Lattice Distortion Effects at Grain Boundaries in Colossal Magnetoresistive Films

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Introduction

The role of strain on the magnetic and magneto-transport properties of colossal magnetoresistance (CMR) films has been reported on widely, both experimentally and theoretically. The strain is due to the strong electron-phonon coupling in this class of materials [1]. One example is the modulation of the Curie temperature T_c of CMR films by the strain in the film [2]. Motivated by measurements of spin-polarized transport in the ferromagnetic phase of polycrystalline manganites [3, 4], we studied grain boundaries in epitaxial manganite films by using local probes: magnetic force microscopy (MFM) [5, 6] and x-ray microdiffraction [7]. Our key finding is that there is an elastic strain gradient at the grain boundaries, which causes the modification of the magnetic properties when compared with those in the grain interior.

Methods and Materials

Epitaxial bicrystal $La_{1-x}Sr_xMnO_3$ films (with $x = 0.3$ and 0.23) were grown by pulsed laser deposition on bicrystal $SrTiO_3(001)$ substrates with 45° misalignment. This article uses pseudocubic notation to describe the crystal orientation of $La_{1-x}Sr_xMnO_3$.

X-ray diffraction measurements to determine the crystal orientation, lattice constant, and thickness of the films were conducted at beamline X16B at the National Synchrotron Light Source at Brookhaven National Laboratory. The scattering data were collected with 7.60-keV energy photons. A beam size of 0.2 mm was selected so that the incident x-rays were confined to one domain of the film during the diffraction measurements. To determine the crystal orientation, we searched for the (10*L*) and (11*L*) diffraction peaks of the films.

The T_c's of the films were measured by using bulk magnetometry (which we call $T_{c,b}$). By using MFM, we imaged the evolution of magnetic domains upon warming.

Local mapping of the strain at the grain boundary of the epitaxial $La_{0.7}Sr_{0.3}MnO_3$ film was performed by using x-ray microdiffraction at beamline 2-ID-D of the APS. A monochromatic 8-keV x-ray beam with a bandwidth of $\Delta\lambda/\lambda = 2 \times 10^{-4}$ was focused to a submicrometer-sized spot at the sample. We measured an upper bound of 0.35 μm for the vertical width of the beam size at the sample location by detecting the K-fluorescence of a Cr knife edge. The sample was mounted vertically on a sample stage with submicrometer translation control, with the grain boundary running along the horizontal direction. This grain boundary orientation choice allows a spatial resolution of 0.35 μm for microdiffraction in the direction perpendicular to the grain boundary (which we call *y*). The 2-D (θ-2θ, *y*) scans for the (002) substrate and film peaks for both domains were performed around the grain boundary region.

Results

From the (10*L*) and (11*L*) diffraction peaks, we infer that on one side of the grain boundary (domain A), the [100] axis is parallel to the grain boundary, and on the other side (domain B), it is rotated by 45° in the plane of the film for both x compositions. The x-ray diffraction results for $x = 0.3$ show that the film is epitaxial and coherently strained, with lattice constants of $a = b = 3.905$ Å and $c = 3.842$ Å (1.0% smaller than the $c = 3.88$ Å of bulk $La_{0.7}Sr_{0.3}MnO_3$). The interference fringes in the diffraction data attest to the smoothness of the film and correspond to a film thickness of 1080 ±20 Å.

The Curie temperatures as measured by SQUID magnetometry were 350 and 339K, respectively, for $x = 0.3$ and $x = 0.23$. As we image the magnetic domains upon warming by using an MFM with a variable temperature sample stage, the magnetic contrast diminishes as we approach $T_{c,b}$. Above $T_{c,b}$, we observe a magnetically inhomogeneous film, with ferromagnetic mesoscale regions forming at the grain boundaries or defects, while most of the film is paramagnetic [5, 6]. These ferromagnetic regions persist up to 20 K above $T_{c,b}$. From the MFM images, we mapped the local T_c as a function of distance from the grain boundary (Fig. 1).

The 2-D (θ-2θ, *y*) scans for the (002) substrate and film peaks on the $x = 0.3$ sample show that there is a slight difference ($\Delta\theta$ of ~0.1°) in the orientation of the *c* axis between the two substrate domains and, similarly,

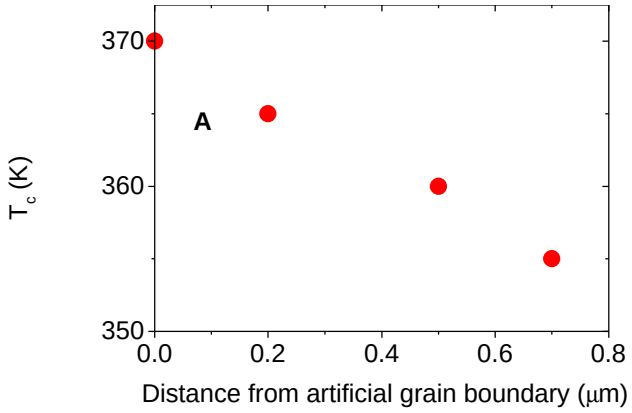

FIG. 1. Local variation of T_c measured by MFM in a $La_{0.7}Sr_{0.3}MnO_3$ film.

between the two film domains on the opposite sides of the grain boundary. This slight difference in the tilt of the *c* axis is sufficient to enable us to locate the grain boundary by detecting the (002) substrate or film peak on either side of the grain boundary and then seeing it disappear as the beam crosses to the other side of the grain boundary as the sample is scanned vertically along *y*. The location of the grain boundary is determined by the condition that the intensity of the (002) reflection drops halfway from its maximum value. The grain boundary locations determined this way by the two substrate peaks and two film peaks are within 2 μm of each other, the difference arising from the hysteresis of the translational motion of the stage.

The results for domain A are displayed in Fig. 1 with the θ-2θ axis converted into a surface normal lattice constant. Similar results were obtained for domain B. The 2θ values at the substrate peaks were used to calibrate the 2θ angle of the goniometer from the known value of c = 3.905 Å. The width of the substrate peak is determined by the resolution in 2θ, which was ~0.06° (equivalent to 0.005-Å resolution in lattice constant) in our setup. The 2-D substrate peak scans show that the substrate lattice constant is not spatially dependent. On the contrary, the same experiment on both film peaks (domain A and B) shows a drastically different effect: the *c* lattice constant increases as we approach the grain boundary.

Discussion

Because of the lattice mismatch between $La_{1-x}Sr_xMnO_3$ (a = b = c = 3.88 Å for x = 0.3) and the $SrTiO_3$ substrate (a = b = c = 3.905 Å), these films are known to have a tensile strain [8] that results in the suppression of the Curie temperature when compared with the bulk [1, 2] and a magnetization vector lying in the plane of the film [8]. The degree of strain depends on the film thickness; partial or complete relaxation of the strain can occur as the film thickness is increased. Our current microscopic studies show that a similar strain modulation can exist on a single film; in such a case, it occurs at the grain boundary. The strain in the interior of the grain relaxes at the grain boundary, yielding a lattice constant at the grain boundary that approaches that of bulk $La_{1-x}Sr_xMnO_3$. This consequently results in a local variation of the Curie temperature, with the Curie temperature at the grain boundary corresponding to the value of the bulk target material (370K) (see Fig. 2 [6]).

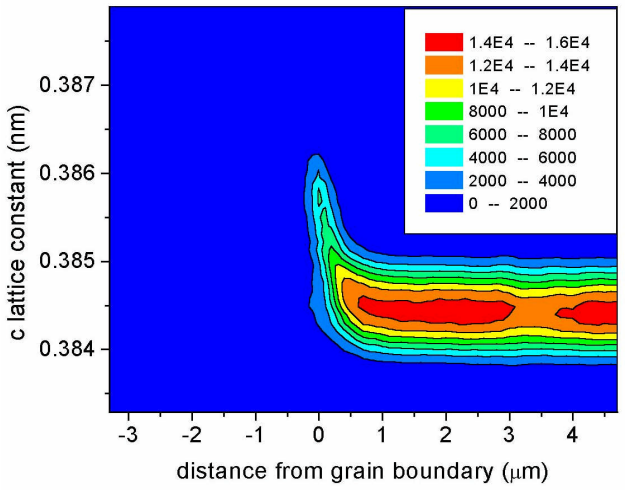

FIG. 2 Strain gradient at the grain boundary on a $La_{0.7}Sr_{0.3}MnO_3$ film.

Acknowledgments

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