Chapter V

Resistive switching in spin filter CoFe$_2$O$_4$ and ferromagnetic La$_{0.67}$Sr$_{0.33}$MnO$_3$ interfaces

In this chapter, we present the observation and analysis of the resistive switching phenomenon at the CoFe$_2$O$_4$ -La$_{0.67}$Sr$_{0.33}$MnO$_3$ interface. An attempt is made to bring out the underlying mechanism by scanning probe microscopy techniques.
5.1 Introduction:

The development of oxide based non-volatile memories having features such as high-density, fast read-write, low energy operation, high endurance under cycling, retention ability and low cost is of great current interest. The GMR and TMR based magnetic random access memories and ferroelectric random access memories (FeRAMs) have been developed. Resistive switching (RS) is an especially interesting phenomenon that has attracted recent attention in view of its potential for alternative, simple and high density non-volatile memory application. This phenomenon has been observed in a wide variety of transition metal oxides, such as manganites, NiO$_2$, TiO$_2$, SrTiO$_3$, and Cu$_2$O$_3$, ZnO and doped oxides such as Cr doped SrZrO$_3$, cobalt doped TiO$_2$, Mn doped ZnO. In these cases, it has been demonstrated that the resistance of a thin film element (typically examined in current-perpendicular to plane geometry) can be reversibly tuned by applying voltage pulses. Unipolar and bipolar switching has been observed in different film based and interface systems, and mechanisms based on filamentary path formation or field induced interface barrier modification have been proposed. Asamitsu et al. first reported the switching in resistance in manganite with electric/magnetic fields and temperature. The compound Pr$_{1-x}$Ca$_x$MnO$_3$ (PCMO) is interestingly a charge ordered (CO) insulator with lowest bandwidth in hole doping regime ($x = 0.1-1.0$) and instability of CO states under these external stimuli lead a large resistance reduction. The other electronic correlations are widely discussed in various models for resistive switching. The interfacial Mott transitions, electronic phase separation, oxygen diffusion, resonant tunneling, polarons, Schottky effects and charge trapping near interface are key mechanisms discussed for resistive switching over time. The microscopic techniques such transmission electron microscopy (TEM), scanning electron microscopy (SEM) and electron energy loss spectroscopy (EELS) have been used to demonstrate filaments in some resistive switching studies. However, the origin of filamentary paths, their formation and rupture are yet not clearly understood in various systems. In addition to that, the filamentary based mechanism alone is not responsible for resistive switching.

Scanning probe microscopy techniques are very efficient tools to study the surfaces and interface of many oxides and their promising use in writing and reading bits with
a very high spatial resolution. In this work our interest was to understand the mechanism of observed resistive switching in the interface system of manganite and cobalt ferrite. In our device configuration the upper layer of CoFe$_2$O$_4$ (CFO) is a ferrimagnetic insulator which is known for its very high magnetostriction coefficient ($\lambda \sim 800 \times 10^{-6}$) and a very efficient spin filtering effect at room temperature. On the other hand, the bottom layer La$_{0.67}$Sr$_{0.33}$MnO$_3$ (LSMO) is a ferromagnetic conductor at room temperature due to broader bandwidth and nearly linear Mn$^{3+}$-O-Mn$^{4+}$ bond. It is known however that small changes in the Mn-O-Mn bond properties on the surface or at the interface of a manganite can change the bandwidth over a wide energy scale that may lead to nanoscale electronic fluctuations, and also modify the transport and magnetic properties significantly.

Herein we report the resistive switching effect at the interface between the spin filter material CFO and mixed-valent room temperature ferromagnetic LSMO. The resistive switching is seen in the form of a sharp transition from high resistive state (HRS) to low resistive state (LRS) exhibiting more than ~100 times change in current. The results examined vis-a-vis the three mechanisms of interlayer transport, namely the space charge limited conduction (SCLC), Schottky and the Poole-Frenkel (PF) mechanism reveal that the resistive switching is interfacial type. A lateral current distribution across the interface shows the interface undergoes an electronic reconstruction from uniform nanoscopic electronic inhomogeneities near grain boundaries to large scale electronic inhomogeneities after switching. The scanning tunneling spectroscopy results suggests that polaron trapping may lead to electronic inhomogeneities responsible for hysteresis and resistive switching. Part of this work was also done jointly with V. Thakare et al. showing a high sensitive magnetic tunable resistive switching.

5.2 Experimental

The heterostructure between CoFe$_2$O$_4$ (CFO) and La$_{0.67}$Sr$_{0.33}$MnO$_3$ (LSMO) was grown using pulsed laser deposition (KrF excimer laser $\lambda=248$ nm, 20 ns pulse duration, laser power 2 J/cm$^2$). The interface grown in a specific way is shown in figure 5.1. First a 100 nm LSMO thin film was deposited on a single crystal (001) LaAlO$_3$ substrate to serve as bottom contact layer. The growth conditions were:
substrate temperature = 700°C, oxygen pressure during deposition = 100 mTorr, oxygen pressure during cooling = 400 Torr. In the second step, a 20 nm LSMO film was deposited on the pre-grown 100 nm LSMO film and immediately afterwards a 4 nm CoFe$_2$O$_4$ (CFO) film was deposited under the same conditions by rotating the target in-situ in PLD chamber. In this way a fresh interface was realized without exposure to air. These films were characterized under high vacuum conditions (better than 10$^{-6}$ Torr) using scanning probe microscopy techniques [SPM 100 by RHK Technologies, USA] and. The AFM was carried out in contact mode using a cantilever of force constant 0.3 N/m in which tip is also coated with Pt in order to carry out the CAFM. The force set point for concurrent imaging of topography and current was optimized by acquiring the force-distance (FD) curves and monitoring the current.

### 5.3 Result & Discussion

The current perpendicular to plane (CPP) transport was studied across these interfaces in which the voltage was varied in a sweeping cycle (- 5 V => 0V => 5V => 0V => -5 V) and the current was recorded. Figure 5.2 (a) shows a typical resistive switching in CFO and LSMO interface in CPP geometry, using the top metal contact of indium. The sharp transition from high resistive state (HRS) to low resistive state (LRS) is seen towards positive polarity (LSMO is the positive terminal) at a threshold voltage ~ 4.45 V (±.05). There is a 100 fold increase in current as seen in figure 5.2 (b). Note the curves also reflect a rectifying behavior below the switching point.

![Device configuration](image)

**Figure 5.1: Device configuration**
Figure: 5.2 (a) The current-voltage characteristics of CFO (4 nm) on LSMO b) at log scale c) dynamic conductance (dI/dV) Inset: dI/dV at log scale
Such diode like characteristics are commonly seen in p-n junction interfaces of doped manganites.\(^1\) Simulations based on semiconductor band theory show that the drift diffusion mechanism, the trap assisted tunneling (caused by oxygen vacancies), and inter-band Zener tunneling dominate in the forward bias, low reverse bias and higher reverse bias, respectively.\(^2\) The other mechanism for such rectification is the formation of Schottky barrier which is seen in the metal-manganite interfaces, particularly in the case of the Pr\(_{0.7}\)Ca\(_{0.3}\)MnO\(_3\) (PCMO).\(^1\) Sawa et al \(^2\) could find similar rectifying character only after depositing a few unit cells of insulating Sm\(_{0.7}\)Ca\(_{0.3}\)MnO\(_3\) (SCMO) on LSMO. We have observed sharp peaks in conductance with hysteretic nature and a shift in zero bias conductance (ZBC) as shown in figure 5.2 (c) and inset figure 5.2 (c1).

We explored the possibility of revealing the mechanism of RS through analysis of three key interlayer transport mechanisms: 1) space charge limited conduction (SCLC), 2) Schottky process, and 3) Poole-Frenkel (PF) mechanism. In space charge limited conduction (SCLC) the Ohmic behavior is modified by Child’s law due to localized states within the band gap of insulator. The Schottky mechanism is purely an interface phenomenon where the current is given by

\[
\ln (I) \propto \sqrt{\frac{e^3}{4\pi\varepsilon_0\varepsilon_r d}} \cdot \frac{V}{kT} \cdot V^{1/2}
\]

The Poole-Frankel (PF) mechanism is associated with the trap states (density of acceptor and donor states near Fermi level in insulators, localized states) and is given by

\[
\ln \left( \frac{I}{V} \right) \propto \sqrt{\frac{e^3}{\pi\varepsilon_0\varepsilon_r d}} \cdot \frac{1}{r \cdot kT} \cdot V^{1/2}
\]

Where \(e\) is electron charge, \(\varepsilon_0\) is permittivity of free space, \(\varepsilon_r\) is the dielectric constant, \(k\) is Boltzmann’s constant, \(T\) is the temperature, \(d\) is the thickness, and \(r\) is a constant having value between 1 and 2 based on the position of the Fermi level.

Figure 5.3 (a) and (b) show the fitting of I-V curves by space charge limited conduction and Schottky emission respectively. The LRS curves are well fitted with SCLC [\(\ln (I)\) vs. \(\ln (V)\)] over the whole bias voltage regime. On the other hand, the
HRS states can be fitted over the low voltage regime by the SCLC mechanism and for higher bias case by the Schottky equation $[\ln(I) \text{ vs. } V^{1/2}]$. The Schottky and SCLC are characteristic of interfacial based RS in contrast to filament formation based mechanism as reported in earlier studies.

**Figure 5.3:** Linear fittings of HRS (black curve) and LRS (red curve) states by (a) space charge limited conduction and (b) Schottky emission
However, it is important to note the current behavior near threshold voltage $V_{th}$ could not be fitted with any of these three mechanisms. The sharp peaks in conductance at threshold voltage can not be explained by any of these mechanisms and are perhaps best discussed in the context of resonant tunneling in semiconductor heterostructures (and also in molecular junctions). In contrast to direct tunneling, the resonant tunneling mainly occurs when the electron first tunnels into localized states inside or near the interface of the barrier layer and then again tunnels outside. The peaks are centered at those energy values when localized states match with the electrode Fermi energy. The resistive switching via resonant tunneling has also been proposed for perovskite oxides. The presence of a single peak in conductance at higher voltage value is suggested to be due to inelastic resonant tunneling which involves the excitation of resonant phonons. Such a sudden increase in current at threshold voltages can be due to resonant tunneling of large number of trapped electrons in localized states inside or near interface of the CFO layer produced either by oxygen vacancies or other defects such grain boundaries. The local removal or addition of electron from the $e_g$ level of Mn$^{3+}$/Mn$^{4+}$ strongly influences the MnO$_6$ octahedra through Jahn-Teller (JT) distortion and involves the phonon contribution. Therefore one would not expect the tunneling to be purely elastic in nature. The resonant tunneling is consistent with polaron based model recently proposed for the hysteresis and negative differential resistance for molecular junction. The magneto-restriction property of CFO can also play an additional role in the inelastic resonant tunneling. The magneto-restriction of CFO could magnetically influence the interface states participating in resonant tunneling and the MnO$_6$ octahedra of LSMO near the interface leading to a magneto-electric coupling. This work jointly done with V. Thakare et al. is under communication.

In order to explore the basic mechanism of resistive switching we carried out scanning probe microscopy studies. Figure 5.3 (a) and (b) shows the atomic force microscopy (AFM) topographic image and concurrently acquired conducting AFM current image taken at (-3V) respectively. The analysis of AFM topographic images gave RMS roughness ~ 0.4 nm. It indicates a smooth growth which is feasible due to compatible lattice constants of spinal and perovskite crystal structures and the fairly high growth temperature allowing surface diffusion.
The spatial distribution of current perpendicular to plane (CPP) through the interface can be seen in CAFM current image under the sample bias ~ - 3 V. It is clearly seen that larger negative current (darker region) could only be observed through grains and a less current near grain boundaries under negative bias. The grain boundary scattering has been reported in the polycrystalline manganite thin film in scanning probe microscopy studies which is consistent with the magneto-transport studies.\textsuperscript{23-25}

\textbf{Figure 5.4:} (a) AFM topographic image (500 X 500 nm). (b) Concurrently acquired CAFM current image under a negative bias – 3 V.
Figure 5.5 (a) shows the current image acquired under a modulated sample bias ($\pm 4$ V) in four regions as marked. It can be noted that the current distribution under positive sample bias is very low through all area without making distinction between grains and grain boundaries. These results demonstrate a clear rectifying behavior of such interface, where large current is seen under negative bias. Such rectification was not seen on bare LSMO thin films, as there is no Schottky interface between the Pt tip and metallic LSMO having nearly same work functions.

![Image](image.png)

**Figure 5.5:** (a) Current image under modulated sample bias ($\pm 3$ V) (b) Current image under modulated sample bias ($\pm 7$ V)
In figure 5.5 (b), as the bias voltage is sufficiently increased the current profile at the interface is entirely different. A constant saturated current (current limit ~ 100 nA) is noted through all the region under positive polarity. These results show that current distribution is entirely different under positive and negative bias polarity. The resistive switching that occurs under negative polarity involves spatial electronic inhomogeneities. On the other hand, under positive bias there is no signature of spatial inhomogeneities and material switches to LRS state with fairly constant charge distribution near the interface. On the other hand, a large spatial electronic inhomogeneity is seen under negative polarity. It may be noted here that the inhomogeneity under relatively higher negative bias polarity is not related to grains and grain boundaries as seen under moderate bias.

We have also measured the current-voltage (I-V) characteristics using conducting AFM tip in direct contact with the sample. Figure 5.6 a and b show the I-V curves recorded under the biasing scheme depicted in figure 5.6 c and d, respectively. These curves invariably show a hysteric loop during the forward and reverse scan. A hysteric loop gets broadened towards positive polarity when a negative pulse is applied after each cycle instead of a continuously varying triangular bias. The broadening of loop clearly shows an influence of pulse duration on the switching behaviour. The broader hysteresis loop implies better retention in the latter case. The switching cycles of current has been shown in figure 5.7 wherein the reading voltage is -0.5 V and writing/erasing voltage ± 7 V.

These results clearly demonstrate that the interface of CFO and LSMO shows resistive switching from low to high resistive state (LRS-HRS) or high to low resistive state (HRS-LRS) at appropriate electric field polarity and strength. Resistive switching (RS) has been observed in a wide range of transition metal oxides (TMO) and migration of oxygen vacancies under bias is a widely accepted mechanism for resistive switching (RS). Szot et al 14 have demonstrated the migration of oxygen vacancies through the network of dislocations. Another group (Kwon et al.) has directly shown the nano-filaments by using high resolution transmission electron microscopy.13
However, the resistive switching in mixed-valent manganites is far more complex due to various ordered phases (charge, orbital and spins) which evolve under external stimuli.\textsuperscript{3-10} The RS in other compounds of manganites family and their interfaces have also been widely explored but there are still no sufficient evidences that can explain a basic mechanism with clarity. The basic model of resistive switching by Rozenberg et al.\textsuperscript{6-7} which is supported by some experimental evidences assumes a spatially inhomogeneous system and oxygen migration as the key phenomenon that strongly influences transport properties. This model agrees with the oxygen diffusion model proposed for resistive switching in manganites.\textsuperscript{8} Under normal conditions, optimally doped La\textsubscript{0.7}Sr\textsubscript{0.3}MnO\textsubscript{3} is not expected to show a large electronic phase separation due to feeble Jahn Teller (JT) distortion. The small amount oxygen vacancies which are always expected in manganites can form a fluctuating charge ordering (CO) state and hence an electronic phase separation (EPS) scenario. It is well established that not an individual property such as CO or defects (ionic vacancies etc) in manganite can explain resistive switching but it is an outcome of all these collective phenomena combined with interfacial effects.
Finally, we also performed scanning tunneling microscopy and spectroscopy (STM/STS) measurements on the same system. Figure 5.8 shows the global average curve of 125 curves taken at equally spaced points in 1 £m² area (shown in inset). All STS curves at all points showed a hysteric loop during forward and reverse scan. The energy gap of high resistive state i.e ~ 0.5 eV was calculated at appropriate current scale where current just departs from Ohmic background. Interestingly, this energy value compares well with the reported polaronic gap (changes at defective sites) in LSMO in STS studies. It is known that the polarons hop through –Mn-O-Mn- bond, therefore, a small delocalization of oxygen ions may be lead to polaron trapping (also leading to electronic inhomogeneities) and therefore STS could measure the polaronic gap which is responsible for the insulating state. A larger electric field with opposite polarity can destroy polaronic state leading to a metallic low resistive state leaving a finite zero bias conductance (ZBC) in STS curves.
Figure 5.8: STS spectroscopy of CFO-LSMO interface: Global average curve of 125 curves taken at equally spaced points in 1 µm² area (shown in inset)

5.4 Conclusion

A giant resistive switching has been observed at the CFO-LSMO interface. The experimental fitting by interlayer transport mechanism reveals that the resistive switching in this case is interfacial type. The dynamic conductance analysis suggests a possible role of inelastic resonant tunneling. A lateral current distribution across the interface shows the interface undergoes an electronic reconstruction from uniform nanoscopic electronic inhomogeneities near grain boundaries to large scale electronic inhomogeneities after switching. The scanning tunneling spectroscopy results suggest that polaron trapping may lead to electronic inhomogeneities responsible for hysteresis and resistive switching. The scanning tunneling spectroscopy results suggest that polaron trapping may lead to large scale electronic inhomogeneities that are suggested to be responsible for the hysteresis and resistive switching.
5.5 References


18. Vishal Thakare, Guozhong Xing, Abhimanyu Rana, Onkar Game, P. Anil Kumar, Arun Banapurkar, Yesappa Kolekar, Kartik Ghosh, Tom Wu, D. D. Sarma, Satishchandra Ogale (*High Sensitivity Low Field Magnetically Gated Resistive Switching in CoFe$_2$O$_4$ (CFO) / La$_{0.67}$Sr$_{0.33}$MnO$_3$ (LSMO) Heterostructure*) communicated
The magnetization data of studied thin film of a) LSMO b) CFO
Figure: STM topographic images under negative sample bias (occupied state image) and positive sample bias (unoccupied state image). The contrast in the grains is higher in occupied state image.

The forward and reverse branch curves taken at two points in a) bright region b) dark region in topography showing the resistive switching is also localized.