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The Effect of Oxygen Vacancies and Strain on the Curie Temperature of $La_{0.7}Sr_{0.3}MnO_3$ Films

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The effects of oxygen vacancies and strain on the magnetism and Curie temperature of $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) thin films deposited by PLD are investigated by changing oxygen partial pressure and increasing the interface mismatch between LSMO and $SrTiO_3$. The presence of oxygen vacancies reduces the double exchange effect between Mn^{3+} and Mn^{4+} ions, and the high-quality crystals effectively increase the Curie temperature of LSMO. Moreover, $SrTiO_3$ simultaneously exerts strain on the upper and lower interfaces of the LSMO film to promote orbital reconstruction of the e_g electrons in the Mn^{3+} ions. These electrons preferentially occupy the $e_g(x^2\text{-}y^2)$ orbit and lead to an enhancement in the in-plane ferromagnetic exchange effect, thereby increasing the Curie temperature. These results suggest that the magnetic properties of these materials can be controlled through artificial structure design and provide guidance for their application in high Curie temperature spintronic devices.

Keywords : $La_{0.7}Sr_{0.3}MnO_3$ films, oxygen vacancies,strain, high Curie temperature

1. Introduction

Doped perovskite manganese oxides $La_{1-x}R_xMnO_3$ (R=Ca, Sr, Ba, etc.) have shown potential for applications such as magnetic sensors, magnetic recording and other electronic devices due to their advantages of colossal magnetoresistance, high spin polarization and half metallicity [1-4]. Additionally, the coupling among the four degrees of freedom of lattice-orbital-charge-spin leads to many unique physical properties [5-8]. Among the doped perovskite materials, $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) has drawn much attention due to its Curie temperature (T_C) being well above room temperature. The T_C and metal-insulator transition characteristics of thin films can be influenced by oxygen pressure, film thickness and substrate strain and so on. The so-called "dead layer" effect occurs when the thin film thickness is reduced to several atomic layers [9-13], which leads to a rapid decrease of the magnetoresistance effect at room temperature, spin polarization, and domain size [14-16]. Different methods have been proposed to circumvent this problem and increase the T_C of ultra-thin LSMO films [17-19]. For example, room temperature ferromagnetism of two atomic-layer thickness LSMO was realized by using the LSMO/$SrRuO_3$ superlattice structure [17]; a canted LSMO antiferromagnetic phase of 10 atomic-layer thicknesses induced by the (110) oriented $SrTiO_3$ substrate was obtained with a T_C of 560 K [19].

The e_g orbit of Mn ions in bulk LSMO is doubly degenerate in a regular octahedron environment and the ferromagnetism is derived from the double exchange between Mn^{3+} and Mn^{4+} ions through oxygen ions. However, oxygen vacancies and oxygen octahedron rotation in the thin films can influence the double exchange between Mn ions, thereby affecting the magnetism and T_C [20-24]. The Mn^{3+} ions are Jahn-Teller active, and the distortion of the oxygen octahedron leads to energy splitting of the e_g orbit. If the environment around the Mn ions can be tuned, the electrons in Mn^{3+} can be regulated to occupy either $e_g(3z^2\text{-}r^2)$ or $e_g(x^2\text{-}y^2)$ orbit. For a (001) oriented LSMO thin film, occupancy of $e_g(x^2\text{-}y^2)$ leads to in-plane double exchange and significantly enhances the ferromagnetism of the film [14]. In this paper, LSMO thin films are prepared by pulsed laser deposition (PLD). The T_C of LSMO is enhanced by controlling oxygen atmosphere (P_{O_2}) and interfacial strain, which provide an experimental basis for the realization of ultra-thin LSMO with high-temperature ferromagnetism.

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2. Experimental Details

LSMO thin films were deposited on $SrTiO_3$ (STO) (001) substrates by PLD. A KrF excimer laser operating at a wavelength of 248 nm and laser energy of 300 mJ/pulse was used for film deposition. The substrate temperature was 700 °C. LSMO films were prepared under a base pressure (5×10^{-5} Pa) and two different oxygen partial pressures (10 Pa and 20 Pa). The thickness of the films was 40 nm. In order to further study the effect of strain on the magnetic properties of LSMO thin films, LSMO/STO bilayer films were prepared under an oxygen partial pressure of 20 Pa. The thicknesses of LSMO and STO were 5 nm and 10 nm, respectively. The substrate temperature of STO thin films was 750 °C. The structure of the sample was analyzed by x-ray diffraction (XRD) and the magnetic measurements were performed using a superconducting quantum interference device magnetometer (SQUID). During the test, the external magnetic field was parallel to the film surface. The variation of magnetic moment with temperature was tested within temperature ranging from 5 K to 390 K, and the applied magnetic field was 5000 Oe.

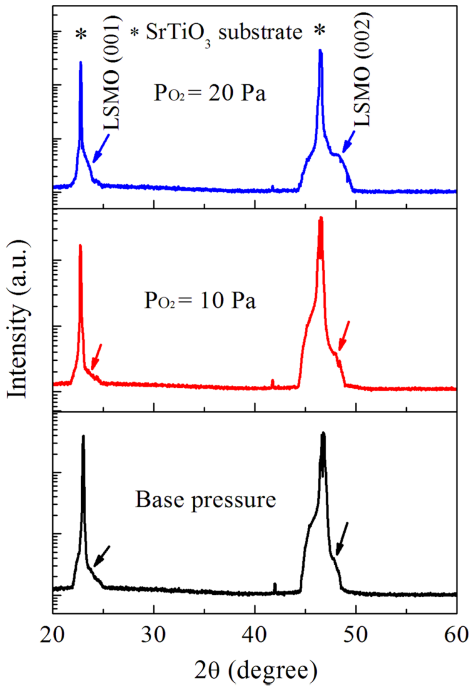

Fig. 1. (Color online) XRD patterns of LSMO films with various oxygen pressures. (a) Base pressure; (b) P_{O_2} = 10 Pa; (c) P_{O_2} = 20 Pa.

3. Results and Discussions

3.1. Effect of Oxygen Atmosphere on Magnetism

The effect of oxygen partial pressure on the LSMO structure and magnetism was determined by analyzing the LSMO films using XRD. Figure 1 shows the XRD patterns of LSMO films under three types of deposition pressures (base pressure, P_{O_2} = 10 Pa and P_{O_2} = 20 Pa). The films exhibit LSMO diffraction peaks at all three deposition atmospheres, which indicates epitaxial growth in the (001) direction. The diffraction peak of the sample deposited under base pressure has the lowest intensity and clearly shifts towards small angles. This can be attributed to the existence of oxygen vacancies leading to the increase of LSMO unit cell parameters [25, 26]. The diffraction peaks of the LSMO thin films deposited in oxygen atmosphere are significantly enhanced compared to that of base pressure, indicating that the oxygen vacancies are reduced and the crystal quality is improved.

The magnetization of LSMO films under different oxygen deposited atmospheres was determined as a function

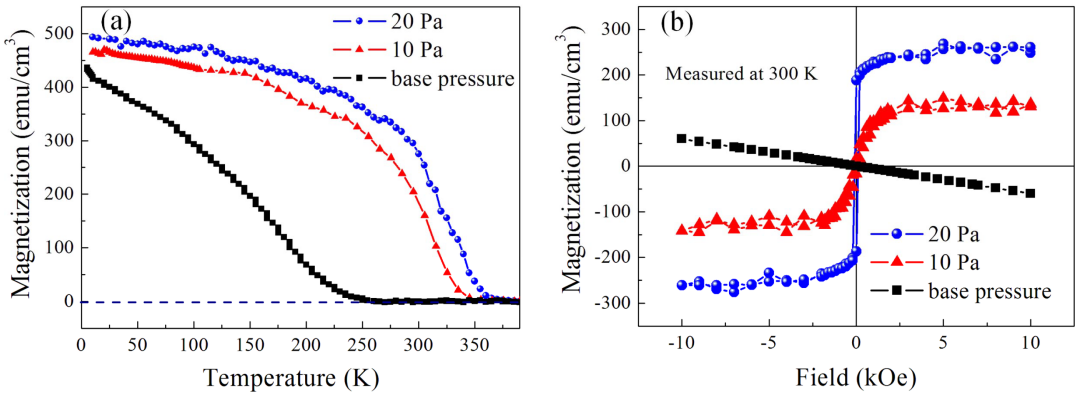

Fig. 2. (Color online) (a) The relationship between the magnetization and temperature for films deposited under different oxygen pressure; (b) The corresponding room temperature hysteresis loop, where the diamagnetic signal from the substrate was subtracted from the data.

of temperature and applied magnetic field, as shown in Fig. 2. The T_C of the film prepared under the base pressure is only 248 K as evident from Fig. 2(a). This is attributed to the presence of a large amount of oxygen vacancies weakening the ferromagnetic exchange between Mn ions, which is consistent with the XRD observations. The T_C of LSMO thin films prepared under oxygen atmosphere are higher than 300 K and increase significantly with the increase of oxygen pressure. The T_C of the sample deposited under oxygen pressure of 20 Pa is about 360 K, which is close to the T_C of bulk LSMO. The corresponding room temperature hysteresis loops of the films deposited under various oxygen atmosphere are shown in Fig. 2(b). Samples deposited under oxygen pressure have an observable room temperature ferromagnetism, in which the saturation magnetization (Ms) of the thin film deposited under oxygen pressure of 20 Pa is 260 emu/cm^3. In contrast, the sample prepared under base pressure is diamagnetic at room temperature. Therefore, the concentration of oxygen vacancies in the LSMO films can be efficiently tuned by varying the deposition oxygen pressure, which further regulates the magnetization and T_C.

3.2. Effect of Strain on Magnetism

In order to investigate the effect of strain on the T_C, LSMO film were prepared with thickness of 5 nm on a (001) orientated STO substrate, followed by a 10-nm-thickness STO film (labeled as LSMO(5)/STO(10)). Strains were applied to the LSMO simultaneously by the substrate and top layer STO. For reference, a monolayer LSMO film (labeled as LSMO (5)) with a thickness of 5 nm was prepared under the same experimental conditions as a control. Figure 3 shows the XRD patterns of LSMO(5)/STO(10) bilayer film with clear LSMO diffraction peaks, indicative of epitaxial growth. Compared to

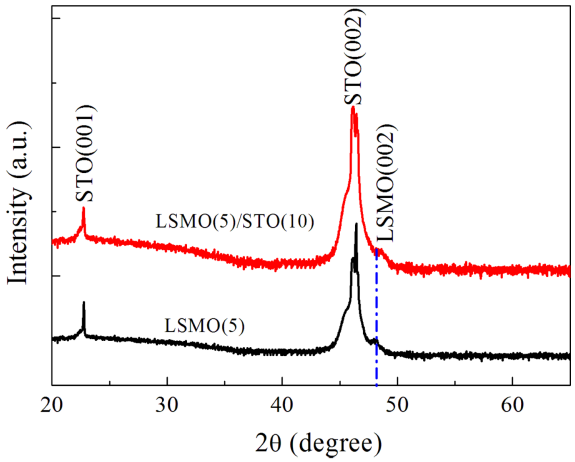

Fig. 3. (Color online) XRD patterns of LSMO(5)/STO(10) bilayer film and LSMO(5) film.

the LSMO(5) film, the LSMO (002) peak in the LSMO(5)/STO (10) bilayer film is shifted towards higher angles. The in-plane lattice constant of (001) oriented STO is 0.394 nm, while that of (001) oriented LSMO is 0.387 nm. Thus, the LSMO film in LSMO(5)/STO(10) bilayers is in a high-tensile strain state, resulting in a decrease of the lattice parameter c in the direction perpendicular to the film plane, resulting the observed shift of the diffraction peak towards higher angles [27].

Figure 4(a) shows the magnetization curves of LSMO(5) thin films and LSMO(5)/STO(10) bilayer films. The T_C for the LSMO(5) monolayers film is about 280 K, which is in contrast to the LSMO(5)/STO(10) bilayer film where a room temperature ferromagnetism is observed with T_C over 330 K. Figure 4(b) shows the corresponding hysteresis loops measured at room temperature and low temperature. Thus, the strains applied to LSMO from the STO layers can significantly improve the T_C and ferromagnetic order of LSMO. A possible explanation for this enhancement

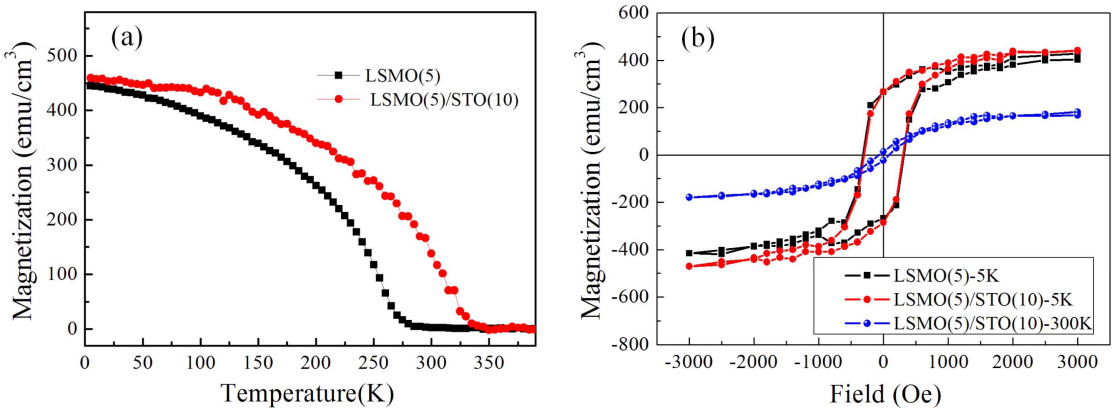

Fig. 4. (Color online) (a) The relationship between the magnetization and temperature of LSMO(5) film and LSMO(5)/STO(10) bilayer film; (b) Hysteresis loops of LSMO(5) film and LSMO(5)/STO(10) bilayer film.

can be expressed as follows: due to strains from STO, the in-plane lattice parameters (a, b) of the (001) oriented LSMO films increase so that the e_g orbital electrons of Mn^{3+} preferentially occupy $e_g(x^2\text{-}y^2)$, which in turn enhances the in-plane double exchange effect [28, 29]. In two-dimensional thin films, the ferromagnetism mainly originates from the in-plane double exchange effect. As a consequence, LSMO(5)/STO(10) has enhanced ferromagnetism along with a significantly higher T_C. It is to be noted that the saturation magnetization of the two samples are almost the same at 5 K but the magnitudes (≈ 450 emu/cm^3) are smaller than that of the LSMO film deposited under 20 Pa oxygen pressure with 40-nm thickness (≈ 500 emu/cm^3), as shown in Fig. 2(a). This may be due to the "dead layer" effect that exists at the interface between the LSMO film and the substrate.

4. Conclusions

LSMO monolayer and LSMO/STO bilayer films were prepared on (001) STO substrate by the PLD method. The effects of oxygen vacancies and strain on magnetism and T_C of LSMO were studied. Reduction of oxygen vacancies in LSMO films can bring about an enhancement in the double exchange effect between Mn^{3+} and Mn^{4+} ions, which can effectively increase T_C. The preferential orbital occupancy of $e_g(x^2–y^2)$ in LSMO induced by tensile strain of STO effectively enhances the role of in-plane ferromagnetic exchange, thereby increasing T_C. The proposed method facilitates the tuning of the magnetism of artificially designed structures and provides guidance for the application of high T_C spintronic devices.

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