Thickness dependence of structural and electrical properties of electron-doped Sr$_{1-x}$La$_x$CuO$_2$ infinite-layer thin films grown by pulsed laser deposition

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Abstract. As the building blocks for all of the high-$T_c$ cuprate superconductors, infinite layer (IL) compounds have the simplest structures and the highest $T_c$ of electron-doped superconductors. However, IL structure is one of the high-pressure forms, which makes it difficult to synthesize a single crystal. Therefore, it is highly desirable to obtain high-quality epitaxial thin films making use of epitaxial effect. Although there are many reported attempts to grow IL thin films on different substrates, no one has systematically studied the thickness dependence of structural and electrical properties of IL thin films. In this report, electron-doped Sr$_{1-x}$La$_x$CuO$_2$ thin films of various thicknesses were deposited on (001) KTaO$_3$ substrate by pulsed laser deposition. It is shown that IL peak shifts to a lower angle with increase of film thickness, indicating the reduction of the tensile strain. With further increase of thickness, there emerges an impurity phase. Transport measurements showed strong influence of the sample thickness on resistivity and $T_c$. For a certain thickness range we have demonstrated that superconductivity will occur. The resistive superconducting transition with $T_c$(onset) = 14.2 K and $T_c$(ρ=0) = 10 K has been observed. A moderate thickness is required to obtain IL thin films with superconductivity.

1. Introduction
As the building blocks for all of the high-$T_c$ cuprate superconductors, infinite layer (IL) compounds have the simplest structures [1] and the highest $T_c$ of electron-doped superconductors [2], enabling fundamental research and improved techniques for synthesizing higher $T_c$ superconductors. However, IL structure is one of the high-pressure forms, which makes it difficult to synthesize a single crystal. Therefore, it is highly desirable to obtain high-quality epitaxial thin films making use of epitaxial effect [3,4]. In the earlier attempts to grow electron-doped IL thin films, SrTiO$_3$ ($a_0=3.905$ Å) was most frequently used for the substrates [5]. IL films on SrTiO$_3$ are compressively strained, and have a smaller in-plane lattice constant ($a_0$) and a larger c-axis lattice constant ($c_0$) than the bulk values, which has been suspected as the reason for the inferior superconductivity of those films. An in-plane tensile strain is considered important to obtain the superior superconductivity of IL films because it makes the removal of interstitial apical-oxygen easier. With a view to introducing the tensile epitaxial strain, Karimoto et al. examined the use of a KTaO$_3$ ($a_0=3.989$ Å) substrate and have demonstrated that the optimally doped Sr$_{1-x}$Ln$_x$CuO$_2$ (Ln=La, Nd and Pr; $x\sim0.1$) films grown on KTaO$_3$ substrates showed the better superconducting properties [6]. On the other hand, thickness is one of the most important parameters to affect the structural and electrical properties of the epitaxial thin films [7-9]. Although there are many reported attempts to grow IL thin films on different substrates [5,6,10-13], no
one has systematically studied the thickness dependence of structural and electrical properties of IL thin films.

In this report, electron-doped $\text{Sr}_{1-x}\text{La}_x\text{CuO}_2$ thin films of various thicknesses were deposited on (001) KTaO$_3$ substrate by pulsed laser deposition (PLD). The influence of film thickness on the structural and electrical properties of the samples was systematically investigated. X-ray diffraction (XRD) patterns showed that IL peak shifted to a lower angle with increase of film thickness, indicating the reduction of the tensile strain induced by the in-plane mismatch. With further increase of thickness, there emerges a modulated superstructure phase which is demonstrated to deteriorate superconductivity. The results indicate that a moderate thickness is required to obtain IL thin films with optimal properties.

2. Experimental Details

The PLD technique was used to deposit $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$ thin films on (001) KTaO$_3$ substrates. In our PLD system, a KrF excimer laser (248nm wavelength, Lambda physic COMPex 102) was used for the ablation of a $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$ target at an energy density of $\sim$2 J/cm$^2$. The base pressure was $10^{-9}$ Torr and the oxygen pressure during the laser deposition was set at 5 mTorr. The target-to-substrate distance was about 43 mm. The depositions were carried out at the substrate temperature of 533 °C. Before the deposition, the KTaO$_3$ substrates were etched chemically by using 0.1% HNO$_3$ with methanol, and then annealed at 1000 °C for one hour in 1 atm oxygen. After the deposition, the films were annealed at the deposition temperature in vacuum for 40 minutes and then cooled naturally to room temperature. Annealing in vacuum can serve as a reducing oxygen process that facilitates the superconductivity properties. Nominal thickness of the films, $t$, was determined by the number of laser shots and the calibrated growth rate. The structural properties of the films were studied by X-ray diffractometer (XRD6000, Shimadzu) using Cu $K\alpha_1$ radiation with $\lambda$=1.5406Å. Electrical properties were measured using a Keithley Hall probe system.

3. Results and Discussion

3.1. Thickness dependence of structural properties

In table 1, three $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$ films with different thickness grown on KTaO$_3$ substrates are presented. X-ray diffraction (XRD) patterns of the films are shown in Fig.1. The single-phase IL structure was successfully obtained for $t < 60$ nm. The IL reflection peaks became stronger and narrower with increase of the film thickness, indicating the improvement of the crystalline quality of the IL films. With further increase in $t$ (e.g., $> 60$ nm), however, an impurity phase (the so-called M-phase [14,15]) emerged and became the main phase for $t > 75$ nm. This result indicates that a moderate thickness is required to obtain high quality single-phase $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$ thin films with the IL-type structure.

| Sample | $t$ (nm) | $c_0$ (Å) | Phase | $\rho$(300 K) (mΩ·cm) |
|--------|----------|-----------|-------|------------------|
| A      | 28       | 3.3905    | IL    | 1.46             |
| B      | 56       | 3.4080    | IL    | 0.26             |
| C      | 105      | 3.6048    | M     | 3.69             |

In addition, the XRD results showed that the (002)IL peak ($2\theta \sim 54^\circ$) shifted towards a lower angle (i.e., $c_0$ expanded) with increasing film thickness, and then disappeared, substituted by the M-phase peak (see, e.g., Fig. 1). The expansion of $c_0$ is consistent with the fact that the in-plane lattice constant of the substrate KTaO$_3$ (3.989 Å) is larger than that of $\text{Sr}_{1-x}\text{La}_x\text{CuO}_2$ bulk (3.949 Å for $x=0.1$). The
mismatch between the substrate and Sr$_{0.9}$La$_{0.1}$CuO$_2$ introduced an in-plane tensile strain to the films due to the epitaxial effect. Due to the tensile strain, $c_0$ of the films is shorter than that of the bulk Sr$_{0.9}$La$_{0.1}$CuO$_2$. The tensile strain is getting weaker as Sr$_{0.9}$La$_{0.1}$CuO$_2$ grows thicker. And this releasing strain has less effect on the vertical lattice constant $c_0$, making $c_0$ larger than that of the thinner films. Thus, $c_0$ increased with increase of the film thickness. Sample B with the optimum thickness of 56 nm has $c_0$ of 3.408 Å, which is very close to the bulk value. Most important of all, sample B showed a resistive superconducting transition.

Figure 1. XRD patterns of Sr$_{0.9}$La$_{0.1}$CuO$_2$ thin films with different thickness grown on KTaO$_3$ substrates.

Figure 2. Temperature dependence of resistivity for samples A, B and C.

For thick Sr$_{0.9}$La$_{0.1}$CuO$_2$ films (see, e.g., sample C), the IL phase disappeared and there emerged a secondary phase – the $2\sqrt{2}a_p \times 2\sqrt{2}a_p \times c$ modulated superstructure, where $a_p$ and $c$ refer to the perovskite subcell parameters [12]. It is believed that this phase forms due to ordering of the Sr and La atoms, as well as of the oxygen atoms and vacancies [14,15]. It is designated as M-phase, which is considered to deteriorate the superconductivity. We suspect that with further increase of the film thickness, the tensile strain which is crucial to the formation of IL phase is reduced and released. Without enough epitaxial pressure induced by the relatively close interaction with substrate, sample C did not achieve superconducting phase.

3.2. Thickness dependence of electrical properties
The transport measurements showed that the resistivity was significantly affected by the thickness of the films (Table 1). Sample B with the optimum thickness had the smallest resistivity; while too thin or too thick samples showed bigger resistivity. We speculate that with too thin thickness, the sample quality was worsen by the imperfect or half-baked crystal structure due to the significant effect of the in-plane lattice mismatch; and with too thick thickness, the impurity phase emerged and destroyed the superconductivity. Thus, for obtaining superconducting samples, thickness is an important factor and a moderate thickness is required.

For most samples with thickness over 65 nm (typically with mixed phases or mainly M-phase), the temperature dependence of resistivity showed a semimetal-like behavior (e.g., sample C, Fig. 2). The room temperature resistivity lies between ~1 mΩ·cm and ~10 mΩ·cm. Superconductivity was observed in a relatively narrow thickness range, 50 nm ≤ $t$ ≤ 60 nm. The resistivity data for sample B showed a superconducting transition with $T_{c, \text{onset}} = 14.2$ K and $T_{c, \rho = 0} = 10$ K (Fig.2). The transition is somewhat large, possibly due to some inhomogeneities. The superconducting transition was also
confirmed by ac susceptibility (data not shown). For samples with thickness less than 50 nm (as for sample A, Fig. 2), no superconductivity was found at low temperatures between $5–100 \text{ K}$. A small but distinct deviation from the semimetal-like behavior was observed (Fig. 2). The temperature at which the curve starts to drop is about 7.4 K. The disappearance of superconductivity strongly suggests that the lattice imperfection or defects in samples with too thin thickness can destroy superconductivity. It is possible that the structural changes could also affect the resistivity.

We should note the difficulty in obtaining resistive superconducting transitions in these materials. Technically, the window for a suitable thickness is quite narrow. It would be instructive to carefully examine the detailed structures and the local compositions for the superconducting thin films. Systematic high-resolution electron microscopy and x-ray microanalysis studies are in progress.

4. Summary

In summary, high-quality electron-doped Sr$_{0.9}$La$_{0.1}$CuO$_2$ films were fabricated by PLD on (001) KTaO$_3$ substrates and the single-phase IL structure was successfully obtained. It was shown that IL peak shifted to a lower angle with increase of film thickness, indicating the reduction of the tensile strain induced by the in-plane mismatch. With further increase of thickness, there emerged a modulated superstructure phase which was validated to deteriorate superconductivity. For a certain thickness range we have demonstrated that (the n-type) superconductivity will occur. The resistive superconducting transition with $T_{c_{\text{onset}}} = 14.2 \text{ K}$ and $T_c (\rho = 0) = 10 \text{ K}$ has been observed, and confirmed by susceptibility measurements. It seems that the most important part of this phenomena is control of the film thickness, but other effects should also be considered. It is an important guide for fabricating Sr$_{1-x}$Ln$_x$CuO$_2$ superconducting films.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant Nos. 50772015 and 10974019), the Special Program for the Ph.D. Subjects in University of the Ministry of Education of China (Grant No. 200800270004) and the Fundamental Research Funds for the Central Universities.

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