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Nonlinear transport in nanoscale phase separated colossal magnetoresistive oxide thin films

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We report a study of the $I$-$V$ characteristics of 2.5–5.4 nm epitaxial La$_{1-x}$Sr$_x$MnO$_3$ ($x=0.33$ and 0.5) and La$_{0.7}$Ca$_{0.3}$MnO$_3$ thin films. While La$_{0.5}$Sr$_{0.3}$MnO$_3$ films exhibit linear conduction over the entire temperature and magnetic field ranges investigated, we observe a strong correlation between the linearity of the $I$-$V$ relation and the metal-insulator transition in highly phase separated La$_{0.5}$Sr$_{0.3}$MnO$_3$ and La$_{0.7}$Ca$_{0.3}$MnO$_3$ films. Linear $I$-$V$ behavior has been observed in the high temperature paramagnetic insulating phase, and an additional current term proportional to $V^\alpha$ ($\alpha=1.5–2.8$) starts to develop below the metal-insulator transition temperature $T_{MI}$. This nonlinear behavior increases with decreasing temperature and increasing magnetic field and is significantly enhanced in ultrathin films with thicknesses close to that of the electrically dead layer. We attribute the origin of the nonlinearity to transport through the nanoscale coexisting metallic and insulating regions. Our results suggest that phase separation is not fully quenched even at low temperatures and high magnetic fields.

I. INTRODUCTION

Correlated oxides such as colossal magnetoresistive (CMR) manganites exhibit diverse electronic and magnetic properties that are tunable via carrier density, magnetic field, and strain,1,2 which make them a promising material platform for the development of nanoscale, multifunctional electronic and spintronic devices.3–11 For example, manganite thin films have been used to build $p$-$n$ junctions and Schottky junction devices that exhibit rectified $I$-$V$ characteristics.4,10

To facilitate the rational design and optimize the performance of such devices, it is important to understand the intrinsic $I$-$V$ relation of manganite thin films. In previous studies, both linear and nonlinear $I$-$V$ behaviors have been reported in CMR manganites.12–20 The nonlinear conduction has been attributed to the melting of the charge ordered states via current,12–14 transport through grain boundaries,15–18 magnetic polarons,19 and nanoscale phase separation.13,20

In this work, we examine the critical role of nanoscale phase separation in nonlinear conduction of epitaxial manganite thin films. We have investigated the $I$-$V$ characteristics of 2.5–5.4 nm epitaxial single crystalline La$_{1-x}$Sr$_x$MnO$_3$ (LSMO, $x=0.33$ and 0.5) and La$_{1-x}$Ca$_x$MnO$_3$ (LCMO, $x=0.3$) thin films. The La$_{0.5}$Sr$_{0.3}$MnO$_3$ films exhibit linear conduction over the entire temperature and magnetic field ranges investigated. In the highly phase separated LCMO and La$_{0.5}$Sr$_{0.3}$MnO$_3$ films, we observe a strong correlation between the linearity of the $I$-$V$ relation and the metal-insulator transition (MIT). Linear $I$-$V$ dependence has been observed in the high temperature paramagnetic insulating phase, and an additional term proportional to $V^\alpha$ ($\alpha=1.5–2.8$) starts to develop in the current below the metal-insulator transition temperature $T_{MI}$. The onset temperature of the nonlinearity increases in magnetic field as $T_{MI}$ increases. The values of the exponent $\alpha$ increase monotonically with decreasing temperature and increasing magnetic field, and the highest exponent has been observed in La$_{0.5}$Sr$_{0.3}$MnO$_3$ films with thicknesses close to that of the electrically dead layer. We attribute the origin of the nonlinearity to transport through the nanoscale coexisting metallic and insulating regions in these phase separated manganite thin films.

II. SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

We have deposited epitaxial LSMO and LCMO films on (001) SrTiO$_3$ (STO) and (110) NdGaO$_3$ (NGO) substrates using off-axis radio frequency magnetron sputtering. The films are grown at 650°C, with 150 mTorr process gas composed of Ar and O$_2$ with the ratio of 2:1. These films are (001) oriented, with no impurity phase observed in x-ray diffraction and a surface roughness of ~2 Å (Fig. S1 in the supplementary material).21 We then pattern the samples into Hall bar and two-point devices with channel widths of 5–20 μm using photolithography followed by the deposition of 30 nm Au electrodes. The $I$-$V$ and magnetotransport measurements have been taken in both two-point and four-point device geometries. The studies have been carried out in a Quantum Design Physical Property Measurement System (PPMS) using external sources (Keithley 2400) and low frequency lock-in techniques.

III. EXPERIMENTAL RESULTS

Figure 1(a) shows the temperature dependence of the resistivity for a 5.4 nm La$_{0.67}$Sr$_{0.33}$MnO$_3$ film grown on STO. At zero magnetic field, the film exhibits a transition from high temperature insulating behavior to low temperature transitions.1

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metallic behavior at $T_{MI} \approx 325$ K. As LSMO is a wide-bandwidth system, its magnetoresistance (MR) is relatively small, with $R(0T)/R(9T) \approx 1.6$ at $T_{MI}$. Figure 1(b) shows the bias voltage dependence of current at temperatures above (350 K) and below the $T_{MI}$ (200 K and 100 K). We observe linear $I-V$ characteristics over the entire temperature range investigated (10 K–350 K). The linearity is preserved in magnetic fields up to 9 T (Fig. 1(c)).

We have then studied an intermediate bandwidth system, La0.67Ca0.33MnO3, which exhibits a lower $T_{MI}$ and more pronounced MR compared with those in LSMO of similar composition. Figure 2(a) shows $\rho(T)$ for a 4.2 nm LCMO film, which shows a $T_{MI} \approx 145$ K and $R(0T)/R(9T) \approx 95$ at $T_{MI}$. At $T > T_{MI}$, the film exhibits linear conduction, similar to what is observed in La0.67Sr0.33MnO3. As the sample is cooled down below $T_{MI}$, however, a nonlinear component of $V$-dependence starts to develop in the current (Fig. 2(b)). This onset of nonlinearity correlates strongly with the MIT. As shown in Fig. 2(a), the LCMO film is in the insulating phase at 160 K, but becomes metallic in a magnetic field of 9 T as $T_{MI}$ shifts to 232 K. Interestingly, the $I-V$ relation at 160 K also changes from linear at 0 T to nonlinear as the film becomes metallic (Fig. 2(c)).

To confirm that the nonlinearity is intrinsic to the LCMO sample rather than due to extrinsic effects such as Joule heating and resistance switching, we have calculated the power density $p = j^2 \rho$, where $j$ is the current density, of different samples with the same device geometry and at the same temperature (see supplementary material for a detailed discussion). Our calculation shows that the maximum power density in the LCMO and La0.67Sr0.33MnO3 samples are comparable at low temperatures, while the nonlinear $I-V$ has only been observed in the LCMO sample. The power density in our sample is also three orders of magnitude lower than the critical values reported for Joule heating in micro-structured LCMO thin films. The observed $I-V$ curve is continuous and fully reproducible as we sweep voltage in different directions and with different speeds, while Joule heating or current induced resistance switching often leads to a sudden softening or even an abrupt change in the current accompanied with hysteresis behavior. More important, as shown in Fig. 2(c), LCMO exhibits a super-linear $I-V$ at 9 T, suggesting higher conductance at higher electric field. This is opposite to what is expected from Joule heating, which should give rise to a sub-linear $I-V$ as the sample is in the metallic phase at 160 K and 9 T. We thus conclude that the nonlinearity in $I-V$ is intrinsic to LCMO thin films.

As we are working with ultrathin epitaxial films, one possible source for the nonlinear $I-V$ behavior is parallel conduction through an electrically dead layer. The existence of an electrically dead interfacial layer has been widely observed in epitaxial manganite thin films and has been attributed to structural or chemical modification at the surface and interface. We have examined the thickness dependence of the transport properties of our La0.67Sr0.33MnO3 films and found the critical thickness for the electrically dead layer to be 3.2 nm. We then worked with a 2.5 nm thick La0.67Sr0.33MnO3 film, which is insulating at all temperatures. The film exhibits linear $I-V$ characteristics in the entire temperature and magnetic field ranges investigated (supplementary material), which suggests that the existence of the electrically dead layer is not the source of the nonlinearity.

The key difference between the La0.67Sr0.33MnO3 and LCMO samples is LCMO is highly phase separated, with coexisting nanoscale metallic and insulating regions. Transport through such a network of metallic regions is percolative, and hopping or tunneling through nanoscale insulating regions can give rise to nonlinear $I-V$ characteristics. To identify the role of phase separation in the nonlinear transport, we have investigated another LSMO system with $x = 0.5$. The ground state of the half doped LSMO is close to the phase boundary between the hole-doped ferromagnetic phase and the electron-doped antiferromagnetic/charge ordered phase, which naturally leads to coexistence of competing phases at
the nanoscale. We have measured two $La_{0.5}Sr_{0.5}MnO_3$ films grown on NGO substrates. The 5 nm sample (denoted as LSMO_A) shows a $T_{MI}$ of 250 K, close to the values observed in thick films. The 3.2 nm sample (denoted as LSMO_B) shows a significantly lower $T_{MI}$ of 135 K (Fig. 2(d)), as the film thickness is close to the electrically dead layer thickness for this composition ($\sim$ 3 nm). Its large MR of $R(0T)/R(9T) \sim 340$ at $T_{MI}$ is a direct manifestation of the presence of enhanced phase separation. The I-V relations of both $La_{0.5}Sr_{0.5}MnO_3$ films closely resemble that of the LCMO films, with linear I-V at high temperature and nonlinear I-V below $T_{MI}$, which can be tuned by a magnetic field. Figures 2(e) and 2(f) show clearly the effects of temperature and magnetic field on the I-V behavior for sample LSMO_B, respectively. We observe linear I-V at 300 K (above $T_{MI}$) and nonlinear I-V at 100 K (below $T_{MI}$). At 150 K, the conduction of the sample is tuned from linear at 0 T to nonlinear in magnetic field of 9 T, while $T_{MI}$ increases from 135 K to 226 K.

In both materials systems, the I-V relation can be well described by the following expression:

$$I = G_0V + G_1V^x,$$

where the nonlinear exponent $x$ is a function of temperature and magnetic field. Figure 3(a) shows the temperature dependence of the exponent $x$ taken on the LCMO sample. At zero magnetic field, $x$ changes from about 1.6 at 130 K to 2.0 at 10 K, showing a monotonic increase with decreasing temperature. In a magnetic field, the nonlinearity emerges at higher temperature and corresponds to a larger $x$, reaching $\sim 2.2$ at 10 K and 9 T. The exponents observed on the half-doped LSMO samples exhibit qualitatively similar temperature dependences (Fig. 3(b)). While sample LSMO_A shows nonlinear exponent values comparable with those observed in the LCMO sample, the exponents are significantly enhanced in LSMO_B. Note that the thickness of LSMO_B is close to that of the electrically dead layer, with a significantly suppressed $T_{MI}$ and enhanced MR, which suggests an enhanced level of phase separation.

We then use the ratio between $G_1$ and $G_0$ (Eq. (1)) to quantify the onset temperature of the nonlinear I-V, and study how it is related to the $T_{MI}$. Figure 3(c) shows the temperature dependence of $G_1/G_0$ for the LCMO sample at different magnetic fields. We define the I-V curve as linear when $G_1/G_0 < 0.05$, which is close to experimental error, and extract the corresponding onset temperature $T_{onset}$. The temperature dependences of both $T_{MI}$ and $T_{onset}$ for LCMO and LSMO_B are shown in Figs. 3(d) and 3(e), respectively. It is clear that for both LCMO and half doped LSMO, $T_{onset}$ increases with $T_{MI}$ in magnetic fields, confirming the correlation between the MIT and the onset of nonlinearity.

**IV. DISCUSSIONS**

In previous studies, nonlinear conduction has been observed in a variety of manganite systems. Besides Joule heating and current induced melting of the charge ordered states, which we have already ruled out, the presence of magnetic polarons, tunneling through grain boundaries, and nanoscale phase separation have also been proposed as possible sources for the nonlinear conduction. For example, it has been suggested that magnetic polarons are responsible for the nonlinear high frequency electrical response in LCMO probed by third harmonic resistance. However, such nonlinearity has only been observed above $T_{MI}$ and showed significant enhancement at temperatures close to the transition temperature, where a high density of magnetic polarons are expected to be activated. In addition, the magnetic polaron induced effect has been found to be suppressed in magnetic field, consistent with the notion that magnetic polarons should collapse in magnetic fields. In sharp contrast, the nonlinear behavior in DC I-V relation reported here is only observed at $T < T_{MI}$ and becomes more pronounced at lower temperatures. Moreover, the nonlinearity is enhanced at high magnetic field. We thus rule out magnetic polaron as the origin of the nonlinear I-V.

Another scenario based on tunneling through grain boundaries has been proposed to account for the nonlinear conduction observed in thin manganite films grown on bicrystal substrates and polycrystalline thin films. It has been shown that there is a large chemical potential difference ($\Delta\mu$), on the order of tenths of the conduction band width, between the insulating and ferromagnetic metallic (FM) phases in doped manganites. As a result, significant band bending forms at the interface between the FM phase and the insulating grain boundary for $T < T_{MI}$, which is close to the magnetic Curie temperature $T_C$. Transport through
such local energy barriers leads to nonlinear \( I-V \) behavior. As \( \Delta \mu \) is proportional to the magnetization of the sample, we expect an enhanced energy barrier and reduced thermal activation at lower temperatures, which leads to enhanced nonlinearity in transport.\(^{17}\)

The picture of nonlinear transport through local energy barriers due to the work function difference between different phases can naturally explain some key features of our observation. First, the nonlinear effect only emerges below \( T_{\text{MI}} \), as band bending occurs at the interface between the insulating and metallic regions. Second, the nonlinearity becomes more pronounced at lower temperatures due to enhanced band bending and suppression of thermal excitation related transport. Although our films are single crystalline and TEM images reveal no grain boundaries, it is important to note that phase separation can lead to coexisting nanoscale insulating regions in the FM phase.\(^{2}\) The nonlinear behavior is only observed in the highly phase separated LCMO and half doped LSMO, revealing clearly the critical role of phase separation. Third, this picture is also consistent with the observation that magnetic field enhances the nonlinear behavior. The presence of a magnetic field increases magnetization, which leads to larger band bending and higher energy barrier. It also reduces the total volume of the insulating phase, which effectively reduces the thickness of the insulating barrier for the charge carriers to tunnel through. It thus makes transport through tunneling more efficient. The low temperature exponent values \( z = 2.0–2.8 \) are close to the calculated value of 7/3 for amorphous semiconductor thin films\(^{33}\) and the exponent of 2.47 reported in discontinuous 2D Au thin films close to a percolation threshold,\(^{26}\) suggesting the strong similarity between our study and transport through highly inhomogeneous, disordered systems. We thus attribute the origin of the nonlinearity to transport through nanoscale phase separated regions.\(^{13,20}\)

This model also explains the different temperature dependences of the nonlinearity and the magnetoresistance. Since the CMR effect is due to the melting of the insulating phase in the presence of magnetic field, MR can be taken as a direct measure of the degree of phase separation in the system. It is known that the MR peaks at temperatures just below \( T_{\text{MI}} \), where a maximum level of phase separation is expected. The fact that our observation is enhanced at low temperatures and high magnetic fields is consistent with the picture that it is the work function difference between different phases that lead to nonlinear \( I-V \), and the degree of the phase separation plays a minor role in determining the \( I-V \) characteristics. An important implication of our results is even at low temperatures and a magnetic field of 9T, where the magnetoresistance becomes relatively weak, phase separation has not been fully quenched. This picture agrees well with previous x-ray scattering studies of the effect of magnetic field on charge/orbitally ordered nanoclusters in manganite.\(^{29}\)

V. CONCLUSIONS

In conclusion, we have observed strong nonlinear conduction in highly phase separated LCMO and half-doped LSMO thin films. The nonlinearity closely correlates with the metal-insulator transition and can be enhanced by magnetic fields and in films with thicknesses close to that of the electrically dead layer. We attribute its origin to transport through energy barriers due to the interfacial work function difference between the nanoscale phase separated insulating and metallic regions. Our results also suggest that phase separation is not fully quenched even at low temperatures and high magnetic fields.

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