

# Pseudogap formation in the metallic state of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ thin films

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We report on scanning tunneling microscopy and spectroscopy (STM/S) studies of epitaxial  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  (LSMO) thin films on a lattice matched (001)  $\text{La}_{0.3}\text{Sr}_{0.7}\text{Al}_{0.35}\text{Ta}_{0.35}\text{O}_9$  substrate for both as-grown and annealed films. In contrast to the as-grown films, the films annealed at 800 °C in air show atomic terraces with spectra that develop a gaplike structure with cooling. We show that the gap structure can be attributed to the predicted pseudogap in the manganites. Unlike several previous reports, we did not find electronic inhomogeneities in LSMO by STM/S. © 2008 American Institute of Physics. [DOI: 10.1063/1.3028072]

Electronic inhomogeneities in the hole-doped manganites have attracted considerable attention with phase separation (PS) into conducting (magnetic) and insulating (non-magnetic) domains emerging as an alternative scenario to the double exchange mechanism for colossal magnetoresistive (CMR) behavior in manganites.<sup>1</sup> While PS is widely accepted as the origin of CMR in some of the narrow bandwidth manganites,<sup>2</sup> its existence is still debatable in the broad bandwidth manganites such as  $\text{La}_x\text{Sr}_{1-x}\text{MnO}_3$  (LSMO) and  $\text{La}_x\text{Ca}_{1-x}\text{MnO}_3$  (LCMO). Scanning tunneling microscopy and spectroscopy (STM/S) is a powerful probe for investigating nanoscale electronic inhomogeneities arising from PS. In the past, several groups reported electronic inhomogeneities with STM/S on the surface of LSMO (Ref. 3) and LCMO,<sup>4</sup> the origin being ascribed to PS. However, other STM groups did not find any signatures of PS.<sup>5-8</sup> Most STM measurements indicate the existence of a hard gap in the metallic state, below the insulator-metal transition temperature  $T_{\text{IM}}$ , of manganites.<sup>5,7,8</sup> From point contact spectroscopy<sup>9</sup> and angle resolved photoemission spectroscopy (ARPES),<sup>10-12</sup> a depression in the density of states (DOS) near the Fermi energy ( $E_F$ ) was found and that was attributed to a pseudogap (PG) in the metallic state. Recent ARPES measurements<sup>12</sup> show that in addition to a broad PG, a quasiparticle (QP) peak exists in the metallic state of a bilayer manganite in a very small region of the Fermi surface, which the authors believed to be the reason behind the observed metallic behavior below  $T_{\text{IM}}$ . The PG seems to arise from the trapping of electrons at all temperatures due to the electron-phonon interaction<sup>13</sup> but the origin of the QP peak is not yet clear. The PG alone is in contradiction with bulk transport measurements and naive Boltzmann transport theory given that the PG becomes more pronounced in the metallic state.<sup>10-12</sup> Unlike the STS measurements, the optical measurements with a weak Drude peak (and a PG) in the metallic state<sup>14</sup> agree with bulk transport. The energy gap, be it a PG or a hard gap, is a strong evidence of trapping of the  $e_g$  electrons, which is an unusual phenomenon in the metallic

state<sup>13</sup> and presents a challenge for researchers. In order to probe the intrinsic inhomogeneities and the PG observed in the manganites, we have performed STM/S measurements on as-grown and annealed  $\text{La}_x\text{Sr}_{1-x}\text{MnO}_3$  (with  $x=0.33$ ) thin films grown by pulsed laser deposition (PLD). The annealing was done at 800 °C for 8 h in air. In this paper we discuss our measurements and observations on both as-grown and annealed LSMO films.

LSMO thin films with  $x=0.33$  and 50 nm thickness were grown on (001)  $\text{La}_{0.3}\text{Sr}_{0.7}\text{Al}_{0.35}\text{Ta}_{0.35}\text{O}_9$  (LSAT) substrates by PLD. Transport and magnetization measurements were performed using Quantum Design physical properties measurement system (PPMS) and magnetic properties measurement system (MPMS) systems. The STM/S measurements were carried out using a homemade variable temperature STM based on an earlier published design<sup>15</sup> and used in our earlier work.<sup>8</sup> The surface of the LSMO thin film at various temperatures was imaged in constant current mode at about 1 V bias. The differential conductance spectra ( $dI/dV$  versus  $V$ ) and STS images were acquired using a modulation technique with an alternating voltage of 50 mV at 2.731 kHz added to the dc bias voltage. We have analyzed the  $d \ln I/d \ln V$  spectra for deconvoluting the voltage dependence of the tunneling matrix element as discussed earlier.<sup>8</sup>

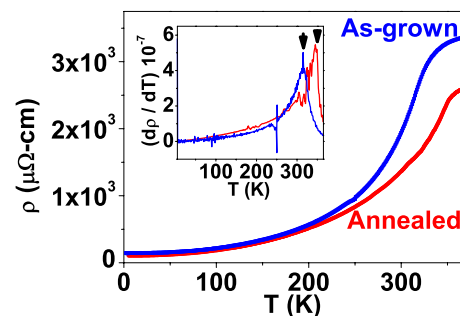


FIG. 1. (Color online) Resistivity ( $\rho$ ) vs temperature plot showing the metal-insulator transition in the as-grown and annealed LSMO thin films. The inset shows  $d\rho/dT$  vs  $T$  plot showing the transitions at 317 and 345 K for the two cases.

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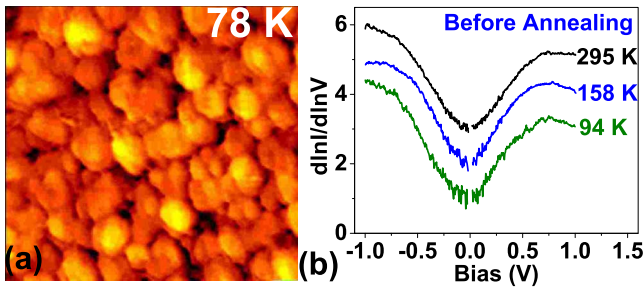


FIG. 2. (Color online) (a) Topographic image (area of  $205 \times 205 \text{ nm}^2$ , bias of 1 V, and current of 0.1 nA) of the as-grown LSMO film at 78 K. (b) Averaged and normalized tunnel spectra of the same film at different temperatures.

For the as-grown films, the resistivity measurements show an insulator-metal transition at  $T_{\text{IM}}=315 \text{ K}$ , as shown in Fig. 1. The change in resistivity with cooling is about  $3 \text{ m}\Omega \text{ cm}$ . The resistivity value at 100 K is  $0.25 \text{ m}\Omega \text{ cm}$  which shows it to be a bad metal. The annealed sample shows a higher transition temperature of 345 K with a smaller magnitude of resistivity as seen from the same figure. The magnetization measurements (not shown here) did not show any measurable change with annealing and in both cases the film shows a biaxial anisotropy with a Curie temperature of 345 K.

Figure 2 shows the topographic image of the as-grown LSMO film at 78 K together with the spatially averaged spectra at different temperatures. We find the surface to be granular with connected grains of  $\approx 20\text{--}30 \text{ nm}$  size and a rms roughness of more than 2 nm. We believe that these films grew in the island growth mode due to a fast growth rate instead of step flow growth mode observed for slower growth rates. The temperature dependent  $d \ln I/d \ln V$  versus  $V$  spectra in Fig. 2(b) did not show much evolution with temperature. Each spectrum here is the average of about 100 spectra at different locations. The detailed STS images (not shown here) show the grain boundaries to be more insulating than the grains. The zero bias conductance (ZBC) deduced from the  $I$ - $V$  spectra is found to be very small and does not change significantly with temperature.

The as-grown films had been exposed to air for 1–2 weeks prior to the measurements which might have modified the surface. Recently Valencia *et al.*<sup>16</sup> reported a change in Mn valency at the surface of a manganite due to the exposure of the films to ambient conditions. However, STM is a surface sensitive technique probing only the top few atomic layers of the surface. The same group also reported that annealing of films restores this valency. Therefore the LSMO films were annealed in air at  $800 \text{ }^\circ\text{C}$  in a temperature controlled box furnace for 8 h to rejuvenate the surface.

Figure 3 shows the topography images of the annealed film at 211 K. The terraces are formed with atomic steps of height  $(0.40 \pm 0.05) \text{ nm}$ . Since the terraces are formed during postgrowth annealing, we did not see a regular step-terrace morphology which is usually seen in the films grown in step-growth mode at high temperatures and low deposition rates. To probe the spatial inhomogeneity in the DOS, if any, we acquired topographic images and conductance maps on the sample surface simultaneously at various temperatures. One such set of images at 211 K is shown in Fig. 3. Here we see very little ( $<5\%$ ) variation in the conductance value as seen in the line cut on a particular terrace. We have taken

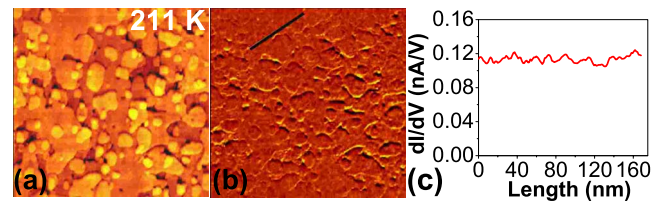


FIG. 3. (Color online) The topographic image (a) of the annealed sample (area of  $524 \times 524 \text{ nm}^2$ ) at 211 K temperature taken under 1 V bias and 0.1 nA current. (b) shows the corresponding conductance image. The plot in (c) shows the line cut of the conductance image along the line marked in (b).

such STS images for areas up to  $2 \times 2 \mu\text{m}^2$  with similar variations in conductance.

The normalized spectra ( $d \ln I/d \ln V$ ) at various temperatures from 310 to 78 K are plotted in Fig. 4(a). At higher temperatures, these spectra are V shaped and a gap-like feature appears far below  $T_{\text{IM}}$ . Here, gaplike means a well-defined kneelike structure at a certain bias (0.2 V for 78 K spectra) below which  $d \ln I/d \ln V$  starts decreasing rapidly. This feature is easily detectable in all the spectra below 150 K. The  $d \ln I/d \ln V$  value at zero bias does not reflect the DOS at  $E_F$  as its value is unity by definition. Therefore we have looked at the ZBC value for fixed junction resistance to understand the behavior of DOS at  $E_F$ . However the variation in the DOS with energy near  $E_F$  is best reflected in the  $d \ln I/d \ln V$  spectra. The ZBC values, inferred from the zero bias slope in the  $I$ - $V$  spectra [see Fig. 4(b)], are finite at all temperatures. All these spectra at different temperatures were acquired at the same tunnel resistance (bias of 1 V and current of 0.1 nA). Further, we find that the ZBC value is slightly increased with cooling [see Fig. 4(b)], while the shape of the normalized spectra becomes more gaplike at the same time. Similar gap feature (PG) has been observed in ARPES (Ref. 10) and optical measurements<sup>14</sup> in the metallic states of LSMO and LCMO.

Given the above two results, i.e., (1) the energy scale associated with the depression in the DOS decreases with temperature while (2) the DOS at  $E_F$  increases, we may surmise that there is a transfer of DOS from high energy to low energies with cooling as the gap reduces with temperature. This appears similar to the spectral weight transfer observed from optical conductivity<sup>14</sup> and ARPES measurements.<sup>10,17</sup> In these two studies, the spectral weight at low energies was found to be unsatisfactory for explaining the metallic resistivity. However, from our data, although we cannot calculate the absolute value of the DOS at  $E_F$ , the general behavior of increasing ZBC with cooling is qualitatively consistent with the metallic behavior at low temperatures.

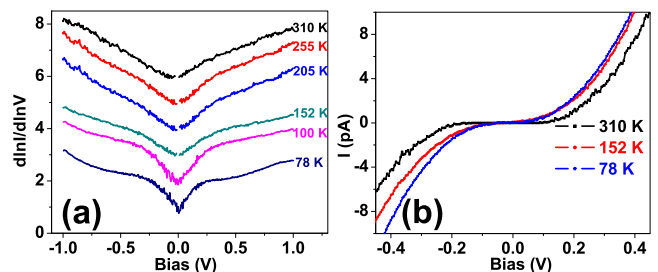


FIG. 4. (Color online) (a) Temperature dependent STS spectra of the annealed sample. The spectra have been offset uniformly for clarity. (b) shows some representative  $I$ - $V$  spectra.

The small sampling depth (a few monolayers) of STM and ARPES and the fact that the surface is less conducting than bulk<sup>18</sup> do raise doubts whether we are probing the intrinsic bulk; however, the weak and localized (in  $\mathbf{k}$ -space) nature of the delocalized quasiparticles and the poor  $\mathbf{k}$ -resolution of these probes makes the detection of such quasiparticles difficult.<sup>12</sup> Thus it is likely that the surface of manganites, at least the broad bandwidth ones, follows the bulk qualitatively but the weak signal arising from these directed quasiparticles requires more careful experiments.

In the present LSMO study, the STS spectra and in particular the ZBC variation with temperature at the surface are consistent with bulk transport. The PG with a finite DOS at  $E_F$  in the metallic state could be a signature of dynamically generated small bubbles of correlated Jahn–Teller polarons as observed by neutron scattering experiments.<sup>19</sup> This scenario also supports coherent polaronic states as observed by ARPES experiments on bilayer manganites.<sup>17</sup> The PG could also be explained from a dynamic PS into metallic and insulating phases as suggested by recent Monte Carlo simulations by Yu *et al.*<sup>20</sup>

In conclusion, our STM/S measurements on LSMO thin films show the formation of a PG in the metallic regime with insignificant electronic inhomogeneities in homogeneous annealed thin films. The detailed spectra show an increase in the DOS at  $E_F$  with a PG indicating the presence of some delocalized carriers that could arise from polaronic correlations in the metallic state.

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