Engineering complex oxide interfaces for oxide electronics
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Chapter 4

Growth, characterization and hot electron transport through SrRuO$_3$ thin films

Abstract

The emerging class of complex-oxide materials, where manipulation of physical properties leads to new functionalities at their heterointerfaces, is expected to open new frontiers in spintronics. For example, SrRuO$_3$ is a promising material where external stimuli like strain, temperature and structural distortions control the stability of electronic and magnetic states, across its magnetic phase transition, useful for spintronics. Despite this, not much has been studied to understand such correlations in SrRuO$_3$. In this chapter, we first present the growth of SrRuO$_3$ thin films on single crystalline substrates and their structural, electrical and magnetic characterization. Epitaxial films were grown using pulsed laser deposition and their growth was monitored using in-situ reflection high energy electron diffraction (RHEED). The deposited films were characterized using atomic force microscopy and X-ray diffraction. Their magnetic and electrical transport studies were also characterized for the different thicknesses. Thereafter, we explore the influence of electron-lattice correlation to electron-transport, at interfaces between SrRuO$_3$ and Nb:SrTiO$_3$ across its ferromagnetic transition, using a nanoscale transport probe and first-principles calculations. We find that the geometrical reconstructions at the interface and hence modifications in the electronic structure dominate the transmission across its ferromagnetic transition, eventually flipping the charge-transport length-scale in SrRuO$_3$. This approach can be easily extended to other devices, in which competing ground states can lead to different functional properties across their heterointerfaces.

4.1 Introduction and Motivation

Complex oxides have propelled a vast research field, establishing themselves as the next frontiers in electronic materials by offering unique prospects to control and manipulate their new functionalities. These materials, typically of the form ABO$_3$, exhibit strong correlations between the charge, spin, orbital and lattice degrees of freedom, leading to modulation of their device properties and are emerging as strong contenders for Beyond Moore technology. In this regard, the growth
and study of SrRuO$_3$ thin films was initially driven by its good metallic characteristics (for oxide systems) and high quality growth in heteroepitaxial structures, which make it ideal for device applications. The increased interest in applications of epitaxial thin film oxide multilayers prompted the metallic SrRuO$_3$ to be integrated into oxide heterostructures and devices as a contact electrode or buffer layer. [1, 2, 3, 4]

The unit cell of SrRuO$_3$ is shown in Figure 4.1(a). The perovskite structure has Sr and Ru ions at the edges and center of the structure, and the RuO$_6$ ions form a framework of corner-sharing octahedra, with a Ru ion at the center of each octahedron and six O ions at the corners. Usually the perovskite structures are tilted or rotated in order to accommodate the large A-site ions; and this results in a variety of symmetries from isometric to tetragonal to orthorhombic to monoclinic depending on the degree of distortion. The unit cell of SrRuO$_3$ are arranged in an orthorhombic lattice, shown in Figure 4.1(b). Since the distortion of the octahedral positions in SrRuO$_3$ is not large, its structure can be also described as pseudocubic (the pseudocubic unit cell, with a lattice parameter of 3.93 Å, is also shown in Figure 4.1(a)).

The significant interest in SrRuO$_3$ thin films arise owing to the deviations of its physical properties from the bulk. The electronic and magnetic properties of SrRuO$_3$ thin films prepared by heteroepitaxy are sensitive to the film thickness [6]. In the bulk, SrRuO$_3$ is an itinerant ferromagnetic metal with a Curie temperature ($T_C$) of
160 K and a saturation magnetization ranging from 1.1-1.7 $\mu$B per formula unit. [7, 8, 10, 11] In thin films, SrRuO$_3$ has been reported to exhibit a lower $T_C$ of 140 K that scales with the thickness of the film and a higher saturation magnetization owing to uncompensated moments emanating at the interface. [12] Although it is considered to be metallic, electron-electron correlations play a significant role in determining the transport properties. As the film thickness is reduced, resistivity in conducting SrRuO$_3$ thin films is found to increase, finally leading to a metal-to-insulator transition for 4 unit cells (u.c.). To comprehend the origin of these non-bulk-like behaviors in SrRuO$_3$ thin films, it is important to understand the physics present in the bulk system. SrRuO$_3$, the lone 4d itinerant ferromagnet among the transition metal oxides offers a unique opportunity to probe electronic and magnetic interactions in a system which is particularly sensitive to the strong correlations. This sensitivity originates as Ru is a 4d system as opposed to the more common 3d ferromagnets. The extended nature of the 4d orbitals leads to unusually strong bonding interactions with neighboring oxygen atoms and correspondingly strong responses to any alteration of these interactions. [13]

Additionally, interfaces coupling SrRuO$_3$ to other complex oxides exhibit novel functionalities, not present in their parent compounds. [14, 15] These primarily stem from broken symmetries at the interface, which when carefully tailored, can lead to unique device functionalities. The microscopic origin of ferromagnetism is supported by the distortions of the oxygen octahedra that are coupled to the degree of hybridization between O 2p and the Ru 4d orbitals. [9] At the interface, an additional distortion originating from the substrate can cause geometrical changes, which strongly influences its magnetic and electronic properties on either side of the $T_C$. This provides an interesting opportunity to study the correlation between magnetism and transport in SrRuO$_3$ across its $T_C$ when integrated in an electronic device.

In this chapter, we first present the results of optimized growth of SrRuO$_3$ thin films of SrTiO$_3$ and Nb:SrTiO$_3$ substrates. We present the characterization of SrRuO$_3$ thin films using AFM, X-ray diffraction methods; which is followed by the magnetic characterization of the thin films for various thicknesses. This is followed by the electronic transport properties of the optimized SrRuO$_3$ films for different thicknesses within a temperature between 10 K and 300 K. Thereafter, we employ a nanoscale transport probe to study such complex correlation across an interface between SrRuO$_3$ on semiconducting Nb:SrTiO$_3$. Principally, this technique allows us to study any material system, whose electronic properties are susceptible to a temperature driven phase transition, while simultaneously allowing us to inves-
4. Growth, characterization and hot electron transport through $SrRuO_3$ thin films

Figure 4.2: (a) Atomic force microscopy (AFM) image of a $(5\times 5\ \mu m^2)$ TiO$_2$ terminated 0.01 wt.% Nb:SrTiO$_3$ substrate before deposition. The root mean square (r.m.s) roughness is 0.20 nm. (b) RHEED spots for such Nb:SrTiO$_3$ substrate before deposition at 600$^\circ$ C and 0.3 mbar of oxygen pressure.

igate its homogeneity across such buried interfaces with a semiconductor, at the nanoscale. This is an important approach for material systems such as complex oxides where small changes in the geometrical properties with thickness or temperature can produce large changes in the electric and magnetic properties. We perform a systematic experimental study to understand the effect of thickness and temperature on electronic transport across thin films of $SrRuO_3$ ($t = 6, 8, 9$ and 10 unit cells) with Nb:SrTiO$_3$ and observe an order of magnitude increase in the transmission in the same device, across its ferromagnetic phase transition. Surprisingly though, we find that this increase originates from an enhanced transmission at the interface between $SrRuO_3$ and Nb:SrTiO$_3$, rather than in the bulk of $SrRuO_3$, and manifests as two different transport lengths at room temperature and below $T_C$. We combine these findings with density functional theory (DFT) calculations to quantitatively understand the role of interface reconstruction, octahedral distortions and exchange splitting in the observed features in electronic transport.

4.2 Growth of $SrRuO_3$ thin films

For the growth of high quality crystalline $SrRuO_3$ films in our study, we use single crystalline SrTiO$_3$ or Nb:SrTiO$_3$ substrates. SrTiO$_3$ is the substrate of choice due to the close lattice matching to $SrRuO_3$ crystals and the availability of the semiconduc-
4.3 Structural characterization of SrRuO$_3$ thin films

The SrRuO$_3$ thin films are all characterized for their surface roughness using the AFM in tapping mode. This enabled the determination of surface roughness, morphology and the height profile of the grown SrRuO$_3$ films. The details on the working principle of AFM has been mentioned in chapter 2. The AFM images of the SrRuO$_3$ films are shown in Figure 4.4. It is observed that with progressive increase in thickness, the surface roughness decreases. The AFM images indicate the typical growth kinetics of SrRuO$_3$ thin films.
Figure 4.3: (a) RHEED oscillation during SrRuO₃ growth. RHEED intensity oscillations saturate indicating the step-flow growth mode. (b) Typical RHEED pattern obtained after depositing 10 u.c. of SrRuO₃. (c) AFM topography image of a 10 u.c. SrRuO₃ film grown on Nb:SrTiO₃ substrate after cooling down to room temperature at a rate of 10° C/min in presence of 100 mbar of oxygen. The r.m.s. roughness of the surface is 0.853 nm.

The growth of SrRuO₃ is sensitive to the underlying substrate termination. Although the substrates are chemically treated to obtain an uniform TiO₂ termination, the high temperature annealing step leads to Sr out-diffusion to the surface thereby causing local regions of SrO terminations. Such locations mainly appear at the terrace edges and with the growth of SrRuO₃, a non-uniform topography of the film is observed. This primarily occurs owing to the different growth rates of SrRuO₃ indicating that it grows faster on TiO₂ terminated sites than on SrO terminations. However, as the film thickness increases, the islands coalesce and the morphology of the substrate is replicated and an uniform topography is rendered. This can be observed from the AFM topography images in Figure 4.4(a,d). As the film thickness increases from 6 u.c. to 10 u.c., the topography becomes smoother and more uniform. The root mean square (r.m.s) roughness for the 6 u.c. film is 0.628 nm and for the 10 u.c. film is 0.853 nm.

In order to investigate the crystal structure of SrRuO₃ on SrTiO₃, we use x-ray diffraction (XRD). Figure 4.5 shows a 2θ – ω scan of a 10 u.c. SrRuO₃ film grown on SrTiO₃ substrate. The absence of other peaks than the (00n) peaks of SrRuO₃ shows
4.4 Magnetic properties of SrRuO$_3$ thin films

Figure 4.4: AFM topography image of (a) 6, (b) 8, (c) 9 and (d) 10 u.c. SrRuO$_3$ films grown on Nb: SrTiO$_3$. Typical growth pattern of SrRuO$_3$ is exhibited. The trenches initially formed owing to the different growth rates disappear as the islands coalesce and an uniform topography is rendered with thicker films.

its single crystalline phase. Owing to a close lattice match between the film and the substrate, the intensity peak positions lie close to each other. The out of plane lattice parameter of this SrRuO$_3$ film is obtained as 4.01 Å, using the equation:

$$\sin \theta_{hkl} = \frac{n \lambda}{2d_{hkl}}$$  \hspace{1cm} (4.1)

where the symbols have their usual meanings as discussed in Chapter 2.

4.4 Magnetic properties of SrRuO$_3$ thin films

SrRuO$_3$ is an itinerant ferromagnet with a Curie temperature ($T_C$) of $\sim 140$ K. [15] The ferromagnetic order is mainly precluded by the extended nature of the 4d orbitals. The large orbital overlap in 4d systems generally results in strong crystal field splitting, wide bands, and a correspondingly low density of states. However, SrRuO$_3$ is highly unusual where the Ru-O orbitals are strongly hybridized, with bonds which are very covalent in character. Electrons freely flow across a network of Ru-O octahedral cages and create an itinerant metal with a strong enhancement to the density of states at the Fermi level originating in hybridized orbitals with mostly
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The importance of the Ru-O hybridization is demonstrated by the contrast between the otherwise similar systems like CaRuO$_3$ and SrRuO$_3$. A slight orthorhombic distortion to the unit cell which causes the two Ru-O-Ru bond angles to be approx. $167^\circ$ and $159^\circ$ respectively.[13, 19] In CaRuO$_3$, with a larger orthorhombic distortion the Ru-O-Ru bond angles are decreased to $150.6^\circ$ and $151.2^\circ$.[13] As a result of this increased octahedral rotation and tilting in CaRuO$_3$, the electron hopping interaction, which is expected to be strongest for a Ru-O-Ru bond angle of $180^\circ$, is much weaker in CaRuO$_3$. [13] Thus, the relative strength of electron correlation effects is higher in CaRuO$_3$ than in SrRuO$_3$ and long range magnetic ordering is suppressed in CaRuO$_3$. Hence the magnetic ordering in SrRuO$_3$ is extremely sensitive to structural alterations, and this change is also depicted as the film thickness increases.

In this section, we present the magnetic properties of 6, 8 and 10 u.c. of SrRuO$_3$ films. The magnetic measurements were performed using an MPMS SQUID magnetometer, which was detailed in chapter 2. The magnetic moment versus temperature curves of 6, 8 and 10 u.c. area as shown in Figure 4.6. These measurements were
4.4. Magnetic properties of SrRuO$_3$ thin films

Figure 4.6: Magnetic moment versus temperature curves recorded on field cooling and in the remanent state for 6, 8 and 10 u.c. samples. A magnetic field of 0.1 T was applied while cooling down. The field was removed at 5 K.

made in an applied field of 0.1 T on field cooling from 300 K and in remanence after removing the applied field at 5 K. All the data are measured in the warm up cycle. The curves show typical ferromagnetic behavior and their respective $T_C$ can be found from the derivative of magnetic moment versus temperature plots. As the film thickness decreases, the transition temperature also decreases exhibiting a subsidence in ferromagnetic stability. The remanent magnetization for the 6 u.c. sample shows an upturn below 20 K indicating some ferromagnetic order at low temperatures. Also with increasing film thickness, a larger Ru content contributes to an enhanced magnetic moment. The magnetic moment versus magnetic field measurement curves of the grown films with magnetic field applied in a direction parallel to the plane of SrRuO$_3$ films are as shown in Figure 4.7. The diamagnetic contributions of the substrate and sample holder were determined from the high-field slope of the magnetic moment and were subtracted; this procedure was chosen, since it is impossible to determine the diamagnetic contribution independently with sufficient precision. The saturation magnetic moments of the samples are close to the bulk magnetic moment, but considerably enhanced as compared to reported values. Such an increment in our films could be understood as a little change in the Ru-O-Ru interatomic distance or bonding angles, which has consequences in changes in the exchange energy among spins. The disorder strongly affects the physical properties of ultrathin SrRuO$_3$ films, resulting in the formation of a layer of higher magnetization at the initial growth stage of ultrathin SrRuO$_3$ films. [12] Also, several reports
attribute this enhancement to the magnetically reconstructed SrRuO$_3$-vacuum interface. [15] However, it was not possible to ascertain this occurrence from our global magnetization measurements.

### 4.5 Electrical transport properties of SrRuO$_3$ thin films

We characterized the electron transport of samples using resistance measurements in the van der Pauw geometries. Samples were placed in a Quantum Design Physical Property Measurement System (PPMS) varying temperature from 10-300 K. As the samples were either square or rectangular, contacts were placed as close to the corners of the films as possible. The resistivity measurements of the samples as a function of temperature are as shown in Figure 4.8. The grown films exhibit metallic behavior within the entire temperature range. Above the T$_C$, the resistivity increases linearly without saturation, confirming a bad metal behavior. The kink in the metallic resistivity curve is indicative of the paramagnetic to ferromagnetic transition, and thus represents the coupled magnetic and electrical behavior. The resistivity of the samples changes slope below the T$_C$, and the origin of this transition is believed to be the suppression of spin dependent scattering in ferromagnetic metals which
4.6 Nanoscale electronic transport across $\text{SrRuO}_3$/ $\text{Nb:SrTiO}_3$

In order to probe electronic transport of the deposited SrRuO$_3$ films, they are patterned with standard UV lithography and further ion beam etched to be defined as devices (detailed in chapter 2). Our experimental nanoscale transport probe is known as ballistic electron emission microscopy (BEEM) (Figure 4.9(a)) which uses...
the scanning tunneling microscope (STM) tip to inject a distribution of hot electrons with energies higher than the Fermi energy \( E_F \). \[21, 22\] In this study, we use a modified Ultra High Vacuum (UHV) STM system from RHK Technology and the measurements are performed at 300 K and 120 K using PtIr metal tips. An electrical contact between the STM tip and SrRuO\(_3\) measures the tunnel current. The device design necessitates an additional contact at the rear-end of Nb:SrTiO\(_3\), for the collection of the transmitted electrons. These injected hot electrons, driven by the applied bias \( V_T \) with respect to the Fermi level of the metal, travel across the metallic base to reach the M-S interface; if their energy is sufficient to overcome the Schottky barrier, they can be collected into the semiconductor conduction bands (Figure 4.9(b)).

To obtain the BEEM spectra, the STM tip is held at a fixed location while \( V_T \) is varied within a voltage range and the collector current is recorded in the constant current mode. As these hot electrons propagate through the SrRuO\(_3\) films, they undergo scattering, which influences the collected current. The collected electrons in Nb:SrTiO\(_3\) are primarily those whose momentum parallel to the interface is conserved, the rest are back-scattered into the SrRuO\(_3\) base layer. These electrons serve as an important parameter to study strong correlations in such metallic oxide thin films and provide information on the homogeneity of the interface electronic structure with high spatial resolution.\[23, 24, 25, 26\] The determination of the relative strengths of such scattering processes (elastic/inelastic) enables a comprehensive understanding of electron transport in complex oxides and allows for designing of new oxide based electronic devices.

### 4.6.1 Thickness and temperature dependent BEEM transmission

The hot electron distribution encounters elastic and inelastic scattering while trans- mitting through the SrRuO\(_3\) metallic base. In this process, the momentum distribution at the M-S interface is broadened, as compared to the injection interface, adding to the reduction of the collected BEEM current \( I_B \). \[27\] These effects get more pronounced as the thickness \( d_{SrRuO_3} \) of the base layer is increased. The normalized BEEM transmission follows an exponential behavior as described by \[21\]:

\[
\frac{I_B}{I_T} = C \times \exp \left[ -\frac{d_{SrRuO_3}}{\lambda_{SrRuO_3}(E)} \right] \tag{4.2}
\]

where \( \lambda_{SrRuO_3}(E) \) is the energy-dependent hot electron attenuation length, \( I_B \) is the collected BEEM current, \( I_T \) is the injected tunnel current and \( C \) is a constant that is the kinematic transmission factor representative of electron transport across the M-S interface. Figure 4.10 shows the BEEM transmission data for various thickness of SrRuO\(_3\) thin films, in their paramagnetic (300 K) and ferromagnetic (120 K)

Figure 4.9: (a) Schematic design of SrRuO$_3$/Nb:SrTiO$_3$ device and measurement scheme. Electrons are injected by the STM tip and BEEM current is collected from Nb:SrTiO$_3$. (b) Energy band profile of the measurement scheme. The Schottky barrier at the SrRuO$_3$/Nb:SrTiO$_3$ interface acts as an energy filter for the transmitted hot electrons.

phases. First we discuss the observation for the paramagnetic phase (Figure 4.10(a)). The transmission for all film thicknesses is low up to a certain bias voltage beyond which, the transmission increases rapidly. This onset in bias voltage corresponds to the local Schottky barrier height (SBH) at the M-S interface. In accordance to the Bell-Kaiser (B-K) model, a plot of the square root of BEEM current versus the bias voltage yields the value of SBH, which in this case is $1.13 \pm 0.03$ eV (Inset, Figure 4.10(a)) [28]. The SBH is extracted from the linear fit of the BEEM current at approximately 0.2 V above the threshold bias voltage. It matches well with our previously extracted values for such an interface [29]. As the thickness of SrRuO$_3$ films is increased, a decrease in transmission is observed. However, the local SBH extracted from measurements on films of different thicknesses are found to be the same, thus providing yet another proof of a high quality growth of atomically sharp M-S interfaces. The representative BEEM spectra shown for each thickness are averages of several spectra taken at different devices and locations.

Electronic transport across the ferromagnetic phase transition in SrRuO$_3$ thin films was studied across its interface with Nb:SrTiO$_3$, in the same set of devices, by performing similar BEEM measurements at 120 K. The characteristic BEEM spectra
Figure 4.10: (a) A plot of BEEM current vs. bias voltage is shown for different thicknesses of SrRuO$_3$ at 300 K. The transmission decreases progressively with increasing film thickness. The curve for 6 u.c. SrRuO$_3$ has been multiplied by 0.5 factor. The inset shows representative local Schottky barrier height (SBH) extracted by the Bell-Kaiser model, for the interface of metallic SrRuO$_3$ and semiconducting Nb:SrTiO$_3$. For all the thicknesses, it is found to be $1.13 \pm 0.02$ eV. The error bars reflect the standard deviation of the measured onset of the BEEM current at a location. (b) The plot of BEEM current vs. bias voltage shows an thickness dependence, similar to what we observe at 300 K. An increased BEEM transmission for all thicknesses is observed compared to 300 K. The curves for 6 u.c. and 8 u.c. of SrRuO$_3$ have been multiplied by 0.5 and the 9 u.c. SrRuO$_3$ curve by a factor 2. The extracted local SBHs for the devices are $1.14 \pm 0.03$ eV, similar to what was observed at 300 K.
are shown in Figure 4.10(b). Similar to our earlier observations, the BEEM transmission progressively decreases with increasing thickness of the films. We find that the hot electron transmission increases by an order of magnitude as compared to its corresponding values at 300 K. The extracted SBH at 120 K, at these interfaces, is found to be 1.14±0.03 eV (Inset, Figure 4.10(b)), which is the same as that obtained in its paramagnetic phase. One can thus safely discard the origin of the enhanced BEEM transmission in SrRuO$_3$ at 120 K, due to differences in the SBH across its magnetic phase transition.

### 4.6.2 Influence of interface and film thickness on electronic transport

An exponential fit of the BEEM transmission for varying thicknesses of SrRuO$_3$ films allows us to extract the (energy dependent) transport length scale known as attenuation length (Equation 1). Above $E_F$, the transmission of hot electrons in SrRuO$_3$ films is mostly governed by inelastic scattering, originating from the availability of increased phase space for hot electrons to decay into [30, 23]. The extracted attenuation length of the carriers reflects the combined effects of inelastic, elastic as well as quasi-elastic scatterings. We plot the transmissions for the paramagnetic and ferromagnetic phase of SrRuO$_3$ at a certain bias voltage of -2 V, shown in Figure 4.11(a).

An important observation is that the BEEM transmission starts to deviate appreciably at 120 K from that at 300 K, with decreasing thickness. This has not been observed earlier in other metallic systems using BEEM. Extrapolation of the data for zero SrRuO$_3$ thickness shows two orders higher transmission, at the interface for ferromagnetic SrRuO$_3$. An exponential fit using Equation 4.2, yields an attenuation length of $1.6\pm0.2$ u.c. in the paramagnetic phase and $0.88\pm0.4$ u.c. in the ferromagnetic phase at -2 V. In Figure 4.11(b), we plot the energy dependence of the attenuation length by fitting the data obtained in Figure 4.10 with Equation 1 for energies above the SBH. We find that the attenuation length decreases with increasing energy, consistent with the enhancement of the density of states (DOS) at higher energies [31]. What is surprising is that in-spite of the enhanced transmission in the ferromagnetic phase, the attenuation length in SrRuO$_3$ is shorter, for all energies at 120 K, than at 300 K.

That for the same material system, i) electron transmission increases significantly across its ferromagnetic phase transition accompanied by ii) an unexpected decrease in the attenuation length in the same phase, is not only intriguing but contrary to existing understanding. A careful analysis of the data in Figure 4.11 was done to ascertain the relative role of inelastic and elastic scattering in order to understand the above observations. If the phase space for inelastic scattering of hot electrons
Figure 4.11: (a) A plot of BEEM current vs. bias voltage is shown for different thicknesses of SrRuO$_3$ at 300 K. Clearly, the transmission decreases progressively with increasing film thickness. The curve for 6 u.c. SrRuO$_3$ has been multiplied by 0.5 factor. The inset shows representative local Schottky barrier height (SBH) extracted by the Bell-Kaiser model, for the interface of metallic SrRuO$_3$ and semiconducting Nb: SrTiO$_3$. For all the thicknesses, it is found to be 1.13 ± 0.02 eV. The error bars reflect the standard deviation of the measured onset of the BEEM current at a location. (b) The plot of BEEM current vs. bias voltage shows an thickness dependence, similar to what we observe at 300 K. An increased BEEM transmission for all thicknesses is observed compared to 300 K. The curves for 6 u.c. and 8 u.c. of SrRuO$_3$ have been multiplied by 0.5 and the 9 u.c. SrRuO$_3$ curve by a factor 2. The extracted local SBHs for the devices are 1.14 ± 0.03 eV, similar to what was observed at 300 K.

changes in SrRuO$_3$ across its ferromagnetic phase transition, it will be reflected in the energy normalized spectrum at 300 K and 120 K for similar thickness of SrRuO$_3$. This has been plotted in Figure 4.12. When normalized at a bias of -2 V, we observe that for both thickness of SrRuO$_3$ film (6 and 10 u.c.), no energy dependence of transmission is observed, leading us to infer that inelastic scattering is not the major contributor in attenuating hot electron transmission. Such an exercise was carried out for all other thickness, and similar conclusions were obtained. As discussed before (Figure 4.11(a)), the interface between SrRuO$_3$ and Nb: SrTiO$_3$, is more transparent to the transmission of hot electrons in the ferromagnetic phase as compared to the paramagnetic phase, suggesting the prominent contribution to be the underlying geometrical changes in addition to possible mismatch of electronic states at either sides of the interface. This apparent conundrum is explained by ab initio calculations performed by our collaborators, taking into account the characteristics of geometries and electronic structures at the interface between SrRuO$_3$ and SrTiO$_3$ along with the quasiparticle renormalization of attenuation length.
4.6. Nanoscale electronic transport across \( \text{SrRuO}_3/\text{Nb:SrTiO}_3 \)

4.6.3 Results of \textit{Ab initio} study of \( \text{SrRuO}_3/\text{SrTiO}_3(001) \) interfaces

To understand the correlation between structural and electronic properties at the interface to the BEEM transmission and to understand the origin of the flipping of the attenuation lengths at 120 K and 300 K, the group of Prof. B. Sanyal at Uppsala University performed \textit{ab initio} density functional calculations. In order to simulate \( \text{SrRuO}_3 \) thin films grown on \( \text{SrTiO}_3 \) (001) substrates, the lattice parameter \( a \) was fixed to the experimental value of the \( \text{SrTiO}_3 \) substrate. 3, 6 and 9 unit cells of \( \text{SrRuO}_3 \) were considered in the low temperature ferromagnetic and room temperature (RT) paramagnetic phases. As a paramagnetic phase with disordered local moments is difficult to simulate within the computational technique, we study the nonmagnetic phase as the RT phase and ferromagnetic phase calculated at 0 K will represent the low temperature (LT) phase. We show in Figure 4.13(a) the supercell with 6 layers of \( \text{SrRuO}_3 \) on 3 layers of \( \text{SrTiO}_3 \). In the following discussions, we will follow the notation shown in Figure 4.11(a), where we denote STOL (or SROL) with \( L=1,2,\ldots \), the L-th layer from the \( \text{SrTiO}_3/\text{SrRuO}_3 \) interface.

To determine the energy dependent attenuation length \( \lambda^{LDA}(E) \), we calculate the mean value over the bands and k-points, at a given energy \( E \), of the product of the modulus of the group velocity along the \( z \) axis \( v_{nk}^z \) and the lifetime \( \tau_{nk} \), which is expressed as:

\[
\lambda^{LDA}(E) = \langle v_{nk}^z \tau_{nk} \rangle \propto \frac{1}{\hbar} \int_{E}^{E_0} \frac{\partial \varepsilon_n(k)}{\partial k_z} \frac{1}{N(\varepsilon)} d\varepsilon
\]  

\( (4.3) \)
where the lifetime is proportional to the inverse of the cumulative density of states from the Fermi level to the energy. We have only considered the $z$-component, as the BEEM transmissions across the M-S interface are measured along this direction. As seen in Figure 4.13(b), the attenuation length $\lambda^{LDA}(E)$ is almost constant in the range between 1.6 and 2.2 eV (above $E_F$) and is greater at 120 K than at RT. In recent works [32, 33], the importance of dynamical correlations in SrRuO$_3$ have been discussed with the aid of dynamical mean field theory. Whereas the dynamical correlations and hence, the temperature dependent quasiparticle weight $Z$ are beyond the scope of LDA, we note that this weight is 1 in LDA and is a multiplicative factor of the spectrum and the velocity. Assuming the same quasiparticle weight for the $e_g$ manifold and neglecting its influence on $\tau$, we get a reduction of the attenuation length, which is more pronounced at lower temperatures. In Figure 4.13(b) we plot the attenuation length multiplying $\lambda^{LDA}$ by $Z$ and observe that under these assumptions, the attenuation length at RT is greater than at 120 K, in agreement with the experimental findings.

### 4.6.4 Variation of the electronic and structural properties of the interface at LT and RT

To understand the experimentally observed enhancement in the interface transmissions at 120 K and 300 K, the electronic and geometric structures of SrRuO$_3$/SrTiO$_3$ interfaces were calculated. Considering the variation in the geometric and magnetic properties, the SrRuO$_3$ thin films can be divided in three regions along the $c$-axis: surface, inner layer and interface region. The calculated densities of states of SrRuO$_3$ along with that of SrTiO$_3$ are shown in Figure 4.14(a) for 9 u.c. of SrRuO$_3$ in the LT ferromagnetic phase and the RT nonmagnetic phases. It is observed that between 1 eV and 2.2 eV (above $E_F$), the DOS in SrRuO$_3$ is dominated by $e_g$ electrons whereas in SrTiO$_3$, the $t_{2g}$ electrons dominate with a larger DOS between 1.2 and 1.4 eV (above $E_F$) in the nonmagnetic phase of SrRuO$_3$. The exchange split $e_g$ state produces a smaller DOS at LT between 1.2 and 1.4 eV (above $E_F$). While the differences between LT and RT phases are observed in all SRO layers, SRO1 layer at the interface needs an extra attention. A distinct feature of $d_{x^2-y^2}$ character (marked by the shaded area) is observed for RT phase in the SRO1 layer along with the renormalization of $e_g$ DOS between 1.2 and 1.3 eV (above $E_F$). This is not an energy shift but is due to an enlargement of the bandwidth. Our calculated hopping parameters, for example, for the 6 u.c. at RT are 580 meV between the $x^2-y^2$ orbitals (corresponding Wannier function shown in Figure 4.14(a) in the SRO1 layer and 540-543 meV for other layers. Also, the hopping mismatch between interface (575 meV) and inner

Figure 4.13: (a) Side view of the slab with 3 layers of SrTiO$_3$ and 6 layers of SrRuO$_3$. Sr, O, Ru and Ti atoms are shown as green, fuchsia, grey and blue balls respectively. In the SRO1 layer, we show the Wannier function corresponding to the $d_{x^2-y^2}$ orbital where red and blue contours are for isosurfaces of identical absolute values but opposite signs. (b) Attenuation length calculated within LDA without and with the quasiparticle weight $Z$. The top and bottom panels show $\lambda_{LDA}$ and $Z\lambda_{LDA}$ respectively in the energy range between 1.6 and 2.2 eV (above $E_F$) for the case with 6 layers of SrRuO$_3$. This energy range is the relevant experimental energy range where the attenuation length was measured. The LT (RT) phase is shown in blue (red).

layers (554-561 meV) is reduced at LT. Thus, we can clearly see that the mismatch between the interface and inner layers is larger at RT. We further note from our DOS calculations that the mismatch of the electronic states at the interface between SrRuO$_3$ and SrTiO$_3$ is larger at RT than at LT. Such elastic scattering effects will lead to a reduction in the BEEM transmission at RT. All these differences in the electronic structures of the two phases strongly suggest the importance of the prefactor $C$ in Equation 1, which influences the BEEM transmission at LT and RT phases.

The difference in the characteristics at the interface for LT and RT phases is quite evident also in the structural properties shown in Figure 4.14(b). The interface reconstruction makes this aspect more evident in the in-plane bond angles compared to the out-of-plane bond angles. For a slab of reasonable thickness (9 u.c. in our case), one can quantitatively identify the surface, inner layers and interface regions by the evolution of the Ru-O-Ru bond angle in the $ab$ plane along the c-axis as shown in Figure 4.14(b). For the 9 u.c. case, a large region of inner layers (properties similar
Figure 4.14: (a) Layer projected DOS (spin-up + spin-down) closer to the interface from STO2 to SRO3 for the 9 u.c. case. The LT (RT) phase is shown in blue (red). The shaded DOS below 1.2 eV in the RT SRO1 layer has $x^2-y^2$ character. The energy range is from 1.0 eV to 2.2 eV (above $E_F$). (b) Ru-O-Ru bond angle in the ab plane as a function of the layer index for LT (solid lines) and RT (dashed lines) phases. The red, green and blue lines represent respectively the 3 u.c., 6 u.c. and 9 u.c. cases. The black dashed line represents the calculated LT bulk value in the same volume setup. The values for the SRO1 layer are indicated by an arrow.

to bulk) exists while this region is not distinctly observed in the 3 u.c. case. Due to the interface reconstruction, the interface layer SRO1 is characterized by a Ru-O-Ru in-plane bond angle having a value between the SrRuO$_3$ and SrTiO$_3$ bulk values. The properties of the inner layers are closer to the bulk. At the surface, we always obtain a bond angle larger than the bulk. Apart from the general differences be-
between bond angles for different regions of the slab, an important observation can be made regarding the bond angles for the LT and RT phases.

It is clearly seen that the difference in bond angle between SRO1 and other SRO layers is larger for the RT phase compared to the LT one. For example, in the 6 u.c. case, the difference in the bond angle between SRO1 and SRO5 is 1.5° for the LT phase, while it is 3.0° for the RT phase (Figure 4.14(b)). This influences the hopping of electrons (as evident from the calculated hopping parameters mentioned above) and hence the transport properties at the interfaces. Therefore, we can conclude that the differences in the geometries and electronic structures between SRO1 and other SRO layers are less dramatic in the LT phase compared to the RT one, which may effectively lead to an enhanced transmission of hot electrons across the interface at LT. The larger mismatch at RT between interface and inner layers will yield a smaller transmission factor (C factor in Equation 1) in the RT phase. Such a substantial influence of geometric and structural changes at the interface leading to strong temperature dependent transport characteristics across the magnetic phase transition in SrRuO$_3$ is a remarkable finding, not observed before in any oxide heterostructure.

4.7 Conclusions

In this chapter, an overview of the growth and the characterization of SrRuO$_3$ thin films used in our studies is provided. The SrRuO$_3$ films are grown using pulsed laser deposition, and their growth is monitored using in-situ RHEED. The grown films were characterized for their structural properties using AFM and XRD, which shows a smooth coherent growth with no secondary phases formed. The growth of ultra-thin films with increasing thickness also provides an opportunity to study the growth morphology of SrRuO$_3$ on SrTiO$_3$ and exhibits its substrate termination growth rate. We observe that as the film thickness increases, such local regions of underlying SrO terminations of the substrate are no longer distinguishable. The magnetic properties of the thin films were studied. They showed a typical ferromagnetic behavior below 140 K for all film thicknesses and indicted the progressive decrease in the $T_C$ with decrease in film thickness. Additionally, we studied electrical transport of the films and observed their good metallic properties for all thicknesses; although with decreasing film thickness the resistivity increases. A strong correlation between the magnetic and electrical properties were also observed as the resistivity curves change slope at $T_C$, indicative of the suppression of spin dependent scattering in its ferromagnetic phase. Correspondingly, we also observed the similar decrease in $T_C$ with film thickness. Finally, we have studied the BEEM
transmission through thin films of SrRuO$_3$ of various thicknesses, interfaced with Nb:SrTiO$_3$ across its magnetic transition. The increase in BEEM transmission at 120 K compared to RT is accompanied by a surprising flipping of the attenuation length. Our first principles calculations indicate strong geometrical reconstructions at the interfaces characterized by Ru-O-Ru bond angles along with distinct features in electronic structures of the Ru-d orbitals, both of which are strongly dependent on the magnetic phases. As a consequence, the importance of the transmission factor in the expression for BEEM current is realized to explain the experimentally observed BEEM transmission data. Moreover, the inclusion of the temperature dependent quasiparticle weight for the calculation of the attenuation length correctly describes the experimental observation at 120 K and RT. The evolution of such unique features in electronic transport in complex oxide heterostructures, across a magnetic phase transition, opens new possibilities to manipulate the electronic and spin degrees of freedom by a selective choice and tailoring of their interfaces. 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.
4.7. Bibliography

Bibliography


