

Magnetic Properties of SrRuO₃ Thin Films Having Different Crystal Symmetries

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This study examined the effect of various types of epitaxial strain on the magnetic properties of SrRuO₃ thin films. Epitaxial SrTiO₃ (001), SrTiO₃ (110), and SrTiO₃ (111) substrates were used to apply different crystal symmetries to the grown films. The films were grown using pulsed laser deposition. The X-ray diffraction patterns of the films grown under optimum conditions showed very clear peaks for the SrRuO₃ film and SrTiO₃ substrates. The saturated magnetic moment at 5 K after 7 Tesla field cooling was 1.2-1.4 μ_B /Ru. The magnetic easy axis for all three types of films was along the surface normal. The magnetic transition temperature for the SrRuO₃ film with lower symmetry was slightly larger than the SrRuO₃ film with higher symmetry.

Keywords : SrRuO₃, thin film, Magnetization, epitaxial strain

1. Introduction

SrRuO₃ (SRO) is a conducting oxide with a ferromagnetic transition at $T_C \sim 160$ K [1, 2]. SRO is commonly used as a metallic electrode in ferroelectric devices on account of its low resistivity and chemical stability [3]. Tunneling junctions with its peculiar negative spin polarization have also been studied [4, 5]. Structural modification caused by epitaxial strain in thin films modulates its magnetic properties significantly [6]. Here, in-plane compressive strain in SRO grown coherently on SrTiO₃ (STO) (001) substrates push the magnetic easy axis normal to the surface and suppresses the T_C of approximately 150 K, while a high aspect ratio in thin film geometry favors an in-plane magnetic easy axis [6].

Lowering the crystal symmetry can induce dramatic changes in the physical properties, as in the case in BiFeO₃ thin film [7]. The crystal structure of BiFeO₃ films grown on STO (111) substrates was monoclinic while bulk BiFeO₃ has a rhombohedral structure. Moreover, the value of polarization of the film increased by almost ten times that that of the bulk BiFeO₃.

In this study, SRO thin films were grown on cubic STO substrates with different surfaces and their magnetic properties were compared [8]. SrTiO₃ (001), SrTiO₃ (110), and SrTiO₃ (111) substrates were used to apply different

crystal symmetries to the films. A cubic (110) substrate can stabilize many distorted perovskite oxides, such as YTiO₃, while a cubic (111) substrate can accommodate hexagonal oxides [9]. A study of SRO films grown on these two types of substrates should provide a wider chance to study interesting oxides with lower symmetry.

2. Experimental

SRO thin films were grown by pulsed laser deposition using KrF excimer laser pulses of 140-250 mJ focused on a stoichiometric ceramic target [10-12]. The films were grown at $T=650$ - 850°C and an oxygen partial pressure during growth of approximately 10-100 mTorr. The typical thickness of the films was determined by an in-situ shadow mask during growth and atomic force microscopy and was 50-100 nm. The growth conditions were fixed in order to allow a reasonable comparison in the structural and magnetization study. Postannealing after growth at higher oxygen partial pressure (> 100 Torr) had a negligible effect on the physical properties within experimental error. The crystal structure of the grown films was examined by high-resolution x-ray diffraction (XRD) with $\text{Cu-}k_\alpha$ radiation, and the magnetic properties of the films were obtained using a superconducting quantum interference device (SQUID) magnetometer. The diamagnetic contribution from the SrTiO₃ substrate was negligible compared with the large ferromagnetic signal taken at 500 Oe, and was neglected in the analysis.

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3. Results and Discussion

First, the growth condition was optimized by growing the SRO film on well-known STO (001) substrates. In this case, the criteria for qualifying the film have been established. These include the surface morphology measurements using atomic force microscopy (AFM), structural identification by XRD, magnetization studies, dc-resistivity measurements etc. Among these, a simple XRD and magnetization studies are the most basic and reliable.

The optimal conditions were found to be $T \sim 760^\circ\text{C}$ and $P(\text{O}_2) \sim 60$ mTorr. Under these conditions, the XRD pattern showed very sharp peaks for the films, as shown in Fig. 1(a). The c -axis lattice constant calculated from the SRO (001) peak was $< 3.960 \text{ \AA}$, which demonstrates good oxygen stoichiometry. It should be noted that a pseudocubic lattice notation for SRO was used for easy comparison. The film quality was also confirmed from the very narrow rocking curve widths of 0.04° .

SRO film grown under a lower oxygen partial pressure can have a c -axis lattice constant as large as $c \sim 4.000 \text{ \AA}$, even though AFM showed an atomically flat surface with a step and terrace structure height of one unit cell of perovskite SrRuO₃ [13]. This lattice expansion compared with that in the bulk was attributed to oxygen deficiencies.

Perovskite oxides with strong spin-orbit coupling usually show large anisotropic magnetic properties, which are sometimes more evident in thin films. The anisotropic magnetic properties of the film were examined by measuring the magnetization of the film with two field directions. The magnetization was measured by cooling the film from room temperature to 5 K under the highest field of 7 Tesla, applying 500 Oe at 5 K and measuring the level of magnetization with increasing temperature. This field-cooling procedure makes the ferromagnetic signal from the very thin film much larger than the paramagnetic or diamagnetic background from the thick substrate.

The field was applied along the surface normal direction, i.e., along [001] and along the in-plane direction of the [100] direction of the substrate. Due to the coherent growth in the cubic (001) substrate, the other in-plane [010] direction was similar to the in-plane [100] direction. Initially, there were two major differences in the magnetization curve of the film compared with that reported for bulk SRO [1]. First, the T_C was suppressed by approximately 10 K. Similar trends have been reported previously and explained in terms of compressive strain [8]. Second, the anisotropy was not so severe. This is due to the fact that the tetragonal symmetry of this film has a higher symmetry than the orthorhombic symmetry of bulk

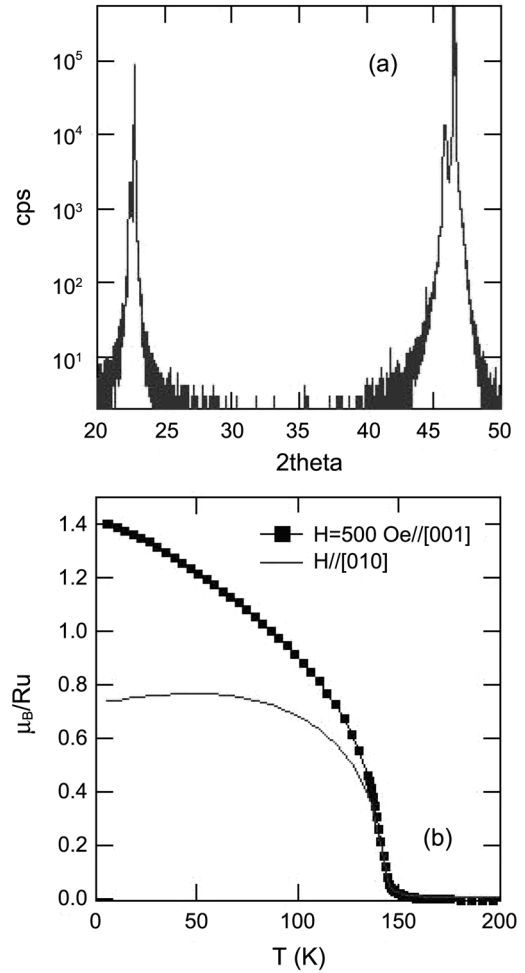


Fig. 1. High resolution XRD θ - 2θ scan (a) and Magnetization measurement (b) for the SrRuO₃ thin films grown on the SrTiO₃ (001) substrate. Sharp and strong peaks for SRO (001) and SRO (002) reflection are clearly visible at the left side of the substrate peaks at $2\theta=23^\circ$ and 46° .

SRO. Moreover, the magnetic easy axis of the SRO is not parallel to either the surface normal or the in-plane direction of the substrate.

Fig. 2 shows a high resolution XRD θ - 2θ pattern and magnetization measurement for the SRO thin film on STO (110) substrate. The film quality was as good as SRO on STO (001) substrate shown in Fig. 1. The magnetization curve showed a very anisotropic behavior, possibly due to the similar crystal symmetry of this SRO film. STO (110) could preserve the orthorhombic symmetry, which is the crystal structure of bulk SRO [1]. The magnetic anisotropy between the two-inplane directions, i.e. [001] and [1-10], was not as large as the huge anisotropy between magnetization along the in-plane direction and along the surface normal direction.

Finally the crystal symmetry of SRO further was reduced by growing the film on top of a STO (111) substrate.

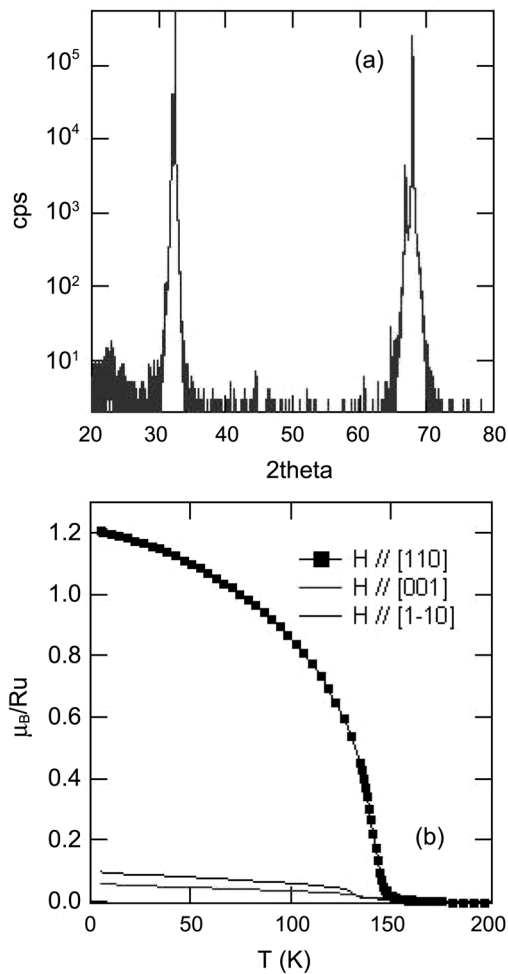


Fig. 2. High resolution XRD θ - 2θ scan (a) and Magnetization measurement (b) for SrRuO₃ thin film on SrTiO₃ (110) substrate. Sharp and strong peaks for SRO (110) and SRO (220) reflection are clearly visible at the left side of substrate peaks near $2\theta=32^\circ$ and 66° .

The SRO film on the STO (111) substrate was not as good as the two types of films described above. Normally, STO (001) and STO (110) substrates can be prepared with the best quality among the various oxide substrates. An atomically flat substrate with a unit cell step height and terrace structure is commercially available. This quality could be obtained using in-situ high vacuum annealing at a higher temperature of approximately 900°C. However, this high quality has not been reported to exist for the STO (111) substrate, which is also evident in the data. Fig 3(a) shows several substrate peaks at $2\theta=40.0^\circ$, which indicates the existence of twin and/or multi grains with different c -axis lattice constants, even though all the above STO substrates with three different directions had been purchased from the same company. Nevertheless, a good SRO film peak could be observed at $2\theta=39.5^\circ$. It should be noted that the y-axis in the XRD pattern is in

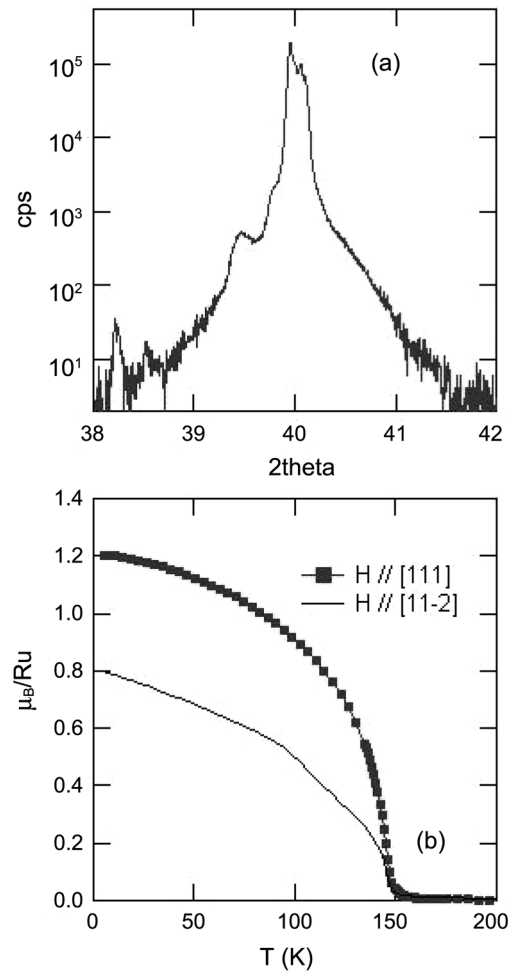


Fig. 3. High resolution XRD θ - 2θ scan (a) and Magnetization measurement (b) for SrRuO₃ thin film on SrTiO₃ (111) substrate. A peak for SRO (111) reflection is clearly visible near $2\theta=39.5^\circ$ at the left side of the substrate peaks near $2\theta=40.0^\circ$. The existence of multiple peaks for the substrate (111) reflection suggests the STO (111) substrate has rather poor quality compared with STO (001) and STO (110) substrate.

log-scale not absolute scale.

The magnetization data in Fig. 3(b) shows that the anisotropy of SRO on STO (111) is more similar to SRO on STO (001) than to SRO on STO (110). However, the sharpness of the magnetization near T_C when the magnetic field is along the surface normal direction is slightly superior to those in the SRO on the STO (001) substrate and the SRO on the STO (110) substrate.

One common observation among the magnetization curves for SRO films on STO (001), (110), and (111) substrate is that the magnetic easy axis is along the surface normal direction. It is possible that a decrease in the ferromagnetic transition temperature and the direction of the magnetic easy axis being along the surface normal rather than in-plane is the result of epitaxial strain from

the substrates. It should be noted that the in-plane lattice mismatch for all three cases is $< 0.5\%$, which is small enough for a coherent growth behavior [8].

4. Conclusions

This study examined the magnetic properties of SrRuO₃ thin films grown on SrTiO₃ (001), SrTiO₃ (110), and SrTiO₃ (111) substrates in order to determine the effect of the crystal structure of the film imposed by epitaxial strain. XRD of the films showed very clear peaks for SrRuO₃ film at the left side of the peaks for the SrTiO₃ substrates, which demonstrates the quality of the films. The magnetic easy axis was found to be along the surface normal direction for all three types of films, and can be explained by compressive epitaxial strain.

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