

# Friday Morning, November 1, 2013

## Electronic Materials and Processing

Room: 102 A - Session EM+NS+TF-FrM

### Nanoelectronic Interfaces, Materials, and Devices/Crystalline Oxides on Semiconductors

**Moderator:** A. Demkov, University of Texas at Austin, K. Kavanagh, Simon Fraser University, Canada, S. Zollner, New Mexico State University

8:20am **EM+NS+TF-FrM1 Growth and Properties of MoS<sub>2</sub> and MoX<sub>y</sub> (X=S,Se and alloys thereof, y=1.5...2) on SiO<sub>2</sub> and Cu(111).** *L. Bartels*, University of California, Riverside **INVITED**

I will present experimental methods for the preparation of MoS<sub>2</sub> and MoX<sub>y</sub> (X=S,Se and alloys thereof, y=1.5...2) on SiO<sub>2</sub> and Cu(111). We investigated the films' structures by low energy electron microscopy and variable temperature scanning tunneling microscopy. The optical properties were probed in the range between room temperature and 5K. For sulfur-selenium alloys, we find an optical bandgap that is tunable between the values observed for pure MoS<sub>2</sub> and MoSe<sub>2</sub> monolayers. Investigation of the chemical properties of the materials show high affinity of the sulfur-deficient materials for adsorption of oxyanion species.

9:00am **EM+NS+TF-FrM3 Tuning Thermoelectric Power Factor in Pnictogen Chalcogenides through S and Cl Doping.** *R.J. Mehta, F. Devender*, Rensselaer Polytechnic Institute, *R.P. Ramprasad*, University of Connecticut, *D. Parker, D.J. Singh*, Oak Ridge National Laboratory, *T. Borca-Tasciuc, G. Ramanath*, Rensselaer Polytechnic Institute

High figure of merit (ZT) thermoelectric materials are attractive for solid state refrigeration of nanoelectronic devices. ZT enhancement is an exacting challenge because it entails achieving high Seebeck coefficient  $\alpha$ , high electrical conductivity  $\sigma$  and low thermal conductivity  $k$ , while these properties are usually unfavorably coupled. We recently demonstrated 25-250% ZT increases in pnictogen chalcogenides [1] by combining sub-atomic percent S doping-induced power factor  $\alpha^2\sigma$  increases [2], and nanostructuring-induced decrease in  $k$ . Here, we show that S and Cl doping alter the electronic band structure near the Fermi level, impacting carrier concentration and mobility pnictogen chalcogenides. In Sb<sub>2</sub>Te<sub>3</sub>, we find that S doping increases  $\alpha$  by suppressing Sb-antisite defect formation. In our quest for optimizing S concentration, we discovered that adventitious Cl confounds the trend between S doping and  $\alpha^2\sigma$ . Synthesis with Cl-free precursors eliminates this effect and we obtain the remarkable result of both  $\alpha$  and  $\sigma$  increasing with S content, contrary to the usually observed inverse correlation between  $\sigma$  and  $\alpha$ . Additionally, we find that Cl doping at a fixed S content result in maxima of these properties at slightly different concentrations. Extended X-ray absorption fine structure analyses reveal that Cl occupies interstitial sites while S occupies Bi sites. We show that these results, together with first principles calculations, provide a framework for obtaining ZT>1.5 by optimizing doping and stoichiometry in pnictogen chalcogenides through the manipulation of the electronic structure near the Fermi level.

1. R.J. Mehta, Y. Zhang, C. Karthik, B. Singh, R.W. Siegel, T. Borca-Tasciuc, G. Ramanath, *Nat. Mater.* 11, 233-240 (2012).

2. R.J. Mehta, Y. Zhang, H. Zhu, D.S. Parker, M. Belley, D. J. Singh, R. Ramprasad, T. Borca-Tasciuc, G. Ramanath, *Nano Lett.* 12, 4523-4529 (2012).

9:20am **EM+NS+TF-FrM4 From High-k Dielectrics to Functional Oxides on Silicon: Find More than Moore in More Moore.** *J. Fompeyrine*, IBM Research - Zurich **INVITED**

Research on oxide materials is a field of intense investigations, in particular for Information and Communication Technologies. This research has been driven since many years from a scientific and a technological perspective.

25 years ago, a scientific community did nucleate around high-Tc superconductivity, and expanded its research interest towards other materials. The motivation remained to understand the fundamentals of the properties of oxides thin films. To reach such an ambitious goal, physical phenomena had to be studied in clean systems, because of the strong coupling between properties and microstructure in oxide thin films. Rather than focusing on obtaining "bulk like" properties, it is more important to control their microstructural characteristics. To that respect, molecular beam epitaxy (MBE) is a well suited technique, although requiring specific design and components.

In a second recent phase, the quest for a replacement gate dielectric in transistors has been a powerful driver to investigate high quality oxide thin films. Replacing SiO<sub>2</sub> with HfO<sub>2</sub> in MOSFETs was a breakthrough for the microelectronic industry. This research is not over, since the replacement of silicon with compound semiconductors could take place within the next years. It will require changes on the materials structure and sequence to be used in dielectric stacks. Nevertheless, because of its ability to control interfaces and to easily combine analytical capabilities with deposition reactors, MBE is also a powerful learning tool to understand the chemistry of interfaces between oxide and semiconductors [2].

The motivation to *understand* or to *exploit* the physical properties of oxide thin films is quite different, but there is clearly cross-fertilization between the various communities. The best example one can give is the development of single crystalline oxides grown directly on semiconductor surfaces. Initially stimulated by the quest for a new gate dielectric, researchers are now able to grow high quality epi-oxide films onto silicon, that can be used as nucleation layers for other "functional" oxides. As expected, the combination of silicon microfabrication techniques with the capability to grow crystalline directly on silicon opens up perspectives for devices exploiting oxide properties with an improved efficiency [3].

The goal of my presentation is to review selected examples of the three phases mentioned, and to highlight exciting research directions in this domain.

[1] J.-P. Locquet et al, *Nature* **394**, 453 (1998)

[2] M. El Kazzi et al, *Appl. Phys. Lett.* **99**(5), 052102 (2011)

[3] S. Abel et al, accepted for *Nature Communications* (2013)

10:00am **EM+NS+TF-FrM6 High Performance Infrared Sensing Using Colloidal Quantum Dots Monolithically Integrated with a Silicon Readout IC.** *J.S. Lewis, E.J.D. Klem, C.W. Gregory, G.B. Cunningham, S. Hall, D.S. Temple*, RTI International, *A. D'Souza, E. Robinson*, DRS Sensors and Targeting Systems, *N. Dhar, Darpa, Mto, P.S. Wijewarnasuriya*, Army Research Laboratories

Low cost is frequently cited as a driver for hybrid and organic electronic devices, but in fact very few applications allow a sacrifice in performance. Here we present a hybrid organic/inorganic device that rivals high performance InGaAs detectors for short wave infrared (SWIR) imaging, and show that the hybrid devices based on colloidal quantum dots (CQDs) offer substantial benefits with respect to wavelength range, integration with Si readout integrated circuits (ROICs), and of course cost. We will present the results for detectors fabricated on passive Si substrates as well as for 320 x 10 arrays fabricated on ROICs. We will discuss recent advances in device architecture and processing that resulted in measured dark currents of 3 nA/cm<sup>2</sup> at room temperature, with sensitivity to 1.7  $\mu$ m. We will show other devices with spectral sensitivity that extends from UV to 2.2  $\mu$ m. For the ROIC-integrated devices we will show dark currents <10 nA/cm<sup>2</sup>. The most significant advantage of the CQD technology is ease of fabrication. The devices are fabricated directly onto the ROIC substrate at low temperatures compatible with ROICs, and arrays can be fabricated at wafer scale. This combination of high performance, dramatic cost reduction, and multi-band sensitivity makes the technology attractive for a variety of applications, which we will discuss.

10:20am **EM+NS+TF-FrM7 Epitaxial Integration of Magnetic Insulators on Silicon.** *A. Posadas*, University of Texas at Austin **INVITED**

In recent years, there has been remarkable progress in the growth of complex magnetic oxides in thin film form. Many novel physical properties such as colossal magnetoresistance, multiferroicity, tunneling magnetoresistance effects, and room-temperature ferromagnetism in dilute magnetic oxides have emerged and are ongoing sources of new ideas and systems for applications in the manipulation of the spin of the electron. Part of this field of complex magnetic oxides are materials that are both ferromagnetic and electrically insulating, a relatively rare combination compared to conducting magnetic materials. Such materials are envisioned to serve as spin filtering tunnel barriers, selectively allowing one particular spin to pass through over the other. In this talk, we will focus on insulating ferromagnets with particular emphasis on their growth on silicon substrates. Three insulating ferromagnetic materials systems will be described including the challenges of growing them in epitaxial form on silicon: EuO, strained LaCoO<sub>3</sub>, and Co-substituted SrTiO<sub>3</sub>. First we describe the use of Eu metal to form a chemical template on Si, similar to the use of 1/2 monolayer of Sr for the growth of SrTiO<sub>3</sub> on Si. We then describe various paths for the growth of EuO on this Eu template. We then describe the use of SrTiO<sub>3</sub> on Si as a pseudo-substrate for growing LaCoO<sub>3</sub>, normally non-magnetic but which becomes ferromagnetic as a result of epitaxial strain, onto silicon. Strain-coupled magnetoresistivity modulation of such LaCoO<sub>3</sub>/SrTiO<sub>3</sub>/Si

heterostructures will be described. Finally, we describe the growth on Si and properties of Co-substituted SrTiO<sub>3</sub>, a ferromagnetic insulator at room temperature that may find potential application in spintronics devices. We discuss the effect of Co concentration on the structural and magnetic properties and also describe theoretical calculations indicating magnetism resulting from cobalt-oxygen vacancy centers.

11:00am **EM+NS+TF-FrM9 Understanding the Origin of the Dead-layer at the La<sub>0.66</sub>Ca<sub>0.33</sub>MnO<sub>3</sub>/SrTiO<sub>3</sub> Interface: A Grazing Incidence X-ray Diffraction and Hard X-ray Photoelectron Spectroscopy Study.** *J. Rubio-Zuazo*, SpLine Spanish CRG beamline at the European Synchrotron Radiation Facility, France, *A. de Andres*, Institute Materials Science of Madrid-CSIC, Spain, *G.R. Castro*, SpLine Spanish CRG beamline at the European Synchrotron Radiation Facility, France

La<sub>1-x</sub>Ca<sub>x</sub>MnO<sub>3</sub>-type perovskite-manganese oxides exhibit a wide variety of interesting physical properties which originate from mutual coupling among spin, charge and lattice degrees of freedom. The perovskite-manganese oxides have, in the Ca doping range between 0.15 and 0.5, a ferromagnetic-paramagnetic (F-M) phase transition accompanied by a metal-insulator (M-I) transition that results in a colossal magneto-resistance behaviour. In bulk La<sub>0.66</sub>Ca<sub>0.33</sub>MnO<sub>3</sub> (LCMO), the transition temperature T<sub>C</sub>, T<sub>MI</sub> rises for 33% Ca doping level reaching values close to room temperature. We have studied a series of epitaxial LCMO films with thickness between 2.4 and 27 nm grown on SrTiO<sub>3</sub>(001) (STO). The magnetic measurements show a severe decrease of T<sub>C</sub> as the film thickness is reduced below 2.4 nm. The atomic structure, as obtained by grazing incidence X-ray diffraction shows that the LCMO films adopt the substrate STO in-plane lattice parameter (1% mismatch) inducing a pseudomorphic growth. The 27 nm film presents a bulk-like crystal structure and space group, but also magneto-transport bulk behavior, while the 2.4 nm film shows a different crystallographic space group and the film is an insulator within the whole temperature range (i.e., no T<sub>C</sub> transition is present). The structure, also observed at the LCMO-STO interface of thicker LCMO films, is based on an anti-correlation between Mn-O octahedra along the three crystallographic directions. This could explain the origin of anomalous magneto-transport or dead-layer behavior in LCMO hetero-structures. These results evidence the strong influence of the interface. The mismatch may be accommodated by the formation of facets, by structural defects or by diffusion-induced changes in stoichiometry or oxygen vacancies. However, in our study no facets were found, but bi-dimensional in-plane reciprocal space maps show a clear lattice relaxation of about 1% suggesting the existence of a stoichiometry change as strain relaxation mechanisms. To understand the relaxation mechanisms a non-destructive compositional depth profile analysis was performed using the Hard X-ray Photoelectron Spectroscopy (HAXPES). The data was fitted with a model in which the La is diffused into the interface, while the Ca is segregated to the surface. The substitution of the Ca<sup>2+</sup> cation for La<sup>3+</sup> results in an LCMO lattice enlargement reducing the mismatch between LCMO and STO. Hence, the first La enriched layer close to the interface will grow pseudomorphic, and in the successive layer Ca concentration increase and consequently a lattice parameter reduction until the bulk lattice parameter is achieved, without energy strain accumulation.

11:20am **EM+NS+TF-FrM10 Monolithic Integration of Rare-Earth Oxides and Semiconductors for On-Silicon Technology.** *R. Dargis*, *A. Clark*, *F.E. Arkun*, *D. Williams*, *R. Smith*, Translucent Inc., *A. Demkov*, *A. O'Hara*, University of Texas at Austin **INVITED**

Increasingly there is a need to integrate functional semiconductors such as III-V's or III-N with low cost manufacturing attainable through existing silicon based technology. Scalability is one of the main issues here, because the cost savings from the Si processing can be only realized if 150-200 mm diameter substrates are used. This could be achievable by formation of the semiconductor layers on the silicon substrates. However, direct growth of the device-grade layers on silicon in many cases is impossible due to difference in crystal structure, huge lattice and thermal expansion mismatch or even chemical reactivity of the compounds. The most of the problems can be solved by introduction of buffer layers that help for stress management. Among the materials of consideration, epitaxial rare-earth oxides have several benefits: beside their crystallographic properties that allow them to be used for stress managing layers, their electrical, optical and thermal properties (good balance between bandgap and electrical permittivity, moderate refraction index, reasonable thermal conductivity) make them useful for additional functions such as electric field suppression layers, high reflectivity heterostructures, optically active heterostructures. In this presentation, some approaches of integration of the epitaxial rare-earth oxides into the emerging advanced semiconductor on silicon technology will be demonstrated. Engineering of the interface between the oxides and the substrate from single crystal to amorphous by controlling the epitaxy process parameters opens way for formation of relaxed or pre-stressed structures that can be used as a template for the growth of III-N

semiconductors on silicon. Polymorphism of some of the rare-earth oxides allows to manipulate their crystal structure from cubic to hexagonal and to grow buffer layers that can be used for germanium on insulator on silicon. Additionally, multilayer silicon-oxide distributed Bragg reflectors with high reflectivity at designed wavelength can be grown with only several pairs of the layers and can be used for light emitting devices.

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