



Users Meeting

Advanced Photon Source
Center for Nanoscale Materials
Electron Microscopy Center

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Thematic Workshop B: Emergent Interfacial Phenomena

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Heterostructures in which different materials are layered together display a range of emergent phenomena, which can be controlled through effects such as geometric confinement and interface structure. Both of these effects can lead to charge transfer and band structure modification giving rise to novel behavior. Understanding and control of these phenomena require advanced deposition and characterization methods, as well as state-of-the-art modeling and theory. This full-day workshop provided a forum for presentations and discussions of current research advances in this important topical area with a focus on research aimed at obtaining a fundamental understanding of the role that microstructure, composition, chemistry and interfaces (including laterally-confining surfaces) play in controlling the emergent phenomena in heterostructures. The workshop covered both experimental and theoretical studies, including the use of *in situ* and *ex situ* characterization and property measurement, and theory and simulations. Speakers from all major sectors of research - academic, national laboratory, and industrial - underscored the breadth as well as importance of this research area, both from a fundamental scientific point of view as well as for emerging and future applications.

Prof. Charles Ahn (Yale) started the workshop by presenting his group's recent work on magnetoelectric coupling in multiferroic heterostructures. Multiferroic materials have been the focus of intense research as the coupling between strain, magnetization, and polarization makes possible new behavior and new functionalities. However, single-phase multiferroic materials, such as BiFeO₃, have a very low magnetoelectric coupling. By combining a ferro- or ferri-magnetic material, such as Fe₂O₃, with a ferroelectric material, such as BaTiO₃, heterostructures with a net larger magnetoelectric coupling may be designed and synthesized. This requires state-of-the-art deposition systems for atomic control of the interfaces, which for oxide materials means oxide molecular beam epitaxy (MBE). Prof. Ahn showed results from Pb[Zr_xTi_{1-x}]₂O₇/La_{1-x}Sr_xMnO₃ (PZT/LSMO) heterostructures grown on SrTiO₃ substrates. PZT is a piezoelectric in which strain or an applied voltage induces a ferroelectric polarization, and LSMO has a phase transition between an antiferromagnetic (AFM) insulator and a ferromagnetic (FM) metal as function of x. The idea with this structure was to control the magnetization in LSMO by inducing polarization in PZT – depending on the interface structure, polarization in PZT will charge accumulation or charge depletion in the LSMO and cause a transition between the AFM and FM states. This is then a path to control the magnetization using electric fields. Magnetoelectric coupling values were two orders of magnitude larger than intrinsic values. The top layer of LSMO was found to undergo changes between AFM and FM alignment relative the next layer LSMO.

Prof. Christian Binek (Nebraska) spoke about electric control of exchange bias. This is a phenomenon that occurs when a ferromagnet is placed in contact with an antiferromagnet. By annealing in a magnetic field the interactions between the antiferromagnet and the ferromagnet lead to an effective unidirectional field on the ferromagnet. The origin of this effective field is the coupling between magnetic moments at the interface between the two materials. The

phenomenon is very important in applications – it is used to control reference magnetic layers in read heads in hard disc drives, as well as in magnetic random access memories. However, once the system has been annealed, the resulting exchange bias cannot be altered reversibly. Prof. Binek's group has demonstrated that in Cr_2O_3 /ferromagnet heterostructures the exchange bias can be controlled by electric fields. Cr_2O_3 is a magnetoelectric antiferromagnet, in which the antiferromagnetic ordering can be affected by electric fields. Because of the structure of Cr_2O_3 , the top (0001) surface on epitaxially grown samples can be brought in a single-domain state in which all surface magnetic moments are aligned. This gives rise to an (out-of-plane) exchange bias on a ferromagnet deposited on top of the Cr_2O_3 . By applying an external electric field, the Cr_2O_3 surface magnetization can be reversed, leading to an observed change in sign of the exchange bias. This effect is observed at room temperature and opens the possibility for interesting device applications.

Prof. Mitra Taheri (Drexel) then spoke on her group's research on *in situ* TEM observations of polarization switching in BiFeO_3 . By using a sample holder that allows for *in situ* biasing with an in-plane electric field, the domain structure and real-time switching behavior can be directly observed. Very different switching behavior and relaxation times are observed for different domains, and the domain motion continues after a voltage pulse that initiates the domain motion. The relaxation mechanism and the precise nature of the switching (ferroelastic or ferroelastic mediated switching) are the subjects of future studies.

The last presentation of the morning was by Prof. Susanne Stemmer (UC Santa Barbara). Her presentation focused on MBE growth of high-mobility SrTiO_3 . While MBE grown GaAs can achieve mobilities in the many millions of cm^2/Vs , MBE grown SrTiO_3 achieves mobilities that are many orders of magnitude smaller. High defect concentrations – impurities, high-energy deposition defects – limit the mobility, and they arise from the unfavorable growth conditions for stoichiometric SrTiO_3 . By using so-called hybrid MBE techniques in which a Ti-precursor that can evaporate is used, thereby limiting off-stoichiometric growth, a larger MBE growth window can be achieved with smaller defect concentrations and larger mobilities.

The keynote presentation for the Workshop was given by Dr. Stan Williams (HP Labs). His group is developing commercial devices using resistance switching structures. These are metal/oxide/metal structures in which the resistance can change reversibly by the application of voltage pulses across the device. These are interesting from an applications point of view because they may allow for non-volatile electronic memories that can be scaled to much smaller dimensions than present Si CMOS technologies, such as NAND-Flash. Furthermore, these structures are embodiments of a fourth fundamental circuit element, the so-called memristor, predicted to exist by Leon Chua in 1971. Even though resistance switching has been known for over 40 years, the nature of the mechanisms has remained elusive. With recently available instruments capable of high spatial resolution for elemental characterization as well as structure and chemical states, great progress has been made. In particular, their group has used beamlines at the ALS and also the Nanoprobe beamline at the CNM for their research. Much of the work in Dr. Williams' group has focused on $\text{Pt}/\text{TiO}_x/\text{Pt}$ structures. Their research has concluded that resistive switching occurs when oxygen vacancies migrate and order under the influence of an electric field. In the conducting state a metallic Magnelli phase (Ti_4O_7) forms – this can be viewed as a condensed phase of oxygen vacancies in TiO_2 . The Magnelli phase acts as a source and sink for oxygen vacancies during the switching. More recently, their group has focused on structures with Ta rather than Ti oxides. Imaging fluorescence at the CNM Nanoprobe beamline at the Ta and Pt L_3 -edge revealed that concentric regions form during resistive switching, with a Ta-rich phase in the center of the regions. Analysis of cross-sections obtained using focused ion beams suggests the Ta-rich region is crystalline Ta_2O_5 .

The next speaker was Dr. James Rondinelli (ANL-XSD), who presented theoretical and modeling work on how to design and engineer polar perovskites from centric polyhedral building blocks. Polar materials must necessarily have broken inversion symmetry so he studies how this inversion symmetry can be broken using only centric polyhedra. Using group-theoretical analyses and *ab-initio* calculations he demonstrated examples of such materials. The work points to rules for how to design new polar materials from simple non-polar building blocks.

Dr. Dillon Fong (ANL-MSD) presented his group's research on the effect of oxygen partial pressure on ferroelectric thin films. It is known that the behavior of ferroelectric thin films, for example fatigue and switching behavior, depends on the oxygen partial pressure and on temperature. The polarization of ferroelectric thin films can affect adsorption behavior on the surface of the films, which opens the possibility for modulating surface catalytic properties. Using *in situ* synchrotron X-ray scattering, the phase diagrams and domain behaviors of PbTiO_3 films grown on SrTiO_3 (001) were correlated with different ferroelectric phases (distinguished by their domain configurations) having charge compensation on bottom and top surfaces. The switching behavior is sensitive to oxygen partial pressure as well as to X-ray and UV-irradiation; irradiation improves the switching induced by changes in the oxygen partial pressure. On the other hand, BaTiO_3 , grown using ozone-assisted metal-organic chemical vapor deposition exhibits much less sensitivity to oxygen partial pressure. Understanding of how the ferroelectric thin films interact with the environment and impose boundary conditions (e.g. substrate clamping or stress) may lead to ways to tune the reactivity on ferroelectric oxide surfaces.

The final presentation was given by Dr. Sang Soo Lee (ANL-CSE). Dr. Lee studies charged interfaces in aqueous solutions using X-ray beamlines at the Advanced Photon Source. The research illustrates novel techniques capable of imaging element-specific structures at complex interfaces, and in this case revealed the distributions of various cations at mineral-water interfaces. The work showed that cations can adsorb in as many as three different species, determined by the number of hydration layers between the cation and the surface.