Chapter III

Study of CMR manganite thin films and surfaces

In this chapter, thin films of CMR manganite (La$_{0.7}$Sr$_{0.3}$MnO$_3$) have been investigated by Scanning Probe Microscopy (SPM) techniques. This chapter is divided in three sections in which a) the effect of unit cell steps on the surface of thin films on localized electronic states, b) the temperature dependent density of states (DOS), and c) the effect of surface topography and grain boundaries on the local electronic transport are examined and presented.
3.1 Nanoscale modulation of electronic states across unit cell steps on the surface of manganite thin films

3.1.1 Introduction

Metal oxides are attracting significant attention during the past decade as functional materials in the realms of both thin films and nanomaterials in view of a range of diverse and fascinating properties they display.\(^1\) It has led to the emergence of the field of oxide electronics which embodies use of metal oxides as device platforms.\(^2\) Currently, most advanced device systems are based on thin film hetero-structures. In the case of oxides, such high quality modulated structures can be grown by techniques such as reflection high energy electron diffraction (RHEED) assisted laser molecular beam epitaxy (MBE) or pulsed laser deposition (PLD), wherein the layer by layer growth mode can be in situ monitored and very smooth surfaces with step configurations are easily realized. As the successive layers of different materials are grown functional interfaces are formed and such interfaces exhibit some unique, unusual and novel physical properties in the domains of transport and magnetism.\(^3\) In these cases it is of interest to know whether and how the step features that get buried in multilayer structures could influence the local physical properties. The vicinal surfaces and steps have been intensively exploited for the crystal growth, nanostructures, electronic components, and catalysts.\(^4\-^8\) The engineered surface step configurations and vicinal surfaces are also interesting supports for self assembled monolayers (SAMs). Hamer et al.\(^4\) demonstrated the atomic structure of Si (001) and electronic reconstruction on surface using scanning tunneling microscopy. The buckling of dimmers in these studies has shown to increase the surface defects. The atomic force microscopy studies on the growth of Ge on Si (001) by molecular beam epitaxy revealed 2D to 3D transition near the steps as a result of strain.\(^6\) Several models have shown that steps are the sites of strain modulation in these systems that can lead to various phenomenons occurring at the surface.\(^7\) However, they can be expected to be of particular significance in systems wherein the strain can influence the properties significantly. Mixed-valent colossal magneto-resistance (CMR) manganites which have been a subject of intense investigations over the past fifteen years are such highly strain sensitive systems wherein the Mn-O-Mn bond property
modulations (via Jahn Teller distortion effects) lead to a dramatically rich phase diagram of ordered phases (magnetic, charge-ordered, orbital-ordered). In this section, we mainly discuss the local electrical properties of unit cell steps on the surface of manganite films grown under real time RHEED monitored conditions, using scanning tunneling microscopy and spectroscopy (STM/STS) techniques. We demonstrate a strong nanoscale electronic state modulation near unit cell step on the surface of La$_{0.7}$Sr$_{0.3}$MnO$_3$ system. This modulation weakens with decreasing temperature.

3.1.2 Experimental details

Highly oriented thin films of La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) of thickness 5 nm and 50 nm were deposited on single crystal SrTiO$_3$ (001) substrates using pulsed laser deposition under reflection high energy electron diffraction monitor. The substrate was annealed in vacuum at 900 °C for 30 min prior to deposition.

The deposition parameters were: substrate temperature 900 °C, oxygen pressure 100 mTorr, laser energy density ~2 J/cm$^2$. The sample was cooled in oxygen at 600 mTorr at a cooling rate 5 °C/min. The deposition rate used was 0.0025 nm / Pulse to ensure high quality of film growth rendering a smooth surface with well defined steps.

The resistivity was measured as a function of temperature using a four probe method. A constant current was passed between two terminals and the corresponding voltage was measured separately from other two terminals.

The scanning probe microscopy and spectroscopy studies were carried out using variable temperature and high vacuum commercial system by RHK technologies, USA (SPM 100). The imaging and tunneling spectroscopy measurements were carried in high vacuum (better than 10$^{-6}$ Torr). The samples were transferred from the growth chamber to the SPM system in a dry ambient and were cleaned with ethanol just before loading them into STM vacuum chamber. The set point used in STM and STS measurements are (0.5 nA current and +0.7 V sample bias).

The tunneling spectroscopy data across steps were acquired simultaneously while imaging to avoid any misinterpretation caused by piezo-drifts. In this way, the exact
pixel locations where the tunneling spectroscopic curves were carried are recorded in the topographic images (shown in topographic images as blue dots). In order to reduce the noise and improve data quality in tunneling spectroscopy, each I-V spectrum was obtained after averaging 100 readings of current value for each voltage step.

3.1.3 Results and Discussion

3.1.3.1 Reflection high energy electron diffraction (RHEED) results

The RHEED oscillations produced in situ during deposition of each unit cell are shown in figure 3.1. The film thickness was calculated with a precision of one unit cell from these oscillations.

![Figure 3.1](image)

**Figure 3.1:** RHEED intensity oscillation monitored on the specular spot during the growth of the LSMO on STO substrate at 900 °C. Inset a1 & a2: RHEED pattern obtained before and after deposition respectively.

The initial intensity gradually drops during the deposition and stables before the completion of deposition, as the thickness of the film increases electron beam intensity decreases due to surface scattering. The insets a1 and a2 show the RHEED pattern obtained before and after deposition. Before deposition, a clear central
specular beam spot on 0th Laue circle was observed without any streaks, which represent an atomically flat surface with distinct surface morphology. During deposition there was an increase in the streakiness and decrease in the brightness of the diffraction spots due to disturbance of the flat surface. The position of diffraction spots does not show any change after deposition, indicating the growth to be epitaxial.

3.1.3.2 Resistivity and Magnetization results

The resistivity and magnetization measurements as a function of temperature, for 5 nm and 50 thin films are shown in figure 3.2 (a) & (b) respectively. The resistivity is plotted on left axis and magnetization on left. These results clearly show a correlation between transport and magnetization in both the films as expected, the resistivity is reduced as the temperature is lowered with a concurrent increase in magnetization. The reported value of LSMO for x = 0.3 is \( \sim 370 \) K and therefore should not show any metal-insulator transition (MIT) at room temperature, as observed in 50 nm films in our case. However, the behavior of 5 nm film is quite surprising as it showed a MIT and a reduced Curie temperature \((T_C) \sim 250 \) K. The ultra thin films have been known to have various scaling effects. Particularly, the strain developed within the films can play a crucial role for the lowering of Curie temperature and MIT as observed here. The other effects are therefore needed to be included in double exchange mechanism to explain the MIT in thin films. At low temperature in double exchange mechanism the only spin down holes hop with background “core spin” \( S = 5/2 \) and there are no propagating up spin hole states which hope in non ferromagnetically aligned \( t_{2g} \) core background at higher temperature. The two-magnon process predicts the resistivity to vary as \( \sim T^{9/2} \), but the manganites usually show the \( \sim T^2 \) dependence which is attributed to electron-electron scattering. However, the resistivity \( \sigma = \sigma_0 + A T^2 \) at higher temperature deviates from \( T^2 \) and vary as \( \sim T^5 \) due to electron-phonon coupling. The slope has been reported to be the function of doping \( x \) and magnetic field.\(^1\)
Figure 3.2: Resistivity/Magnetization Vs temperature curves for LSMO thin films of (a) 5 nm and (b) 50 nm thicknesses.

Figure 3.3 shows the comparison for the two cases of LSMO films of thickness 5 nm and 50 nm. The films of 50 nm show a linear behaviour in most of region due to electron-electron scattering. However, the ultra thin films clearly show the deviation and therefore other stronger correlation effects should play important role.
Particularly, the large deviation towards higher orders of resistivity change suggests the role of electron-phonon coupling. Interestingly, the deviation from $\sim T^2$ in figure 3.3 can also be observed at much lower temperature where magnon scattering cannot account for resistivity. At low temperatures where magnetization should saturate and the exchange interaction of the electrons with the ordered spin forms a periodic potential which alone cannot be a source of scattering. Indeed, the electron-phonon interaction is the source of residual resistivity at very low temperatures in manganites. The JT effect in manganites play important role for electron-lattice interaction. Theoretical studies have shown that the strong polaronic transport can explain the basic physics of these manganites in the deep ferromagnetic metallic phase.

![Figure 3.3: Resistivity Vs $T^2$ plot for LSMO thin films of thickness 5 nm and 50 nm](image-url)
3.1.3.3 Scanning tunneling microscopy and spectroscopy results

Figure 3.4 (a) and (b) show the STM topographic images (1 µm X 1 µm) of 5 nm films taken at 300 K and 105 K, respectively. These images show clear unit cell steps created during layer by layer growth mode.

Figure 3.4: STM Topographic images of La$_{0.7}$Sr$_{0.3}$MnO$_3$ (1 µm X 1 µm) with set point (sample bias 0.7 V, current 0.5 nA) taken at (a) 300 K and (b) at 105 K. The unit cell steps on the surface are resolved, the blue dots represents the point where tunneling spectroscopy were carried out.

Figure 3.5 (a-d) shows the tunneling spectroscopy curves performed across these steps. These curves were acquired simultaneously with imaging to avoid any misinterpretation caused by piezo-drifts, and the exact pixel locations are shown in topographic images [(Figure 3.5 (a-d))] as blue dots. Interestingly, the tunneling spectroscopy performed across any step always invariably showed a nanoscale modulation effects. A large gap structure was encountered just at the step edge and a relatively conducting characteristic was encountered nearby just away from the step edge. The probe point dependent statistical variation of the data recorded at 300 K taken at the step edge and just away from it is shown in figure 3.5 (a) and 3.5 (b), respectively. Figure 3.5 (c) and 3.5 (d) show the corresponding results recorded at 105 K.
Figure 3.5: STS spectra across unit cell steps; (a, b) statistical behavior of I-V curves at the edge of step and away respectively at 300 K, (c, d) at 105 K.

We estimated the energy gap from the I-V curves by defining $V_-$ (positive) sample bias voltage where the tunneling current departs from the Ohmic background by a threshold amount ($\sim 1\ pA$ in this case) as suggested by others.\textsuperscript{9} It can be seen from figure 3.5 (a, b) that the value of the gap ($\Delta = V_+ - V_-$) at 300 K for insulating phase encountered at the step edge varies from $\sim 0.4\ eV$ to more than $\sim 1\ eV$. On the other hand, the value of the gap for the relatively conducting phase present just away from the step edge is $\sim 0.2\ eV$ and lower. The gap values for the insulating and conducting phases at 105 K are $\sim 0.4$ and $\sim 0.2$ (and lower), respectively. Interestingly, the insulating gap structure in the data at 105 K is tightened as compared to that in the data at 300 K. The data corresponding to the conducting phase is nearly invariant with temperature.
Steps on Si (001) surface have been studied using scanning tunneling microscopy and also their electronic states have been calculated theoretically. However, manganites are interestingly complex systems and their electronic properties depend on various factors. Lattice distortions, in particular, change Mn-O-Mn bond length and angle, and thereby the electron bandwidth of the system. In our case, the large nanoscale modulation with a gapped structure encountered near a step edge may be attributed to the local stress developed by steps that distort the lattice and disperse the electronic states. Since this stress necessarily has a gradient across the step, a modulation of electron states and variation in energy gap values across the step edge can be understood. Figure 3.6 shows the spread of 256 curves obtained spatially at equally spaced (16 X 16) matrix points in 500 nm² area. Both the films show a distribution in gap which includes step related modulating or other kink sites where the density of states are expected to change. The spread is clearly large at room temperature in thinner films.

Figure 3.6: The spatial distribution of tunneling characteristics on the surface of LSMO thin film of thickness (a) 5 nm (b) 50 nm
3.2 Evidences of pseudogap (PG) and polaronic transport in deep ferromagnetic metallic (FMM) state of manganite

3.2.1 Introduction

It is known that manganites exhibit a rich electronic and magnetic phase diagram due to a complex interplay between charge, orbital, spin and lattice degree of freedoms. The double exchange mechanism alone could not explain metal-insulator transition and CMR effect in manganites completely. The lattice effects play a particularly crucial role in the transport properties, either through tolerance factor influencing the neighboring atoms orbital overlap i.e bandwidth, accompanied by various orbital and spin ordered phases. The dynamical electron-phonon coupling has been predicted in manganites in which there is an instantaneous deviation of atom position from its ideal crystallographic position with the instantaneous deviation of electron configuration surrounding it from the average value. In recent angle resolved photoemission spectroscopy (ARPES) studies where the FS of manganites is mapped, showed that the FS was well defined in deep ferromagnetic metallic state of manganite. Therefore, it is of interest to analyze the density of states at low temperatures, particularly near the unit cell steps. In this section, we discuss the temperature evolution of density of states (DOS) probed by scanning tunneling spectroscopy.

3.2.2 Experimental details

The DOS was calculated from I-V curve numerically using the SPM software by RHK Technologies and later smoothed using Fast Fourier Transform. In temperature dependent tunneling spectroscopy, the global average of DOS was calculated numerically from the average of 256 I-V curves (100 samples at each point) acquired at equally spaced (16 X 16) matrix points in 1 µm² area. The resolution in spectroscopy was increased to detect the depletion in density of states (DOS) near Fermi region using variable gap spectroscopy technique. The variable gap spectroscopy takes advantage of exponential dependence of current on the width of tunneling gap. The tip is simultaneously moved by 2 Å towards the surface as the...
bias voltage is reached to its minimum, it increases the minimum observed current by 100 times. The current readings are later divided by 100 to normalize the data compared to the values acquired in normal conditions. All I-V curves were also smoothened using Fast Fourier Transform, as these curve showed noise in pico-ampere range.

### 3.2.3 Results and Discussion

Figure 3.7 shows DOS curves at different temperatures (deviation ± 2 K). This is the global surface average which does not distinguish between near or away from the step.

![DOS curves at different temperatures](image)

**Figure 3.7:** Spatially averaged DOS curves of 256 points (100 samples at each point) taken at different temperatures in deep metallic state.

The gap at low enough temperatures where the manganite is in deep metallic state is called pseudogap (PG) as reported earlier and its origin has been discussed.12-18
In figure 3.7, we could detect a sharp PG of ~ 0.5 eV in the DOS at 200 K and below. The averaging of curves above 200 K is not reasonable because of the two phase mixture. Note that the gap structure is somewhat broad at 200 K, which is on the high temperature side at which some admixture of second phase in the electronic phase separation scenario can be envisioned. The PG also seems to reduce at 105 K with a distribution.

Wei et al\textsuperscript{13} have reported a gap in DOS with very sharp edges at ± 0.5 eV in La\textsubscript{0.7}Ca\textsubscript{0.3}MnO\textsubscript{3} (LCMO) at 77 K. Mitra et al\textsuperscript{14} have also reported the depletion in the DOS in LSMO and LCMO single crystals down to 4.2 K and have found the depth of depletion to be more in LCMO compared to LSMO. The formation of PG has been reported recently in LSMO in STS studies wherein a knee-like gap feature in DOS was seen at the temperatures below 150 K.\textsuperscript{15} The charge ordered (CO) Nd\textsubscript{0.5}Sr\textsubscript{0.5}MnO\textsubscript{3} and Pr\textsubscript{0.5}Sr\textsubscript{0.5}MnO\textsubscript{3} compounds have shown gaps of ~ 0.5 eV and ~ 0.4 eV, respectively in STS studies.\textsuperscript{16-17} Biswas et al\textsuperscript{16} have identified the existence of gap at low temperature with the charge ordered (CO) state because the gap opened up near T\textsubscript{CO} and the gap value of ~ 0.5 eV compared well with the nearest neighbor Coulomb repulsion energy. Wei et al\textsuperscript{13} have explained the gap in optimally hole doped LCMO as a result of JT distortion as the gap energy compared well with JT coupling energy. The temperature evolution of DOS has also been studied in angle resolved photoemission spectroscopy (ARPES) studies. Mannella et al.\textsuperscript{12} showed a PG in FM ground state of bilayer manganite similar to that in high temperature superconductors (HTS)\textsuperscript{19}. They found that the Fermi surface of LSMO is sharply defined in the FM state, where electron-phonon coupling leads to quasiparticles (QP) ‘polarons’. Theoretical investigations have also proposed the persistence of dynamic JT polarons in the FM phase far below TC.\textsuperscript{11} The EPS and nanoscale charge-orbital fluctuations caused by nesting of Fermi surface are other important issues in the context of PG.\textsuperscript{20}

Figure 3.8 compares the DOS distribution just at and just away from a step edge at 105 K. The PG is clearly larger at the step edge than just away from it. This modulation of PG can be attributed to the trapping of polarons at the step edge acting as a defect. The dashed line in Fig. 3.8 is the same curve as the 105 K data shown in Figure 3.7, which corresponds to the global area average. It falls in between the two curves corresponding to the at the step edge and near the step edge curves, as
expected. Interestingly, the PGs seen in figure 3.7 & 3.8 are also asymmetric in spectral weight near the edges. Such asymmetry in gap is commonly discussed in high temperature superconductors (HTS) due to particle-hole asymmetry. The asymmetry in occupied and unoccupied states has been reported for cuprates using tunneling and photoemission spectroscopy and is found to be characteristic of high temperature superconductors. However similar asymmetry in DOS which is also seen in manganites is not much discussed.

![Graph](image)

**Figure 3.8:** DOS behavior near step at 105 K. The black curve is the average of DOS curves at the step edge and red curves shows average of DOS curves just away from step edge. The dotted curve show the global average curve at 105 K.

In STS measurements on manganites at low temperature, the local injection (extraction) of electron near the Fermi level can perturb the local electronic state of the system. For instance, in hole doped manganites, the occupied and unoccupied states just near $E_F$ are formed from filled Mn$^{3+}$ (eg) bands and empty Mn$^{4+}$ (eg) bands, respectively. The distribution of Mn3+ and Mn4+ not only influences the electron
hopping but also the distribution of J-T distortion in real space. Thus addition or removal of electrons are not necessarily equivalent processes in the tunneling context and may cause the asymmetry. This issue needs to be addressed in more details.

The other issue that the I-V curves are not positioned symmetrically vis a vis the Fermi level as seen in Fig. 3.9. These curves show different $V_+$ (positive sample bias) and $V_-$ (negative sample bias) values for any current value.

![Figure 3.9: Asymmetry in tunneling spectroscopy: Two I-V curves taken at 105 K (black curve) and 145 K (red curve).](image)

Raychaudhuri and coworkers$^{14, 24}$ explained this asymmetry in tunneling conductance by considering trapezoidal potential barrier and fitted the curve by incorporating the work functions of probe and sample separately into conductance ($dI/dV$) relation rather than using the average of these two. This asymmetry which is the function of temperature in this case can in fact be due to the Fermi level is not positioned exactly
in middle of the bandgap. The Fermi level for an intrinsic semiconductor can be written as

\[ E_F = \frac{E_C + E_V}{2} - \frac{3kT}{4} \ln \left(\frac{m_e}{m_h}\right) \]

Where \( m_h, m_e \) are hole and electron effective mass respectively. Therefore, the Fermi level of an intrinsic semiconductor is not exactly lie at the middle of the bandgap. The later term is called chemical potential and can be estimated by mid gap value \( i.e \)

\[ \frac{V_+ + V_-}{2} = \mu = -\frac{3}{4} k_B T \ln \left(\frac{m_e}{m_h}\right) \]

The chemical potential is \( \sim -10 \) meV at 105 K giving \( m_e/m_h \sim 2.8 \). This can be understood since the electrons are dressed up with JT distortion and not holes, therefore must show higher effective mass and low mobility than holes during vacuum tunneling experiments.
3.3 Study of polycrystalline La$_{0.7}$Sr$_{0.3}$MnO$_3$ thin films

3.3.1 Study of Annealing effect

Annealing is known to render enhanced structural quality, sharper phase transition and higher Curie temperature in the films. However for any spintronic device the interface properties and lateral homogeneity are more critical parameters, making it desirable to find out whether the layers near the surface of manganite films are also improved or otherwise by such annealing treatment. It is also reported that the microstructure and grain boundaries strongly influence electronic transport in nanostructured manganite films that can be controlled by annealing. Further, the internal strain is found to be affected by post synthesis treatments and can dramatically change the electronic and magnetic properties of La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) films. The annealing is also known to increase the Mn$^{4+}$/Mn$^{3+}$ ratio due to self doping. The motivation of this work was to explore the effects of high temperature annealing on surface electronic properties of LSMO.

The LSMO thin films studied herein are 100 nm thick, deposited on (001) LaAlO$_3$ (LAO) substrate using pulsed laser deposition (PLD). A KrF pulsed Excimer laser ($\lambda=248$ nm, 20 ns pulse duration, laser power 2 J/cm$^2$) was used for this experiment. During deposition, the substrate temperature was kept at 750 ºC with oxygen pressure 100 mTorr. The sample was cooled in the presence of oxygen at 400 Torr. The sample was subsequently annealed ex-situ at 800 ºC for 2 hrs in an oven at 1 atm. The annealing implemented in air is not expected to cause oxygen loss.

The scanning probe microscopy and spectroscopy studies were carried out using variable temperature and high vacuum commercial system by RHK technologies, USA (SPM 100). The imaging and tunneling spectroscopy measurements were carried in high vacuum (better than 10$^{-6}$ Torr). The samples were transferred from the growth chamber to the STM/SPM system in a dry ambient and were cleaned with ethanol just before loading them into STM vacuum chamber. The set point used in STM and STS measurements are (0.5 nA current and +0.7 V sample bias).
The scanning tunneling microscopic topographic images before and after annealing are shown in figure 3.10 (a) and (b) respectively. The topographic results depict that there is a surface modification induced. The film before annealing has aligned fine grains ~ 10-20 nm diameters with RMS roughness of ~0.2 nm. On the other hand, after annealing, the film surface topography was transformed into flat terraces of ~ 50-100 nm width, with RMS roughness of ~1.3 nm. The enhanced RMS roughness and topographic modification were also confirmed from the atomic force microscopy.

Figure 3.10: Annealing effect on surface topography: STM images of the surface of polycrystalline LSMO thin film (a) before and (b) after annealing, respectively

Figure 3.11 shows the I-V characteristic of LSMO film before and after annealing, each curve is the spatial average of of 256 I-V curves (100 samples at each point) acquired at equally spaced (16 X 16) matrix points in (500 nm X 500 nm) area. The electronic property of thin films is remarkably modified after annealing inducing an overall enhanced metallic character. The metallic character can be quantified in terms of zero bias conductances (ZBC) from tunneling characteristics. The ZBC can be obtained by fitting the liner region of curve near zero bias. The dotted lines in figure represent the fitted region. The estimated values of ZBC for un-annealed and annealed films are 6.6 X 10^{-11} and 1.3 X 10^{-9} respectively. Therefore, the conductance is increased by twenty times.
The increase in ZBC can be due to the broadening of electron bandwidth resulting into enhanced mobility. The topographic results indicate the formation of flat terraces and reduction of granular nature, and thereby reducing the grain boundary scattering.

![Graph showing I-V curves](image)

**Figure 3.11:** Annealing effect on tunneling spectra: Two I-V curves of as grown LSMO thin film (black curve) and annealed films (red curve).

### 3.3.2 Occupied and Unoccupied state imaging

The topographic images and their histogram under negative and positive sample bias of un-annealed film are shown in Fig 3.12 (a) and (b) respectively. The histogram of an image is the distribution of pixels percentage frequency with respect to different heights and the peak represents the maximum pixels for a particular height. A net increase in Z height is seen in the histogram of the unoccupied-state image. The increase in height comes from the net increase in current under negative bias indicating that it is easier to add an electron than to extract it from the LSMO film. In occupied-state image obtained using sample bias of -200 mV, four electrons *i.e* (three
t_{2g} and one e_g) of Mn^{3+} and three electrons (t_{2g}) of Mn^{4+} below the Fermi level contribute to the tunneling current.

On the other hand, in the unoccupied-state image obtained using tip bias of + 200 mV, the brighter regions should correspond to the presence of Mn^{4+} (localized holes) which have high density of unoccupied eg states just above Fermi level and give rise to relatively high tunneling current. J. X. Ma et al.\textsuperscript{24} also found a significant increase in current in unoccupied-state image of La_{5/8-0.3}Pr_{0.3}Ca_{3/8}MnO_3 (LPCMO) with atomic resolution that was attributed to the presence of localized holes (Mn^{4+}). The localized variation in contrast in the topographic image is useful in finding such spatial variation of Mn^{3+} and Mn^{4+} (hole) rich regions in real space. Some brighter spots in unoccupied state image in Fig 3.12 are missing in occupied state image and vice versa giving strong indications of the presence of Mn^{4+} (holes) and Mn^{3+} rich regions.

\textbf{Figure 3.12:} Occupied and unoccupied state imaging: (500 X 500 nm) constant current image and the corresponding brightness histogram (a) under negative sample bias (-200 mV, 15 pA) (b) under positive sample bias (+200 mV, -15 pA)
3.3.3 Conducting atomic force microscopy (CAFM) results

The presence of grain boundaries is known to enhance the magnetoresistance (MR) effect.\textsuperscript{1} Therefore various experimental methods have been applied to understand the behavior of GB in manganites. Indeed, the spin polarized tunneling can occur between grains. Here, the role of grain boundaries (GB) in polycrystalline growth of epitaxial thin of manganites has been examined by conducting AFM. Figure 3.13 shows the atomic force microscopy image of topography and the concurrently acquired current image. The bright and dark contrast represents the conducting and insulating region observed near the grains boundary. These results clearly demonstrate the conducting path network and electronic inhomogeneities near the grain boundaries. The GBs can be explained by an interface between two grains. There is a natural structural distortion and also a bend bending between grains. Therefore, the Schottky interface between grains control the transport and give rise to such conducting path network and produce electronic inhomogeneities.

Figure 3.13: Conducting AFM imaging: (1 μm X 1 μm) image of (a) Topography by AFM and (b) current by CAFM.
3.4 Conclusions

In conclusion, the surface properties of CMR manganite thin films formed by pulsed laser deposition are studied using scanning probe microscopy techniques. The important findings are summarized below:

1. The ultra thin films of LSMO (5 nm) show a significant reduction of the Curie temperature ($T_C \sim 250$ K) due to strong strain effects. The electronic states near the edge of a unit cell step on the surface of these films is examined by the STM/STS techniques showing a strong nanoscale modulation in the vicinity of unit cell steps on the surface. At room temperature (non-ferromagnetic state) we observe a large gap at the step edge and a lower gap just away from the step. In the deep metallic ferromagnetic region at low temperature the step related modulation progressively weakens.

2. A well defined pseudogap $\sim 0.5$ eV was detected in the density of states (DOS) probed by tunneling spectroscopy in deep FMM state of LSMO. The pseudogap originates from strong electron phonon coupling and polaronic transport in these systems. The pseudogap has been demonstrated to change at the step edge working as defective sites. The electron effective mass is found to be $\sim 2.7$ times the hole effective mass in these systems due to the polaronic transport.

3. Post growth annealing and grain boundary effects in polycrystalline manganite films are studied using SPM techniques. The surface topography shows a clear change from aligned fine grains to flat terraces after annealing. The large reduction of the gap in tunneling spectroscopy after annealing is observed confirming the enhanced metallic nature. The imaging of occupied and unoccupied states showed an asymmetry and localized increase in contrast (due to current) due to possible presence of $\text{Mn}^{3+}$ and $\text{Mn}^{4+}$ rich regions. The conducting AFM studies revealed the conducting path networks and electronic inhomogeneities near the grains boundaries.
3.5 References


Appendix

XRD Result

HRTEM Result: