Wednesday Afternoon, November 12, 2014

Electronic Materials and Processing
Room: 314 - Session EM-WeA

High-K Dielectrics for 2D Semiconductor
Moderator: Andrew C. Kummel, University of California at San Diego

2:20pm **EM-WeA1 Adding New Functionalities to CMOS Integrated Circuits Via Directed Self-Assembly**, ***Theresa Mayer***, Penn State University **INVITED**

With CMOS nearing the physical limits of scaling, the future of the semiconductor industry is at a critical point. The International Technology Roadmap for Semiconductors identifies the growing need to interface new nanoscale materials and devices with Si CMOS architectures to sustain nanoelectronic circuit scaling (more-*of*-Moore) and to discover entirely new electronic systems (more-*than*-Moore). This talk will describe new directed self-assembly process to position large, diverse, and interchangeable arrays of nanowire sensors or sheets of alternative electronic materials onto fully-processed Si CMOS circuits. The wires or sheets are fabricated off-chip from many different materials tailored for a specific function. Electric-field forces are then used direct different populations of these materials to specific regions of the chip, while also providing accurate registry to a predefined feature on the chip. Following assembly, conventional lithographic processes can then be used to define the nanodevices and connect them to the Si circuit. Several material and device integration examples will be discussed, including the directed assembly of metal-oxide nanowire device arrays as well as monolayer 2D transition metal dichalcogenide crystal materials.

3:00pm **EM-WeA3 Band Gap Engineering of 2D Semiconductor Materials *via* Atomic Layer Deposition of TiOPc on Graphene and MoS_2**, ***Pabitra Choudhury***, New Mexico Institute of Mining and Technology, *A.C. Kummel*, University of California at San Diego

Metal phthalocyanine (MPc) molecules are composed of a metal atom and a surrounding pthalocyanine ligand ring. The metal-ligand interaction and molecule-surface interaction are the two most important parameters, which controls the various physical and chemical properties of this adsorption system of MPc molecules onto the substrate. MPc molecules can potentially be employed for electrostatic doping of non-reactive substrates (for example 2D semiconductor materials), will lead to various applications such as sensors and electronics, and hence MPc become a model system for surface chemistry and nanotechnology. Tytanyl pthalocyanine (TiOPc) is another interesting molecule of pthalocyanine family having anisotropic intermolecular interactions. In this study, TiOPc electrostatic interactions with two nonreactive 2D semiconductor substrates, graphene and MoS_2, were studied. We have carried out first principle density functional theory (DFT) calculations and theoretical analysis to explore the structural and electronic properties of mono- and bi-layer of TiOPc molecule on both graphene and MoS_2. The adsorption of mono- and bi-layer films of TiOPc on graphene shows that there is a net 0.047 electrons and 0.016 electrons per TiOPc molecule charge transfer takes place from the graphene surface, respectively. Conversely, a net amount of 0.058 electrons and 0.029 electrons per TiOPc molecule charge transfer take place to the MoS_2 surface in case of mono- and bi-layer of TiOPc, respectively. Moreover, we find that the bandgaps of graphene/TiOPc(mono-and bi-layer) and MoS_2/TiOPc(mono-and bi-layer) heterostructures decrease with increasing number of TiOPc layers. Our results suggest that the band gap of 2D semiconductors, MoS_2/TiOPc and graphene/TiOPc heterostuctures, could be engineered with atomic layer precision by controlling the number of TiOPc layer deposited on the 2D substrate, which could serve as a potential candidate for both sensor and advanced electronics applications.

3:20pm **EM-WeA4 $HfSe_2$ Thin Films: 2D Transition Metal Dichalcogenides Grown by MBE**, ***Ruoyu Yue***, *A. Barton, X. Peng, N. Lu, R. Addou, S. McDonnell, L. Chen, J.Y. Kim*, University of Texas at Dallas, *L. Colombo*, Texas Instruments, *M. Kim, R.M. Wallace, C.L. Hinkle*, University of Texas at Dallas

The growth of high-quality, layered $HfSe_2$ thin films by molecular beam epitaxy (MBE) on a variety of substrates is demonstrated for the first time. The cross-section of $HfSe_2$ thin films on highly ordered pyrolytic graphite (HOPG) shows the layered structure of crystalline $HfSe_2$ with an atomically sharp interface between the $HfSe_2$ and HOPG, verifying the van der Waals epitaxy. Crystalline $HfSe_2$ thin films with preferred orientation and hexagonal top surface symmetry are characterized by RHEED, STM, and XRD with a measured lattice constant consistent with the theoretical prediction of the 1-T phase. The stoichiometry (Hf: Se) of crystalline $HfSe_2$ on HOPG, measured by XPS, is very close to 1:2 and the in-plane and out-of-plane vibration mode peaks of the 1-T structure of $HfSe_2$ is confirmed by Raman spectroscopy. It is also noted that the crystal quality of the $HfSe_2$ changes as a function of substrate with the best growth results obtained on inert, hexagonal symmetry surfaces. These results indicate that the growth of novel TMDs by MBE is achievable and opens the possibility for exciting new 2D heterostructures and devices.

4:20pm **EM-WeA7 Phonons, Scattering, and Semiclassical Transport Studies in 2D Materials and Devices**, ***Massimo Fischetti***, *W.G. Vandenberghe*, The University of Texas at Dallas **INVITED**

Basic ideas from pseudopotentials and semiclassical-transport will be used to discuss the properties of some novel 2D materials considered for post-Si-CMOS applications. First, it will be shown that in order to scale devices to 5 nm, simple electrostatic scaling laws demand the use of these two-dimensional materials, despite the daunting processing challenges they pose. Graphene will be considered discussing how its outstanding electronic properties become much less interesting when used as a component of some non-ideal structure, such when supported and gated and/or in nanoribbon form. A couple of very interesting ideas will be discussed next: 1. The Bose-Einstein condensation in bilayer systems (motivating UT-Austin's BiSFETs) as an example of how issues of practical implementation may regrettably transform an excellent idea into a pure academic exercise; and 2. Monolayer tin ("stannanane") as a 2D topological insulator with potential applications in spintronics and low-power high-performance devices. Besides discussing its potential electronic properties, the likelihood of actually fabricating such a material will be discussed on the basis of *ab initio* thermodynamics.

5:00pm **EM-WeA9 *In Situ* Transmission Electron Microscopy of Oxides on TMDs**, ***Moon Kim***, *N. Lu, J. Oviedo, X. Peng, J. Wang, G. Lian, A. Azcatl, S. McDonnell, R.M. Wallace*, The University of Texas at Dallas, *S. Vishwanath, H. Xing*, University of Notre Dame **INVITED**

Over the past two years, transition metal dichalcogenide (TMD) materials, as 2-D crystals, have attracted much interest for a wide range of electronic and optoelectronic device applications. Yet, uniform deposition of sub-10 nm dielectrics on 2-D materials remains challenging.There is a great demand for the visualization and analysis of interfaces and defects in 2-D crystals and gate oxides, which play an important role in the growth and properties of heterostructures. Site-specific cross-sectional TEM imaging and associated techniques have become essential in providing detailed atomic scale information. High angle angular dark field (HAADF)-scanning transmission electron microscopy (STEM) can be used to investigate the atomic structure and chemistry of TMD-oxide interfaces and defects. *In-situ* TEM techniques such as heating and electrical/mechanical probing can also provide information regarding the dynamic behavior of the materials/devices of interest.

Herein, we report our results on HfO_2 and Al_2O_3 thin films deposited on MoS_2 by atomic layer deposition and $SnSe_2$ FETs with an Al_2O_3 gate oxide. Our *in-situ* TEM work on 2-D materials will also be presented. Based on our study, a possible growth mechanism of oxides on TMD with different surface treatments has been proposed [1,2]. These unique and effective site-specific and *in-situ* analysis tools can be widely applied to other gate oxides of interest.

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

[1] ACS Nano, **7**, 10354–10361, 2013.

[2] Applied Physics Letters, **104**, 111601, 2014.

5:40pm **EM-WeA11 Effects of Neutron Irradiation of Ultra-Thin HfO_2 Films**, ***Kai-wen Hsu***, University of Wisconsin-Madison, *H. Ren*, Applied Materials, *R.J. Agasie*, University of Wisconsin-Madison, *L. Zhao*, *Y. Nishi*, Stanford University, *J.L. Shohet*, University of Wisconsin-Madison

In order to investigate neutron-induced effects on HfO_2 resistive random-access memory (RRAM), HfO_2 films are subjected to irradiation by neutrons with energies above 1 MeV. Changes in the defect state concentrations of HfO_2 may lead to changes in the states of memory which has the potential to convert a "0" into a "1" in RRAM or vice versa.

Electron-spin resonance (ESR) is used to detect defect-state concentrations of the HfO_2 film deposited on high-resistivity substrates. Additionally, leakage currents of HfO_2 films are also measured to support the ESR data.[1]

Neutron irradiation at low fluence decreases the Pb-type and E' defect levels in ultra-thin HfO_2 films because electrons can fill existing states. These electrons come from electron-hole pairs generated by neutron interactions with silicon and oxygen. Thus, a low fluence of neutrons "anneals" the sample. However, when neutron fluence increases, more neutrons collide with oxygen atoms and cause them to leave the lattice or to transmute into different atoms. This causes the E' state concentration to increase. The changes in the number of defect states lead to changes in leakage currents.

This work was supported by the Semiconductor Research Corporation under Contract 2012- KJ-2359 and by the National Science Foundation under Grant CBET-1066231.

[1]K-W Hsu, H. Ren, R.J. Agasie, S. Bian, Y. Nishi, and J.L. Shohet, *Applied Physics Letters* **104** 032910 (2014)

6:00pm **EM-WeA12 Nucleation of Low Temperature HfO_2 Atomic Layer Deposition on InGaAs using Various Native Oxide Removal Techniques**, ***Tyler Kent***, University of California at San Diego, *K. Tang*, Stanford University, *S. Lee*, *C.Y. Huang*, *V. Chobpattana*, University of California at Santa Barbara, *K. Sardashti*, *M. Edmonds*, University of California at San Diego, *R. Droopad*, Texas State University, *P.C. McIntyre*, Stanford University, *A.C. Kummel*, University of California at San Diego

One of the major obstacles impeding the advancement of III-V MOSFETs is the large density of interfacial trap states (D_{it}) at the high-k/III-V interface. Poor nucleation of the gate oxide can lead to dangling bonds, strained bonds, and metallic bonds which contribute to D_{it}; additionally, low nucleation density requires a thicker oxide to avoid pinholes which increase gate leakage. The nucleation of HfO_2 was studied using tetrakis(ethylmethylamino)hafnium (TEMAH) and H_2O on the InGaAs (001) and InGaAs (110) surfaces at low temperature, 120 ˚C, using atomic layer deposition (ALD). Low temperature ALD reduces subcutaneous oxidation of the channel when this is an activated process. The pulse and purge times of the oxidant and reductant were varied and their impact on the nucleation of HfO_2 were studied by fabricating MOSCAPs and extracting the D_{it} using the full interface surface state model. All samples had 10 cycles of an in-situ pre-ALD surface clean developed by Choptabanna and Carter which utilizes atomic H and TMA. The effectiveness of the ex-situ buffered oxide etch (BOE) was examined by fabricating samples with and without this clean. The BOE was more effective on the (001) samples since the non-BOE samples had a larger D_{it} and a higher C_{max} indicating poor nucleation of the HfO_2. The dispersion in accumulation remained constant indicating the BOE had an immediate effect on the interface, rather than deep traps in the oxide. The BOE and non-BOE (110) samples had a nearly identical $C_{max,}$ $D_{it,}$ and dispersion in accumulation indicating the nucleation of HfO_2 is not as dependent on the BOE as the (001) surface. This result obviates the need for the BOE allowing an all dry process on InGaAs(110) and is likely a result of the inherent stability of the (110) surface compared to the (001) surface.

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