Engineering complex oxide interfaces for oxide electronics
Roy, Saurabh
Chapter 6

Influence of ferroelectric polarization on hot electron transport through BiFeO$_3$

Abstract

Oxide heterointerfaces exhibit a strong correlation between spin, charge and orbital degrees of freedom among its constituent thin films thus presenting them as strong contenders for multifunctional devices. To address such novel functionalities, it is important to understand the interfacial phenomena and tune them accordingly by external electric, magnetic or optical inputs. However, the pristine electronic structure of these interfaces till now have been determined using the invasive high resolution scanning transmission electron microscopy (HR-STEM) or synchrotron-radiation studies. Here we present a novel technique to ascertain the electronic structure of a buried interface of metal-ferroelectric semiconductor, and provide a direct evidence of the ferroelectric polarization control of the interfacial energy band alignment. We grow heterostructures of Au/BiFeO$_3$/Nb:SrTiO$_3$ on either terminations of the Nb:SrTiO$_3$ substrates, fabricate devices and probe hot electron transport across these heterostructures. Exploiting the dependence of the ferroelectric polarization of BiFeO$_3$ on the terminating site of a substrate, local Schottky barrier heights (SBH) reveal the influence of the interfacial charges on the energy band alignment of the device, without application of any external bias across the interfaces. This novel technique can be extended to further study the detailed interface physics of oxides and accordingly tune their fundamental properties.

6.1 Introduction and Motivation

Ferroelectrics form a large sub group of dielectric materials, majorly defined by two characteristics. First is the existence of spontaneous electric polarization, and second is a response of this polarization to an external electric field, i.e. the polarization must be reversible when a sufficiently large electric field is applied in the opposite direction. Ferroelectric materials are important contenders for non-volatile electronic devices, including memory devices. Research on these materials normally deal with the mechanism of the formation of spontaneous polarization, the relationship of this polarization to the atomic and electronic structure, the control of ferroelectric polarization, and the use of ferroelectric materials in electronic
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Figure 6.1: Schematic of a typical ferroelectric hysteresis loop. The vertical axes marks the remnant polarization ($P_r$) and the saturation polarization ($P_s$). Figure adapted from [1].

devices. The ferroelectric polarization directions can be switched by the application of an external electric field due to the coupling of the electric field $E$ and the polarization $P$. This coupling reflects the change of relative energy $E.P$. The response of the polarization to the applied electric field produces a hysteresis loop which could be measured experimentally, as shown in Figure 6.1.

Perovskites are a large family of materials which exhibit a broad range of physical properties including ferroelectricity, ferromagnetism, magnetoelectric coupling, and superconductivity. [2, 3, 4, 5] An ideal perovskite with a chemical formula of ABO$_3$ has a cubic unit cell. By symmetry this cubic structure does not possess an inherent polarization and thus is not ferroelectric. Within this large family of perovskites, a few of them are ferroelectric. Structurally, Goldschmidt presented an empirical theory for a tolerance factor ($t$) connecting the structure of the perovskite and the ionic sizes of its constituents, which is defined by

$$t = \frac{R_A + R_B}{\sqrt{2}(R_B + R_O)}$$  \hspace{1cm} (6.1)

where $R_A$, $R_B$ and $R_O$ are the radii of A, B and O atoms respectively. For a value of $t$>1, the structure prefers a ferroelectric state with a polar distortion of B atom (for example, BaTiO$_3$). For $t$<1, rotational distortion of the oxygen octahedra suppresses ferroelectricity (for example, SrTiO$_3$ and CaTiO$_3$). Thus, ferroelectricity is sensitive
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Metal MetalFerroelectric
Charge distribution
Voltage
Electric field

Figure 6.2: A schematic of (a) a short circuited structure of an electrode-ferroelectric structure with the polarization displayed; (b) the charge distribution in presence of perfect electrodes; (c) charge distribution; (d) voltage; and (e) electric field profiles in presence of realistic electrodes. Note: the ferroelectric film is completely insulating.

to strain due to its strong effect on the atomic structure of the ABO$_3$ unit. The in-plane strain induced by the substrate influences the phase diagram of a ferroelectric thin film, and this effect is widely used nowadays for the growth of ferroelectric heterostructures with modified ferroelectric properties. Even in a paraelectric material, such as SrTiO$_3$, epitaxial strain may induce a ferroelectric phase. [6]

With progressive decrease in thicknesses of ferroelectric thin films and their active use in devices, the measured properties reflect the entire system of films, interfaces, electrodes, and substrates; and the ferroelectric thin films thus can not be considered in isolation. With the growth of ferroelectric thin films on substrates, their properties are often considerably different from those of their bulk parent material. The electronic properties also have a characteristic behavior in thin-film form. While bulk ferroelectric materials are usually treated as good insulators, with decreasing film thickness, it becomes more appropriate to treat them as semiconductors with a fairly large band gap.

Conventionally, ferroelectricity has been believed to exist just in bulk materials and disappear as the dimensions of a ferroelectric material goes down to the
Influence of ferroelectric polarization on hot electron transport through BiFeO$_3$ nanoscale. This is because the depolarizing field in ferroelectric increases as the dimension of the materials is reduced. The depolarization effect on nanoscale ferroelectric can be understood from Figure 6.2. [7] The depolarizing field is opposite to the direction of ferroelectric polarization. With ferroelectric polarization being normal to the interface, the screening charges from the electrode compensate the ferroelectric polarization charge at each interface. For ideal metal, the polarization charges are perfectly compensated at both interfaces and therefore no depolarizing field emerges in the ferroelectric film. However, in reality the effect of interface polarization charge is not fully compensated due to the incomplete screening by the electrode. The screening charges are distributed in a vicinity of the interface. The net charge distribution results in a voltage jump at each interface from the electrode. With both electrodes short-circuited, the voltage drop in the ferroelectric film from one interface to the other leads to the depolarizing field opposite to the polarization. This field depends inversely on the thickness of the ferroelectric film. Therefore, when the dimension of the ferroelectric film is down to a critical size, the depolarizing field will be strong enough to suppress the ferroelectricity.

Switching the polarization of such films requires a metallic contact, raising fundamental issues on the behavior of the interface between the ferroelectric layer and the electrode. In addition to the depolarizing field, the partially covalent nature of the bonds in the ferroelectric changes the band structure with respect to that of a perfectly ionic compound. Intense theoretical activity has been deployed to understand the electronic structure and band alignment at the interface. [8, 9, 10, 11, 12, 13, 14] First principles calculations can even predict an Ohmic barrier. Pintilie et.al. have extended semiconductor theory of the metal-insulator interface to the case of ferroelectric capacitors, including the effect of the polarization on the band line-up and consequential transport properties. [15]

Realizing the formation of the electrode interface and the relation between the polarization charges and the electronic properties of the interface is crucial in controlling the polarization switching and the magnitude of leakage current. These two are important considerations in the read-write processes in nonvolatile memories. [16] The influence of the polarization and electrode interface is better studied using good quality epitaxial ferroelectrics, avoiding in this way the deleterious effects of the grain boundaries (large extrinsic contribution to the dielectric constant, back-switching effect, low carrier mobility, etc. [17, 32, 19] In the ferroelectric capacitors based on high-quality epitaxial films the hysteresis loop is rectangular, which can be attributed to the absence of pinning centers for the ferroelectric domains, associated with grain boundaries. This also represents a very efficient mechanism for the
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Figure 6.3: PFM images (topography and phase) of electrically polarized locations. (a) PFM images after polarizing a 3x3 µm² area. The top image shows the topography image and the bottom one, the phase contrast. (b) PFM images after five successive scans of reading out the ferroelectric polarization of the written location. The phase contrast image shows no impression of polarization. Applied voltage 8 V to the sample.

screening of the depolarization field during the switching process. The last one may be related to the height of the potential barriers at the electrode interfaces, which seems to be influenced by the magnitude and orientation of the ferroelectric polarization. [37, 28]

Despite these important theoretical advances, there is little direct experimental data, due to the intrinsic difficulty of measuring the electronic structure of a buried interface. Determination of the electronic structure of such a device is even more challenging in traditional electrical characterizing methods. Several groups have conducted electrical measurement on these systems [22, 23, 24] but they do not directly probe the microscopic interfacial electronic structure. A recent study exhibited the resistive switching behavior of semiconducting ferroelectric BiFeO₃. [25] The semiconducting behavior of BiFeO₃ has been exploited in the demonstration of polarization-controlled charge transport [37, 27] and switchable photovoltaic effects. [28, 29] The latter behavior was qualitatively explained by a transition from a Schottky to an Ohmic contact at the interface, driven ferroelectrically. [30] Here, we demonstrate a novel non-destructive technique to probe the ferroelectric polarization dependence of the transport of hot electrons through a metal-BiFeO₃-semiconductor stack and reveal the interfacial electronic structure in a non-invasive
way. A combined study of STM topography and BEEM current provides a quantitative picture of the spatial uniformity of the potential landscape of the buried metal-semiconductor interface at the nanometer scale. However, a fundamental issue lies in switching the ferroelectric polarization of an ultra-thin film of BiFeO$_3$ without the use of a metallic bottom electrode. This arises as a result of incomplete screening of the charges at the interface with the semiconductor causing the generation of a depolarizing field that strongly impacts the switchability of its ferroelectric state. An attempt of switching the polarization state of a thin BiFeO$_3$ film grown on Nb:SrTiO$_3$ is as depicted in Figure 6.3. After polarizing a selected area, successive PFM phase images show progressive decrease in the phase contrast; thereby confirming a local charging phenomena to appear in the contrast initially, and not a change in ferroelectric polarization. Several such locations were probed for switching the local polarization state, all yielding similar results. A solution to studying the differently polarized state of BiFeO$_3$ films was arrived at by growing the film on different terminations of the substrate, which yields the ferroelectric polarization either towards the interface or away from it.

### 6.2 Interface control of polarization state

Atomically sharp interfaces between complex oxides reveal newer functionalities in heterostructures. Recently, in a study by Yu et al. [31], it was demonstrated that the ferroelectric polarization of a thin film is inherently controlled by the interfacial chemical termination. They explored this phenomena by growing BiFeO$_3$ thin films on conducting La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) bottom electrode and tuned the valence mismatch at the interface. With the aid of RHEED, thin films of BiFeO$_3$ were grown with atomic sharpness on either terminations of LSMO. When the two structures (FeO$_2$-BiO-MnO$_2$-La,SrO and BiO-FeO$_2$-LaSrO-MnO$_2$) were probed for their ferroelectric properties using a PFM, the as grown polarization of the sample directly correlated with the interface termination of the heterostructure. They observed that samples possessing the MnO$_2$ termination had polarization upwards (pointing up outwards the interface) whereas the ferroelectric polarization was pointing downwards (pointing down into the interface) for the films possessing LaSrO terminations (Figure 6.4).

Such a dependence was studied by density functional theory (DFT) calculations based on the atomic scale electrostatic potentials across two non-equivalent interfaces, as shown in Figure 6.5. They observed an increase in the potential gradient when the direction of polarization was against the preferred direction of electrostatic
potential and it resulted in an enhancement of the depolarizing field for a specific polarization direction. This potential gradient were composed of two major contributions, ferroelectric depolarizing field and the electrostatic potential difference between two non-equivalent interface, however the major contribution to the preference of ferroelectric polarization direction originated from the valence mismatch at the interface.

They extended this study for different interfaces and tabulated the presence of preferred polarization direction for thin films of BiFeO$_3$ grown on different substrate terminations. Thus, this result provides us a route to obtain different bulk polarization directions of BiFeO$_3$ when grown on differently terminated substrates thereby providing us with an opportunity to circumvent the issue of polarizing different regions of the same ferroelectric film in different directions. A growth of BiFeO$_3$ on the TiO$_2$ and SrO terminations of Nb:SrTiO$_3$ would eventually lead to ferroelectric polarizations towards and away from the interface.

### 6.3 Sample growth, fabrication and measurement technique

BiFeO$_3$ thin films were grown using pulsed laser deposition on both SrO and TiO$_2$ terminations of Nb:SrTiO$_3$ substrates (Nb = 0.01 wt. %). The initial steps of chemically terminating the substrate prior to deposition has been mentioned before in details. To attain an uniform SrO termination of the substrate, 1 unit cell (u.c.) of SrO is deposited on the previously TiO$_2$ terminated substrate. Subsequently, 4 nm
thick BiFeO$_3$ films were deposited on either samples. Epitaxially, these films were grown at a substrate temperature of 670°C from a target with 11% excess Bi to main-
tain the stoichiometry of volatile Bi. The background oxygen pressure was kept at 0.3 mbar, the fluence at 2 J/cm$^2$ and a pulse repetition rate of 0.5 Hz. The target to substrate distance was kept at 58 mm. Simultaneously during the growth of the film, reflection high energy electron diffraction (RHEED) specular spots were used to monitor the quality of film grown. Figure 6.6 (a, b) shows the AFM topography scan and their corresponding RHEED spots after the growth of BiFeO$_3$ on SrO and TiO$_2$ terminations, respectively. This was followed by patterning device structures of 250 $\mu$m x 650 $\mu$m using standard UV lithography and ion beam etching technique. Thereafter, the sample was patterned again to selectively deposit 10 nm of Au on the device area followed by the deposition of top and bottom contacts of Au (100 nm) and Ti (75 nm)/Au (75 nm), respectively. For BEEM studies, a modified commercial STM system from RHK Technology was used. The samples were studied both for their macroscopic I-V characteristics as well as with BEEM at a local scale. The primary difference in studying the electrical transport across the interface lies in the application of voltage across the metal-semiconductor (M-S) interface. The measurements were all done at room temperature (300 K), and thermionic emission theory was used to ascertain the Schottky barrier height and the quality of the M-S interface. Additionally, since the injection current in BEEM experiments is in the order of nanoamperes (nA), the zero bias resistance of the device assumes importance in collecting the BEEM current. In the devices shown above, the zero bias current is sufficiently low to obtain spectroscopy data. In BEEM, no bias is applied to the M-S interface and thus, the injected hot electrons enter the conduction band by virtue of their kinetic energy after traveling through the film and across the interface. The BEEM current, $I_B$ is recorded over a local area of a few nanometers (nm), at a constant tunnel current, $I_T$, while varying the $V_T$. $I_B$ clearly depends on the thickness of the metallic over layer and decreases exponentially with increasing thickness. Each specific location on the device was probed with 150-200 spectra and many locations on different devices were averaged to obtain the representative BEEM spectrum. Figure 6.6 (e) shows the schematic of the measurement set-up. At each of these locations, the local SBH was extracted from the onset of their respective BEEM current using the Bell-Kaiser (B-K) model.

6.4 Polarization control of energy band alignments

In order to understand the formation of electrode interface and the relation between polarization charges and the electronic properties of the device, a composite energy band diagram of the system is required. Here we consider an asymmetric heterostructure consisting of thin metallic films, an n-doped semiconductor
Figure 6.6: (a, b) AFM image of 4 nm BiFeO$_3$ deposited by PLD on SrO and TiO$_2$ terminated substrates (left and right). Their corresponding root mean square (rms) roughness is 0.26 nm and 0.42 nm, respectively. The corresponding images of the specular RHEED spots are shown below. (c) Schematic representation of the device and the BEEM measurement set-up.

(Nb: SrTiO$_3$) and a ferroelectric thin film. Although BiFeO$_3$ is electrically insulating in bulk, oxygen vacancies play a very important role in controlling the conduction in thin films. These oxygen vacancies present themselves as n-type defect states in the band gap that enables thermally activated electrons to be promoted to the conduction band. This conduction through BiFeO$_3$ thin films can be controlled by different oxygen content, either by altering the cooling rate or oxygen pressure after growth, but otherwise growing under similar conditions. This renders the device to have two interfaces, i.e. metallic thin film-BiFeO$_3$ and BiFeO$_3$-Nb: SrTiO$_3$. 

These two interfaces are discussed separately. We start with the BiFeO$_3$-Nb:SrTiO$_3$ interface. From previous studies, the energetic positions of the conduction band (CB) and valence band (VB) edges of Nb:SrTiO$_3$ without the applied sample bias (at zero sample bias) are extracted to be -0.06 V and -3.26 V, respectively. [34] The energetic positions of the CB and VB edges of BiFeO$_3$ without the applied sample bias are 1.33 V and -1.37 V. [34] With presence of no additional dopant concentrations, the Fermi level of BiFeO$_3$ is situated close to the middle of the gap. A high level of doping in Nb:SrTiO$_3$ makes it a degenerate semiconductor. The built-in potential at the Bi/FeO$_3$/Nb:SrTiO$_3$ interface can be determined based on the difference of the work function between them. The work function of Nb:SrTiO$_3$ is 4.08 eV and BiFeO$_3$ is 4.70 eV. [35] Consequently, when Nb-SrTiO$_3$ and the as-grown P-down state in BiFeO$_3$ are joined together, the ideal value of built-in potential ($\phi_{bi}$) is 0.62 eV. Some of the electrons from Nb:SrTiO$_3$ spontaneously move into BiFeO$_3$ because the Fermi level of BiFeO$_3$ is lower than that of Nb-SrTiO$_3$ and such a movement of electrons causes negative charges to accumulate in BiFeO$_3$ depletion layer. Without considering the contribution of the as-grown polarization, the band structure of virgin BiFeO$_3$/Nb:SrTiO$_3$ can be schematically plotted in Figure 6.7.

In accordance to earlier theoretical estimations, the surface charge neutrality level ($\phi_0$) is located 2.20 eV above the valence band edge. [36] The $\phi_{bi}$ value of 0.62 eV suggests that the Fermi level at the interface is below $\phi_0$ resulting in a positively charged BiFeO$_3$-Nb:SrTiO$_3$ interface. However, in order for it to be a stable system, the as-grown interface trap charge prefers to be zero, suggesting the Fermi level of BiFeO$_3$ approaches the surface charge neutrality level at the interface. This consideration motivates the as-grown polarization state to be downward. The positive bound charges of the as-grown P-down state in BiFeO$_3$ will assist the reduction of the unwanted positive trapped charges at the hetero-interface. Consequently, the depolarization field resulting from the as-grown polarization contributes to a wider electron region of the band at the interface, as schematically indicated in Figure 6.7(c).

According to the model proposed Pintilie et. al. [32], the ferroelectric polarization can influence the built-in potential as $\Delta \phi = \phi_{bi}' - \phi_{bi} = \pm P \delta / \epsilon_0 \epsilon_S$, where $\phi_{bi}'$ is the built-in potential with contribution from polarization, $\phi_{bi}$ is the built-in potential without contribution from polarization, $\epsilon_0$ is the permittivity of free space, $\epsilon_S$ is the static dielectric constant, $P$ is ferroelectric polarization, and $\delta$ is the thickness of an interface layer between the polarization surface charge and the physical interface with the metallic system. For BiFeO$_3$ films, the ferroelectric polarization value $P$ is
approximately 60 $\mu$ C/cm$^2$, and the reported low-frequency dielectric constant is approximately 100. The variation in the built-in potential $\Delta \phi$ can then be estimated as 0.38 eV for a $\delta$ value of the order of 0.4 nm. With these values of $\phi_{bi} (0.62 \text{ V})$ and $\Delta \phi (0.38 \text{ V})$, the predicted $\phi'_{bi}$ for a downward polarized BiFeO$_3$ is 1.00 V. Similarly for the polarization up scenario, the ideal built-in voltage $\phi'_{bi}$ is deduced to be 0.24 V from $\phi_{bi} (0.62 \text{ V})$ and $\Delta \phi (0.38 \text{ V})$. Such a behavior, previously observed, is attributed to the screening of the ferroelectric polarization at the interface by oxygen vacancies. [37] [38] Figuratively, the band alignment at the heterointerface for polarization up situation is shown in Figure 6.7(d). However, in this scenario the
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Figure 6.8: Schematic diagram of the energy bands at the interface of Au and BiFeO$_3$ for the different polarization states of BiFeO$_3$.

depolarization field from the negatively bound charges result in an upward bending of the band and produces a narrow depletion region near the interface.

On the other hand, the interface of the metallic thin film on semiconducting BiFeO$_3$ aligns its energy bands in accordance to the conventional Schottky barrier theory. This situation is far simplified; a change in the ferroelectric polarization state of BiFeO$_3$ causes a change in the interface potential of BiFeO$_3$ thereby causing a change in the band alignment. From the above discussions, we can hereby construct the composite band diagram of the entire system as shown in Figure 6.8.

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The electronic transport studies on the samples mainly comprised of both macroscopic current-voltage ($I$-$V$) measurements and further local scale investigations using BEEM. Figure 6.9 shows the $I$-$V$ characteristics of the samples at 300 K. Each plot is a representative of multiple measurements on several devices on the same sample and all of them show good diodes. The $I$-$V$ characteristics show clear rectifying behavior, where the forward biased current shows a linear increase in the semilog scale, whereas no current flows in the reverse bias. This linear increase and a strong asymmetry in $I$ is consistent with the thermionic emission over a Schottky barrier, as expected from the asymmetry of the energy profiles. However, a measure of dependence on this charge transport phenomena is given by the ideality factor
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Figure 6.9: Electrical (I-V) characteristics of $\text{Au/BiFeO}_3/\text{SrO-Nb: SrTiO}_3$ and $\text{Au/BiFeO}_3/\text{TiO}_2-\text{Nb: SrTiO}_3$ devices at RT (300 K). Inset shows a schematic of the electrical connections. The straight line fit is the thermionic emission fit allowing an extraction of the Schottky barrier height and the ideality factor.

(n). Classical thermionic emission current does not depend on the Schottky barrier width but only on the barrier height; which yields an ideality factor of 1. The forward bias characteristics were fitted with thermionic emission theory to extract the Schottky barrier height (SBH) at zero bias and the ideality factor.

The measurement schematic for the I-V characterization is as shown in Figure 6.9 (inset). As the Au-BiFeO$_3$ forms a M-S interface, a peak in electrical potential profile of height $e\Phi_B$ is formed, and this barrier height is modified by the polarization state of BiFeO$_3$ (up or down). The macroscopic SBH for the two polarization states of BiFeO$_3$ are extracted to be 1.25±0.02 eV (Au/BiFeO$_3$/SrO-Nb: SrTiO$_3$) and 1.06±0.02 eV (Au/BiFeO$_3$/TiO$_2$-Nb: SrTiO$_3$). A simple Schottky-Mott model for a M-S junction would expect a SBH of 1.8 eV considering the work function of Au to be 5.1 eV and the electron affinity of BiFeO$_3$ as 3.3 eV. The experimentally extracted SBH deviates from the expected value and clearly shows an additional interface effects determining the final energy band line-ups. The ideality factors for Au/BiFeO$_3$/SrO-Nb: SrTiO$_3$ (1.2) and Au/BiFeO$_3$/TiO$_2$-Nb: SrTiO$_3$ (1.3) can attribute to charge transport mechanisms like tunneling or thermally assisted field emission being prevalent across the interface. However, the barrier heights extracted for BiFeO$_3$ grown on SrO and TiO$_2$ terminations were different thereby indicating an influence of polarization in the SBH obtained from macroscopic I-V measurements.

The hot electron transmission at several locations through the metallic overlay-
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Figure 6.10: BEEM spectra for the Au/BiFeO$_3$/SrO-Nb:SiTiO$_3$ and Au/BiFeO$_3$/TiO$_2$-Nb:SiTiO$_3$ devices at RT (300 K). Each spectrum is a representative of several spectra taken at the same location. For each device, three such BEEM spectra are represented which provides an idea of the uniformity in BiFeO$_3$ thin films growth on SrO and TiO$_2$ terminations of SiTiO$_3$.

ers and across the Au/BiFeO$_3$/TiO$_2$-Nb:SiTiO$_3$ and Au/BiFeO$_3$/SrO-Nb:SiTiO$_3$ are shown in Figure 6.10. In both cases, the BEEM transmission is found to increase sharply with increasing $V_T$ beyond a certain tip bias, while $I_T$ is kept constant. Many such spectra were taken to ascertain the uniformity of the hot electron transport property of the devices. These hot electrons are injected by the STM tip across the vacuum tunnel barriers into the Au overlayer. These hot electrons propagate through the film and are scattered both elastically and inelastically in the process, and reach the unbiased Au-BiFeO$_3$ interface. A few of these electrons that possess enough energy and satisfy the stringent moment conservation criteria, overcome the Schottky barrier and enter the conduction band of the 4 nm thick BiFeO$_3$ thin film. As the carriers enter the BiFeO$_3$ thin film and travel across it by virtue of their kinetic energy, they will, due to the band bending at the BiFeO$_3$-Nb:SiTiO$_3$ interface, be accelerated away from the interface into the conduction band of the Nb:SiTiO$_3$ and constitute the BEEM current. As is evident from the energy band diagrams, the electric field at the BiFeO$_3$-Nb:SiTiO$_3$ interface always aids in transmitting charge carriers away from the interface. A change in the sign of polarization charge only changes the magnitude of the electric field at this interface. Consequently, the highest energy barrier that hot electrons encounter in their transmission is the interface between the metallic over-layer and the BiFeO$_3$. Since the electric potential at this interface is directly related to the ferroelectric polarization state of BiFeO$_3$, measuring a change in the SBH at this interface reflects its polarization state. This can be
obtained from the onset of the BEEM transmission beyond a certain threshold voltage (corresponding to the SBH). Using the B-K model [33], we obtain the local SBH for Au/BiFeO$_3$ interface by extrapolating the straight line so as to intersect the voltage axis in the plot of the square root of the BEEM transmission versus the applied voltage, as shown in Figure 6.11. The measurements indicated an extracted SBH of $1.56\pm0.03$ eV for Au/BiFeO$_3$/SrO-Nb: SrTiO$_3$ devices and a value of $1.07\pm0.03$ eV for Au/BiFeO$_3$/TiO$_2$-Nb: SrTiO$_3$. The SBH directly corresponds to the collected BEEM current for the two samples. We observe a higher $I_B$ for Au/BiFeO$_3$/TiO$_2$-Nb: SrTiO$_3$, indicating a larger number of transmitted electrons that can overcome the SBH and contribute to the BEEM current. In either devices, the injected hot electrons travel the same thickness of Au overlayer, and thus undergo similar attenuation. A difference of an order of magnitude in the BEEM transmission for the two devices point to the dissimilar energy barriers. Furthermore, a wide spread in the BEEM current in Au/BiFeO$_3$/TiO$_2$-Nb: SrTiO$_3$ hints the non-uniform growth of BiFeO$_3$ on TiO$_2$ termination. The SBH extracted from different locations and devices from either samples are represented in the histogram shown in Figure 6.11 (inset).

Although location-wise, a slight deviation in the extracted SBH was observed for the two kinds of samples, a clear difference in the energy band line-ups at the Au and BiFeO$_3$ interface was observed, indicating a tuning of the barrier potential by virtue of its ferroelectric polarization. In order to confirm the observed phenomena, we grew a heterostructure of metallic LaSrMnO$_3$ (LSMO)/BiFeO$_3$/SrO-Nb: SrTiO$_3$. Here in place of Au, a thin film of LSMO (3.5 nm) is grown on a similar 4 nm thick BiFeO$_3$ film on SrO terminated Nb: SrTiO$_3$ substrate. Devices were fabricated on the sample in a similar fashion as mentioned earlier. Preliminary $I$-$V$ characterization of the sample shows a good rectifying diode with an extracted SBH of $1.33\pm0.02$ eV and an ideality factor of 1.3, Figure 6.12(a). The leakage current at zero bias is sufficiently low ($10^{-10}$ Amps) and hot electron transport studies were performed on this sample. The representative BEEM spectra are obtained by sweeping the tip bias while simultaneously recording the $I_B$ at a constant tunnel current injection. The local SBH extracted from these measurements, using the B-K model [33] is $1.74\pm0.03$ eV as shown in Figure 6.12(b), which are comparable to the previous sample with similar direction of polarization. We thus clearly establish the dependence of the grown polarization state of BiFeO$_3$ on the extracted SBH from the devices.

Interfaces between two oxides are known generate novel electronic phases that are not accessible in bulk. In the case of BiFeO$_3$ grown on TiO$_2$/SrO-Nb: SrTiO$_3$, our study provides an opportunity understand the role played by the heterointerface is stabilizing the polar phase of BiFeO$_3$; whose origin lies in the coupling between
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Figure 6.11: The extracted SBH at the Au/BiFeO\textsubscript{3} interface Schottky interface, obtained by plotting the square root of the normalized BEEM current $I_B$ vs. $V_T$ and fitting it with the B-K model at 300 K. The inset shows the corresponding occurrences of the distribution of SBH obtained at different locations for both the devices. The error bars reflect the standard deviation of the measured onset of the BEEM current at a location.

The concept of interfacial coupling rests on the idea that the substrate tends to translate its octahedral pattern to the film grown on top of it. Magnitude and sense (in-phase or out-of-phase) of these rotations determines the electronic and magnetic properties. The stability of the polar phase of BiFeO\textsubscript{3} lies in the interface charge, misfit strain and octahedral tilt at the interface of substrate. The interface selection of the ferroelectric polarization is due to the preference of SrO or TiO\textsubscript{2} interface to stabilize either an in-phase or out-of-phase rotation pattern in BiFeO\textsubscript{3} about the film-normal direction. The TiO\textsubscript{2} terminated interface enables the BiFeO\textsubscript{3} film to have a complete FeO\textsubscript{6} octahedron, and as in the bulk the film prefers to adopt an out-of-phase rotation of the octahedron. This results in a more energetically favored state which causes a polar atomic displacement. In contrast, the SrO termination leads to FeO\textsubscript{6} octahedra with nearest neighbor interactions determined by the Sr or Bi cations. Since SrFeO\textsubscript{3} has a structural tendency to adopt an in-phase rotation about the film normal which presents a lowest energy configuration, which causes a stronger interaction between the Bi cation and the oxygen octahedra, altering the cationic displacement thereby manifesting as a different polarized state. Such a change in ferroelectric polarization in our samples is captured by a respective variation in the energy band alignment at its interface with a metal. Under
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Figure 6.12: (a) Electrical (I-V) characteristics of LSMO/BiFeO$_3$/SrO-Nb:SrTiO$_3$ devices at RT (300 K). Inset shows the representative schematic of the set-up. (b) Representative BEEM spectra of the device, an average of several spectra taken at various locations and on different devices. The inset shows the extracted SBH of 1.74±0.04 eV. The error bars reflect the standard deviation of the measured onset of the BEEM current at a location.

normal circumstances, detection of out-of-plane polarization in ultra-thin films becomes quite challenging and even more without a bottom electrode. Recently, such studies have been conducted using annular dark field (ADF) scanning transmission electron microscopy (STEM) on thin films which determine the atomic positions at the heterointerface to determine the polarization state. Our technique, on the other hand gives an indirect knowledge of the ferroelectric polarizations in ultra-thin films [39].

6.6 Conclusion

In conclusion, we have demonstrated a novel way of studying the different polarization states of BiFeO$_3$ thin films obtained by atomically precise control of the interface using BEEM. The as-grown polarization states of BiFeO$_3$ thin films were engineered by its growth on SrO and TiO$_2$ terminated Nb:SrTiO$_3$ substrates. Macroscopic I-V characteristics of the both the samples showed good rectifying diode, but the extracted SBH of samples where BiFeO$_3$ was grown on SrO terminations (down-polarized) consistently showed a higher value than the one grown on TiO$_2$/Nb:SrTiO$_3$ (up-polarized). The samples were characterized for hot electron transport across the heterointerface. From the collected BEEM current, the extracted SBH from the B-K
fit clearly showed a higher potential barrier for Au/BiFeO$_3$/SrO-Nb:SrTiO$_3$ than for the sample with BiFeO$_3$ grown on TiO$_2$ terminations. To confirm this observation, we fabricated another sample (LSMO/BiFeO$_3$/SrO-Nb:SrTiO$_3$), which is also polarized upwards, and studied hot electron transport through it. The extracted SBH was similar to the sample with BiFeO$_3$ grown on SrO termination. Our experiments have extended the conventional device design in BEEM to detect the ferroelectric polarization effects, allowing a manifestation of the polarization states as different SBH in our measurements. Utilizing the unique capabilities of BEEM, the electronic potential landscape of the buried interface can be mapped out at a nanoscale. Such studies could be instrumental in understanding the role of adsorbates acting as screening charges.

Bibliography

6. Influence of ferroelectric polarization on hot electron transport through BiFeO$_3$