Thin Film
Room 102B - Session TF+SA+MI-TuM
Thin Films for Synchrotron and Magnetism Applications

Moderators: Joshua Ballard, Zyvex Labs, Divine Kumah, North Carolina State University

8:00am **TF+SA+MI-TuM1 Achieving High-Temperature Ferromagnetic Topological Insulator by Proximity Coupling***, **Valeria Lauter,*** Oak Ridge National Laboratory

Topological insulators (TIs) are insulating materials that poses conducting surface states protected by time-reversal symmetry, wherein electron spins are locked to their momentum. This exclusive property offers novel prospects for creating next-generation electronic and spintronic devices, including TI-based quantum computation. Introducing ferromagnetic order into a TI system without compromising its distinctive quantum coherent properties could lead to a realization of a number of innovative physical phenomena. In particular, achieving robust long-range magnetic order at the TI surface at specific locations without introducing spin scattering centers could open up new potentials for devices. Here, we demonstrate topologically enhanced interface magnetism by coupling a ferromagnetic insulator (FMI) to a TI (Bi_2Se_3); this interfacial ferromagnetism persists up to room temperature, even though the FMI (EuS) is known to order ferromagnetically only at low temperatures (< 17 K). The induced magnetism at the interface resulting from the large spin-orbit interaction and spin-momentum locking property of the TI surface is found to greatly enhance the magnetic ordering (Curie) temperature of the TI/FMI bilayer system. Due to the short range nature of the ferromagnetic exchange interaction, the time-reversal symmetry is broken only near the surface of a TI, while leaving its bulk states unaffected [1]. The topological magneto-electric response originating in such an engineered TI could allow for an efficient manipulation of the magnetization dynamics by an electric field, providing an energy efficient topological control mechanism for future spin-based technologies. Work supported by U.S. DOE, Office of Science, BES.

[1]F. Katmis, V. Lauter, F. Nogueira, B. Assaf, M. Jamer, P. Wei, B. Satpati, J. Freeland, I. Eremi[5], D. Heiman, P. Jarillo-Herrero, J. Moodera, “Achieving high-temperature ferromagnetic topological insulating phase by proximity coupling”, *Nature 2016*

8:20am **TF+SA+MI-TuM2 Soft X-ray Induced Spin Crossover Transition at Room Temperature***, **Paulo Costa**, X. Zhang, S. Beniwal,* University of Nebraska-Lincoln*; A.T. N'Diaye,* Lawrence Berkeley National Laboratory*; J-F. Létard,* Université de Bordeaux*; P.A. Dowben, A. Enders,* University of Nebraska-Lincoln

The spin crossover Fe(II) complex (SCO) of the type $[Fe(H_2B(pz)_2)_2(bipy)]$ has been previously shown to exhibit spin state transitions between its low spin (LS) and high spin (HS) states as a response to external stimulus such as electric fields, temperature changes, and light. It is well established that this SCO complex exhibits a crossover from its LS state to the HS state if the temperature is increased above approximately 150 K. It is demonstrated here that this spin crossover can be suppressed by mixing the SCO with strongly dipolar *p*-benzoquinonemonoimine zwitterion (PZI) molecules, so that unlike before, the LS state still prevails even at room temperature (RT). With the metastable LS state now locked in at RT, a spin state transition to the HS state can now be triggered optically by soft X-rays over a relatively short time of several minutes. This process is fully reversible, as cooling the mixture to 78 K has been shown to de-excite it back to its original LS state. Experiments were performed using X-ray absorption spectroscopy measurements (XAS) with synchrotron radiation tuned to the Fe L_3 absorption edge as well as accompanying magnetic moment measurements taken by a superconducting quantum interference device (SQUID). The effects of temperature, photon flux, and the stoichiometric ratio between SCO and PZI in the mixture were systematically studied, and the results will be presented here. This study provides a demonstration that the spin crossover transition temperature can be tailored to create a material that exists in a meta-stable LS state at RT wherein spin states can then be switched optically.

8:40am **TF+SA+MI-TuM3 Probing Thermochromic Phase Transitions in ALD VO_2 using Synchrotron Radiation***, **Alexander Kozen,*** U.S. Naval Research Laboratory*; H. Joress,* Cornell University*; V.D. Wheeler, C.R. Eddy, Jr.,* U.S. Naval Research Laboratory

VO_2 is a thermochromic material, one class of “smart materials” that are receiving considerable interest due to a sharp semiconductor to metal (S-M) phase transition that occurs at a specific, material dependent temperature (T_c = 68˚C for VO_2). The S-M transition occurs as a result of a phase transition between a semiconducting monoclinic phase below T_c and a metallic tetragonal phase above T_c. While VO_2 has been widely utilized as a microbolometer material for IR detectors, current deposition processes used to fabricate thin film VO_2 (PLD, MBE, sputtering) are not adequate to realize complex device architectures. Use of ALD to deposit VO_2 thin films allows for uniform, low temperature coating of large area 3D substrates that could open the door to new applications.

Temperature dependent *in-situ* grazing incidence synchrotron XRD was utilized to probe lattice strain and structural reordering in both as-deposited (amorphous) and annealed (polycrystalline) ALD VO_2 thin films during the S-M transition. GIXRD allows us to selectively sample the bulk or the film-substrate interface of thin ALD films with excellent depth resolution, while the high flux provided by the synchrotron (10^{12} photons/s) enables fast data collection. Initial results show that as-deposited ALD VO_2 films are polycrystalline at the VO_2-sapphire interface, while the bulk of the as-deposited VO_2 is amorphous. Annealing VO_2 on sapphire in an oxygen-rich environment forms a fiber-textured polycrystalline VO_2 film with a more pronounced S-M transition. We will discuss how substrate selection, ALD growth and processing conditions, and film thickness influence VO_2 morphology and/or structure and relate these materials properties to device data.

The authors wish to acknowledge Cornell University's CHESS synchrotron facilities for GIXRD work and The Office of Naval Research for support. Dr. Kozen acknowledges support by the ASEE-NRL postdoctoral fellows program.

9:00am **TF+SA+MI-TuM4 Standing-wave Synchrotron Photoemission Studies of Electronic Structure in $SrTiO_3$-$LaCrO_3$ Superlattices***, **Ryan Comes,*** Auburn University*; S.C. Lin,* University of California, Davis*; C.T. Kuo,* Lawrence Berkeley National Laboratory (LBNL)*; L. Plucinski,* FZ Juelich*; S. Spurgeon,* Pacific Northwest National Laboratory*; D. Kepaptsoglou, Q. Ramasse,* SuperSTEM*; J.E. Rault,* Synchrotron SOLEIL*; S. Nemsak,* Forschungszentrum Juelich GmbH, Germany*; C. Fadley,* Lawrence Berkeley National Laboratory (LBNL)*; P.V. Sushko, S.A. Chambers,* Pacific Northwest National Laboratory

The polar discontinuity at the interface between $SrTiO_3$ (STO) and $LaCrO_3$ (LCO) has been shown to produce a varying band alignment between the two materials with a built-in potential gradient.[1] We have recently shown that this built-in potential gradient can be harnessed to induce a polarization in STO-LCO superlattices through interface engineering.[2] This work demonstrated that by controlling interfacial termination between layers we can induce a built-in polarization in STO, with Ti cations displaced off-center in surrounding oxygen octahedra. To further study this system, we have synthesized a series of STO-LCO superlattices with varying interfacial and surface terminations for synchrotron standing-wave x-ray photoemission measurements.[3] These measurements make use of Bragg diffraction from the superlattice to induce an x-ray standing wave that can be scanned across a single period of the superlattice. Through careful material design, we have achieved the strongest standing-wave effects to date, enabling angle-resolved photoemission measurements of electronic dispersion in both the STO and LCO layers of the material. Density functional theory models of the electronic structure of the superlattices are used to corroborate our experimental results with the expected behavior. Monochromated, aberration-corrected scanning transmission electron microscopy electron energy-loss spectroscopy (STEM-EELS) measurements also enable further studies into changes in electronic behavior at interfaces.

[1] S.A. Chambers, L. Qiao, T.C. Droubay, T.C. Kaspar, B.W. Arey, and P.V. Sushko, Phys. Rev. Lett. **107**, 206802 (2011).

[2] R.B. Comes, S.R. Spurgeon, S.M. Heald, D.M. Kepaptsoglou, L. Jones, P.V. Ong, M.E. Bowden, Q.M. Ramasse, P.V. Sushko, and S.A. Chambers, Adv. Mater. Interfaces, (2016). DOI: 10.1002/admi.201500779

[3] A.X. Gray, C. Papp, B. Balke, S.-H. Yang, M. Huijben, E. Rotenberg, A. Bostwick, S. Ueda, Y. Yamashita, K. Kobayashi, E.M. Gullikson, J.B. Kortright, F.M.F. de Groot, G. Rijnders, D.H.A. Blank, R. Ramesh, and C.S. Fadley, Phys. Rev. B **82**, 205116 (2010).

9:20am **TF+SA+MI-TuM5 *In Situ* Synchrotron X-ray Studies of Complex Oxide Thin Film Growth*, Dillon Fong,*** Argonne National Laboratory**INVITED**

Functional materials based on complex oxides in thin film form offer new and exciting strategies for meeting many of our outstanding energy challenges through systematic control of layer sequencing, strain, etc. However, the synthesis of such oxide films can be a major challenge even when utilizing reactive molecular-beam epitaxy (MBE), a powerful deposition technique that allows the construction of materials atomic plane by atomic plane. To understand the fundamental physics of oxide growth by reactive MBE, we present *in situ* surface x-ray diffraction results on the growth of $SrTiO_3$ and SrO-$SrTiO_3$ thin films on (001)-oriented $SrTiO_3$ substrates. For homoepitaxy, we compare sequential deposition (alternating Sr and Ti monolayer doses) with that of co-deposition of Sr and Ti, both in a background of oxygen pressure, and observe drastically different growth pathways due to the presence of a TiO_2 double layer. For heteroepitaxial growth of Ruddlesden-Popper SrO-$SrTiO_3$ films, we find that layers rearrange dynamically, resulting in layer sequences distinct from the shutter sequence. In general, the starting surface structure and composition, in combination with local thermodynamic considerations, strongly influence our ability to atomically construct new complex oxides.

Work at Argonne, including the Advanced Photon, is supported by the U.S. Department of Energy.

11:00am **TF+SA+MI-TuM10 Probing CVD Growth Mechanisms of SiC with *In Operando* Synchrotron-based X-ray Diagnostics*, Philip DePond,*** *A.A. Martin, J.H. Yoo, M. Bagge-Hansen, J. Lee, S. Elhadj, M. Matthews, T. van Buuren,* Lawrence Livermore National Laboratory

Laser chemical vapor deposition (LCVD) of ultra-hard coatings, such as SiC, offers sub-mm spatial control over composition and phase, while addressing multiple growth processes under the same conditions for comparison. Normally, optimization requires extensive and costly “cook and look” experiments. Using an in situ approach instead, we develop fundamental insights into the growth mechanisms to unravel the complex roles of deposition parameters. We have conducted a series of in operando synchrotron-based X-ray absorption experiments that interrogate the LCVD growth region during growth. SiC was grown in a compact, portable CVD system from tetramethylsilane using a CW 532nm YAG to achieve laser-based pyrolytic precursor decomposition. We will present the results of Si K-edge (1.8keV) X-ray absorption near-edge structure (XANES) measurements conducted concurrently for the film during LCVD growth with an emphasis on the effects of variation of temperature, flow, substrates, and pressure conditions.

11:20am **TF+SA+MI-TuM11 Unusual Effects in Organic Thin Film Growth as Revealed by the Use of *In Situ* Real Time Synchrotron X-ray Techniques*,*** *R.K. Nahm, H.J. Bullen, T. Suh,* ***James Engstrom,*** Cornell University

The effects of molecular scale events on the growth of crystalline thin films has been long been an active area of research as the resulting thin film properties depend sensitively on the microstructure. The growth of high quality, smooth thin films in the vast majority of these systems is favored at low rates of growth and high substrate temperatures. Here we report on the growth of thin films of tetracene, an organic semiconductor that possesses one less aromatic ring as compared to the much more studied pentacene. We examine the growth on SiO_2 using *in situ* real time X-ray synchrotron radiation and *ex situ* atomic force microscopy (AFM). First, using *in situ* X-ray reflectivity, we observe a transition from 3D island growth to 2D layer-by-layer growth as the growth rate of tetracene is *increased* on SiO_2 at room temperature, T_s ~ 30 °C. This unusual phenomenon, 2D growth favored at higher rates, has not been observed in previous work with pentacene, despite the similarities between these two molecules. Results from AFM indicate that tetracene may tend to quickly traverse “upwards” on thin film features such as the edges of islands, making these thin films susceptible to reorganization during and/or after growth. Thus, at sufficiently high rates of growth the rate of admolecule attachment at the tetracene island/SiO_2 substrate edges effectively outcompetes the rate of upward step-edge transport, and 2D growth results. We find additional evidence for this mechanism by examining the effect of substrate temperature. In particular we find that the transition to 2D growth occurs at a lower rate of growth at a substrate temperature of T_s ~ 0 °C, consistent with suppression in the rate of upward transport at lower values of T_s. Finally, we have also examined the evolution of the thin film crystal structure in real time using *in situ* grazing incidence X-ray diffraction. Many thin film organic semiconductors are known to crystallize in different structures, and tetracene is no exception. At room temperature we find that first a thin film phase grows, then, after a delay, a bulk phase begins to grow, while the growth of the thin film phase saturates. We also find that the film thickness at which X-ray scattering from the bulk phase becomes apparent is found to vary with deposition rate. These phenomena are also dependent on substrate temperature. For example, for the range of thin films thicknesses examined, we found no evidence for growth of the bulk phase at the lower substrate temperature, T_s ~ 0 °C. These results highlight the potential complexity of crystalline thin film growth in what appears to be a very simple system, tetracene on SiO_2.

11:40am **TF+SA+MI-TuM12 Understanding the Effect of Nitrogen Plasma on Plasma Assisted Atomic Layer Epitaxy of InN Monitored by Real Time GISAXS*, Neeraj Nepal,*** *V. Anderson, S.D. Johnson, D.J. Meyer, B.P. Downey, A.C. Kozen,* US Naval Research Laboratory*; Z.R. Robinson,* SUNY College at Brockport*; D.R. Boris, S.C. Hernández, S.G. Walton,* US Naval Research Laboratory*; K.F. Ludwig,* Boston University*; C.R. Eddy, Jr.,* US Naval Research Laboratory

III-N semiconductors have found application in a variety of technologies such as high power transistors, emitters, detectors, and solar-cells. The relatively high growth temperature of common III-N synthesis techniques has impeded further development and application of the materials due to challenges with miscibility gaps and strain related to thermal expansion mismatch with non-native substrates. To address these challenges, Plasma assisted atomic layer epitaxy (PA-ALE) offers a new approach to low temperature III-N growth and can be used to epitaxially grow InN by using alternative pulses of trimethylindium and nitrogen plasma [1]. Since growth using this technique is far from thermodynamic equilibrium, understanding how nitrogen plasma affects nucleation and growth kinetics is essential for development.

Real-time grazing incidence small angle x-ray scattering (GISAXS) measurements at the Cornell High Energy Synchrotron Source were used to study the effect of variation in nitrogen plasma pulse conditions on PA-ALE of InN at 250 °C. Current results show the evolution of GISAXS characteristics such as the correlated peak (CP) length scale in the Yoneda Wing (YW) directly relates to the surface roughness, impurities, and electrical properties of the material. During the initial cycles of InN growth, the diffuse specular reflection broadens and CPs start to evolve along the YW with different correlated length scales. For the nitrogen plasma pulse time (t_p) of 15 seconds, the CPs have two different correlated length scales of 33.36 and 8.38 nm. With increasing t_p to ≥ 20s (the empirically optimal pulse length), a YW with only one CP evolves and the longest correlated length scale of 11.22 nm is for $T_p = 25s$. The correlated length scale of this single CP decreases to 10.75 nm for $t_p = 30s$. Additionally at $t_p = 25s$, the growth rate is largest (0.035nm/cycle – consistent with previously reported self-limited growth [1]) with root mean square surface roughness and carbon impurity at or below AFM and XPS sensitivity limits, respectively. The nature of GISAXS CP correlated length scale directly relates to the material quality. GISAXS also shows that the N_2/Ar flow ratio significantly affect the nucleation and growth of InN. Based on various *ex situ* characterization methods, the quality of the PA-ALE grown films is similar or better than the material grown by conventional growth methods, for example, molecular beam epitaxy at higher temperature (>400 °C).

[1] Nepal et al., Cryst. Growth and Des. **13**, 1485 (2013).

12:00pm **TF+SA+MI-TuM13 Spintronics Based on the Chiral Induced Spin Selectivity (CISS) Effect*, Yossi Paltiel,*** The Hebrew University, Israel*; R. Naaman,* The Weizmann Institute of Science, Israel

The high level of energy dissipation associated with the present semiconductor-based integrated-circuit technology limits the operating frequency of the devices. Therefore there is interest in new concepts that may solve this problem. One such concept that attracts considerable attention nowadays combines spins with electronics (spintronics). In principle, the application of spintronics should result in reducing power consumption of electronic devices and efficiency should be closer to the thermodynamic limit.

Two major issues complicate the use of spintronics; material problems and the inefficiency in producing spin-polarized current. Spintronics devices usually require the use of complicated structures of magnetic material layers and the need for permanent magnetic layers puts constrains on the miniaturization of these devices. In addition, high currents are required to produce highly polarized spin current which results in induced heating.

We present a new concept in which spin current is produced by using the spin selectivity in electron transport through chiral molecules, termed Chiral-Induced Spin Selectivity (CISS). The CISS effect allows realization of simple local and power efficient spintronics devices. Studying the CISS effect, we found that chiral molecules, especially helical ones, can serve as very efficient spin filters at room temperature, with no need for a permanent magnetic layer. Recently, by utilizing this effect we demonstrated a simple magnetless spin based magnetic memory. Moreover, we show that when chiral molecules are adsorbed on the surface of thin ferromagnetic film, they induce magnetization perpendicular to the surface, without the application of current or external magnetic field.

The CISS-based spintronics technology has the potential to overcome the limitations of other magnetic-based memory technologies and to facilitate the fabrication of inexpensive, high-density memory and other spintronics elements.

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