the Fermi energy to values about 3.5 eV below the Fermi energy for an applied B-field along [110] both for majority-spin and minority-spin electrons. The polarization is about 60% at -3.2 eV below E-Fermi. For 0.13 ML adsorbed FePc the spin polarization is somewhat reduced and is rotated from [110] towards [100] in the plane of the sample. We interpret this rotation as due to a strong coupling of the orbital moment of FePc with the conduction electrons of the Fe substrate. At a coverage of ~0.25 ML the polarization is reduced to ~0 and then at higher coverage (~1 ML) it increases to about 1/2 of the initial polarization. These data suggest that paramagnetic molecular species are useful for modifying the interfaces of spin-valve devices. A mechanism for this effect will be presented.

5:40pm **MI+OX-WeA12 Magnetic Configurations of $Ni_{80}Fe_{20}$/Ir Superlattices**, ***G.J. Mankey***, University of Alabama, *J. Hwang,* Lane College, *N. Pachauri, E.A. Manoharan, P.R. LeClair,* University of Alabama, *H. Ambaye, V. Lauter*, Oak Ridge National Laboratory

Antiferromagnetically coupled superlattices consisting of ferromagnetic (FM) layers separated by nonmagnetic (NM) spacer layers exhibit a wide range of magnetization behavior as a function of applied field. The magnetic configurations depend on the magnetization, thickness and anisotropy of the FM layers and the strength and type of magnetic coupling through the NM layers. The dependence of the magnetic configurations on applied magnetic field can be estimated with one-dimensional micromagnetic models that find the minimum energy configurations of the average magnetization vectors within the ferromagnetic layers1. A set of Ni80Fe20/Ir superlattice samples was designed to compare the measured magnetization curves as a function of applied field to magnetization curves generated by a micromagnetic model. The Ni80Fe20 layers were sputter deposited with an in-plane magnetic field, to induce uniaxial anisotropy within these layers. Both the FM layer thickness and number of superlattice periods were varied. FM layer thicknesses were verified by magnetometry and x-ray reflectivity analysis. The Ir NM layer thickness was tuned to the thickness for maximum antiferromagnetic coupling strength. Ir was chosen because the coupling strength has strong temperature dependence, increasing by about a factor of two as the temperature is reduced from 300 K to 5 K. A detailed comparison of the modeled and experimental magnetization curves enables a parameterization of the micromagnetic model that shows applying a magnetic field generates a complex magnetic structure in finite superlattices for multiple repeats. This complex structure, with twisted magnetic configuration is measured for a 16-repeat superlattice structure using polarized neutron reflectivity. Analysis of the polarized neutron reflectivity data for the applied magnetic field along the hard axis of the FM layers allows the determination of the detailed magnetic configuration.

1. U. K. Robler and A. N. Bogdanov, Phys. Rev. B 69, 184420 (2004).

The authors gratefully acknowledge financial support from DOE award DE-FG02-08ER46499. Research at Oak Ridge National Laboratory’s Spallation Neutron Source was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy.

Surface Science
Room: 21 - Session SS+EN+OX-ThM

Catalysis and Photocatalysis on Oxides
Moderator: Z. Dohnalek, Pacific Northwest National Laboratory

8:00am **SS+EN+OX-ThM1 Photoelectrochemical Water Splitting under Sunlight Irradiation using Oxynitride Electrodes Fabricated by Particle Transfer Method**, *K. Domen, **J. Kubota***, The University of Tokyo, Japan **INVITED**

Hydrogen production through the photoelectrochemical (PEC) water splitting is one of the attractive ways to convert solar energy to storable chemical energy. The availability of powder semiconductor materials through coating methods for preparing photoelectrodes is a one of strong point of PEC cells. Even if the surface is a rough particle layer, the electrolyte solution automatically forms the desirable solid-liquid interface for whole semiconductor surfaces, where photoexcited carriers are separated by electric field.

Oxynitride and oxysulfide materials are promising candidates for photoelectrodes for water splitting. Among them, $LaTiO_2N$ has a proper band structure from the view point of driving solar water splitting. The material shows photocatalytic hydrogen and oxygen evolutions in half reactions using sacrificial reagents, indicating that the material have a proper band structure to drive PEC water splitting. $LaTiO_2N$ absorbs visible light up to 600 nm (E_g = 2.1 eV), so that they can capture more solar energy than oxide photocatalysts, which typically have absorption in the UV region. Photoelectrodes based on the material have been studied extensively, however, the photocurrent was low due to the rack of good preparation method of the electrode.

In the present study, we report a novel fabrication method of photoelectrodes for PEC water splitting using semiconductor powders. This method, which we have termed the particle transfer (PT) method, is shown to be applicable to a variety of semiconductor powders. $LaTiO_2N$ was demonstrated to exceed those prepared by the conventional method of photoelectrode fabrication from powder materials.

8:40am **SS+EN+OX-ThM3 Multi-step Photooxidation of CO on TiO_2(110)**, ***G.A. Kimmel***, *N.G. Petrik*, Pacific Northwest National Laboratory

TiO_2 is an important photocatalyst with many practical applications. However, a detailed understanding of the relevant physical and chemical processes for the photocatalysis remains elusive. We have studied the photooxidation of CO adsorbed on rutile TiO_2(110) during UV irradiation with ~1 ms time resolution. Previous investigations with ~0.1 s resolution found that the maximum CO_2 photon-stimulated desorption (PSD) signal occurred for the first data point and then decreased monotonically with increasing irradiation time. However our experiments with improved time resolution show that the initial rate of CO_2 production is zero, and then increases smoothly to a maximum before decreasing at longer irradiation times. Experiments varying the UV photon flux show that the CO_2 PSD kinetics are proportional to the photon fluence but are independent of the photon flux (for the range investigated). The photon fluence required to reach the maximum CO_2 PSD signal increases as the initial coverage of chemisorbed O_2 increases – an effect that we attribute to changes in the initial charge state of the chemisorbed O_2. These results demonstrate that the production of CO_2 proceeds through the formation of stable precursor. The angular distribution of the photodesorbing CO_2, which is peaked at ~40° with respect to the surface normal perpendicular to the BBO rows, is also consistent with the production of CO_2 from a precursor state. Previously, the photooxidation of CO on TiO_2(110) was believed to occur in a single non-thermal reaction step: $CO + O_2 + h\nu \rightarrow CO_2 + O_{ad}$. However, our results show that the photooxidation of CO requires at least two non-thermal reaction steps – one to form the precursor and a second to produce the CO_2. We will compare the experimental results to DFT calculations and discuss the role of photo-generated electrons and holes in the photooxidation of CO. These results show that the photooxidation of CO on TiO_2 is more complicated than previously appreciated.

9:00am **SS+EN+OX-ThM4 Design of Band Engineered Photocatalysts using Titanium Dioxide**, *S.W. Ong, **D.E. Barlaz**, E.G. Seebauer*, University of Illinois at Urbana Champaign

Difficulties in achieving control over carrier concentration have impeded progress toward tailoring the electric fields in semiconducting oxide photocatalysts based upon principles of electronic band engineering drawn from classical optoelectronics. The present work demonstrates such principles using the model case of methylene blue photo-oxidation over thin-film anatase TiO_2 grown by atomic layer deposition. The carrier concentration in the polycrystalline semiconductor is controlled over a range of 2.5 orders of magnitude via an unconventional means - film thickness, which indirectly influences the concentration of electrically active donor defects at grain boundaries. Over this range, the reaction rate constant varies by more than a factor of 10, and is well described by a quantitative one-dimensional model for photocurrent. The model suggests that the changes in rate result fundamentally from variations in the width of the space charge layer near the surface. Electrical characterization of the films by capacitance-voltage measurements and ultraviolet photoelectron spectroscopy, together with detailed physical characterization by a variety of techniques, confirm this picture. Prospects for better control of grain boundary donor defects through film synthesis procedures are discussed.

9:20am **SS+EN+OX-ThM5 Adsorption of CO_2 on Oxygen Precovered TiO_2(110) Surfaces**, ***X. Lin***, *Y. Yoon, N.G. Petrik, G.A. Kimmel, Z. Li, Z.-T. Wang, B.D. Kay, I. Lyubinetsky, R. Rousseau, Z. Dohnalek*, Pacific Northwest National Laboratory

Rutile TiO_2(110) was employed as a model oxide surface to investigate the adsorption behavior of CO_2 by means of scanning tunneling microscopy (STM) and density functional theory (DFT). STM images of partially reduced TiO_2(110) surfaces obtained before and after *in-situ* dosing of CO_2 molecules at 50 K show that CO_2 adsorbs preferentially on oxygen vacancy (V_O) sites. Since the reaction of CO_2 with oxygen adatoms (surface hydroxyl groups) may lead to the formation of carbonate (bicarbonate), O_2 (H_2O) was predosed to form oxygen adatom (hydroxyl) covered TiO_2 surfaces. On the oxygen precovered surfaces, CO_2 molecules were found to preferentially bind on the Ti sites next to oxygen adatoms (O_a's) and form CO_2/O_a complexes, while on hydroxylated surfaces no interactions were observed between CO_2 and hydroxyl groups. CO_2 binding to O_a's is weak as revealed by the dissociation of the CO_2/O_a complexes at 50 K where CO_2 diffuses away along the Ti row. The weak binding indicates that CO_2 is bound to O_a only via dispersion forces. Temperature dependent studies (100 - 150 K) show that the CO_2 binding energy next to O_a's is smaller by ~20 mV than that on V_O's. At 50 K, however, the adsorption of CO_2 on V_O is partially hindered by the higher adsorption barrier. CO_2 molecules diffusing between two CO_2/O_a complexes are found to move fast compared to the STM sampling rate and are imaged as a time average of all CO_2 binding configurations on Ti sites. DFT studies reveal the rotation-tumbling mechanism for CO_2 diffusion with a very low diffusion barrier (~ 50 meV) in agreement with the experiment.

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X.L. is grateful for the support of the Linus Pauling Distinguished Postdoctoral Fellowship Program at PNNL. This work was supported by the US Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences & Biosciences. A portion of the research was performed using EMSL, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory (PN NL). PNNL is a multiprogram national laboratory operated for DOE by Battelle.

9:40am **SS+EN+OX-ThM6 Probe of NH_3 and CO Adsorption on the Very Outermost Surface of a Porous TiO_2 Adsorbent Using Photoluminescence Spectroscopy**, ***A. Stevanovic***, *J.T. Yates, Jr.*, University of Virginia

The photoluminescence (PL) of powdered TiO₂ at 529.5 nm (2.34 eV) has been found to be a sensitive indicator of UV-induced band structure modification. As UV irradiation occurs, the positive surface potential changes and shifts the depth of the depletion layer. It was found that UV light (3.88 eV) induces a positive surface potential which diminishes band bending in n- type TiO₂ and enhances PL1. Also, adsorbates modify the PL intensity by exchanging charge with TiO₂, producing a change in the surface band bending structure.

In addition, we employ photoluminescence (PL) spectroscopy to probe the development of adsorbed layers on the very outermost surface sites of a porous solid adsorbent (TiO₂) in a depth of 20 nm where the meso-pores, separating 30-80 nm TiO₂ particles, join the gas phase2. In parallel, we also employ transmission infrared (IR) spectroscopy to gain insight into the extent of adsorption averaged over the entire depth of the diffusion process. The combination of the two surface spectroscopies (PL and IR) allows one to observe the kinetics of transport of adsorbate molecules between the very outermost surface region (where adsorption

first occurs) and the interior of the powdered substrate. The transport is governed by the surface mobility of the adsorbate molecules, and hysteresis effects in adsorption/desorption are observed.

References:

1. Stevanovic, A.; Buttner, M.; Zhang, Z.; Yates, J. T., Jr., Photoluminescence of TiO2: effect of UV light and adsorbed molecules on surface band structure. *Journal of the American Chemical Society* **2012,** 134, (1), 324-32.

2. Stevanovic, A.; Yates, J. T., Jr., Probe of NH(3) and CO Adsorption on the Very Outermost Surface of a Porous TiO(2) Adsorbent Using Photoluminescence Spectroscopy. *Langmuir : the ACS journal of surfaces and colloids* **2012,** 28, (13), 5652-9.

Work supported by the Army Research Office.

10:40am **SS+EN+OX-ThM9 Site-Specific Photocatalytical Reactions of O_2 on $TiO_2(110)$**, ***Z.-T. Wang,*** Pacific Northwest National Laboratory, *N.A. Deskins,* Worcester Polytechnic Institute, *I. Lyubinetsky*, Pacific Northwest National Laboratory

Photo-stimulated reactions on TiO_2 have attracted much attention due to the variety of potential applications ranging from a hydrogen production by water splitting to environmental remediation through organic pollutant oxidation. In majority of these processes, the oxygen plays a crucial role. A better understanding of the fundamental aspects of oxygen on TiO_2 can potentially lead to improvements or developments of the TiO_2 applications. We present the direct observation at an atomic level with high-resolution scanning tunneling microscopy of photostimulated reactions of single O_2 molecules on reduced $TiO_2(110)$ surfaces at 50 K. The critical relation between photoreactivity and adsorption sites on TiO_2 is demonstrated. Two distinct reactions of O_2 desorption and dissociation occur at different active sites of terminal Ti atoms and bridging O vacancies, respectively. These two reaction channels follow very different kinetics. While hole-mediated O_2 desorption is promptly and fully completed, electron-mediated O_2 dissociation is much slower and is quenched above some critical O_2 coverage. Density functional theory calculations indicate that both coordination and charge state of an O_2 molecule chemisorbed at specific site largely determine a particular reaction pathway.

11:00am **SS+EN+OX-ThM10 Bond Selectivity in the Activation of *n*-alkanes on PdO(101)**, ***J.F. Weaver***, *A. Antony, C. Hakanoglu, F. Zhang,* University of Florida, *A. Asthagiri*, The Ohio State University

We have investigated initial C-H bond selectivity in the activation of propane and *n*-butane on PdO(101) both experimentally and computationally. Temperature-programmed experiments using different propane isotopologues reveal a strong preference toward primary C-H bond cleavage of propane on PdO(101); about 90% of the propane molecules which react do so by primary C-H bond activation. Direct measurements of the initial dissociation probability of various *n*-butane isotopologues also demonstrate a high selectivity for primary C-H bond activation of *n*-butane on PdO(101) at low coverages. Unlike propane, however, TPRS experiments show that the preference for primary C-H bond cleavage of *n*-butane diminishes with increasing molecular coverage. Calculations using dispersion-corrected DFT reproduce the selectivity toward primary C-H bond cleavage of propane and *n*-butane on PdO(101), and predict that alkane C-H bond scission occurs heterolytically on the oxide surface. The calculations suggest that greater substituent polarization in the 1-alkyl transition structures is responsible for the lower energy barriers for primary vs. secondary C-H bond activation of alkanes on PdO(101).

11:20am **SS+EN+OX-ThM11 Photoresponse, Electronic Transport and Magnetic Properties of Ti-doped $(Cr_xFe_{1-x})_2O_3$**, ***S.E. Chamberlin***, *T.C. Kaspar, M.E. Bowden, V. Shutthanandan, S.A. Chambers, M.A. Henderson*, Pacific Northwest National Laboratory

There is widespread interest in discovering materials that can effectively harvest sunlight in the visible region of the electromagnetic spectrum in order to drive chemical processes on surfaces. Hematite (Fe_2O_3) has received renewed interest recently as the active photoanode in photoelectrochemical (PEC) water splitting to store solar energy as H_2. Hematite has three key advantages which make it appealing: it is very abundant, it has a bandgap of 2.2 eV, which is suitably narrow to harvest incident solar radiation, and it is sufficiently stable in the aqueous solutions required for PEC water splitting. However, hematite is a charge-transfer insulator with extremely poor electron and hole mobilities, which results in short hole diffusion lengths and ultrafast recombination of photogenerated electron/hole pairs before charge separation can occur. Substitutional Ti(IV) at an Fe(III) site should be a donor, and epitaxial Ti-doped α-Fe_2O_3 exhibits significantly enhanced conductivity relative to pure hematite when grown under certain conditions by oxygen-assisted molecular beam epitaxy (OAMBE) on α-$Al_2O_3(0001)$ substrates.[1] In addition, Mashiko *et al.*[2] have shown that the bandgap of pure hematite can be reduced to 1.7 eV by alloying with Cr(III) in epitaxial films. Combining these approaches is expected to result in material with both a reduced bandgap and favorable electrical conductivity, which will facilitate visible-light photoactivity. Heteroepitaxial thin films of $(Fe_{1-x}Cr_x)_2O_3$ and $(Fe_{1-x-y}Cr_xTi_y)_2O_3$ were deposited on α-$Al_2O_3(0001)$ substrates by OAMBE. Film quality was monitored *in situ* by reflection high energy electron diffraction (RHEED). *In situ* x-ray photoemission spectroscopy (XPS) was utilized to characterize the charge states of the cations. Film crystallinity and lattice parameters were determined *ex situ* by high resolution x-ray diffraction (HRXRD). Rutherford backscattering spectrometry (RBS) in both random and channeling geometries confirmed the film stoichiometry, and elucidated the degree of substitution of the cations in the lattice. Preliminary optical absorption measurements and photochemistry experiments will be presented.

1. B. Zhao, T. C. Kaspar, T. C. Droubay, J. McCloy, M. E. Bowden, V. Shutthanandan, S. M. Heald, and S. A. Chambers, Phys. Rev. B 84, 245325 (2011).

2. H. Mashiko, T. Oshima, and A. Ohtomo, Appl. Phys. Lett. 99, 241904 (2011).

11:40am **SS+EN+OX-ThM12 A Nonadiabatic Mechanisms of Inequilibrium Charge Carriers Production in Pd/n-GaP Schottky Nanodiode Exposed to Atomic Hydrogen**, ***S.V. Simchenko***, *V. Styrov*, Azov State Technical University, Ukraine

Since the recent discovery of production of electronic flows in Schottky diodes with nanosized "top" metal layer due to ballystic metal-to-semiconductor transport of hot electrons formed by the surface exoergic chemical reaction, e.g. [1], this effect attracts attention of scientists owing to its fundamental and practical potential. Here we invastigate a new system of that kind, namely Pd-(n)GaP planar Schottky diod (15 nm Pd-layer) placed in the atmosphere of atomic hydrogen. We found the steady-state current flow through the system under consideration in perpendicular direction to the metal surface on which the hydrogen atoms stationary recombine into molecules.

We elaborated a new approach to detect production of the inequilibrium charge carriers via nonadiabatic channel by observing the current-voltage characteristic of the Schottky diode in the presence and absence of the atomic flux incident on the structure. The nonequilibrium nature of the additional carriers is confirmed by kinetics measurements: the current drops to its initial value in the absense of atoms practically momentarily once the atoms are "switched off" and jumps immediately to its excited value when atoms are "switched on" (at the given temperature of the structure and the fixed forward voltage bias on the structures). We were able to draw some quantitative information about the processes of generation of nonequilibrium electron-hole pairs in the reaction of recombination of hydrogen atoms on Pd-surface and their transport in the metal film. The short circuit current is expressed in terms of yield of the chemoexcited carriers and probability of their survival while traveling through the Pd-film.

For a 1V forward bias the current drastically grows from 3 nA to 950 uA; thus the bias allows gaining chemicurrent value as large as five orders of magnitude. This result can be of significant importance for the practical applications of the nonequilibrium chemiconductance and chemicurrents in Schottky nanostructures including sensing and chemical-to-electricity energy conversion.

[1] B. Georgen, H.Nienhaus, W.H. Weinberg, E. McFarland. *Science*, 294**,** 2521 (2003)

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Gotlib-Vainshtein, K.: OX+EM+MI+NS+TF-MoM11, 3
Grampeix, H.: EM+TF+OX+GR-MoA9, 5
Gray, A.X.: MI+OX-WeA1, 14
Greene, A.: EM+TF+OX+GR-MoM3, 1
Greiner, M.T.: OX+SS+TF+MI-MoA7, 6
Grundmeier, G.: OX+SS+TF+MI-MoA11, 7
Guerrero, J.: EM+TF+OX+GR-MoA9, 5

— H —

Hakanoglu, C.: SS+EN+OX-ThM10, 18
Harl, R.R.: SS+OX-WeM4, **10**
Harrell, W.R.: SS+OX-WeM3, 10
Harriss, J.E.: SS+OX-WeM3, 10
Hassibi, A.: EM+OX-WeA1, 13
He, C.: OX+EM+MI+NS+TF-MoM10, 3
He, X.: MI+OX-WeA10, 15
Heald, S.M.: SS+OX-WeM5, 11
Hellman, F.: MI+OX-WeA1, 14
Henderson, M.A.: SS+EN+OX-ThM11, 18
Herdiech, M.W.: OX+SS+TF+MI-MoA2, 6
Herrera-Gomez, A.: EM+TF+OX+GR-MoA9, 5
Herrero-Albillos, J.: MI+OX-WeA1, 14
Heyns, M.: EM+TF+OX+GR-MoA1, 4
Highland, M.J.: IS+AS+OX+ET-WeM3, 9
Hikita, Y.: OX+EM+MI+NS+TF-MoM3, **2**
HIllion, F.: IS+AS+OX+ET-WeM11, 10
Hinkle, C.L.: EM+TF+OX+GR-MoA4, 4
Hordagoda, M.: MI+OX-WeA9, 15; OX+EM+MI+NS+TF-MoM1, **2**
Hossain, T.: EM+TF+OX+GR-MoM9, 1
Hwang, J.: MI+OX-WeA12, 16
Hyde, R.H.: MI+OX-WeA9, 15; OX+EM+MI+NS+TF-MoM1, 2

— I —

Ilton, E.S.: SS+OX-WeM9, 11
Ismail-Beigi, S.: OX+SS+TF+MI-MoA2, 6

— J —

Jang, W.C.: EM+OX-WeA7, 13
Jeon, H.T.: EM+OX-WeA7, 13
Jeon, H.Y.: EM+OX-WeA7, **13**
Jia, Q.: IS+AS+OX+ET-WeM3, 9
Jiang, S.: EM+TF+OX+GR-MoA1, 4
Jobbins, M.M.: IS+AS+OX+ET-WeM1, 9
Joly, Y.: SS+OX-WeM5, 11
Jung, W.: EM+OX-WeA1, 13
Jupille, J.: SS+OX-WeM6, **11**

— K —

Kaiser, A.M.: MI+OX-WeA1, 14
Kakekkhani, A.: OX+SS+TF+MI-MoA2, 6
Kalfon-Cohen, E.: OX+EM+MI+NS+TF-MoM11, 3
Kandel, S.A.: IS+AS+OX+ET-WeM1, 9
Kaspar, T.C.: IS+AS+OX+ET-WeM2, 9; SS+EN+OX-ThM11, 18; SS+OX-WeM5, **11**
Kaufman-Osborn, T.: EM+TF+OX+GR-MoA3, **4**
Kay, B.D.: SS+EN+OX-ThM5, 17
Kayani, A.: OX-TuP6, 8
Keun, S.K.: IS+AS+OX+ET-WeM3, 9
Khodadadi, B.: MI+OX-WeA2, 14
Khvalkovskiy, A.: MI+OX-WeA7, 15
Kiantaj, K.: EM+TF+OX+GR-MoA3, 4
Kim, D.J.: IS+AS+OX+ET-WeM2, 9
Kim, H.J.: EM+OX-WeA11, **14**
Kim, J.: EM+TF+OX+GR-MoM6, 1
Kim, M.J.: EM+TF+OX+GR-MoA4, 4
Kimmel, G.A.: SS+EN+OX-ThM3, **17**; SS+EN+OX-ThM5, 17
Kreil, J.: MI+OX-WeA2, 14
Kronast, F.: MI+OX-WeA1, 14
Krounbi, M.: MI+OX-WeA7, 15
Krueger, P.: SS+OX-WeM6, 11
Kubota, J.: SS+EN+OX-ThM1, **17**
Kuhness, D.: SS+OX-WeM12, 12
Kummel, A.C.: EM+TF+OX+GR-MoA3, 4
Kwon, Y.H.: OX+EM+MI+NS+TF-MoM2, **2**

— L —

Langfitt, Q.: OX-TuP6, 8
Lauter, V.: MI+OX-WeA12, 16
Laver, M.: OX+EM+MI+NS+TF-MoM10, 3
LeClair, P.R.: MI+OX-WeA12, 16
Lee, D.Y.: IS+AS+OX+ET-WeM1, **9**
Lee, J.H.: OX+EM+MI+NS+TF-MoM2, 2
Lee, J.R.I.: IS+AS+OX+ET-WeM6, 9
Lee, J.S.: EM+OX-WeA7, 13; EM+TF+OX+GR-MoA3, 4
Lee, J.Y.: OX+EM+MI+NS+TF-MoM2, 2
Leighton, C.: OX+EM+MI+NS+TF-MoM10, **3**
Li, Z.: SS+EN+OX-ThM5, 17
Liang, T.: OX+SS+TF+MI-MoA1, 6; OX-TuP1, 8; OX-TuP3, 8
Lin, X.: SS+EN+OX-ThM5, **17**
Linder, B.P.: EM+TF+OX+GR-MoA7, 5
Locquet, J.P.: IS+AS+OX+ET-WeM9, 9
Lottis, D.: MI+OX-WeA7, 15
Lu, N.: EM+TF+OX+GR-MoA4, 4
Lu, Z.-H.: OX+SS+TF+MI-MoA7, **6**
Lucero, A.T.: EM+TF+OX+GR-MoM6, **1**
Lyubinetsky, I.: IS+AS+OX+ET-WeM2, 9; SS+EN+OX-ThM5, 17; SS+EN+OX-ThM9, 18

— M —

MacDonald, A.H.: EM+OX-WeA1, 13
Madisetti, S.: EM+TF+OX+GR-MoM3, 1
Manandhar, S.: OX-TuP6, 8
Mangham, A.N.: SS+OX-WeM5, 11
Mankey, G.J.: MI+OX-WeA12, **16**
Manoharan, E.A.: MI+OX-WeA12, 16
Martin, F.: EM+TF+OX+GR-MoA9, 5
Martinez, E.: EM+TF+OX+GR-MoA9, **5**
Martinez, J.: OX-TuP4, **8**
Martirez, J.: SS+OX-WeM10, 11
Mau, X.: EM+OX-WeA1, 13
Maxisch, M.: OX+SS+TF+MI-MoA11, 7
McCleskey, T.M.: IS+AS+OX+ET-WeM3, 9
Merckling, C.: EM+TF+OX+GR-MoA1, **4**
Merrill, M.D.: IS+AS+OX+ET-WeM6, 9
Mewes, T.: MI+OX-WeA2, 14
Meyer III, H.M.: EM+TF+OX+GR-MoM9, 1
Meyer, D.J.: EM+OX-WeA8, 13
Moon, K.: MI+OX-WeA7, 15
Moore, R.: EM+TF+OX+GR-MoM3, 1
Morales, E.: SS+OX-WeM10, **11**
Morgante, A.: SS+OX-WeM6, 11
Mukherjee, D.: MI+OX-WeA9, **15**; OX+EM+MI+NS+TF-MoM1, 2
Mukherjee, P.: MI+OX-WeA9, 15; OX+EM+MI+NS+TF-MoM1, 2

— N —

Nachimuthu, P.: OX-TuP6, 8
Nagaiah, P.: EM+TF+OX+GR-MoM3, 1
Nandasiri, M.I.: OX-TuP6, **8**
Narayanan, V.: EM+TF+OX+GR-MoA7, 5
Nasir, A.N.: EM+OX-WeA12, **14**
Nefedov, A.: OX+SS+TF+MI-MoA10, 7
Negreiros, F.R.: SS+OX-WeM12, 12
Nelin, C.J.: SS+OX-WeM9, 11
Nepal, N.: EM+TF+OX+GR-MoM9, 1
Netzer, F.P.: SS+OX-WeM12, **12**
Ney, A.: SS+OX-WeM5, 11
Ney, V.: SS+OX-WeM5, 11
Nie, X.W.: OX-TuP1, 8
Nikitin, V.: MI+OX-WeA7, 15
Noei, H.: OX+SS+TF+MI-MoA10, 7
Novak, S.: EM+TF+OX+GR-MoM3, 1
Ntwaeaborwa, O.M.: SS+OX-WeM11, **11**

— O —

Ogitsu, T.: IS+AS+OX+ET-WeM6, 9
Oktyabrsky, S.: EM+TF+OX+GR-MoM3, **1**
Ong, S.W.: SS+EN+OX-ThM4, 17

— P —

Pachauri, N.: MI+OX-WeA12, 16
Pan, X.: SS+OX-WeM1, **10**
Park, C.M.: MI+OX-WeA7, 15
Park, J.G.: EM+OX-WeA7, 13
Park, Y.: EM+OX-WeA11, 14
Peckerar, M.: EM+OX-WeA9, 13
Peres, P.: IS+AS+OX+ET-WeM11, 10
Perret, E.: IS+AS+OX+ET-WeM3, 9
Pesin, D.: EM+OX-WeA1, 13
Petrik, N.G.: SS+EN+OX-ThM3, 17; SS+EN+OX-ThM5, 17
Phillpot, S.R.: OX+SS+TF+MI-MoA1, 6; OX-TuP1, 8; OX-TuP3, 8; OX-TuP4, 8
Potbhare, S.: EM+OX-WeA9, 13
Povey, I.M.: EM+TF+OX+GR-MoA6, 4
Prokes, S.M.: EM+TF+OX+GR-MoA10, 5

— Q —

Qiao, L.: OX-TuP5, 8
Qin, X.: EM+TF+OX+GR-MoM5, **1**
Quintero, M.: OX-TuP6, 8

— R —

Rangan, S.: OX+SS+TF+MI-MoA6, **6**
Rappe, A.M.: SS+OX-WeM10, 11
Reddy, D.: EM+OX-WeA1, 13
Register, L.F.: EM+OX-WeA1, **13**
Robertson, J.: EM+TF+OX+GR-MoM10, **2**
Rodriguez, L.N.J.: IS+AS+OX+ET-WeM9, **9**
Rogalev, A.: SS+OX-WeM5, 11
Rogers, B.R.: SS+OX-WeM4, 10
Rousseau, R.: SS+EN+OX-ThM5, 17
Rowe, J.E.: MI+OX-WeA11, **16**
Rozen, J.: EM+TF+OX+GR-MoA7, 5
Ruggieri, C.: OX+SS+TF+MI-MoA6, 6
Ruppalt, L.: EM+TF+OX+GR-MoA10, 5

— S —

Saitoh, E.: IS+AS+OX+ET-WeM10, 10
Sandin, A.A.: MI+OX-WeA11, 16
Santana, J.: MI+OX-WeA10, 15
Schafer, S.: MI+OX-WeA2, 14
Schmitt, J.: OX+EM+MI+NS+TF-MoM10, 3
Schneider, C.M.: MI+OX-WeA1, 14
Schuhmacher, M.: IS+AS+OX+ET-WeM11, 10
Seebauer, E.G.: SS+EN+OX-ThM4, 17
Sementa, L.: SS+OX-WeM12, 12
Shaat, S.K.: SS+OX-WeM11, 11
Sharma, M.: OX+EM+MI+NS+TF-MoM10, 3
Shutthanandan, V.: OX-TuP6, 8; SS+EN+OX-ThM11, 18
Shyam, R.: SS+OX-WeM3, **10**
Simchenko, S.V.: SS+EN+OX-ThM12, **18**
Sinnott, S.B.: OX+SS+TF+MI-MoA1, 6; OX-TuP1, 8; OX-TuP3, 8; OX-TuP4, 8
Sodeman, I.: EM+OX-WeA1, 13
Sosolik, C.E.: SS+OX-WeM3, 10
Srikanth, H.: MI+OX-WeA9, 15; OX+EM+MI+NS+TF-MoM1, 2
Srinadhu, E.S.: SS+OX-WeM3, 10
Stadermann, M.: IS+AS+OX+ET-WeM6, 9
Stair, P.C.: OX+SS+TF+MI-MoA3, **6**
Stevanovic, A.: SS+EN+OX-ThM6, **17**
Styrov, V.: SS+EN+OX-ThM12, 18
Sukenik, C.N.: OX+EM+MI+NS+TF-MoM11, 3
Surnev, S.: SS+OX-WeM12, 12
Swart, H.C.: SS+OX-WeM11, 11
Szulczewski, G.J.: MI+OX-WeA2, **14**

— T —

Tallarida, M.: IS+AS+OX+ET-WeM9, 9
Tang, X.: MI+OX-WeA7, 15
Thevuthasan, S.: OX-TuP6, 8
Tokranov, V.: EM+TF+OX+GR-MoM3, 1
Torija, M.: OX+EM+MI+NS+TF-MoM10, 3

— V —

van Buuren, T.: IS+AS+OX+ET-WeM6, 9
Van Elshocht, S.: IS+AS+OX+ET-WeM9, 9
Varela, M.: OX+EM+MI+NS+TF-MoM10, 3
Varga, T.: OX-TuP6, 8
Verdini, A.: SS+OX-WeM6, 11
Vescovo, E.: MI+OX-WeA10, 15; MI+OX-WeA11, 16
Voznyuk, V.: MI+OX-WeA7, 15

— W —

Wagner, M.: SS+OX-WeM12, 12
Walker, G.: SS+OX-WeM4, 10
Wallace, R.M.: EM+TF+OX+GR-MoM1, **1**; EM+TF+OX+GR-MoM5, 1
Wang, J.: MI+OX-WeA10, 15
Wang, J.-P.: MI+OX-WeA3, **15**
Wang, Y.: OX+SS+TF+MI-MoA10, 7
Wang, Z.-T.: SS+EN+OX-ThM5, 17; SS+EN+OX-ThM9, **18**
Watts, S.: MI+OX-WeA7, 15
Weaver, J.F.: SS+EN+OX-ThM10, **18**
Wei, D.: EM+TF+OX+GR-MoM9, **1**
Wheeler, V.D.: EM+OX-WeA8, 13
Wilhelm, F.: SS+OX-WeM5, 11
Witanachchi, S.: MI+OX-WeA9, 15; OX+EM+MI+NS+TF-MoM1, 2
Wittstock, A.: IS+AS+OX+ET-WeM6, 9
Woicik, J.C.: OX+SS+TF+MI-MoA9, 6
Wöll, Ch.: OX+SS+TF+MI-MoA10, 7
Wood, B.C.: IS+AS+OX+ET-WeM6, 9
Worsley, M.A.: IS+AS+OX+ET-WeM6, 9
Wu, N.: MI+OX-WeA10, **15**

— X —

Xing, G.: EM+OX-WeA3, **13**

— Y —

Yakimov, M.: EM+TF+OX+GR-MoM3, 1
Yakou, F.: SS+OX-WeM5, 11
Yao, K.: OX-TuP3, **8**
Yates, Jr., J.T.: SS+EN+OX-ThM6, 17
Yckache, K.: EM+TF+OX+GR-MoA9, 5
Yesilkoya, F.: EM+OX-WeA9, 13
Yilmaz, D.E.: OX+SS+TF+MI-MoA1, **6**; OX-TuP3, 8
Yoon, Y.: SS+EN+OX-ThM5, 17

— Z —

Zapotok, D.W.: EM+OX-WeA8, 13
Zhang, F.: SS+EN+OX-ThM10, 18
Zhang, K.H.L.: OX-TuP5, 8