Nanoscale modulation of electronic states across unit cell steps on the surface of an epitaxial colossal magnetoresistance manganite film

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(Received 11 March 2010; accepted 22 May 2010; published online 30 June 2010)

The nature of electronic states near the edge of unit cell steps on the surface of epitaxial $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) thin films grown by real-time reflection high energy electron diffraction monitored pulsed laser deposition is examined by scanning tunneling microscopy and scanning tunneling spectroscopy techniques. It is observed that the electronic states are strongly modulated near the step edge with considerably high gap at the edge and low gap on the terrace. This modulation weakens at low temperature. The temperature evolution of the density of states and the nature of gap in deep metallic state of LSMO are also discussed. © *2010 American Institute of Physics*. [doi:10.1063/1.3455886]

Metal oxides have been attracting significant attention during the past decade as functional materials.[1–7] High quality modulated structures of oxide can be grown by reflection high energy electron diffraction (RHEED) assisted laser molecular beam epitaxy or pulsed laser deposition (PLD), wherein very smooth surfaces with step configurations are easily realized. Such surface steps are known to be the sites of strain modulation in a system.[8–11] Mixed-valent manganites are highly strain sensitive systems wherein the Mn–O–Mn bond property modulations [via Jahn–Teller (JT) distortion effects] lead to a dramatically rich phase diagram of ordered phases (magnetic, charge-ordered, and orbital-ordered).[1–4] In this work, we demonstrate a strong nanoscale electronic state modulation near a unit cell step on the surface of the $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) system.

The epitaxial thin films of $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) of thickness 5 nm were deposited on single crystal $SrTiO_3$ (001) substrates using PLD under RHEED monitoring. The substrate was annealed in vacuum at 900 °C for 30 min prior to deposition. The deposition parameters were as follows: substrate temperature 900 °C, oxygen pressure 100 mTorr, and 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 STM/STS measurements were carried out using variable temperature SPM system by RHK Technologies, USA (SPM 100) in high vacuum conditions (better than 10^{-6} Torr). The STS was used in variable gap mode to increase spectroscopic energy resolution. The RHEED oscillations produced *in situ* during deposition of each until cell are shown in Fig. 1(a). The film thickness was calculated with a precision of one unit cell. The insets a1 and a2 show the RHEED pattern obtained before and after deposition. The position of diffraction spots does not show any change after deposition, indicating the growth to be epitaxial. The resistivity and magnetization measurements for 5 nm thin films are shown in Fig. 1(b). These data show that the insulator–metal transition temperature (T_{IM}) and the Curie temperature (T_C) are close to 250 K for 5 nm film. The lowering of the critical temperatures below the reported bulk value (~370 K) (Ref. 4) can be attributed to stronger strain effects in thinner films. Figures 1(c) and 1(d) show the STM topographic images (1×1 μm^2) 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.

Figures 2(a)–2(d) show the tunneling spectroscopy curves performed across these steps. These curves were acquired simultaneously with imaging to avoid any misinter-

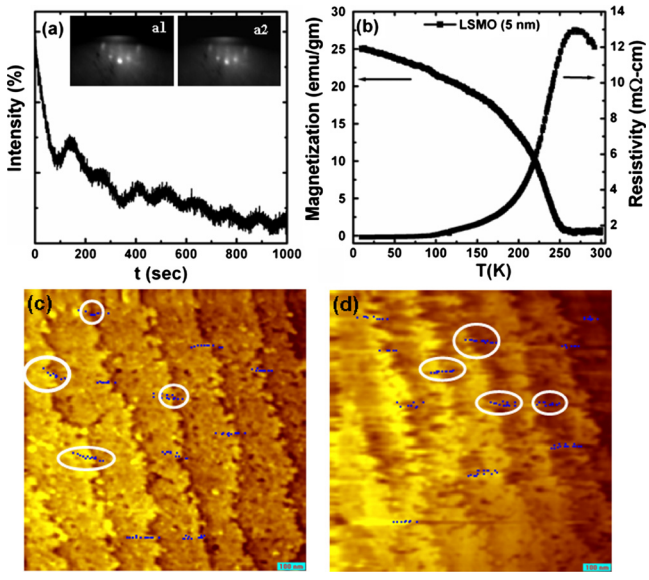

FIG. 1. (Color online) (a) RHEED intensity oscillation monitored on the specular spot during the growth of the LSMO on STO substrate at 900 °C. Inset a1 and a2: RHEED pattern obtained before and after deposition, respectively. (b) Resistivity/magnetization vs temperature curves for LSMO thin films of 5 nm thickness. STM topographic images (1×1 μm^2) with set point (sample bias 0.7 V, current 0.5 nA) taken at (c) 300 K and (d) 105 K.

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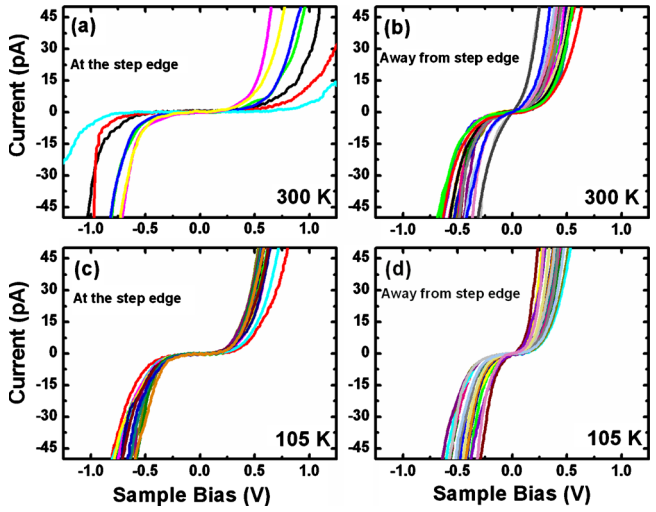

FIG. 2. (Color online) Statistical behavior of I–V curves at the edge of step and just away from the step, respectively, at [(a) and (b)] 300 K and [(c) and (d)] 105 K.

pretation caused by piezodrifts, and the exact pixel locations are shown in topographic images [Figs. 1(c) and 1(d)] as 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 in the data recorded at 300 K taken at the step edge and just away from it is shown in Figs. 2(a) and 2(b), respectively. Figures 2(c) and 2(d) show the corresponding results recorded at 105 K.

We estimated the energy gap from the I–V curves by defining $V_-(V_+)$ negative (positive) sample bias where the tunneling current departs from the ohmic background by a threshold amount (1 pA in this case) as suggested by others.[12] It can be seen from Figs. 2(a) and 2(b) that the value of the gap ($\Delta = V_+ - V_-$) at 300 K for insulating phase encountered at the step edge varies from ~0.4 eV to more than ~1 eV. On the other hand, the value of the gap for the relatively conducting phase present just away from the step edge is ~0.2 eV and lower. The gap values for the insulating and conducting phases at 105 K are ~0.4 eV and 0.2 eV (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 STM and also their electronic states have been calculated theoretically.[13–15] However, in manganites lattice distortions 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.

In Fig. 3(a), we show DOS curves calculated by averaging 256 curves (100 samples at each point) acquired at equally spaced points at different temperatures (deviation ± 2 K). This is the global surface average which does not distinguish between near or away from the step. 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.[16–20] In Fig. 3(a), 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 (EPS) scenario can be envisioned. The PG also seems to reduce at 105 K with a distribution.

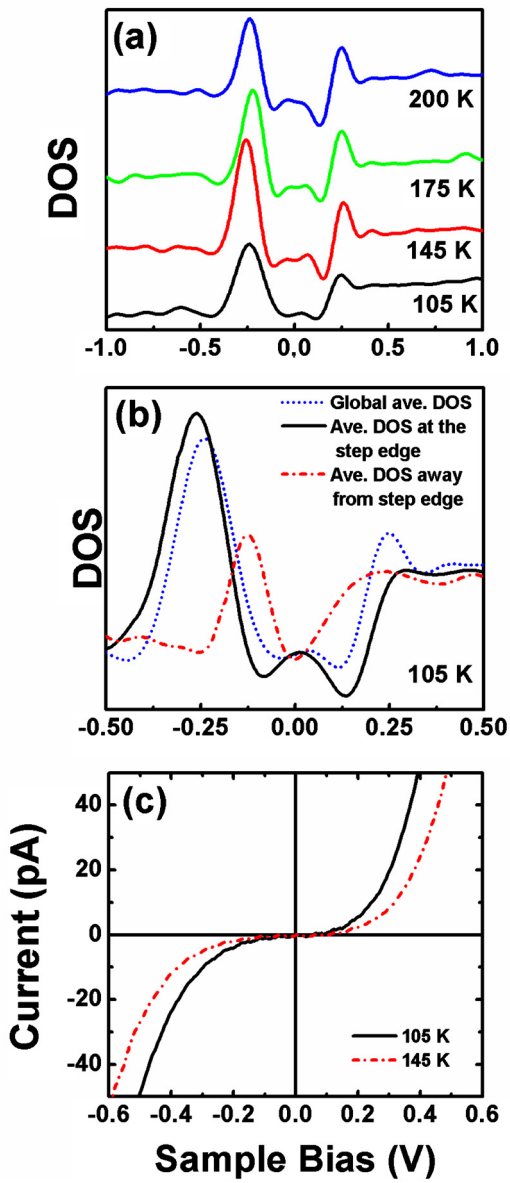

FIG. 3. (Color online) (a) Spatially averaged DOS curves of 256 points (100 samples at each point) taken at different temperatures. (b) DOS behavior near step at 105 K: the solid line represents the average of DOS curves at the step edge and the dashed-dotted line represents the average of DOS curves just away from step edge. The dotted curve shows the global average curve at 105 K. (c) Two I–V curves taken at 105 K (solid line) and 145 K (dashed-dotted). Each curve is average of curves taken at 256 points (100 samples at each point).

Wei *et al.*[16] have reported a gap in DOS with very sharp edges at ±0.5 eV in $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) at 77 K. Mitra *et al.*[17] 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 kneelike gap feature in DOS was seen

at the temperatures below 150 K.[18] The charge ordered (CO) $Nd_{0.5}Sr_{0.5}MnO_3$ and $Pr_{0.5}Sr_{0.5}MnO_3$ compounds have shown gaps of ~0.5 eV and 0.4 eV, respectively, in STS studies.[19,20] Biswas *et al.*[19,21] have identified the existence of gap at low temperature with the CO state because the gap opened up near T_{CO} and the gap value of ~0.5 eV compared well with the nearest neighbor Coulomb repulsion energy. Wei *et al.*[16] have explained the gap in optimally hole doped $La_{0.7}Ca_{0.3}MnO_3$ (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.[22,23] Mannella *et al.*,[23] in recent ARPES measurement, showed a PG in FM ground state of bilayer manganite similar to that in high temperature superconductors (HTSs). They found that the Fermi surface of LSMO is sharply defined in the FM state, where electron–phonon coupling leads to quasiparticles "polarons." Theoretical investigations have also proposed the persistence of dynamic JT polarons[24,25] in the FM phase far below T_C. The EPS and nanoscale charge-orbital fluctuations caused by nesting of Fermi surface are other important issues in the context of PG.[26,27] Figure 3(b) 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(b) is the same curve as the 105 K data shown in Fig. 3(a), 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 given in Fig. 3(b), as expected.

Interestingly, the PGs seen in Figs. 3(a) and 3(b) are also asymmetric in spectral weight near the edges. Such asymmetry in gap is very common in HTS due to particle-hole asymmetry.[28] However, similar asymmetry in DOS which is also seen in manganites[16,17] is not much discussed. 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.[12] Thus addition or removal of electrons are not necessarily equivalent processes in the tunneling context and may cause the asymmetry.[17] This issue needs to be addressed in more details.

It is seen from Fig. 3(c) that the I–V curves are not positioned symmetrically vis a vis the Fermi level. These curves show different V_+ (positive sample bias) and V_- (negative sample bias) values for any current value. From this asymmetry, we have calculated mid gap value, i.e., $(V_+ + V_-)/2$ that gives chemical potential $(\mu) = 3/4\ k_B T \ln(m_h/m_e)$, where m_h (m_e) are hole (electron) effective masses. The chemical potential is ~−10 meV at 105 K giving m_e/m_h ~2.8, that closely matches with the value observed in layered manganites.[12] This can be understood since the holes are not dressed up with JT distortion unlike electrons, therefore, must show lighter effective mass and higher mobility during vacuum tunneling.

In conclusion, a strong modulation of the electronic states is noted in the vicinity of a step on a manganite film surface. At room temperature (nonferromagnetic 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 but a well defined PG is still seen, which is also different at the step edge and just away from it.

The authors wish to acknowledge funding from DAE (BRNS) and Indo-Australian strategic research fund ST020078. K.B. and N.V. are partially supported by ARC discovery grant. S.B.O. also acknowledges CSIR network Grant No. NWP0051.

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