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The electric and magnetic properties of epitaxially grown $A_{0.5-x}La_xSr_{0.5}MnO_3$ (A=Pr, Nd) thin film*

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The epitaxial (single crystal-like) $Pr_{0.4}La_{0.1}Sr_{0.5}MnO_3$ (PLSMO) and $Nd_{0.35}La_{0.15}Sr_{0.5}MnO_3$ (NLSMO) thin films are prepared and characterized, and the electric and magnetic properties are examined. We find that both PLSMO and NLSMO have their own optimum deposition temperature (T_o) in their growing into epitaxial thin films. When the deposition temperature is higher than T_o, a c-axis oriented but polycrystalline thin film grows; when the deposition temperature is lower than T_o, the thin film tends to be a-axis oriented and also polycrystalline. The most important point is that for the epitaxial PLSMO and NLSMO thin films the electronic phase transitions are closely consistent with the magnetic phase transitions, i.e. an antiferromagnetic phase corresponds to an insulating state, a ferromagnetic phase corresponds to a metallic state and a paramagnetic phase corresponds to a semiconducting state, while for the polycrystalline thin films the electronic phase transitions are always not consistent with the magnetic transitions.

Keywords: epitaxial, polycrystalline, thin film, electric and magnetic phase transition
PACC: 7127, 7130, 7360, 7530V

1. Introduction

In general, a material used for making electronic devices or for fundamental research purposes should be prepared into a thin film, because it may be comparable with a single crystal in both structure and physical property. Usually the thin film is polycrystalline, though it shows highly oriented growth. As a consequence, the transport property of such a thin film cannot reflect the intrinsic feature of the material. In this case, the film possesses complicated electric and magnetic phase transitions with temperature varying, and cannot show the same consistency between transport feature and magnetic phase as the single crystal does.[1] Therefore, for fundamental research and application, it is necessary to make the material into a thin film that is not only preferentially oriented but also epitaxially (single crystalline-like) grown. $A_{0.5-x}La_xSr_{0.5}MnO_3$ (ALSMO, A=Pr, Nd)[2,3] is the same typical half (0.5) Sr-doped compounds.[2−9] Its bulk sample shows a series of magnetic and electric phase transitions, and two kinds of colossal magnetoresistance effects (CMR) at T_N and T_C were observed in a lower magnetic field.[2] But the intrinsic relation between the electronic phase and magnetic phase remains to be studied. For this purpose it is necessary to find out a reasonable approach to growing the high-quality epitaxial thin films.

In the present work, we first fabricate the $Pr_{0.4}La_{0.1}Sr_{0.5}MnO_3$(PLSMO) thin films on single crystal (100) $SrTiO_3$ (a=3.905 Å)[10] substrates by using pulsed laser deposition (PLD) technique. The results show that the most important condition for the epitaxial growth of PLSMO thin films is the deposition temperature (T_d). Only when T_d is about 700°C, can we obtain real PLSMO epitaxial thin films. The films are characterized by x-ray diffraction (ϕ-scan), atomic force microscopy (AFM), etc. Deviated from 700°C, no epitaxial film can be obtained at all. Above 700°C

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(up to 740°C), the films are c-axis oriented but polycrystalline. Below 700°C, the mixture of c-axis and a-axis oriented polycrystalline thin film is obtained. The pure a-axis orientation polycrystalline films are formed at 580°C. The consistency between electronic and magnetic phase transitions holds true only for the epitaxial thin films, but not for the c- and a-axis oriented but polycrystalline thin films. In addition, in order to further prove the influence of the deposition temperature on the growth of the film, we have also prepared the $Nd_{0.35}La_{0.15}Sr_{0.5}MnO_3$ (NLSMO)[3] thin films, because both NLSMO and PLSMO have similar crystal structures and electronic and magnetic phase transitions. Our experiment shows their results to be similar to those of PLSMO films. By optimizing the growth conditions we obtain high-quality epitaxial thin films of PLSMO and NLSMO, and find the corresponding electronic and magnetic phase transitions, indicating that the deposition temperature plays an important role in the epitaxial growth of the PLSMO and NLSMO thin films.

2. Experiment

The PLSMO films and NLSMO films were grown on (001) $SrTiO_3$ and (001) $LaAlO_3$ substrates respectively by using pulsed laser deposition (PLD) method. The KrF excimer complex 205 (λ=248 nm) was operated at a repetition rate of 4 Hz. The pulse duration was 25 ns, and pulse energy 180 mJ. The substrates were held in flowing oxygen atmosphere with a pressure of 40 Pa and 42 mm far from the target. After deposition, the samples were annealed in a static oxygen atmosphere (P_{O_2}=8.1×10^{4}Pa) for 30 min in order to obtain a homogeneous oxidization, and then cooled down to room temperature at a cooling rate of about 10°C·min^{-1}. With all the conditions above fixed, we fabricated PLSMO and NLSMO thin films at various deposition and annealing temperatures. The thicknesses of the films were all about 300 nm that were measured by a Dektak-II A profilometer. It was reported that the critical thickness for strain relaxation was about 50–100 nm for most material films.[11,12] Then it is reasonable to assume the stress from the substrate to be completely relaxed in the present films. In addition, our preliminary experimental results indicate that the influence of anneal temperature on the preparation of the thin films is similar to the influence of deposition temperature on the preparation of the thin films, thus we always maintain the anneal temperature being the same as the deposition temperature in all the preparation processes of the films. In the present work, the deposition temperature was changed from 500°C to 800°C with a step of 20°C. The phase purity and crystal structure were characterized by x-ray diffraction with an M18AHF x-ray diffractometer by $\theta-2\theta$ scan and ϕ-scan ((Cu Kα, λ=0.15406 nm). The cation content of all the films was checked by electron dispersive analysis within an error less than 5%. For transport measurement, four Ag electrodes with an area of $\leq 8\times10^{-3}$ cm^2 and a thickness of ∼200 nm were deposited on the surface of the films by DC magnetron sputtering through a shadow mask. The separation between electrodes with potentials applied remained being 3 mm in order to guarantee that the current to be measured could uniformly pass through the sample. The $R-T$ curves were recorded with the temperature increasing from 5 K to 300 K in the fixed magnetic fields of 0 T and 1 T by using a superconducting quantum interference device (SQUID) magnetometer. At the same time, the temperature-dependent magnetization ($M-T$) curves were also measured by SQUID.

3. Results and discussion

3.1. PLSMO thin films

3.1.1. Structure characterization

Figure 1 shows the $\theta-2\theta$ scanning results of the PLSMO films grown on (100) $SrTiO_3$ (STO) substrates at the deposition temperatures of 580 K, 700 K and 740 K, respectively. The three films are named as film 1, film 2 and film 3 correspondingly. For the PLSMO bulk, $a\approx b\approx c/\sqrt{2}$.[3] In this article, the peaks of the films are indexed based on the PLSMO unit cell that could be regarded as a pseudocubic structure. For this unit cell,[6] $a_c=b_c=\sqrt{a^2+b^2}/2=3.825$Å, and $c_c=c/2=3.889$Å, the subscript "c" here denotes the pseudocubic perovskite unit cell. It is shown in Fig.1(a), Fig.1(c) and Fig.1(e) that the $(100)_c$ and $(001)_c$ diffraction peaks of the films are observed respectively corresponding to deposition temperatures of 580°, 700° and 740°. The FWHM (full width at half maximum) of the $(100)_c$ peak of film 1 is 0.22°, the $(001)_c$ peaks of film 2 and film 3 are 0.19° and 0.23°, respectively, indicating that these films are all of single phase with the

singular orientation. The out-of-plane lattice parameter of film1 is 3.829 Å, which is very close to a_c of single perovskite unit cell (3.825 Å). While the out-of-plane lattice parameters of film 2 and film 3 are 3.880 Å and 3.882 Å, respectively, which are obviously different from 3.825 Å but close to the c_c of unit cell (3.889 Å). It clearly shows that film 1 is *a*-axis oriented and both film 2 and film 3 are *c*-axis oriented.[13]

The ϕ-scan (in-plane rotation) measurements around the $(011)_c$ of film 1 and $(110)_c$ of film 2 and film 3 are shown respectively in Fig.1(b), Fig.1(d) and Fig.1(f); $\phi = 0°$ was set along the STO (100) direction and tilt angle $\alpha = 45°$. Four peaks are clearly observed in Fig.1(d) and no peak appears in Fig.1(b) and Fig.1(f), which indicates that film 2 is an epitaxial *c*-axis oriented film, while both film 1 and film 3 are only singular oriented but polycrystalline films. The optimum deposition temperature (T_o) for the epitaxial growth of the PLSMO thin films is 700K. Figure 1(g) shows the ϕ-scan result around the $(110)_c$ peak of the substrate STO, which shows that the substrate is of high-quality single crystal.

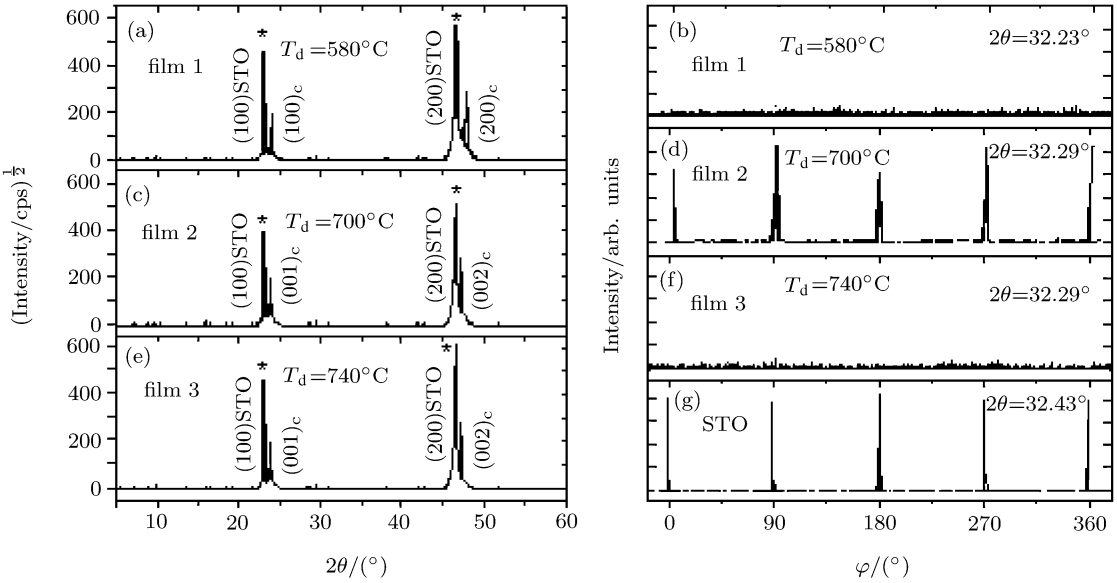


Fig.1. Room-temperature $\theta - 2\theta$ and ϕ-scan XRD results of typical PLSMO thin films deposited at various temperatures, the reflexes of the substrate are indicated by *. Four peaks of ϕ-scan are clearly observed in Fig.1(d) that serve as an indicator for the epitaxial growth of the film 2 (comparable with substrate in Fig.1(g)).

Surface morphologies of film 1, film 2 and film 3 were observed with atomic force microscopy (AFM). The results are shown in Fig.2. For film 1, film 2 and films 3, the root-mean-square roughnesses R_{rms} are estimated to be 36.2 Å, 8.38 Å and 43.7 Å, respectively; while the average roughnesses R_{ave}, 19.3 Å, 4.77 Å and 22.6 Å respectively. These results indicate that the thin films with perfect structure also have smooth surfaces. Film 1 (Fig.2(a)) and film 3 (Fig.2(c)) are not epitaxial films, showing relatively rough surface.

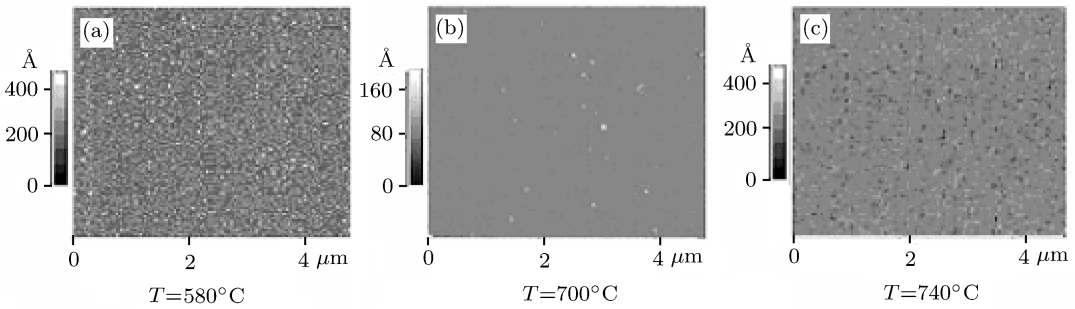


Fig.2. Surface AFM images of film 1 (a), film 2 (b) and film 3 (c). The epitaxial film has a very smooth surface.

3.1.2. Magnetic characterization

The temperature-dependent magnetization ($M-T$) curves were measured for the above three films separately in the magnetic fields of 0.02 T and 1 T by zero magnetic field cooling. The field was applied parallel to the film plane. The results are shown in Fig.3. It can be seen from this figure that when the temperature increases from 5 K to 300 K, the films change first from antiferromagnetic to ferromagnetic at the *Néel* temperature $T_{\rm N,}$ and then become paramagnetic at Curie temperature $T_{\rm C}$. $T_{\rm N}$ and $T_{\rm C}$ for film 2 are about 152 K and 280 K, respectively, which are defined as the temperatures that correspond to the left and right inflexions of the $M-T$ curves,[6] where $\mathrm{d}M/\mathrm{d}T$ reaches a maximum. By the same route, it is found that the *Néel* temperature of film 1 and film 3 is a little higher than the *Néel* temperature of film 2, and the *Curie* temperature of film 1 and film 3 is slightly lower than the *Curie* temperature of film 2. The differences between them are all less than 10 K, which indicates that these films have almost the same magnetic properties, no matter whether they are epitaxial or polycrystalline films. That is to say, for the later, the grain boundary has inconsiderable influence on the magnetic phase transitions of the films, because the volume of the grain boundary is so small compared with the grain body.

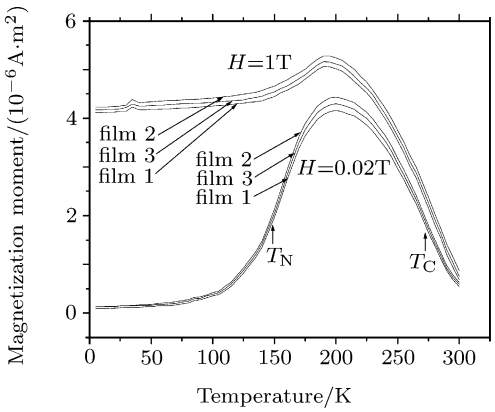


Fig.3. Temperature-dependent magnetizations in the magnetic fields of 0.02 T and 1 T for the above three typical PLSMO films.

3.1.3. Transport properties in magnetic field

The measurements of the resistance (R–T) curves of these films were performed separately in the magnetic fields of 0 T and 1 T with zero magnetic field cooling. Figure 4(a) displays the $R-T$ curves of film 1 (a-axis oriented film). In a magnetic field of 0 T, film 1 undergoes an insulator–metal phase transition at $T_{\rm IM}$ (35 K), and then becomes semiconductor at $T_{\rm MS}$ (278 K). Under an applied magnetic field of 1T, the insulator–metallic transition temperature $T_{\rm IM}$ decreases from 35 K to 30 K, and the metallic-semiconductor transition temperature $T_{\rm MS}$ increases from 278 K to 300 K and more. Corresponding to the above two transitions, there are two magnetoresistance effect (MR) peaks in the MR–T curve (see the inset of Fig4.(a)) where MR=(R(0)-R(H))/R(0).[2] It is noticed that $T_{\rm MS}$ (278 K) is close to $T_{\rm C}$ (∼276 K) but $T_{\rm IM}$ (30 K) is apparently lower than $T_{\rm N}$ (∼153 K). From the $M-T$ curve, in a temperature range from 5 K to 153 K, the film is in the antiferromagnetic state, correspondingly, it should be come an insulator, but the transport measurement shows the metallic behaviour between 35 K and 153 K, similar to the property of a-axis oriented $Pr_{0.5}Sr_{0.5}MnO_3$ film.[13] This may be suggested that there are percolating channels within the film body that is responsible for the conductance.

Figure 4(c) displays the $R-T$ curves of film 3 (c-axis oriented film). As mentioned above, film 3 also has magnetic phase transition from antiferromagnetic to ferromagnetic and then becomes paramagnetic when the temperature increases up to 300 K. The transport measurement shows that, however, the film appears as an insulator in the whole temperature range no matter whether the magnetic field is applied or not. This property is similar to the electric property of c-axis oriented $Pr_{0.5}Sr_{0.5}MnO_3$ film.[13]

Film 2 (epitaxial film) has its own feature of the transport as shown in Fig.4(b). Obviously, at a zero magnetic field, film 2 shows phase transition from insulator to metal at $T_{\rm IM}$ (148 K), and then becomes semiconductor at $T_{\rm MS}$ (282 K). When the magnetic field increases to 1 T, the $T_{\rm IM}$ decreases to 137 K and the $T_{\rm MS}$ increases to 300 K and more. $T_{\rm IM}$ and $T_{\rm MS}$ are almost equal to $T_{\rm N}$ and $T_{\rm C}$, respectively, at the same magnetic field. It clearly indicates that between 5 K and T_{IM} ($T_{\rm N}$), film 2 becomes an antiferromagnetic insulator; in the temperature range from T_{IM} ($T_{\rm N}$) to $T_{\rm MS}$ ($T_{\rm C}$), film 2 turns to a ferromagnetic metal; when the temperature increases to above $T_{\rm MS}$ ($T_{\rm C}$), film 2 becomes a paramagnetic semiconductor. The transport behaviour is consistent with the magnetic phase transition very well. The properties in this case resembles the electronic and magnetic properties of the epitaxial $Pr_{0.5}Sr_{0.5}MnO_3$ film[14] and the $Pr_{0.5}Sr_{0.5}MnO_3$ single crystal.[1] As shown in the in-

set of Fig.4(b), there are two remarkable MR peaks appearing at T_N and T_C, which are about 12% at T_N and about 9% at T_C, so is the PLSMO bulk.[2]

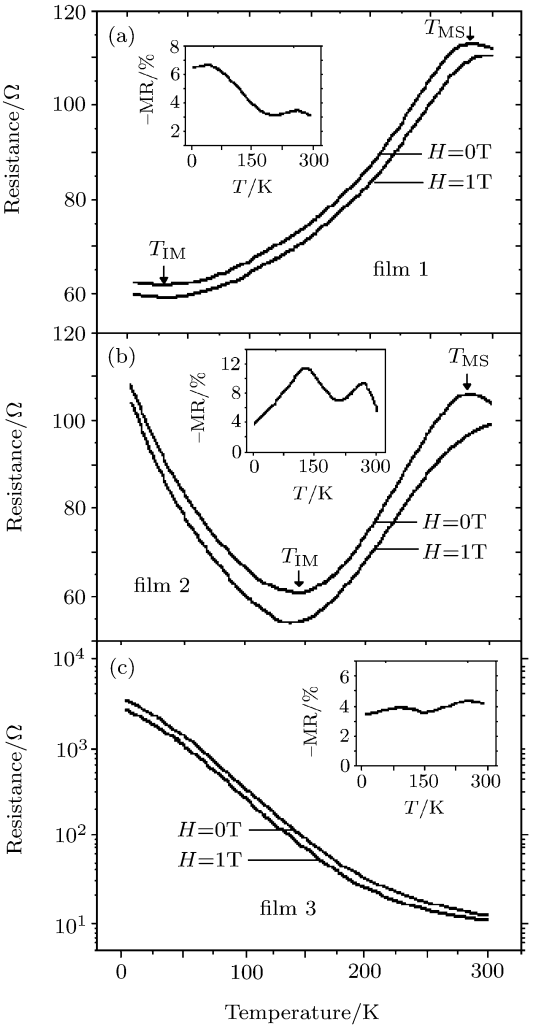


Fig.4. Temperature-dependent resistances for the above three PLSMO films. For the epitaxially grown film (film 2), the consistency between transport and magnetic phase transition (in Fig.3) is clearly observed.

From the $M-T$ and $R-T$ curves of these three films, it is obvious that the epitaxially grown thin film (film 2) is the only film of which the electric transport behaviour is consistent with the magnetic phase transition well, while the electric transport properties of singular oriented polycrystalline thin films (film 1 and film 3) are not consistent with their magnetic phase transitions. Such a remarkable difference may be attributed to the grain boundaries existing in the film 1 and film 3, rather than in the epitaxially grown film, film 2. This may be understood as follows. The grain boundary may have a second phase due to the composition segregation and spin random, which may not sensitively influence the magnetic phases, but it is more likely to remarkably influence the transport property of the thin film due to the blocking and scattering effects.

3.2. NLSMO thin films

The crystal structure and electronic and magnetic properties of the $Nd_{0.35}La_{0.15}Sr_{0.5}MnO_3$ (NLSMO) bulk are very similar to those of the PLSMO bulk.[3] In order to confirm the influence of the deposition temperature on the film growth, we also fabricated the NLSMO thin films at various deposition temperatures. The $\theta-2\theta$ scan and ϕ-scan results indicate that the epitaxial and c-axis oriented single-phase film (film 2) can be obtained at about 720°C. When the temperature increases to 750 °C, the film remains c-axis oriented but becomes polycrystalline (film 3). As the temperature decreases to 620°C, the deposited film shows being a-axis oriented (film 1). The optimum deposition temperature (T_o) for the epitaxial growth of the NLSMO thin films is 720°C.

The temperature-dependent magnetization ($M-T$) curves of the NLSMO films are shown in Fig.5. All the films change first from antiferromagnetic to ferromagnetic at about 131 K (T_N), and then becomes paramagnetic at about 273 K (T_C). These films have almost the same magnetic properties as those of the PLSMO thin films.

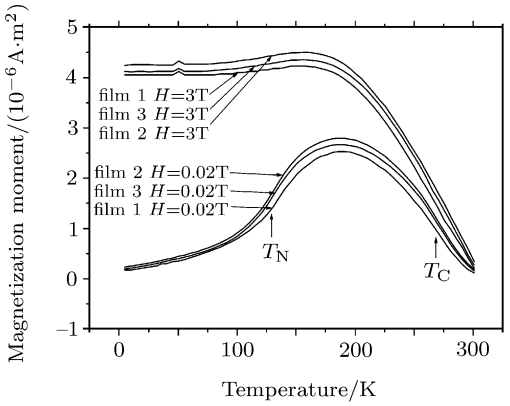


Fig.5. Temperature-dependent magnetizations at magnetic fields of 0.02 T and 3 T for the NLSMO films.

Figure 6 displays the temperature-dependent resistance ($R-T$) curves of the NLSMO films. At the magnetic field of 0 T, and the temperature increasing from 5 K to 300 K, the case is very similar to that of PLSMO. Film 1 undergoes an insulator–metal phase transition at T_{IM} (45 K), and then becomes a semiconductor at T_{MS} (285 K). The applied magnetic field,

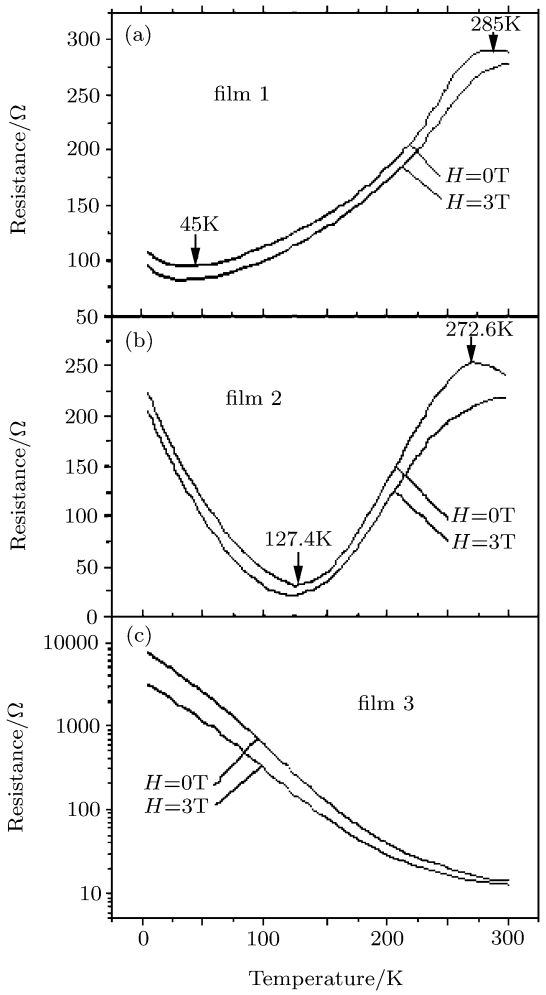


Fig.6. Temperature-dependent resistances for the NLSMO films, the consistency between electronic transport and magnetic transitions can be observed very well.

3 T, can decrease the T_{IM} from 45 K to 40 K and increase the T_{MS} from 285 K to above 300 K. T_{IM} and T_{MS} are very different from the T_N and T_C, respectively. Film 3 behaves as an insulator in the whole temperature range, without any electronic phase transition appearing. While film 2 shows an insulator–metal phase transition at about 127.4 K, and then becomes a semiconductor at about 272.6 K, at the zero magnetic field. The temperatures of 127.4 K and 272.6 K are very close to T_N (131 K) and T_C (273 K), respectively. Between 5 K and T_N, film 2 becomes an antiferromagnetic insulator. From T_N to T_C, the film 2 turns to a ferromagnetic metal. Above the T_C, film 2 becomes a paramagnetic semiconductor. The electronic phase transitions of film 2 are consistent with its magnetic phase transitions very well.

4. Conclusions

In the present work, we have investigated the growth conditions of the PLSMO and NLSMO epitaxial thin films. It is found that the deposition temperature plays the most important role in the growth of the films. At the optimum deposition temperature (T_o), the epitaxial (single crystal-like) and *c*-axis oriented thin films can be obtained. When the temperature is higher than T_o, the *c*-axis oriented single-phase but polycrystalline thin films grow. When the temperature is lower than T_o, films tend to be *a*-axis oriented polycrystalline. A comparison between the epitaxially grown PLSMO and NLSMO thin films clearly shows an exact consistency between the electronic phase transitions and the magnetic phase transitions; while for the *a*-axis and *c*-axis oriented polycrystalline PLSMO and NLSMO thin films, their electronic phase transitions basically are not consistent with the magnetic phase transitions, which may be attributed to the grain boundaries in the polycrystalline PLSMO and NLSMO thin films, because the grain boundaries where the segregated phase and random spin scattering exist have remarkable influence on the transport properties but no obvious influence on magnetic phase transitions of the thin films. However, the real epitaxial thin film can be obtained only in a very narrow deposition temperature range.

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