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THICKNESS DEPENDENCE OF MORPHOLOGY IN $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ THIN FILMS

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$\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ (LCMO) thin films with the thickness from 4 nm to 50 nm were fabricated by the off-axis magnetron sputtering technique. Single crystal (001) SrTiO_3 (STO), (0001) sapphire (ALO), and (001) yttrium-stabilized ZrO_2 (YSZ) were used as substrates. The surface morphology of thin films was characterized by atomic force microscope (AFM). The surface morphology of the thin films depends on the thickness. Thin films on STO substrate with the thickness less than 20 nm show a wave-like morphology, which indicates a two-dimension growth mode. With the thickness increasing, some cracks and grains appear on the surface, which indicates the release of the lattice strain due to the lattice mismatch between the substrates and the films. The morphology became smoother with the thickness more than 30 nm, which indicates the full relaxation in strain for the films. The surface roughness and the average grain size increase with the thickness. The morphology for LCMO growing on ALO and YSZ shows a rougher surface than that on STO. The rough surface morphology may indicate the wide metallic-to-insulating transition in transport properties.

Keywords: $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ thin film; morphology; Atomic force microscopy; lattice strain

1. Introduction

The doped colossal magnetoresistance (CMR) manganite perovskites, especially their thin films, have been extensively studied over the past decade due to their potential use in data storage devices or sensors^[1–3]. The structure and the physical properties of manganites are highly sensitive to the preparation conditions and

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the substrate. For this reason, structural deformations or modified transport properties are often observed. Such behavior appears when the growth conditions, the thickness of the film and the substrate are changed. The effects have often been explained by the substrate-induced strain [4–6]. Thus, the understanding of the microstructure for manganite thin film is useful to understand its physical properties. The magnetoresistance (MR) at low field (LFMR) for manganites can be enhanced by the fabrication of tri-layer tunnel junctions or polycrystalline films [7–9]. Experiments have proved that the enhancement of the LFMR response is due to the spin-polarized tunneling across the grain boundaries in the film [7–8]. Zhao et.al [9] have fabricated the LCMO films with the ordered surface microstructures to improve the LFMR. Hwang et al [10] have found that the polycrystalline samples can also enhance LFMR. There is no report about the relation between the thickness and surface morphology for LCMO films, which may be useful to know how the surface morphology affects the transport properties. In the present contribution, the surface morphology of LCMO films with varying the thickness and the substrates is reported.

2. Experimental procedures

The LCMO films with nominal thickness from 4 nm to 50 nm were deposited on (001) SrTiO_3 (STO), (001) Yttrium-stabilized ZrO_2 (YSZ), and (0001) sapphire Al_2O_3 (ALO) substrates by modified off-axis r.f. magnetron sputtering [6,11]. A deposition atmosphere is consisting of a mixture of oxygen and argon with the ratio of the partial pressure of $P_{\text{O}_2}:P_{\text{Ar}}=1:3$. The total sputtering pressure was kept between 1.2 and 1.6×10^{-1} mbar. The LCMO layer was deposited onto the substrate which was heated to $750 - 770^\circ\text{C}$. An rf-power of 75W was applied to the cathode, generating a power density of $4\text{W}/\text{cm}^2$. The growing rate was $0.6\text{--}0.7$ nm/s. After deposition, the thin films were further treated by in-situ annealing in an oxygen atmosphere at $400 - 500^\circ\text{C}$ for about 20~30 minutes. The surface morphology was recorded by Nanoscope IIIa atomic force microscope (AFM: Digital instruments) using contact mode.

3. Results and Discussions

The thickness dependence of morphology for LCMO films deposited on STO was shown in Fig. 1. For LCMO film with the thickness of 4 nm, a wave like surface morphology was clearly observed (see Fig. 1a). The transverse waves and the vertical waves divided the surface into lots of strip-like islands scattering on the surface regularly (see Fig. 1b). The strip-like islands are $5\text{ }\mu\text{m}$ in length and $2\text{ }\mu\text{m}$ in width. The average roughness of the surface is about 3 nm, according to the AFM image. The lacking of the "rounded grains" on the surface of the film indicates that the film grows according to the Franck and Van der Merwe growth mode^[12].

Fig. 2 shows that the thickness dependence of morphology for LCMO films deposited on STO with the thickness from 8 nm to 50 nm. With the thickness

Fig. 1. AFM images for $La_{2/3}Ca_{1/3}MnO_3$ film with the thickness of 4 nm. The vertical scale is 20 nm for (a) and 100 nm for (b).

increasing from about 5 ML (Fig. 1b) to 11 ML (Fig. 2a), the surface becomes flatter except for several dots with the size of $0.2\ \mu\text{m}$ scattering on the surface. These dots are accumulated from the strain due to the lattice mismatch, which will be discussed below. With further increasing the thickness of the film, small grains with the size below $0.05\ \mu\text{m}$ appeared and distributed homogenously on the surface (Fig 2b). The in-plane average size of the grains is less than $0.1\ \mu\text{m}$. The grains become larger with the thickness of LCMO film. When the thickness of the film is larger than a critical thickness, T_c , which can be determined from the Thouless' model [13], where strain accumulated in the film will be released by the appearance of cracks on the surface, which has been observed in Fig.2c. The in-plane average size is about $0.15\ \mu\text{m}$ for the thickness of 50 nm (see Fig. 2d).

The morphology is normally determined by the growth mode. Usually we consider three basic growth modes [12], i.e. island growth mode, layer growth mode and the mode involving the formation of one or several initial two-dimensional layers followed by three-dimensional nucleation and growth on top of the original growth layer. The growth of the layer is determined by many factors such as the chemical potential of the substrate surface, the interaction between the substrate atoms and the layer atoms, the roughness of the substrate, the lattice mismatch between the substrate and the layer, and so on. Many researchers [2,7,9,14] believed that grains and cracks on the surface of the film usually relax strain. The lattice parameters for LCMO and STO are $3.86\ \text{\AA}$ [13] and $3.905\ \text{\AA}$ [15], respectively. The lattice mismatch is about 1.2% [15]. The film will be full-strain for the thickness less than 4 nm, which drives the atom accumulation in wave-like shape to release the strain energy measured by surface X-ray diffraction, which will be reported elsewhere. The interlayer between the substrate and the film and the surface layer of the film for all substrates were also observed by grazing X-ray reflection measurements in our previous studies [6,16]. Our above results together with our previous researches prove that the growth mode for LCMO grown on STO is from two-dimensional growth mode (with the thickness below 20 nm) to dotted mode. The flat surface morphology was observed when the thickness is larger than 30 nm. The averaged roughness of the surface is

Fig. 2. Thickness dependence of morphology for $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ thin films on SrTiO_3 substrate. The vertical scale for all image is 20 nm. The thickness is 8 nm (a), 12 nm (b), 30 nm (c) and 50 nm (d).

from about 4.3 nm (8 nm) to 1.6 nm (50 nm). The thicker the film is, the flatter the film is. There are several relatively larger grounded islands observed on the surface, which are to release the strain energy induced by the lattice mismatch. The partial relaxation in layer forms some dislocations in the layer to release the lattice strain. These dislocations divide the layer into small grains. These grains distribute on the surface uniformly. The grains connect each other and become larger which induce the film growth layer by layer. The above discussions show that the growth of the film with the thickness below 20 nm is two-dimensional. Fig. 1 and Fig. 2 clearly indicate that the initial growth of the film on LCMO is in full-strain state, and with the thickness increasing, strain energy is accumulated in the film and makes cracks when the thickness reaches a critical value, where, the strain energy beyond the ability of the film endurance.

Besides the thickness, the substrate affects the surface morphology of the layer. Fig. 3 is the AFM images for 50 nm LCMO films deposited on YSZ and ALO. Comparing with 50 nm LCMO film with relatively big and rounded grains deposited on STO (Fig. 2d), there are lots of grains with different size and height appearing on the surface of the LCMO thin films deposited on YSZ and ALO substrates. The surface for LCMO on YSZ and ALO is rougher than that on STO, which was also proved by grazing incident X-ray scattering technique. The distribution of the grains on the surface is random. We attribute the difference to the larger lattice mismatch.

The lattice strain can be deduced by the lattice mismatch between substrate

Fig. 3. Substrate affects the surface morphology for $La_{2/3}Ca_{1/3}MnO_3$ film. The thickness of $La_{2/3}Ca_{1/3}MnO_3$ film is 50 nm. The substrates are Al_2O_3 (a) and Yttrium stabilized ZrO_2 (b).

and the layer. The in-plane lattice mismatch δ is given by

$$\delta = \frac{a_{\text{substrate}} - a_{\text{LCMO}}}{a_{\text{substrate}}}$$

and the in-plane lattice constants of $La_{2/3}Ca_{1/3}MnO_3$, Al_2O_3 , $SrTiO_3$, YSZ are respectively $3.86 \text{ \AA}^{[13]}$, $4.7591 \text{ \AA}^{[17]}$, $3.905 \text{ \AA}^{[15]}$ and $5.14 \text{ \AA}^{[17]}$. Therefore, the mismatches on ALO, STO and YSZ are respectively 18.9%, 1.2% and 24.9%. The in-plane lattice mismatch for LCMO deposited on YSZ and ALO is much larger than that on STO. The larger lattice mismatch induced a transient layer between LCMO and the substrate for releasing the strain, which has been observed by grazing incident X-ray reflectivity. The transient layers for 50 nm LCMO deposited on ALO and YSZ are 1.7 nm and 4.1 nm, respectively.

For the layer deposited on STO substrate, grains are uniform and distribute on the surface homogeneously. Comparing with film deposited on STO substrate, the surface morphology for the layer on YSZ (Fig. 3b) is similar to that on ALO (Fig. 3a), and grains are relatively bigger. The roughness of the surface for LCMO on YSZ and ALO is larger than that on STO. We argue that the lattice mismatch plays an important role in the surface morphology for LCMO films. The lattice mismatch between STO substrate and LCMO film is only 1.2%, which is relatively small, and the strain induced by lattice mismatch is relatively small, thus, small and low grains may form to relax the strain. On the other hand, the lattice mismatch between LCMO film and YSZ substrate is about 20%, the strain induced by lattice mismatch is very big. Then, bigger and higher grains are needed to relax larger strain. These results can be used to explain the transport properties of LCMO films, which is clearly discussed in the reference 6.

4. Conclusion

In summary we have studied the morphology of the surface of $La_{2/3}Ca_{1/3}MnO_3$ (LCMO) thin films grown on $SrTiO_3$, Al_2O_3 and Yttrium stabilized ZrO_2 substrates with different thickness. The surface morphology of the films depends

strongly on the thickness and substrate. The film grows in two-dimensional initially and then grows in two-dimensional and dotted mode. The lattice mismatch plays an important role in surface morphology. Strain from lattice mismatch is gradually relaxed when the thickness is beyond the critical value. Grains and cracks result in big roughness.

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