Engineering complex oxide interfaces for oxide electronics

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Summary

A complex interplay of physics and chemistry in transition metal oxides determines their electronic, magnetic, and ferroic properties enabling a wide range of applications of these materials. The extreme sensitivity of these properties to structural distortions and crystal symmetry offers many routes to control and engineer new functionalities in these materials, and the interfaces between different complex oxides giving rise to interesting and unexpected new behavior. It is well understood that the macroscopic characteristics are often governed by micro- and nanoscopic elements like interfaces, grain boundaries, defects, and dislocations. Exploration of these features led to the discovery of 2D electron gas in oxide heterointerfaces, ferroelectric domain wall conduction and polarization controlled tunneling in ferroelectric films. Further progress in these studies is limited by the nanoscopic nature of the studied objects and their strong correlations to charge, structure and orbital degrees of freedom. In recent times, the nanoscale obstacle has been addressed by development of advanced scanning probe microscopy (SPM) techniques. However, understanding of phenomena at the nanoscale remains a challenge; typically in probing characteristics of feature sizes, when their extent is smaller than the probe dimensions. A promising pathway to study the physical responses originating from the nanoscopic feature is to employ a technique capable of resolving features and phenomena with high spatial resolution, to which scanning tunneling microscopy (STM) is the fittest choice.

A canonical multifunctional material system which has attracted a lot of research interest is $BiFeO_3$. It exhibits a large ferroelectric polarization and G-type antiferromagnetism with high transition temperatures (Curie temperature is 1100 K and Neel temperature is 673 K), making it appealing for applications in memory devices. Among other interesting aspects of $BiFeO_3$ thin films, locally enhanced conductiv-

ity of the ferroelectric domain walls have gathered a lot of interest, underlining the strong correlations between electronic structure and crystal symmetry. Owing to the coupled ferroelectric and magnetic property of $BiFeO_3$, it is theoretically proposed that the local symmetry at the ferroelectric domain wall might significantly affect the Fe-O-Fe canting angles thereby changing the magnetic interaction from antiferromagnetic to ferromagnetic superexchange. As this feature is prevalent only at the domain walls, lack of proper techniques to probe the domain walls has made this observation elusive. The capabilities of the technique of ballistic electron emission microscopy (BEEM) has been used in this study to investigate electronic transport across a functional interface with an oxide semiconductor at the nanoscale.

Conventionally, multiferroic $BiFeO_3$ thin films are grown on a conducting bottom electrode of $SrRuO_3$ whose thickness again dictates the density of 71° and 109° domain walls. In order to probe these ferroelectric domain walls in a current perpendicular to plane configuration using BEEM, it was imperative to first electrically characterize the interface between metallic $SrRuO_3$ and the substrate (Nb:$SrTiO_3$), which is the semiconducting analogue of $SrTiO_3$. Chapter 4 focuses on hot electron transport across the functional interface of $SrRuO_3$/Nb:$SrTiO_3$ where interestingly the interface transmission increases by orders of magnitude across the ferromagnetic transition of $SrRuO_3$. This observation was confirmed for $SrRuO_3$ films of various thicknesses, and we found that the hot electron attenuation length in $SrRuO_3$ was consistently lower in the low temperature ferromagnetic phase, contrary to the BEEM transmission across the interface at this temperature. We established that the geometrical reconstructions at the interface and hence modifications in electronic structures dominate the transmission across its ferromagnetic transition, eventually flipping the charge-transport length-scale. This approach of tuning heterointerfaces by coupling structural, electronic and magnetic properties can be extended to other material systems with promising prospects for future oxide electronic and spintronic devices.

Interestingly using the high spatial resolution of BEEM, we found that the buried electronic landscape of the $SrRuO_3$/Nb:$SrTiO_3$ interface depended critically on the underlying substrate termination. We engineered the substrate termination, which tailored the energy band alignments across the metal-semiconductor interface; yielding the Schottky barrier height (SBH) to be 0.2 eV higher for SrO termination as compared to TiO_2 termination. Such a surprising finding at a non-polar interface was also probed locally using high resolution transmission electron microscopy (HR-STEM) and identified the origin to be the disparate atomic plane stacking at the interface for SrO and TiO_2 terminations. This study emphasized the extra control

of substrate termination on the band line-ups (SBH) thereby acting as an additional degree of freedom at non-polar oxide interfaces, relevant for numerous device applications.

In addition to establishing interesting features at the functional interface of $SrRuO_3$ /Nb:$SrTiO_3$, it was required to nanoscopically probe the different ferroelectric states of $BiFeO_3$. In Chapter 6, we present a novel technique to ascertain the electronic structure of a buried interface of metal-ferroelectric-semiconductor; providing a direct evidence of the ferroelectric polarization control of interfacial energy band alignment. Here we exploit the substrate Nb:$SrTiO_3$ termination (SrO or TiO_2) to tailor the ferroelectric state of $BiFeO_3$ thin films. This further influences the energy barrier at the interface of $BiFeO_3$ with metal, which is reflected in different SBH for the different polarization states. The study opens new avenues to investigate the ferroelectric potential landscape of a buried interface. Even though the influence of ferroelectric polarization on BEEM current was understood, the device design forbids making local changes in the polarization direction as no underlying bottom electrode exists in the device.

This was circumvented by an alternate device geometry by utilizing the semiconducting property of $BiFeO_3$ to act as a collector. This device design relaxes our stringent dependence on Nb:$SrTiO_3$ as the semiconducting oxide substrate, thereby allowing $BiFeO_3$ to be grown on different lattice matched substrates. With $BiFeO_3$ grown on $SrRuO_3$ thin bottom electrode, specific domain patterns of 71°, 109° or 180° could be written using piezo force microscopy (PFM). This device geometry enables one to investigate charge transport across a metal and $BiFeO_3$ film with different ferroelectric domains. As the STM tip scans across two adjoining domains, the altered electrostatic potential at the metal-$BiFeO_3$ interface for the different polarizations change the energy barrier at its interface with the metal. This will influence the collected BEEM current, thereby providing an opportunity to locate the buried ferroelectric domain wall. Owing to different conductivities of the 71°, 109° or 180° domain walls, local scale transport studies will reveal different characteristics pertaining to the domain walls, and directly correspond to the oxygen vacancies. This way, the proposed ferromagnetic nature of the domain walls could also be probed by growing a spin valve stack and studying the spin dependent BEEM current in a magnetic measurement for the different domain walls.

Our first studies on probing interfaces between $BiFeO_3$ and metals using the new variant of BEEM shows a low BEEM current for the grown devices. Hot electron scattering in the thin metallic overlayer is expected to be minimal, according

to existing reports in identical metallic films. However, the dissimilar crystal and band structure at the metal-$BiFeO_3$ interface acts as a major source of scattering thereby reducing the BEEM current. Further, the electronic properties of $BiFeO_3$ needs to be characterized for such thin films to establish its semiconducting nature and correlate the same with bulk crystals. This is crucial as the BEEM transmission strongly depends on the conservation of parallel momentum across the interface. A large band structure mismatch between the metal and the semiconductor causes higher elastic scattering, which could be a prime reason for such low transmission. With different film-substrate lattice mismatch, electronic properties like band gap and density of states (DOS) that are strongly dictated by the changes in Bi-O bond lengths could be engineered for tailoring its semiconducting property, and thus the BEEM transmission. Further, with a choice of substrate and growth parameters, the super tetragonal phase of $BiFeO_3$ could also stabilized, which could exhibit different electronic properties of the grown film. This unique probing ability of BEEM in this novel geometry could be extended to the study of other material systems too (e.g. $BaTiO_3$, $TbMnO_3$ and other oxide materials) particularly to locally characterize the charge transport at the domain walls and explore novel functionalities therein, at the nanoscale. With a properly tailored semiconducting film, this method establishes itself as a major probing technique for features of size smaller than the dimension of the probe.