



Preparation and conducting performance of LaNiO_3/Ag film and its interface reaction

Wenqing Yao, Haipeng Yang, Yu Chang, Yongfa Zhu*

Department of Chemistry, Tsinghua University, Beijing 100084, PR China

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Abstract

LaNiO_3 thin film with perovskite structure was successfully prepared on Ag substrate via an amorphous heteronuclear complex $\text{LaNi}(\text{DTPA})\cdot 6\text{H}_2\text{O}$ as a precursor. The influences of precursor concentration and PEG additive with different molecular weight on the texture of the film were carefully studied. The interface states of LaNiO_3/Ag film were revealed by using AES analysis. The effect of annealing time on the interface diffusion of the LaNiO_3/Ag film was shown by using AES depth profile spectrum. The relationship between the electric resistivity of the film and the environmental temperature was measured by using four-probe method. The results showed the film had good metallic conductivity from 300 down to 77 K. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

Mixed rare earth metal oxide materials, especially the thin film materials have generated considerable interest in recent years [1–3]. The study of these kinds of thin films has extended their application fields, and benefits to fabricate novel thin film devices and find new physical effect [4,5]. Also it helps to clarify the underlying mechanism of high temperature superconductors, sensors, catalysts and gas separator, etc. [2,6,7].

LaNiO_3 with perovskite structure shows metallic character, which is quite uncommon in oxides. It is well known to be a rhombohedrically distorted perovskite, which exhibits a metallic character down to 4.2 K [8]. The electrical and magnetic properties of this oxide are governed by strong electronic correlation effects. Thus, it is important to investigate the effect of the preparation route and calcination conditions on the crystalline structure and morphology of synthesized LaNiO_3 films. These factors are considered important due to their effect on electronic properties, which could affect the conductivity [3].

Much work has been done on the preparation and the characterization of LaNiO_3 powder and on thin films [3,9,10]. These films are mainly on substrate of

* Corresponding author. Tel.: +86 10 62783586;

fax: +86 10 62787601.

E-mail address: zhuyf@mail.tsinghua.edu.cn (Y. Zhu).

non-metals such as Si. However, there had serious diffusion of Si into the film and Si signal was found in the LaNiO_3 layer. This diffusion reaction could impede the crystallization of the LaNiO_3 species and increase the electric resistivity of LaNiO_3 film [3]. It is important to get more pure LaNiO_3 films with high conducting performance to satisfy its numerous applications. This work tries to solve this problem. There had little work done on metal substrate. Different preparation methods of the perovskite oxides have been studied [11,12]. Comparing with traditional ways, amorphous complex method had many advantages [13,14]. This work attempts to synthesize LaNiO_3 thin films on metal substrate of Ag via amorphous complex, reveal the influence of precursor concentration and PEG additive on the texture of the LaNiO_3 thin film, and study the interface state between the LaNiO_3 film and the Ag substrate. The effect of annealing time on the interface diffusion and the conducting performance of the film are also studied in present work.

2. Experimental section

2.1. Synthesis of $\text{LaNi(DTPA)} \cdot 6\text{H}_2\text{O}$ precursor

Firstly, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ powder with a molar ratio of 1:1 were dissolved in distilled water. Then 1.0 mol/l NaOH solution was added in drops into the transparent green mixture solution with stir. In this process, fresh $\text{La}(\text{OH})_3$ and $\text{Ni}(\text{OH})_2$ deposited. Adjusting the pH value to 8.0, green colloidal depositions of $\text{La}(\text{OH})_3$ and $\text{Ni}(\text{OH})_2$ separated out totally. The depositions were washed with distilled water for several times to remove the excess OH^- . Then, mixture precipitates were added into calculated quantity of diethylenetriaminepentaacetic acid (H_5DTPA) solution. It was stirred and heated at about 80°C to promote the dissolution and reaction until the mixture became a blue transparent solution mixture. After vaporized slowly at room temperature, the solution became a piece of transparent glass-like material $\text{LaNi(DTPA)} \cdot 6\text{H}_2\text{O}$.

The precursor solution of $\text{LaNi(DTPA)} \cdot 6\text{H}_2\text{O}$ was prepared by dissolving it into distilled water and certain amount of PEG water solution was added into the precursor solution.

2.2. Preparation of LaNiO_3/Ag thin film

Ag sheet was cleaned in deionized water using ultrasonic. The precursor films with various thicknesses were formed on Ag sheet by spin coating precursor solution with a definite concentration. The spin rate and spin time was 3000 rpm and 50 s for quickly spin, 1000 rpm and 3 s for slowly spin, respectively. The LaNiO_3 film was obtained by annealing the precursor film sample in air at a heating rate of $3^\circ\text{C}/\text{min}$. Then, the sample was kept at various pre-set temperatures and maintained for a definite period of time to promote the formation of perovskite-type LaNiO_3 thin film.

2.3. Analysis techniques

The auger electron microscope (AES) spectra were obtained using PHI 610 SAM system. A coaxial electron gun with a single pass cylindrical mirror analyzer (CMA) was used. The energy resolution of the CMA was set at 0.3% to obtain a good energy resolution. For AES analysis, the electron beam energy and the beam current were 3.0 keV and $0.5 \mu\text{A}$, respectively. The electron beam was incident at an angle of 30° with respect to the specimen surface. The base pressure of the analysis chamber was better than 3.9×10^{-9} Torr. During the depth profile analysis, the energy and beam current of the Ar ion beam were 3.0 keV and $6 \mu\text{A}$, respectively. The diameter of beam was 1 mm, and the sputtering rate was calibrated to be 30.0 nm/min by using thermal oxidized SiO_2 thin film. The electron charge effect was not found for the film sample during AES analysis.

X-ray diffraction (XRD) experiments were carried out in Bruker D8 Advance X-ray diffractometer with $\text{Cu K}\alpha$ radiation.

The X-ray photoelectron spectroscopy (XPS) spectra were obtained using PHI 5300 ESCA system with $\text{Al K}\alpha$ X-ray source. The power of 250 W and the pass energy of 37.5 eV were used during the experiment. The base pressure of the analysis chamber was better than 3×10^{-9} Torr. All spectra were calibrated using the binding energy of C 1s (285.0 eV) as a reference.

SEM experiments were carried out in CSM950 scanning electron microscopy.

The resistance was measured with a four-probe method in an air flow. The measurement experiment was carried in the potentiostat/galvanostat electrochemistry analyzer Model 283. The electrical current was 1 mA.

3. Results and discussion

3.1. Influence of precursor concentration on the texture of the film

The morphology of the film was studied by SEM. Fig. 1 shows the SEM photos of the LaNiO_3/Ag thin films prepared with differently concentrated precursor

solutions. All samples were calcined at $600\text{ }^\circ\text{C}$ for 2 h. When the concentration of the precursor solution was low (10 wt.%), the thin film was smooth and compact, and no micro-crack was observed on the surface of the film. When the concentration became higher (15 wt.%), the surface of the film became uneven. Some micro-cracks were observed on the surface of the films prepared with a high concentrated precursor

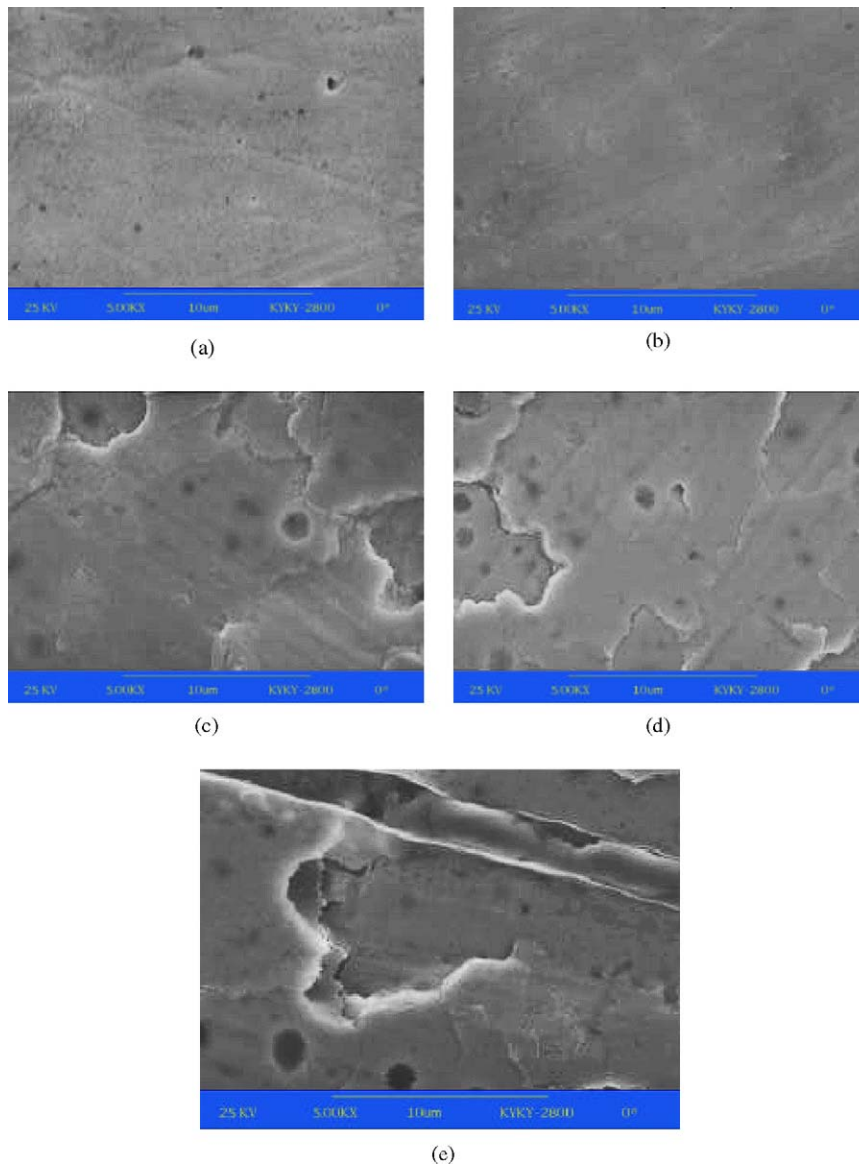


Fig. 1. SEM photos of the texture of LaNiO_3/Ag thin film with different precursor concentration: (a) 5% ($\times 5000$); (b) 10% ($\times 5000$); (c) 15% ($\times 5000$); (d) 20% ($\times 5000$); (e) 25% ($\times 5000$).

solution (25 wt.%). This result indicated that the surface morphology of the thin films could be improved by decreasing the concentration of the precursor. With lower concentration, the thin film could be smoother and compact. But if the concentration of the precursor solution was too low, the film obtained by spin coating one times was very thin. Fig. 1a shows the SEM photos of the LaNiO_3/Ag thin films prepared with 5 wt.% precursor solutions. There are many holes in the film. These holes are the pits of the Ag substrate. The film is too thin to cover up them. In order to get thicker high quality film, it is important to choose appropriate concentration of the precursor solution and to spin coating repetitiously.

3.2. Influence of PEG additive on the morphology of the thin film

Polyethylene glycol (PEG), a kind of tackifier, was used to increase the viscosity of the solution and improve the quality of the thin film. The influence of

the additive on the surface morphology was investigated by using SEM. When the additive concentration was low in the precursor solution, the effect of the PEG on the morphology of the LaNiO_3 thin film was not obvious. When the additive concentration was high, the film became uneven. This phenomenon could be seen before the film was calcined. As to high concentration precursor solution, some micro-cracks and other defects such as dropped spots were found on the SEM without PEG additive. After certain amount of PEG was added into the precursor solution, the micro-cracks and the dropped spots disappeared. The improvement of the surface morphology probably resulted from the dispersion effect of the thermal stress in the thin film by the additive of PEG. It interrupts the formation of crystal and tends to form amorphous film. The above results illustrated that PEG additive can greatly improve the morphology of the LaNiO_3 thin film.

The influence of PEG additive with different molecular weight on the surface morphology of the

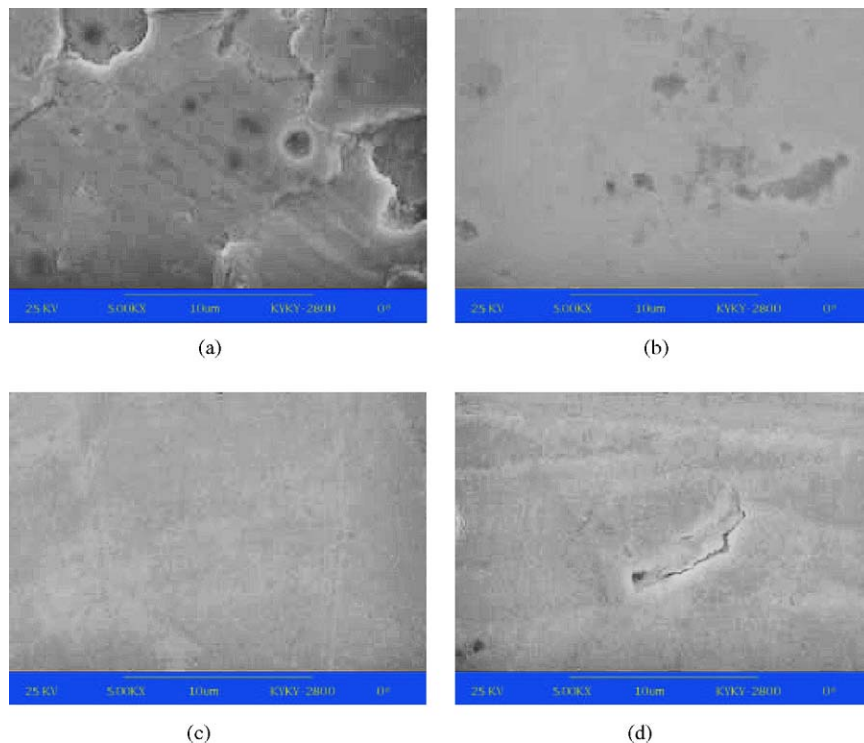


Fig. 2. Effect of additive PEG (0.02 wt.%) on the texture of LaNiO_3/Ag thin film with the precursor concentration of 15%: (a) no PEG ($\times 5000$); PEG 800 ($\times 5000$); (c) PEG 4000 ($\times 5000$); (d) PEG 11000 ($\times 5000$).

LaNiO₃ thin film was described in Fig. 2. The LaNiO₃/Ag film sample was prepared by using the precursor solution with a concentration of 15 wt.% and the PEG concentration of 0.02 wt.%. When the PEG additive was not used, the surface of the film is rough (Fig. 2a). After 0.02 wt.% PEG 800 was added into the precursor solution, the surface becomes evenness but still have pits (Fig. 2b). When 0.02 wt.% PEG

4000 was added into the precursor solution, the quality of the film is improved greatly. The surface of the film is evenness and no pits and cracks are found (Fig. 2c). When the molecular weight of PEG is changed to 11000, some cracks appears in the surface of the film (Fig. 2d). With the increase of the molecular weight of PEG, the viscosity of the precursor solution increased. The ion migration ratio and ion exchange ratio

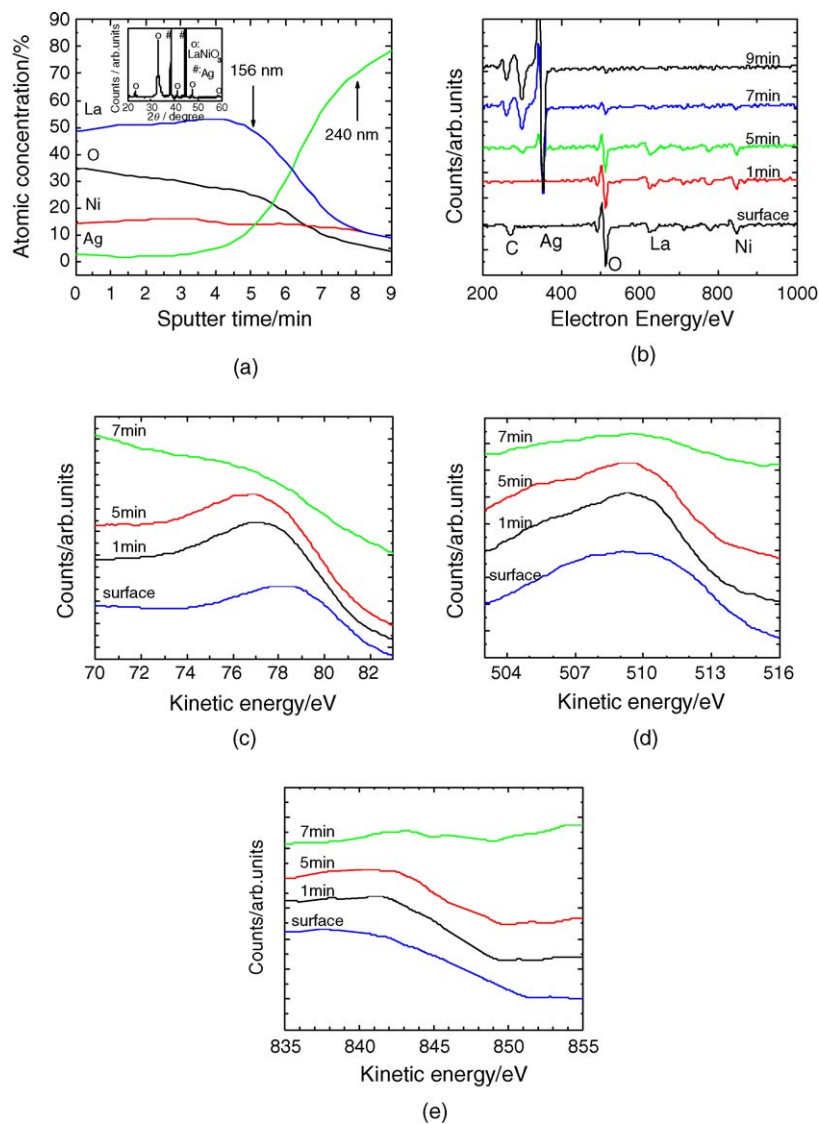


Fig. 3. AES results of the six-layer LaNiO₃/Ag thin film calcined at 600 °C for 2 h. The inset in fig a was the XRD pattern of the LaNiO₃/Ag thin film. (a) AES depth profile spectrum; (b) AES qualitative analysis of the six-layer film with different depth; (c) La MNN; (d) O KLL; (e) Ni LMM.

decreased correspondingly [15]. This would interrupt the nucleation process and thus decrease the thermal stress in the thin film, and improve the morphology of the film. On the other hand, the chains of PEG would adsorb ions in the precursor solution. The very long chain would adsorb more ions around it and lead to the distribution of ions in the precursor solution become inhomogeneous. Thus, the use of the highest molecular weight of PEG here (PEG 11000) led to the cracks in the film surface. The optimum molecular weight of PEG here was 4000.

3.3. Interface states of LaNiO_3/Ag film

The chemical compositions of a six-layer LaNiO_3/Ag thin film were determined by using XPS. The film was calcined at $600\text{ }^\circ\text{C}$ for 2 h. There were La, Ni, O and C in the surface of the film. The element carbon comes from the atmosphere, which is a typical

contamination for non-vacuum stored samples [16]. The binding energies of La, Ni and O are consistent with that of LaNiO_3 in literature [17], which proved the formation of LaNiO_3 species on the Ag substrate. XRD patterns of the LaNiO_3 thin film was shown in the inset of Fig. 3a. The peaks of Ag were extraordinarily strong because Ag was used as substrate. The other peaks could be attributed to the perovskite structure of LaNiO_3 , indicating the crystallization of LaNiO_3 on the substrate of Ag.

Fig. 3a showed a typical AES depth profile spectrum of the six-layer LaNiO_3/Ag thin film sample calcined at $600\text{ }^\circ\text{C}$ for 2 h. The composition of the six-layer thin film was distributed homogeneously with the depth. The thickness of the LaNiO_3 film was about 156 nm.

In order to clarify the interface species, the chemical states of La, Ni, Ag and O were studied by using AES qualitative analysis and AES line shape

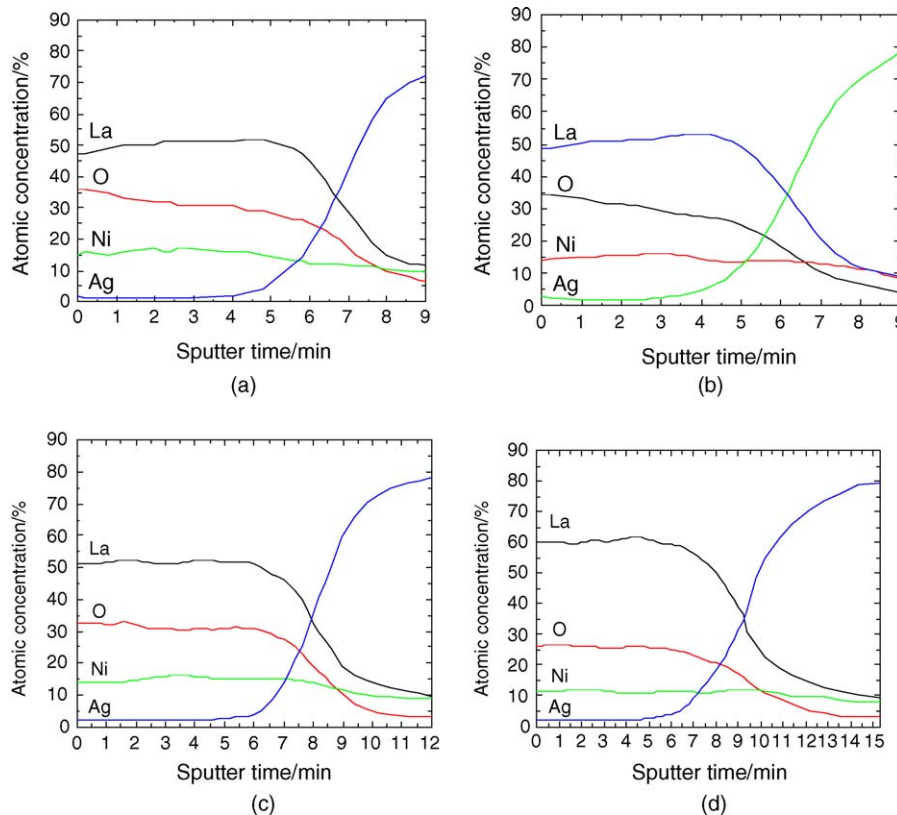


Fig. 4. AES depth profile spectrum of the LaNiO_3/Ag thin film samples calcined at $600\text{ }^\circ\text{C}$ for different annealing time: (a) 1 h; (b) 2 h; (c) 4 h; (d) 6 h.

analysis. Fig. 3b showed AES qualitative analysis of the six-layer film with different depth. There were La, Ni, O and C in the surface of the film. The element C was from the atmosphere. At the depth of sputtering 1 min, there were no carbon was found in the AES qualitative analysis curve. In the interface layer (sputtering 5–7 min), the signal of La, Ni and O decreased gradually and Ag increased inchmeal. When it reached to the substrate, there was only Ag could be found. This was consistent with the AES depth profile spectrum (Fig. 3a). AES line shape analysis were shown in Fig. 3c–e. Fig. 3c showed the line shapes of La MNN at various depths of the the six-layer film calcined at 600 °C for 2 h. Based on Fig. 3c, the kinetic energy of La MNN decreased from 78.4 to 76.5 eV when the depth increased from the LaNiO₃ surface layer to the Ag substrate (sputtered for 7 min). In the surface layer, the composition was LaNiO₃ and the La MNN kinetic energy of 78.4 eV can be contributed to the LaNiO₃ species. In the inner film, with increasing depth, the La MNN peaks shifted to the low kinetic energy of about 77 eV. This showed that the chemical atmosphere of La in the surface layer was different from that in the inner layer. However, the kinetic energy of O KLL and Ni LMM had little change, showing unitary chemical environment.

3.4. Effect of annealing time on the interface diffusion of the LaNiO₃/Ag film

Fig. 4 showed typical AES depth profile spectrum of the six-layer LaNiO₃/Ag thin film samples calcined at 600 °C for different annealing time. With the prolonging of the annealing time, the diffusion layer became wider. But the interface diffusion was greatly depressed. Even for the film annealing 6 h, though the interface between the layer and the substrate was quite wide, there was no serious diffusion of Ag into the film. The thickness of diffusion layer with different

Table 1
The relationship between annealing time and corresponding thickness of diffusion layer

Annealing time (h)	Thickness of diffusion layer (nm)
1	80.5
2	84
4	91
6	136.5

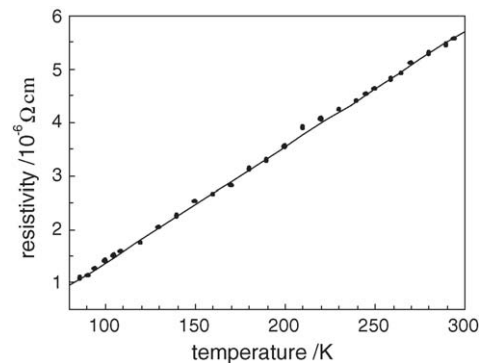


Fig. 5. Electrical resistivity of LaNiO₃/Ag film calcined at 600 °C for 2 h as a function of temperature.

annealing time was shown in Table 1. If the annealing time is lower than 4 h, there is a very thin interface layer.

3.5. Conducting performance of the LaNiO₃/Ag film

The relationship between the electric resistivity of the film calcined at 600 °C for 2 h and the environmental temperature was measured by using four-probe method. The results showed the film had good conductivity and its resistivity decreased linearly as temperature decreased from 300 down to 77 K, showing a metallic property. At room temperature (300 K), the electric resistivity of the LaNiO₃/Ag film is about 5.71 μΩ cm, showing good conducting performance (Fig. 5).

4. Conclusions

LaNiO₃ thin film with perovskite structure on metal substrate of Ag was synthesized by using amorphous heteronuclear complex LaNi(DTPA)·6H₂O as a precursor. The synthesized film showed very good metallic conducting performance. Both precursor concentration and PEG additive can affect the morphology of the thin film. When the precursor concentration was 10 wt.%, a smooth film without microcrack can be obtained. When 0.02 wt.% PEG 4000 was added into the precursor solution, the quality of the film is improved greatly. AES results showed that the optimized annealing process is calcined at 600 °C for 2 h.

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