Direct measurement of strain effects on magnetic and electrical properties of epitaxial $SrRuO_3$ thin films

Q. Gan, R. A. Rao, and C. B. Eom
Department of Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina 27708

J. L. Garrett and Mark Lee
Department of Physics, University of Virginia, Charlottesville, Virginia 22903

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By lifting an epitaxial thin film off its growth substrate, we directly and quantitatively demonstrate how elastic strain can alter the magnetic and electrical properties of single-domain epitaxial $SrRuO_3$ thin films (1000 Å thick) on vicinal (001) $SrTiO_3$ substrates. Free-standing films were then obtained by selective chemical etching of the $SrTiO_3$. X-ray diffraction analysis shows that the free-standing films are strain free, whereas the original as-grown films on $SrTiO_3$ substrates are strained due to the lattice mismatch at the growth interface. Relaxation of the lattice strain resulted in a 10 K increase in the Curie temperature to 160 K, and a 20% increase in the saturation magnetic moment to 1.45 μ_B/Ru atom. Both values for the free-standing films are the same as that of the bulk single crystals. Our results provide direct evidence of the crucial role of the strain effect in determining the properties of the technologically important perovskite epitaxial thin films. © *1998 American Institute of Physics.* [S0003-6951(98)02008-7]

Over the last decade, the scientific and technological importance of perovskite oxide materials has grown tremendously because they possess a wide range of unusual and useful physical properties, such as high T_c superconductivity, colossal magnetoresistance (CMR), and ferroelectricity. Both electronics applications and many scientific experiments focus on synthesizing these oxide materials in the form of epitaxial thin films or heterostructures. However, as is true for most cases of heteroepitaxial film growth, the lattice mismatch and the thermal expansion mismatch between the thin film and substrate materials cause considerable microstructural strain in films. As a result, the properties of epitaxial perovskite thin films can be quite different from the intrinsic properties of the corresponding bulk crystalline materials. For example, Jin *et al.* first observed ''colossal'' MR values ($\sim 10^6\%$) in epitaxial perovskite $La_{0.67}Ca_{0.33}MnO_x$ thin films on $LaAlO_3$ substrates.[1] In contrast, bulk polycrystalline $La_{0.67}Ca_{0.33}MnO_x$ exhibits a relatively low MR value (40%–100%).

The influence of strain on the properties of epitaxial perovskite thin films has been actively studied recently. The most commonly used approach is to grow epitaxial thin films of varying thickness on substrates with different lattice mismatches to induce different strain states.[1–4] However, this method cannot isolate strain effects from property changes due to other mechanisms such as variation of crystalline quality with substrate, presence of impurities arising from interdiffusion with the substrate, thickness dependence of the strain distribution, as well as possible stoichiometry changes resulting from strain stabilization.[5] There are also other indirect methods which explain the property changes of the strained thin films based on studies of hydrostatically pressure-strained bulk perovskite materials.[6–8] However, bulk samples under hydrostatic pressure are subjected to an isotropic compressive strain whose effects can be quite different from the anisotropic mixture of compressive and tensile strains that result from heteroepitaxial film growth.

In order to determine the intrinsic strain effect on the properties of epitaxial perovskite thin films, all other effects mentioned above need to be removed or kept constant. An ideal method is to study the same thin-film sample before and after strain relaxation. In this report, we present exactly such direct measurements on how strain changes the magnetic and electrical properties of epitaxial $SrRuO_3$ thin films by using a lift-off technique to obtain strain-free films. $SrRuO_3$ is an isotropic metallic perovskite with a $GdFeO_3$-type structure undergoing a ferromagnetic transition at 160 K. Unlike other oxides such as $YBa_2Cu_3O_7$ and $La_{0.67}Ca_{0.33}MnO_x$, $SrRuO_3$ is chemically very stable, which allows us to prepare lift-off or free-standing thin films by selective chemical etching of substrates. Since there is no lattice coherency requirement in the films after they are lifted off the substrate, the elastic strain should be relaxed, i.e., the lift-off thin films should be strain free.

The $SrRuO_3$ thin films were deposited by 90° off-axis sputtering under the conditions described elsewhere.[9] Vicinal (001) $SrTiO_3$ substrates with 2°, 4°, and 8° miscut toward [010] axis were used. The thickness of the thin films was about 1000 Å. Due to the small lattice mismatch with $SrTiO_3$ ($\sim$0.64% smaller than $SrRuO_3$), epitaxial $SrRuO_3$ thin films should coherently grow on the substrates, and thus, are subjected to a compressive stress in the plane. X-ray analysis indicated that these epitaxial $SrRuO_3$ thin films grown on vicinal (001) $SrTiO_3$ substrates are single domain with [110] normal to the substrate surface.[10] Scanning tunneling microscope study of the surface morphology suggests that these thin films grow in a step flow growth mode.[11] After deposition, the as-grown $SrRuO_3$ thin films on 0.25 in.×0.25 in. $SrTiO_3$ substrates were diced into two rectangular-shaped pieces of almost equal sizes. One piece from each pair was used to establish the reference characteristics for as-grown, strained samples. The other was used to prepare a lift-off thin-film sample by selectively etching the $SrTiO_3$ substrate with an acid (50% HF: 70% $HNO_3:H_2O = 1:1:1$) solution.

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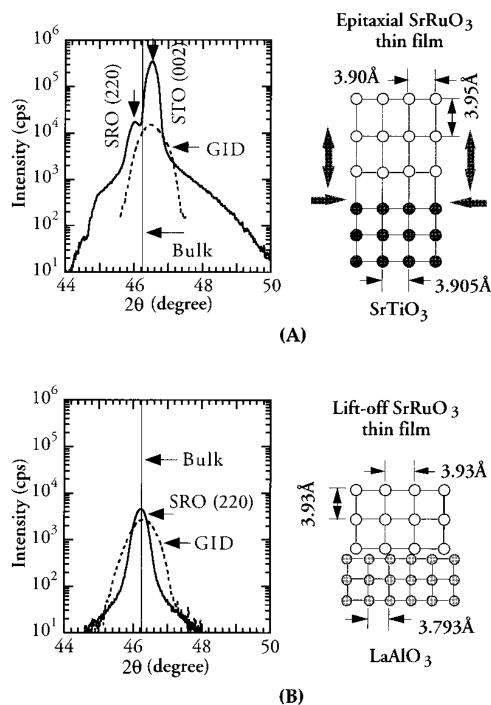

FIG. 1. X-ray diffraction normal (solid line) and grazing incident diffraction (GID) (broken line) $\theta-2\theta$ scans, and schematics of lattice arrangements for (A) an as-grown (elastically strained) $SrRuO_3$ thin film on a vicinal (001) $SrTiO_3$ substrate and (B) a lift-off strain-relaxed $SrRuO_3$ thin film. The vertical line indicates the 2θ angle for $d_{(220)}$ of bulk $SrRuO_3$.

This etchant does not chemically affect the $SrRuO_3$. The free-standing lift-off thin film was then settled onto a (001) $LaAlO_3$ substrate for mechanical support. The top surface of the lifted-off $SrRuO_3$ thin film was slightly roughened, probably due to the strain relaxation.

The complete strain states of the films were studied by using a four-circle x-ray diffractometer. The out-of-plane lattice parameter, $d_{(110)}$, was determined by normal θ–2θ scans. The in-plane lattice parameters were determined by both a least-squares method using several off-axis reflections and by grazing incidence diffraction (GID). The data from both methods were consistent. Figure 1(A) shows a typical normal θ–2θ scan and a GID θ–2θ scan of (002) or $(\bar{2}20)$ plane for the as-grown thin film on 8° miscut (001) $SrTiO_3$. For comparison, the 2θ value corresponding to $d_{(220)}$ of the bulk material is represented by a vertical line. The in-plane lattice parameters of $SrRuO_3$ were found to be 3.90 ± 0.01 Å, very close to that of $SrTiO_3$ (3.905 Å). Therefore, epitaxial $SrRuO_3$ thin films grow coherently on $SrTiO_3$ substrates, which is consistent with cross-sectional transmission electron microscope studies.[12] The in-plane lattice parameters, which are smaller than that of bulk $SrRuO_3$ (3.93 Å), indicate that the film is subjected to a biaxial compressive strain in the plane of the film ($\epsilon_{xx}=\epsilon_{yy}=-0.67\%$). From the 2θ value of the normal scan in Fig. 1(A), the out-of-plane lattice parameter was found to be 3.95 Å, larger than that of bulk materials, demonstrating a uniaxial tensile strain along [110] direction ($\epsilon_{zz}=0.50\%$) in the film. This tensile strain is due to the in-plane biaxial compressive stress.

The strain state of lifted-off $SrRuO_3$ thin-film samples was also determined by x-ray diffraction. Figure 1(B) shows both normal and GID θ–2θ scans for the lift-off thin film. As can be seen, both the in-plane and out-of-plane lattice param-

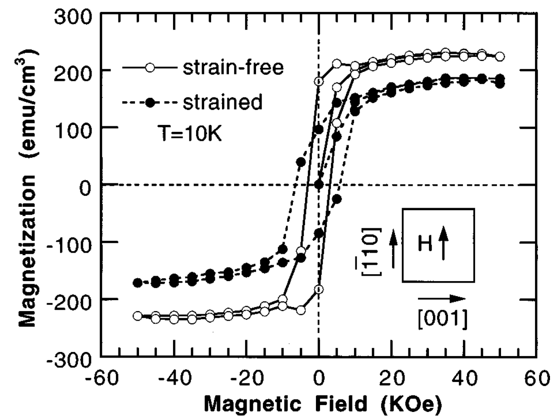

FIG. 2. The magnetization vs applied magnetic-field curves for both a strained and a strain-relaxed $SrRuO_3$ thin film measured at 10 K.

eters (~3.93 Å) of the lift-off film are the same as that of the bulk material. This implies that the as-grown $SrRuO_3$ thin film is subjected to an elastic strain which is fully relaxed after lift-off. Because the only difference between the as-grown and lifted-off samples in each pair was the strain state, we can directly measure how strain alters the magnetic and electrical properties of epitaxial $SrRuO_3$ thin films.

The strain effect on magnetic properties was investigated with a superconducting quantum interference device magnetometer. The magnetization (M) was measured as a function of magnetic-field (H) applied parallel to the surface. Single-domain epitaxial $SrRuO_3$ films showed an anisotropic behavior in the plane with $[\bar{1}10]$ being the easy axis and [001] being the hard axis for magnetization.[13] The M versus H curves measured at 10 K with H along the easy axis for both strained and strain-relaxed films originally grown on 8° miscut $SrTiO_3$ substrates are shown in Fig. 2. The saturation magnetic fields are almost the same for both samples, in the range of 25–30 KDe, but the saturation magnetization is significantly increased (~20%) in the strain relaxed film. At $H=40$ KDe, the calculated saturated moments are 1.45 μ_B/Ru atom for the strain relaxed film (which is the same as that for bulk single crystals[14]) and only 1.15 μ_B/Ru atom for the strained film. There is a ~5% uncertainty in the above values due to the difficulties in accurately determining the volume of the films. We also notice that the shape of the M versus H hysteresis loops are quite different. For example, at zero field, the remnant magnetization (M_r) is about 75% of the saturation magnetization moment in the strain-relaxed film, while it is only 50% in the strained film. However, the strain-relaxed film is easy to ''switch'' due to its smaller coercive field H_c of 3 KDe as compared to a H_c of 7 KDe for the strained film. Normally, these magnetic quantities are sensitive not only to lattice strain, but also to impurity, grain boundary, and defect structures. However, because these factors are identical in the strained and strain-relaxed sample pairs, the differences in magnetic behavior are directly attributable to the strain relief.

We also measured the magnetization as a function of temperature in an applied field of 500 De along the easy axis. These data were taken after the $M(H)$ curves of Fig. 2, so the magnetization follows the upper branch of the hysteresis curve. As shown in Fig. 3, the strain-relaxed $SrRuO_3$ thin film shows a sharp magnetization onset at about 160 K and does not saturate with temperature as T approaches 0 K. The

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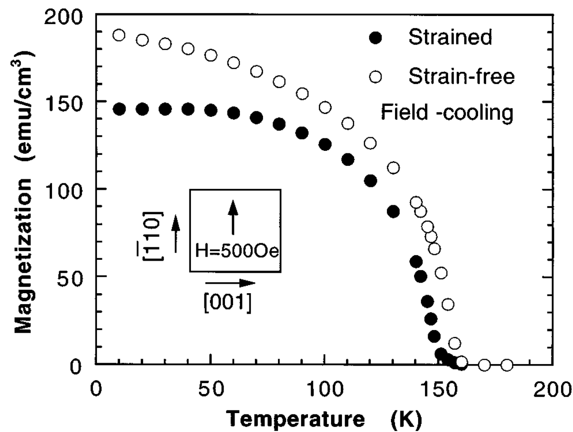

FIG. 3. The magnetization vs temperature curves for both a strained and a strain-relaxed $SrRuO_3$ thin film.

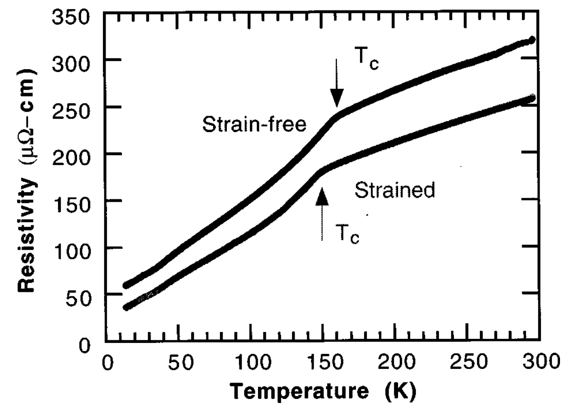

FIG. 4. The resistivity vs temperature curves for both a strained and a strain-relaxed $SrRuO_3$ thin film. The arrows indicate the Curie temperature T_c.

unsaturated magnetization is attributed to the strong magnetocrystalline anisotropy of $SrRuO_3$.[15] The functional form of $M(T)$ and the T_c of the strain-relaxed film are also similar to those of the bulk single crystals.[14] However, the strained film has a broader ferromagnetic transition with an onset at 150–154 K, and its magnetization becomes temperature independent at low temperatures. The broad magnetic transition indicates that the strain state is inhomogeneous in the strained film, resulting in magnetic domain alignment over a wide temperature window. Unlike the strain-relaxed films where only the magnetocrystalline anisotropy plays a role in determining the magnetization in a given crystallographic direction, additional residual stress anisotropy also should be considered in the strained thin films. This may explain why the magnetization saturated only in the strained film as shown in Fig. 3. The suppression of both T_c and magnetization moment in the strained thin films is believed to result primarily from a change in the spin–spin coupling since this coupling is very sensitive to interatomic distances. The change of the lattice parameters affects the overlapping of Ru:$t2g$ and O:$2p$ orbitals to which form a narrow π^* band that is responsible for the ferromagnetism.[16]

The strain effect on the electrical transport behavior was studied by measuring resistivity as a function of temperature using the Van der Pauw method. As shown in Fig. 4, the general features of resistivity behavior for both strained and strain-relaxed thin films are the same, such as metallic behavior and a sharp kink corresponding to the Curie temperature T_c. There is some uncertainty in the absolute resistivity values of the strain-relaxed films because the lift-off films are very fragile and could be easily damaged when being loaded onto the $LaAlO_3$ substrate. We actually can see microcracks on the strain-relaxed film, which may be responsible for the higher resistivity as compared to the strained film. We found that the resistively measured T_c significantly increased from about 150 K for the strained film to about 160 K when the elastic strain was relaxed, which is consistent with our magnetization measurements. Above T_c, the resistivity for both strained and strain-relaxed samples linearly increased with temperature with almost the same slope. Below T_c, the resistivity for strain-relaxed film decreased faster with decreasing temperature, which is due to the stronger magnetization in that film. These property changes are attributed to the structural distortion, which results from the elastic strain inherent to all lattice-mismatched epitaxial film growth.

In summary, our results provide unambiguous, quantitative evidence for the defining role played by strain in altering the important macroscopic electrical and magnetic physical properties of epitaxial perovskite thin films. It is clearly evident that strain arising from lattice mismatch with the substrate is responsible for reducing the Curie temperature, broadening the ferromagnetic transition, and reducing the saturation magnetic moments by significant amounts. All these properties recover to bulk values once the strain is relieved, showing the strain effects to be truly elastic. Because the chemical and physical concerns in $SrRuO_3$ thin-film heteroepitaxy are very similar to most other perovskite oxides, it is expected that strain plays a similarly important role in degrading or in some cases possibly enhancing the interesting scientific and technological properties of this class of materials.

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