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Conduction and magnetoresistance in doped manganite grain boundaries

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Grain boundary diffusion has been used to increase selectively the doping in grain boundaries of doped lanthanum manganite thin films. We show that this doping strongly modifies the temperature dependence of the grain boundary resistance and the form of the conductance versus voltage characteristic. The low field magnetoresistance associated with the grain boundary is altered following doping, but is not necessarily enhanced. This behavior is interpreted in terms of a doping-induced suppression of the local Curie temperature in the region of the grain boundary. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1569430]

Since the discovery of large low-field magnetoresistance (MR) in grain boundaries of doped lanthanum manganites[1–3] and other materials exhibiting colossal magnetoresistance, there has been considerable speculation regarding the nature of the grain boundary and the conduction mechanisms through it.[4] Models for the transport in grain boundaries have included elastic spin polarized tunneling,[1] inelastic tunneling,[5,6] hopping conduction through a nonmagnetic interface,[4] and tunneling through an interfacial depletion layer.[7] To some extent, research in this area has paralleled that on the physics of grain boundaries in high temperature superconductors. One of the experiments which has improved the understanding of the superconductor system has been the observation of enhanced critical currents in selectively doped grain boundaries.[8] In this letter we report the results of experiments in which manganite grain boundaries were selectively doped by a similar technique. In contrast to the superconductor experiments, in which increasing the transparency of the grain boundary is of great technological importance, we were interested in determining the role of electron tunneling in the low-field MR and the doping was aimed at decreasing the transparency. Unlike recent publications[9,10] which aimed to segregate a second, insulating phase at the grain boundary our experiments aimed only to modify the A-site cation doping within the grain boundary.

Epitaxial films of $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) were grown by laser ablation on (001) $SrTiO_3$ bicrystal substrates. The doping of the LCMO was achieved by the subsequent deposition of a $CaMnO_3$ (CMO) thin film on the LCMO under the same deposition conditions. Details of the deposition process can be found elsewhere.[8] The substantial difference in diffusion rate between the epitaxial film and the grain boundary has been shown to lead to selective doping of the grain boundary with an increased transparency consequent on reduced band bending at the interface.[8]

The phase diagram of the $La_{1-x}Ca_xMnO_3$ system is well understood with the ferromagnetic metallic phase existing only for $x<0.5$; thus, CMO shows activated transport over the whole temperature range of our experiment and at low temperatures contributes negligibly to the conductivity. Thus, the aim of the experiment was to enhance the disorder-induced enhanced resistivity of the grain boundary and to create a structure which was closer to a simple tunnel barrier. The level of doping enhancement was varied by changing the thickness of the CMO layer deposited onto the LCMO.

The films were patterned using conventional photolithography and argon ion milling into a series of measurement tracks which crossed the grain boundary. A variety of Wheatstone bridge structures were patterned in order that the properties of the grain boundary itself could be determined.[3] In addition, each sample contained tracks that did not cross a grain boundary and therefore could be used to determine the properties of the epitaxial bilayer. Au contact pads were deposited by dc sputtering and lift-off. The samples were measured between room temperature and 4.2 K in a dip probe with an integrated solenoid to provide magnetic field.

Plain tracks without a grain boundary were measured to assess the interdiffusion within the epitaxial films. Normalized resistance versus temperatures $[R(T)]$ data from these

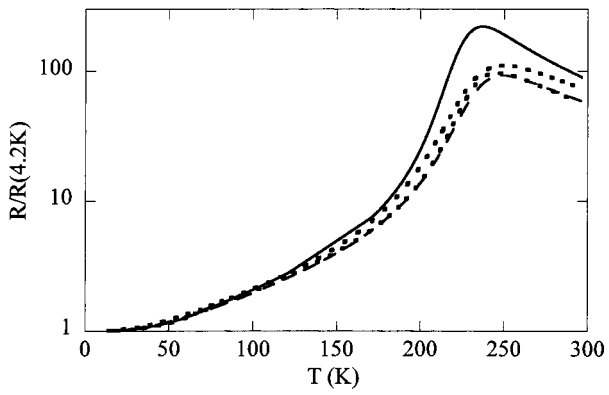

FIG. 1. Resistance (normalized to the value at 4.2 K) vs temperature for a series of films. The solid line is from a plain LCMO film; dashed line LCMO (100 nm)/CMO (50 nm) bilayer film, dotted lines LCMO (100 nm)/CMO (100 nm) bilayer films.

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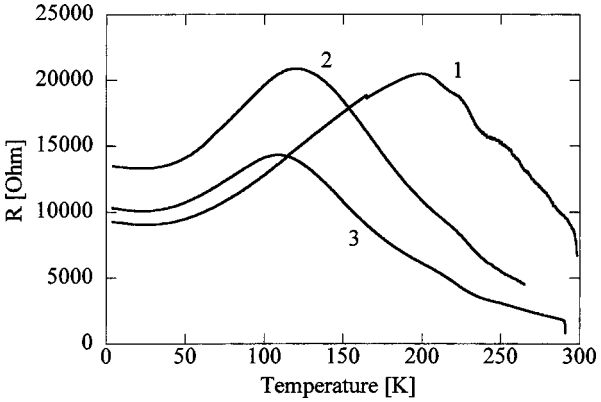

FIG. 2. Output resistance (offset voltage/current) from Wheatstone bridges containing 23 24° symmetrical grain boundary crossings per arm. Curve 1 is from a plain 100 nm LCMO film, curves 2 and 3 are from LCMO 100 nm/CMO 50 nm and LCMO 100 nm/CMO 100 nm bilayer films, respectively.

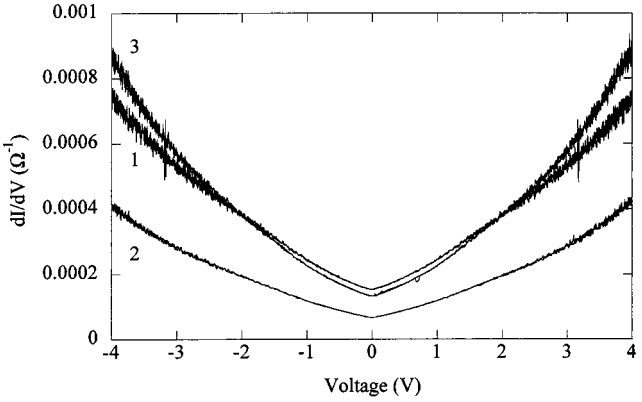

FIG. 3. Differential conductance at 4.2 K vs voltage characteristics from Wheatstone bridges containing 23 22.4° symmetrical grain boundary crossings per arm. (1) Plain 100 nm LCMO film, (2) LCMO 100 nm/CMO 50 nm, and (3) LCMO 100 nm/CMO 100 nm.

tracks are shown in Fig. 1. If significant interdiffusion had occurred, the increased Ca doping would be expected to reduce the peak resistance temperature (T_p) since increasing the Ca doping above 0.33 reduces T_p. It is evident from the data in Fig. 1 that T_p is not suppressed by the doping—if anything it is slightly higher in the bilayer samples. The lower normalized resistance of the bilayer samples above T_p is a consequence of the parallel conductance of the CMO doping layer which has a comparable hopping resistivity to LCMO; at low temperatures the LCMO layer alone contributes to the conduction. These results show that if interdiffusion occurs it is limited to a few atomic layers at the interface and that the bulk of the LCMO is unaltered during the bilayer growth.

Wheatstone bridge structures were used to measure the temperature dependence of the grain boundary resistance. Figure 2 shows curves from 24° symmetric grain boundaries with different doping levels. It can be seen that any imbalance in the bridges (which would lead to the measurement of interconnection tracks and so result in a series resistance drop at the metal–insulator transition temperature T_p) is small and we can be sure that the measurement correctly represents the properties of the grain boundary.

The undoped grain boundary shows broadly similar behavior to that previously observed,[11] with a peak resistance temperature around 200 K. Figure 2 shows that doping results in a change in the form of the resistance versus temperature behavior, with a reduction in the temperature at which the grain boundary resistance reaches a maximum and a consequent increase in the low temperature resistance. This is the result which might be expected on the basis of a model in which the metal–insulator transition of the material in the grain boundary is suppressed by local strain in the grain boundary region.[4] The additional doping has further suppressed the transition temperature and so lowers the peak resistance temperature in accordance with the aim of the experiment.

The conductance versus voltage characteristics for the undoped and doped material are compared in Fig. 3. There is a significant difference between the shape of the doped and undoped curves. Although qualitatively quadratic in form, neither curve is an especially good fit to the Simmons' model[12] of electron tunneling in that all show a cusp at zero bias. A better fit can be obtained to the Glazman–Matveev theory for multistep tunneling,[13,14] but it is unclear whether parameters obtained from the fit are necessarily physical. To avoid excessive heating, the measurements did not reach the high voltages reported by Gunnarsson *et al.*[6]

As has been observed previously,[11] the effect of the magnetic field is to shift the conductance vs. voltage curves vertically, consistent with a model in which the magnetization direction of the electrodes but not the barrier properties are altered by an applied field. However, doping clearly affects the nature of the transport process across the grain boundary. A more detailed study of the conductance voltage characteristics is being prepared as a separate publication.

Irrespective of the level of doping, all tracks containing a grain boundary showed the hysteretic double peak MR structure typical of manganite grain boundaries.[2,3,5,11,15] The low field MR from a grain boundary is associated with the relative misorientation of the local moments on either side of the grain boundary and, especially in a multiple track Wheatstone bridge, is heavily averaged over all domain orientations. Thus, irrespective of the precise mechanism underlying the MR, it is hard to achieve the 180° spin misorientation which should lead to the largest MR. The MR can be maxi-

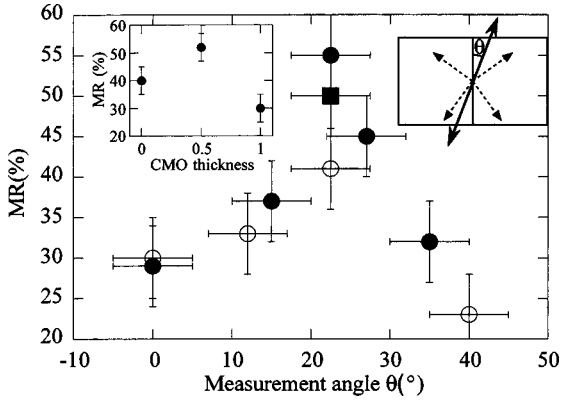

FIG. 4. Magnetoresistance vs applied magnetic field angle from Wheatstone bridges containing 23 24° symmetrical grain boundary crossings per arm. Open circles are data from a plain 100 nm LCMO film, solid symbols from LCMO 100 nm/CMO 50 nm. Inset: MR vs relative CMO/LCMO thickness. The inset diagram shows a plan view of the applied magnetic field angle and the (110) directions in the bicrystal substrate.

mized by varying the angle (illustrated in the inset to Fig. 4) within the plane of the film between the applied magnetic field direction and the grain boundary. Figure 4 shows comparative data from doped and undoped grain boundaries. It can be seen that the maximum MR in both cases is obtained for angles close to 22°. The magnetocrystalline anisotropy in unstrained LCMO leads to an easy axis lying along the (110) directions.[16] It can be seen from the schematic inset to Fig. 4 that for θ close to 20° the difference in the magnetic reversal of the two electrodes is maximized.

It can also be seen from Fig. 4 that the MR in the doped grain boundary is significantly higher than in the plain material, although the error bars are large reflecting the imprecision in field alignment and the run to run variation in the peak MR measured. The maximum MR of 24° bicrystal bridge structures with different doping levels is shown in the inset to Fig. 4. Although the MR is increased slightly by the first doping procedure, it is clear that it is strongly reduced by further doping.

In this letter we have presented grain boundary data from Wheatstone bridge structures. It is important to stress that a balanced bridge structure measures the difference between the grain boundaries and the comparable undisordered regions in the arms which do not contain a grain boundary. At low temperatures, where the intragranular resistance is low (see Fig. 1) the bridge output is essentially that of the boundary in isolation. At high temperatures, particularly above T_p the measured resistance falls as high resistance activated transport dominates in the intragrannular material. Thus, the rate at which the output resistance tends to zero at high temperatures provides a further measure of the properties of the doped grain boundary material. From Fig. 2 is it evident that doping substantially suppresses the bridge output resistance above T_p and we can therefore conclude that in the doped material the transport in the grain boundary is more dominated by hopping than in the undoped boundary whose excess resistance remains substantial above T_p.

The results presented in this letter show that the effect of doping, at least in terms of the changes to the barrier resistance can be understood on the basis of a metal–insulator transition which is suppressed to lower temperature, consistent with the expected changes in the doping of the grain boundary material. At least for the first doping stage, this is reflected in a more insulating intergranular barrier and, hence, a higher MR. These results are consistent with the model of Gunnarsson *et al.*[6] in which the suppressed magnetic order in the barrier would lead to a higher effective tunnel barrier. The conductance versus voltage response and the high temperature behavior, however, suggests that the effect of doping is more complex and leads to more substantial changes in the structure of the barrier consistent with the fall in MR at high doping. The likelihood is that low levels of doping can enhance the quality of the barrier, but that higher levels depress the Curie temperature of the regions of the electrodes from which tunneling is occurring.

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