

Electrical Properties of SrRuO₃ Thin Films with Varying *c*-axis Lattice Constant

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We studied the effect of the variation of the lattice constant on the electrical properties of SrRuO₃ thin films. In order to obtain films with different volumes, we varied the substrate temperature and oxygen pressure during the growth of the films on SrTiO₃ (001) substrates. The films were grown using a pulsed laser deposition method. The X-ray diffraction patterns of the grown films at low temperature and low oxygen pressure indicated the elongation of the *c*-axis lattice constant compared to that of the films grown at a higher temperature and higher oxygen pressure. The in-plane strain states are maintained for all of the films, implying the expansion of the unit-cell volume by the oxygen vacancies. The variation of the electrical resistance reflects the temperature dependence of the resistivity of the metal, with a ferromagnetic transition temperature inferred from the cusp of the curve being observed in the range from 110 K to 150 K. As the *c*-axis lattice constant decreases, the transition temperature linearly increases.

Keywords : SrRuO₃, thin film, resistivity, lattice constant, ferromagnetic transition

1. Introduction

SrRuO₃ (SRO) is a conducting oxide and has a ferromagnetic transition at $T_c \sim 160$ K [1, 2]. Due to its low resistivity and chemical stability, SRO has frequently been used as a metallic electrode in ferroelectric devices [3]. Tunneling junctions with a peculiar negative spin polarization have also been realized [4, 5].

The stabilization issue of the ferromagnetic properties of thin films by the introduction of strain and oxygen vacancies has been widely studied [6, 7]. Herein, the oxygen vacancies and off-stoichiometry in SRO films coherently grown on SrTiO₃ (STO) (001) substrates elongate the volume of the films, while their T_c value decreases with increasing resistivity.

Oxygen vacancies in perovskite oxides can induce a drastic change of the physical properties. For example, in contrast to the bulk SrTiO₃ which has a cubic structure and is not ferroelectric, SrTiO₃ films grown on SrTiO₃ (001) substrates with oxygen vacancies have an elongated tetragonal structure and has a finite polarization [7].

Herein, we grew SRO thin films on cubic STO substrates with different off-stoichiometries. In order to obtain

grown films with different oxygen contents, we changed the growth temperature and oxygen pressure during the growth without post-annealing.

2. Experimental

SRO thin films were grown using a pulsed laser deposition method with KrF excimer laser pulses of 200 mJ focused on a stoichiometric ceramic target [8-10]. The films were grown at temperatures $T = 650$ - 750 °C and the oxygen partial pressure during the growth was in the range of about 20-100 mTorr. The typical thickness of the grown films was measured using in-situ reflection high-energy electron diffraction during the growth and further confirmed by x-ray reflectivity measurements. We varied the growth temperature and the oxygen pressure, while the other growth conditions were kept fixed, in order to achieve a reasonable comparison in the structural and electrical study. The films were cooled down just after the growth without any further post-annealing process. The crystal structure of the grown films was identified using a high-resolution x-ray diffractometer (XRD) with $Cu-k_\alpha$ radiation and the dc-resistivity of the films was obtained by a four-probe method.

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3. Results and Discussion

First, we grew SRO films on STO (001) substrates while varying the growth conditions. In this case, many parameters were used for qualifying the films. These include surface morphology measurements obtained using atomic force microscopy, structure identification using XRD, magnetization studies, and DC-resistivity measurements. Among these, we used structure identification and DC-resistivity measurements to obtain some insights into the correlation between the structure and electrical properties.

The SRO films grown under various conditions showed a wide range of *c*-axis lattice constants. We varied P(O₂) from 20 to 100 mTorr and *T* from 650 to 750°C. Under these conditions, the XRD spectra of the films showed a large shift of the peaks, as shown in Fig. 1. The *c*-axis lattice constant calculated from the SRO (002) peak was 4.000 Å for a film grown at P(O₂) of 20 mTorr, which demonstrates the presence of a large amount of oxygen vacancies. On the other hand, the *c*-axis lattice constant for a film grown at P(O₂) of 100 mTorr reached 3.960 Å, which demonstrates the existence of good oxygen stoichiometry. Note that we used pseudo-cubic lattice notation for SRO to facilitate the comparison [11]. It is known that SRO films grown under a low oxygen pressure can have a *c*-axis lattice constant as large as $c \sim 4.000$ Å, though the atomic force microscopy measurements showed an atomically flat surface having a step and terrace structure with a height of one unit cell of perovskite SrRuO₃ (not shown here) [12]. These lattice expansions compared to that in the bulk may be attributed to the oxygen deficiency of the film due to the change of the oxygen pressure during the growth.

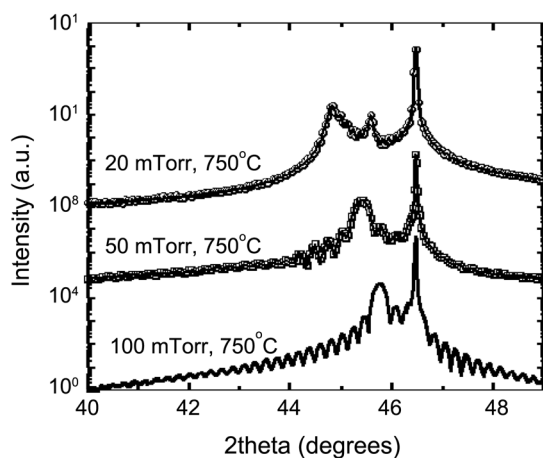


Fig. 1. High resolution X-ray θ - 2θ scan for SrRuO₃ thin films on SrTiO₃ (001) substrates.

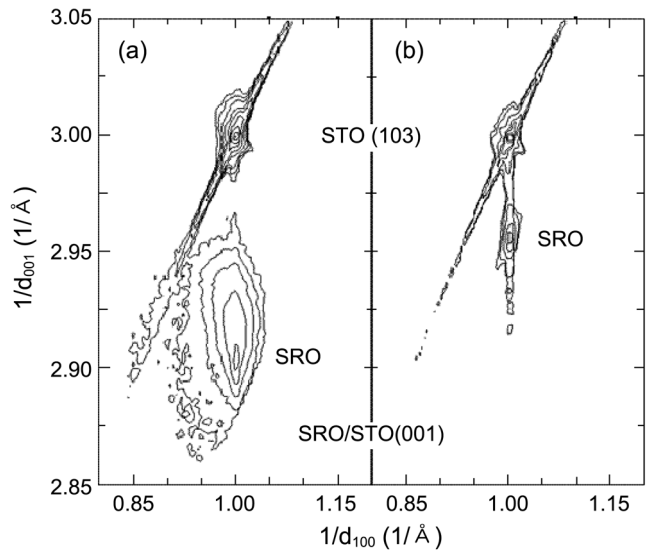


Fig. 2. High resolution X-ray reciprocal space mapping for the SrRuO₃ thin films grown (a) at 20 mTorr and (b) at 100 mTorr.

Along with the expansion of the *c*-axis lattice constant, we also tried to measure the in-plane lattice constant. Reciprocal space mapping data was collected around the STO (103) peak using high-resolution XRD. As shown in Fig. 2, the SRO films grown at oxygen pressures of both 20 and 100 mTorr maintained their in-plane lattice constant, which is well clamped by the STO substrate. The SRO peak has the same position as that of the STO peak along the [100] direction confirming that the in-plane lattice constant of the film is the same as that of the substrate, while the shift of the SRO film peak along the [001] direction indicated the elongation of the *c*-axis lattice constant. In spite of the oxygen deficiency of the SRO film, its in-plane lattice constants retained the values of the STO substrate.

The strong hybridization between the Ru *d*-orbital and O *p*-orbital enhances the sharp density of states near the Fermi level, leading to Stoner-type ferromagnetism [2, 13]. For this reason, the oxygen vacancies can affect not only the structure, but also both the metallic and magnetic properties of SRO [6, 7]. We measured dc-resistivity of the SRO film with different oxygen contents. The resistivity of the oxygen deficient film showed a higher value than those of the other films, as shown in Fig. 3(a). Furthermore, the monotonically increasing average slope of the curves of the resistivity in Fig. 3(b) implies the enhanced scattering rate of the carriers with oxygen vacancies and their localized electrons [13]. A systematic increase in the resistivity of the films and average slope of the resistivity curves is observed with decreasing oxygen pressure during the growth.

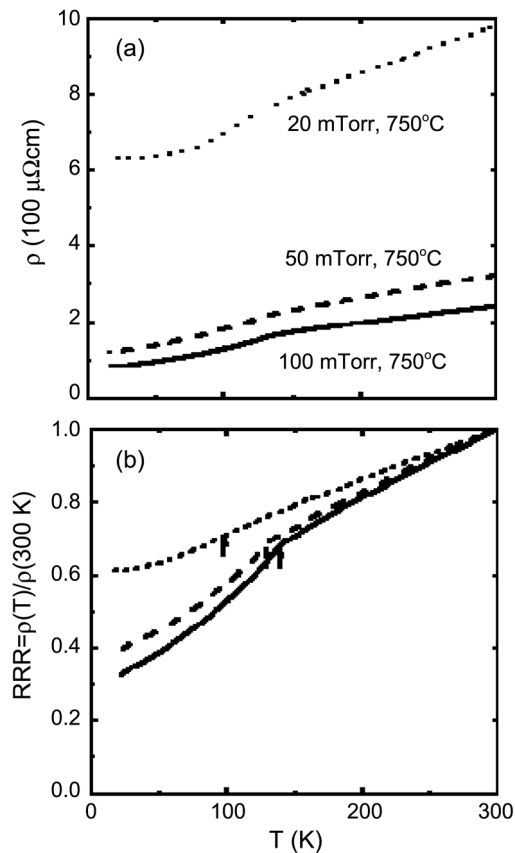


Fig. 3. (a) DC-resistivity and (b) normalized resistivity with respect to the resistivity value at 300 K for the SrRuO₃ thin films.

Ferromagnetic transition diminishes spin disorder scattering in the resistivity, thus resistivity curve shows cusp indicated by arrows as shown in Fig. 3(b) [2, 13]. In Fig. 3(b), T_C decreases by about 30 K as the oxygen pressure during growth decreases. Since SRO shows ferromagnetic ground states caused by the strong hybridization between oxygen and ruthenium, the oxygen vacancies can easily diminish the hybridization strength and increase the resistivity. Following the Stoner model, T_C is proportional to the density of states near the Fermi level and, therefore, we can explain the changes of both T_C and the resistivity in terms of the density of states.

To obtain further insight into this behavior, we mapped T_C in terms of the corresponding x-ray diffraction peak position. As shown in Fig. 4, the change of T_C possesses some correlation with the shift of the SRO (002) peak position. As the c -axis lattice constant increases from 3.960 Å to 4.000 Å with a fixed in-plane lattice constant, T_C diminishes at a rate of 49 K/Å³, which is much smaller than the rate of 400 K/Å³ observed for the polycrystalline sample [6, 11]. [note that a pseudo-cubic unit cell volume is assumed.] The different rate of change of T_C suggests

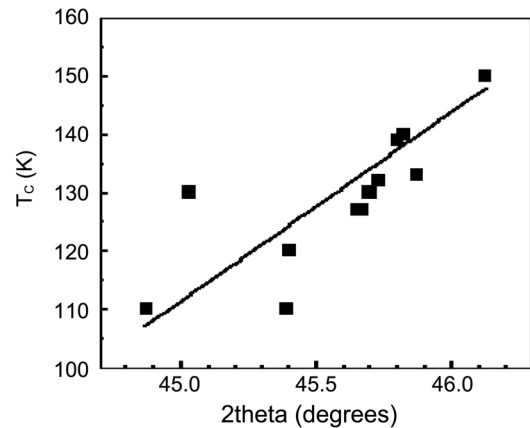


Fig. 4. Ferromagnetic transition temperature versus X-ray 2θ value of SrRuO₃ (002) peak for the SrRuO₃ thin films.

that the compressive strain in the films also plays an important role in stabilizing the ferromagnetic ground states, as well as the oxygen vacancies, while bulk SrRuO₃ expands its volume in the isotropic direction.

Finally, we discuss the effect of the oxygen vacancies in the SRO films on their electrical and structural properties. Oxygen vacancies reduce the hybridization between ruthenium and oxygen, which destabilizes the Stoner ferromagnetism and decreases T_C . In addition, these oxygen deficiencies also generate charged defects and cause the unit cell volume to expand in order to compensate the Coulomb repulsion between the uncompensated charges. The interplay between the volume expansion and in-plane compressive strain mainly elongates the c -axis lattice constant of the film.

4. Conclusions

We investigated the structural and electrical properties of SrRuO₃ thin films grown on STO (001) substrates, in order to study the effect of the oxygen deficiency of the films constrained by the epitaxial strain. The ferromagnetic phase transition temperature of the films grown at low oxygen pressures was suppressed. Both the expansion of the volume and enhancement of the dc-resistivity, which could be explained by the oxygen vacancies and compressive in-plane strain.

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