Grain Boundary Structures in La$_{2/3}$Ca$_{1/3}$MnO$_3$ Thin Films

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Grain Boundary Structures in La$_{23}$Ca$_{13}$MnO$_3$ thin films

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Abstract

As with many other oxide-based compounds that exhibit electronic behavior, structural defects have a strong influence on the electronic properties of the CMR manganites. In this work, we have studied the effect of grain boundaries on the transport properties and on the local orientation of magnetization. Thin films of the perovskite-related La$_{23}$Ca$_{13}$MnO$_3$ compound were deposited onto bicrystal substrates using pulsed laser deposition. Transport measurements showed some enhancement of magnetoresistance across the grain boundary. The structure of the boundary was evaluated by electron microscopy. In contrast with the highly meandering boundaries typically observed in bicrystals of high temperature superconductors, the boundaries in these films are relatively straight and well defined. However, magneto-optical imaging showed that the local magnetization was oriented out of the plane at the grain boundary while it was oriented within the plane in the grains on either side. This coordinated reorientation of local magnetization near the grain boundary leads to enhanced magnetoresistance across the boundary in low fields.
Introduction

The observation of colossal magnetoresistance behavior (CMR) in perovskite-related manganites has led to considerable interest in these materials both to understand the underlying behavior and to develop these materials for magnetic sensor and recording applications. In these complex oxides, it is anticipated that the microstructure and structural defects will play an important role in their CMR properties due to the strong mutual coupling between electron, spin and lattice structure. The influence of defects on CMR properties is made more complex by the effect of strain introduced by such defects. For example, the effect of strain on the magnetic and transport properties of CMR thin films has been addressed in a number of studies.[1-7] This effect is likely to lead to complicated interactions between defects and CMR properties.

One example of the interaction between structural defects and CMR properties is the influence of grain boundaries on magnetoresistance (MR). The presence of grain boundaries has been demonstrated to enhance MR, particularly in the low-field regime. This effect has been demonstrated in through number of studies in polycrystalline thin film and bulk samples.[8-10] Studies on bicrystal thin films have further confirmed this effect.[11-13] In polycrystalline films, a large increase in resistivity and MR is observed over a wide range of temperatures, with a decreasing grain size leading to increasing resistivity and MR.[8] Systematic measurements on thin film bicrystals demonstrated that the enhancement in MR was a function of misorientation angle.[13]

The origin of the enhanced MR at grain boundaries is not yet clear, although several models have been proposed. Gu, et al.[10] and Gupta, et al.[8] each proposed that magnetic disorder at or near the grain boundary contributes to this behavior. In small applied fields, the grains become magnetically ordered, but the grain boundaries remain disordered leading to excess scattering due to spin-disorder. As the magnitude of the field is increased, the spins at the boundary are aligned and the resistance across the boundary is reduced. Steenbeck, et al.[11] demonstrated that the MR characteristics of a thin film bicrystal grain boundary could be modified through post-deposition annealing. Based on these results, they concluded that annealing led to the creation of a barrier region of modified material and transport properties showed tunnel junction-like behavior. Isaac, et al.[13] proposed a similar effect in which a region of modified material near the grain boundary leads to the enhancement of MR. However, based on the strong dependence of MR with misorientation angle, they suggest that an alternative to a tunneling mechanism in which the resistivity of this layer varies with misorientation and transport does not occur via tunneling.

In this work, we have studied the MR behavior and structure of grain boundaries in thin film bicrystals. In particular, we have studied the magnetic structure near the grain boundary using magneto-optical imaging. Based on this work, we propose an alternative
mechanism for the enhancement of MR at grain boundaries. This mechanism differs from those discussed above in that we find a coordinated reorientation of local magnetization rather than disorder leads to enhanced magnetoresistance across the boundary in low fields.

**Experiment**

Bicrystal thin films of the La$_{2/3}$Ca$_{1/3}$MnO$_3$ CMR compound were prepared by pulsed laser deposition onto bicrystal SrTiO$_3$ substrates. Films of several different misorientation angles were produced. In each case, the boundary in the underlying substrate was nominally a symmetric [001] tilt boundary with a misorientation angle $\Theta$. For convenience, all boundaries will be described simply by the misorientation angle $\Theta$. Generally, a series of samples with different misorientation angles were produced in a single run to minimize variations from deposition to deposition. All of the films discussed in this work were between 1000 and 1200Å in thickness. The Curie temperature each of the films was between 250 and 260K. The films were characterized structurally by x-ray diffraction (XRD) and electron microscopy. XRD revealed highly oriented films with narrow rocking curves (less than 0.1°), consistent with single crystal growth on each part of the bicrystal. Transmission electron microscopy confirmed the single crystal nature of growth and was used to study the structure of the grain boundary separating each half of the film. Transport measurements were carried out by patterning a single microbridge across the boundary. The geometry of the bridge was selected to enhance the measurement of the grain boundary resistance by narrowing only at the grain boundary. A similar bridge was patterned in the grains on either side of the boundary to allow comparative measurements. The magnetization patterns in the films and boundaries were imaged using magneto-optical methods. The imaging conditions were established such that magnetization pointed upward, out of the plane of the film was brightest, magnetization pointed downward was darkest, and magnetization in the plane of the film was of intermediate values. The magneto-optical imaging was carried out over a wide range of fields, orientations, and temperatures. Previously we have described the magnetic and domain structure found in single crystal films.[14, 15] In this work we concentrate on the structure at the grain boundaries.

**Results and Discussion**

A typical example of the transport properties measured across a grain boundary and within an adjacent grain is shown in Fig. 1. In this figure, the resistance measured for each bridge is normalized to the maximum value for each bridge. From this data, a relatively larger decrease in resistance with the application of small fields can be observed for the grain boundary as compared to the grain. Qualitatively, this enhanced low field magnetoresistance at the grain boundary is similar to that reported in previous...
Although we have not completed measurements of MR for all of our bicrystal samples, the work of Isaac, et al. demonstrates a strong dependence of MR and the specific resistance of the boundary (the product of the boundary resistance and boundary area) on the misorientation angle. [13]

Transmission electron microscopy (TEM) of the boundaries has shown that they are similar to those observed in other perovskite-based oxides. An example of the type of structure observed is shown in Fig. 2 for a 45° boundary. The misorientation between the two grains is confirmed by the inset diffraction pattern which was obtained from a selected area that contained portions of each grain. As is typical of this type of bicrystal substrate, there is a small deviation from the nominal misorientation angle of 45°. The structure of the boundary shows small steps or facets. It is not clear whether these steps are due to the small deviation from 45° (approximately 0.3°) or due to the growth mechanism of the film. In either case, the deviation from perfect linearity in these films appears to be much smaller than that observed in high temperature superconducting thin films [16], suggesting a different growth mechanism.

The magnetic structure near the grain boundary was studied by magneto-optical imaging. An example of the type of image obtained is shown in Fig. 3a. In this image, for a 36.8° grain boundary, strong magnetic contrast is observed along the grain boundary. This image represents the remnant magnetization after ramping the field in one direction in the plane of the film. The bright contrast at the boundary indicates that the net magnetization at the boundary is pointed upward out of the plane of the film while the gray contrast within the grains indicates magnetization within the plane of the film. Typically, as the field is ramped from the zero-field cooled condition, the bright contrast develops along the boundary while the contrast within the grains remains relatively unchanged. For larger applied magnetic field, the contrast at the boundary disappears as the magnetization at the grain boundary is forced to lie within the plane of the film (and parallel to the applied field). As the field is reduced to the remnant magnetization, the bright contrast reappears along the boundary. Upon field reversal, the bright contrast is again reduced until at sufficiently high fields, a uniform dark contrast appears along the boundary, indicating a reversal of the magnetization obtained for field in the opposite direction.

The uniform contrast along the boundary indicates a net magnetization of the boundary. On the length-scale of the magneto-optical technique, in this case of order 2-5 μm, this implies ordered spins along the grain boundary, but the alignment of these spins is not parallel to those within the grains. This observation is in contrast with assumptions that spins are disordered at the grain boundary. However, it is clear that the coordinated reorientation of spins near the boundary can lead to an increase in resistance for transport across the boundary. At higher magnetic fields, roughly consistent with those at which the resistance peaks, the spins near the boundary begin to orient within the plane and the
resistance decreases. Thus, this effect provides a reasonable explanation for enhanced MR at grain boundaries.

The dependence of this reorientation of spins on boundary misorientation angle is shown by the example in Fig. 3b. This image is from a 10° grain boundary and is collected under similar conditions as those for Fig. 3a. Qualitatively, this lower angle boundary demonstrated the same behavior as the higher angle counterpart: bright contrast along the boundary as small fields were applied, but then decreasing contrast as the field was further increased. In the case of this lower angle boundary, however, the bright contrast at the grain boundary is significantly less intense than that observed at the higher angle boundary. Thus, the assumption that excess scattering due to the local reorientation of spins at the boundary leads to enhanced MR is consistent with this data and with the data of Isaac, et al.[13]

The origin of this coordinated reorientation of spins near the boundary is not clear, nor are the microscopic details of the length-scale over which this reorientation takes place. However, we speculate that strains (elastic energy) associated with the grain boundary lead to this effect. The energy of a grain boundary depends on all parameters that define the boundary, including the grain boundary plane. Nevertheless, a simplified expression for the energy of low angle grain boundaries illustrates the strong dependence of boundary energy on misorientation angle, Θ. According to Read[17], the expression for the energy, E, of a low angle boundary of misorientation Θ can be approximated as

\[ E = C \Theta (A - \ln \Theta) \]

where C and A are constants that include details of the elastic constants and Burgers vector of the dislocations that comprise the boundary. Thus, if the grain boundary energy is indeed the key parameter, this expression predicts a strong dependence on Θ as observed in these experiments and manifested in MR as shown by Isaac, et al.[13]

Conclusion

We have studied the effect of grain boundaries in the colossal magneto-resistive compound La_{2-x}Ca_xMnO_3. In the bicrystal thin films studied in this work, transport measurements were used to confirm the enhancement of magneto-resistance across a grain boundary. Transmission electron microscopy was used to evaluate the structure of the boundaries which were found to be similar to those in other complex oxide systems. Magneto-optical imaging revealed a coordinated local reorientation of spins near the grain boundary, in contrast to speculation of spin disorder at grain boundaries. We have proposed that strain associated with the boundary leads to this local reorientation, and this model correctly predicts the strong dependence on misorientation angle for both our magneto-optic data and published transport data.
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Figure Captions

Figure 1  Normalized resistance as a function of applied magnetic field measured across the grain boundary and within a grain. The field was applied normal to the film plane, the bicrystal misorientation was 24°, and the temperature was 5K.

Figure 2  Bright-field zone axis transmission electron micrograph of a 45° bicrystal grain boundary. The inset selected area diffraction pattern reveals a small deviation from the nominal misorientation angle.

Figure 3  Magneto-optical images of (a) a 36.8° grain boundary and (b) a 10° grain boundary. Both images are taken at remnant magnetization.
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Figure 1