Chapter 1

Introduction and Outline

1.1 Introduction

In recent decades, one of the most active and promising areas of research in condensed matter physics has been employing complex oxides and their heterostructures. With the advent of new growth and measurement techniques, a wealth of novel magnetic and electronic ground states have been found in complex oxide heterointerfaces. The interest in these materials stems from their multifunctional properties, such as the coexistence of different types of magnetic ordering, ferroelectricity, charge-, and orbital ordering, all promoted by a strong interplay between spin, charge, and orbital degrees of freedom \[1, 2, 3, 4, 5, 6\]. These materials represent a clear advancement over conventional Si-based technology as their physical properties can be tuned; and when used in devices, leads to functionalities not realized in conventional electronics. The tunability of this already diverse playground of competing ground states and interactions is greatly multiplied in thin films and their heterostructures by the addition of parameters such as substrate induced strain and interfacial electronic reconstruction.

In the family of complex oxides, multiferroic materials have attracted a lot of research owing to their coupled ferroelectric and magnetic properties; which leads to additional functionalities. Pioneering studies on the room temperature multiferroic material BiFeO\(_3\) reported an unusual electrical conductivity across ferroelectric domain walls in an otherwise insulating BiFeO\(_3\) thin films at room temperature \[7, 8\]. Using conductive atomic force microscopy, the local conductivity of the artificially written ferroelectric domains and their walls were mapped out. The conduction at 180° domain walls in BiFeO\(_3\) was found to be rather significant in those samples whereas 109° walls conducted less and little conduction was observed at 71° walls. The reduction of bandgap, associated with the suppression of ferroelectric distortions, at the domain walls was proposed to be responsible for the conduction. This was an exciting revelation and BiFeO\(_3\) proved to be an excellent platform to probe and look for new functionality in such nanoscopic domain walls and simultane-
ously exploit it for potential oxide electronics and spintronic applications. Although the mechanisms of tailoring ferroelectric and magnetic properties were explored in BiFeO$_3$ thin films using both experimental and theoretical simulations, only a few studies exist in engineering these nanoscopic domains walls (1-2 nm) to probe their electronic and magnetic properties [9, 10].

Initial studies using AFM and its variants allowed a straightforward access to local mechanical, structural, electromechanical, dielectric, piezoelectric, and magnetic properties of ferroic materials. As an example, domain imaging, domain patterning, and spectroscopy performed with these techniques ushered new insights into local switching processes in ferroelectrics [11, 12]. However, the resolution and the analysis of the features and the accompanying processes were typically governed by the properties of the probe. Scanning probes employed in such related AFM techniques have since then undergone significant modifications enabling more detailed investigation of such novel functional properties [13, 14]. In this context an important technique that has only been recently introduced to study correlation effects to electron transport in complex oxide heterointerfaces is a valuable addition [15]. Based on the well known principle of the Scanning Tunneling Microscope (STM), this technique is known as the Ballistic Electron Emission Microscopy (BEEM), and has been used in this thesis to unravel new features in electron transport at the nanoscale, across heterointerfaces in devices based on complex oxides such as ferroelectric materials. Such a technique provides insights into the correlation between local electronic transport and reconstructions at the buried interface due to changes in the perovskite structure, manifested as a change in bond angle, that originates from the polarization discontinuity at the domain walls.

Despite the attention in probing the nanoscale transport phenomena in ferroelectric domain walls of BiFeO$_3$, many aspects regarding its origin are not fully understood; particularly at interfaces with different buffer layers, raising open questions on the linkage between electronic properties to its intrinsic order parameters as well as to their structure and symmetry. Initial studies indicated the role of the electrostatic potential change at the domain walls creating a large electric field that promotes an asymmetric charge distribution around the walls, where electrons and oxygen vacancies concentrate on the opposite sides. This increases the charge density at the domain wall, presumably enhancing the local conductivity [7]. Further research showed the role of these screening charges accumulating towards the bottom of the conduction band of an intrinsically small bandgap BiFeO$_3$ (2.7 eV), giving rise to increased conductivity [16]. The contribution of defects controlling the conduction has also been emphasized in a separate study [18]. Apart from the origin of
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Figure 1.1: A representative schematic of a novel route to electronically study the interesting phenomena and functionalities of oxide heterointerfaces using BEEM. The interplay between the various degrees of freedom manifest as different charge transport properties for such devices, and probing them at a nanoscale builds a fundamental understanding of complex oxide interfaces. This allows us to engineer such material systems for future devices to be more precisely fine-tuned to specific applications. In this thesis, a major emphasis is given to realize the strong influence of interesting properties at oxide heterointerfaces to charge transport, at a nanoscale.

In all these efforts done so far, SrRuO$_3$ has been widely used to control the polarization switching and magnitude of leakage current in BiFeO$_3$.

In order to probe the electronic transport properties of the domain walls in BiFeO$_3$, the first key requisite is to investigate the influence of the bottom conducting electrode (either SrRuO$_3$ or doped SrTiO$_3$) to electron transport in a device geometry. For our study, we adopted a current perpendicular to the plane device geometry of BiFeO$_3$ and SrRuO$_3$ on a n-type semiconducting substrate of SrTiO$_3$, as the technique of BEEM necessitates. Here, we use a well characterized Nb-doped SrTiO$_3$ substrate as the semiconductor. In BEEM, the transmission of hot electrons are
used to study local differences in transport in thin films and across their interface with semiconductors, relying on the principle of an energy filter at the metal-semiconductor interface to map out the conductivity landscapes, thus allowing us to study the influence of strong correlation in this process. A systematic study necessitated a first characterization of the SrRuO$_3$/Nb: SrTiO$_3$ interface; and this provided novel insights into the electronic transport at a local scale across a functional interface, hitherto unexplored. We find that the geometrical reconstructions at the interface owing to phase transitions are strongly correlated to the electronic structures thereby influencing charge transport. The crucial role of the local substrate termination on the the energy landscape of an oxide heterointerface is demonstrated, thereby providing yet another tool to tailor device performances. Combining a suite of techniques that can simultaneously probe and correlate local structural changes to electronic transport in the same device will be instrumental in furthering oxide electronics and oxide spintronics.

## 1.2 Scope of this thesis

The work presented in this thesis aims to provide a better fundamental understanding of hot electron transport and its correlation with other physical properties across complex oxide heterointerfaces. Here we have used the energy band alignment at the oxide metal-semiconductor interface as a parameter to unravel novel features at interfaces, crucial for development of all-oxide devices. Here is a chapter wise content of the thesis:

- **Chapter 2** presents an array of experimental techniques used for the growth and characterization of epitaxial thin films of complex oxides used in this thesis. The experimental details on the device design and fabrication are discussed along with a detailed description of the nano-scale measurement technique used to perform electronic charge transport through the thin oxide films and across their heterointerfaces.

- **Chapter 3** discusses the fundamental principles of energy band alignment at the complex oxide heterointerface followed by an introduction to the commonly used models describing the Schottky barrier height. This is followed by the main concepts of hot electron transport and Ballistic Electron Emission Microscopy (BEEM) including the various scattering mechanisms of the hot carriers in this transport technique.

- **Chapter 4** explores the influence of electron-lattice correlation to electron-transport, at interfaces between SrRuO$_3$ and Nb: SrTiO$_3$ across its ferromagnetic transi-
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We find 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 in SrRuO$_3$.

- **Chapter 5** presents the crucial role that the terminating surface of the substrate has on the Schottky interface and electron transport through metallic SrRuO$_3$ on semiconducting Nb doped SrTiO$_3$. This is manifested as the differences in the height of the Schottky barriers at the SrO and TiO$_2$ surface terminations of the substrate, and its origin lies in the different interfacial atomic plane stacking of SrRuO$_3$, as confirmed by High-Resolution Scanning Transmission Electron Microscopy (HR-STEM) studies. First-principles density functional theory calculations conform with our experimental findings.

- **Chapter 6** investigates the influence of bulk polarization state provided by the underlying substrate termination, to hot electron transmission in BiFeO$_3$. This is ascribed to the altered potential landscape at the electrode-BiFeO$_3$ interface for different ferroelectric polarization, thus allowing us to locate the domain walls.

- **Chapter 7** introduces a novel technique based on BEEM to investigate the electronic transport at domain walls in BiFeO$_3$. This variant of the conventional BEEM technique utilizes the leaky nature of an otherwise insulating BiFeO$_3$ film to act as a semiconductor to collect the BEEM current. This technique potentially scores over the conventional scanning probe techniques used so far. This indicates a novel route to study the nanoscopic ferroelectric domain walls of BiFeO$_3$ thin films.
Bibliography