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Effect of thermal annealing on transparent conductive $LaNiO_3$ thin film prepared by an aqueous method

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Dense, crack-free and uniform lanthanum nickel oxide (LNO) thin films were prepared by an aqueous method on various substrates, such as single crystal silicon, microcrystalline glass ceramic (GC) and amorphous glass. The effects of various thermal annealing temperatures on the microstructure, interface and electrical properties of the LNO films were investigated by XRD and SEM with the EDX and a four-probe method, respectively. It was found that with the increase in thermal annealing temperature, the LNO film on Si substrates displayed a structure change from pseudocubic to rhombohedral and was accompanied by the appearance of a NiO impure phase, while the LNO film on a GC substrate diffused into the substrate. In these cases, the film resistivity was increased. As a result, a LNO thin film with a resistivity of $2–3 \times 10^{-5}\ \Omega \cdot m$ was achieved by thermally annealing at 750–800°C for 1 hour in air. The measurement of the surface resistance under different temperatures shows that the LNO film possesses better high temperature stability. Its transmittance spectrum was also observed.

1. Introduction

Lanthanum nickel oxide (LNO) is a typical metallic oxide with a perovskite-like structure. Using it as an electrode, ferroelectric nonvolatile memory is shown to be fatigue-free up to 10^{11} cycles [1], in which the fatigue property of ferroelectric thin film is obviously improved. In addition, the change in electronic configuration of the transition nickel element makes the LNO possess many wonderful properties, such as electrocatalytic and magnetic properties [2, 3]. Because of this, the study on the relationship of preparation, structure and properties of the LNO has become considerably important. In this paper, the LNO film was prepared by an aqueous method, and the effects of thermal annealing on the structure, the interface as well as the electrical and optical properties of the thin films were investigated in detail.

2. Experimental

The LNO precursor solution was synthesized by an aqueous method. The preparation procedure is schematically described in the flow chart in Fig. 1. Lanthanum oxide and nickel nitrate were used as the starting materials. First, the lanthanum oxide was dissolved in a water solution with acetic acid to synthesize lanthanum acetate, and then the water solutions of lanthanum acetate and nickel nitrate were mixed. The pH value of the solution was adjusted by the addition of acetic acid to obtain a stable solution of LNO. The 5% polyvinyl alcohol (PVA) water solution was employed as the stabilizing agent to promote formation of thin films by adjusting the viscosity of the solution. A clear and stable precursor solution of 0.6 M concentration was finally obtained.

Single crystal silicon, microcrystalline glass ceramics (GC: $K_2O{\cdot}SiO_2{\cdot}Al_2O_3$) and amorphous glass were chosen as substrates. The LNO films were fabricated by spin coating onto the substrates at 2500 rpm for 15 seconds, followed by heat treatment at 600°C for 3 minutes for pyrolysis, nucleation and prevention of cracks. The process was repeated several times to obtain the desired thickness film, before the thermal annealing

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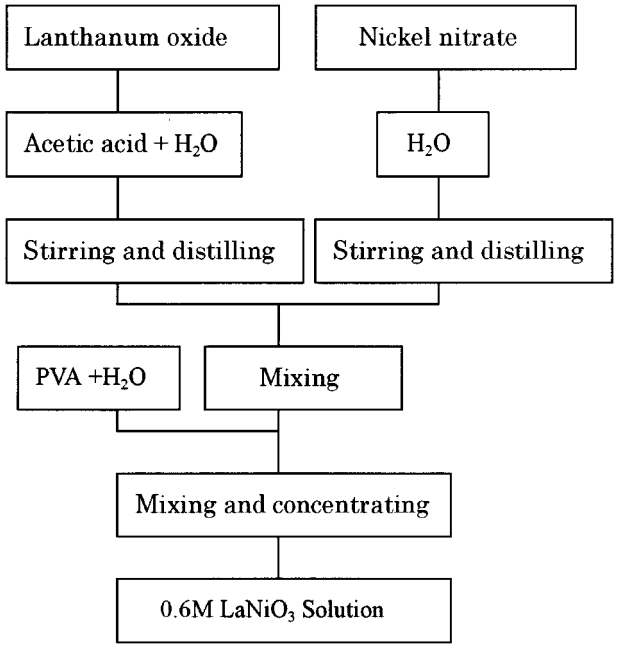

Figure 1 Flow chart of synthesis process of the LNO precursor.

process in air at 600–900°C for 1 hour. This process was determined by the thermal analysis characteristics. The effects of the thermal annealing temperatures on microstructure and interface structure were investigated by X-ray diffraction (XRD) and scanning electronic microscopy (SEM). The resistivity of the LNO film was evaluated by a four-probe method. Its transmittance spectrum was also observed by a spectrophotometer.

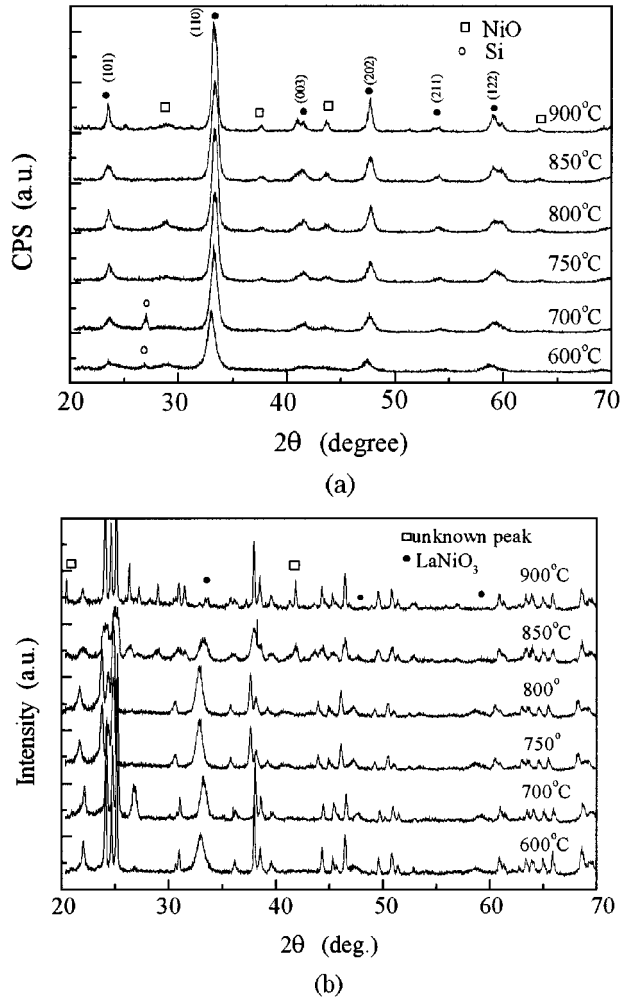

Figure 2 XRD patterns of the LNO films: (a) Si and (b) GC substrates.

3. Results and discussion

3.1. Structure analysis

Fig. 2a shows the XRD patterns of LNO films annealed at various temperatures on Si substrates. At below 600°C, the LNO film is in the amorphous state. The LNO film shows a pseudocubic structure with the lattice parameter $a = 3.84$ Å at 600°C, which corresponds to a distorted perovskite structure. With an increase in the thermal annealing temperature, the intensity of the XRD peaks is enhanced and the peaks have a tendency to be divided into doubles. This indicates that the LNO film structure transfers from pseudocubic to rhombohedral. On the other hand, with increasing thermal annealing temperature, the adsorbed Ni^{3+} atoms would become unstable and a higher tendency of reduction from Ni^{3+} to Ni^{2+} could occur. This corresponds to the impure NiO phase which appeared in the XRD patterns.

The LNO thin films on GC substrates remain pseudocubic structures at 600°C, which are the same as the films on Si substrates. However, the intensity of the XRD peaks has been increasing up to 800°C and then reduced so seriously that some peaks almost disappear (shown as in Fig. 2b). At 900°C, some unknown peaks appear, and the color of the LNO film changes to white from dark brown. This may be caused by the diffusion of the film into the substrate.

Figs 3a and b respectively show the SEM micrographs of the surface and cross section of the LNO thin films on Si substrates after annealing at 600°C. Dense, crack-free and uniform LNO film with a thickness of 0.8 μm was obtained. Its grain size is around several tens of nanometers. The interface between the LNO film and the Si substrate shows an island-type growth mode. It is too difficult to form the preferentially oriented LNO films; therefore, We could not obtain any preferred orientation in the LNO films.

The surface structure of the LNO film on a GC substrate (Fig. 3c) is the same as that on a Si substrate at 600°C, but the surface of the film began to change with increasing of annealing temperature. Fig. 3d shows the surface micrograph of the film after annealing at 900°C. It seems discontinuous. As aforementioned, the color of the film changed from dark brown to white, which is the same color as the GC substrate. We originated a conjecture on the diffusion of the LNO into the GC substrate. To prove this, the film/substrate interface property was further investigated by EDX.

To avoid too many curves on one picture in the EDX analysis, the Si and Ni elements were chosen as representative of the composition of the GC substrate and the LNO film, respectively. The line scanning results for elements in the neighborhood of the film/substrate interface are shown in Fig. 4. After annealing at 600°C, three parts consisting of the LNO film, the interface and the substrate could be clearly observed. However, no interface appeared in the film annealed at 900°C. The Si content increases with the increase in the depth and

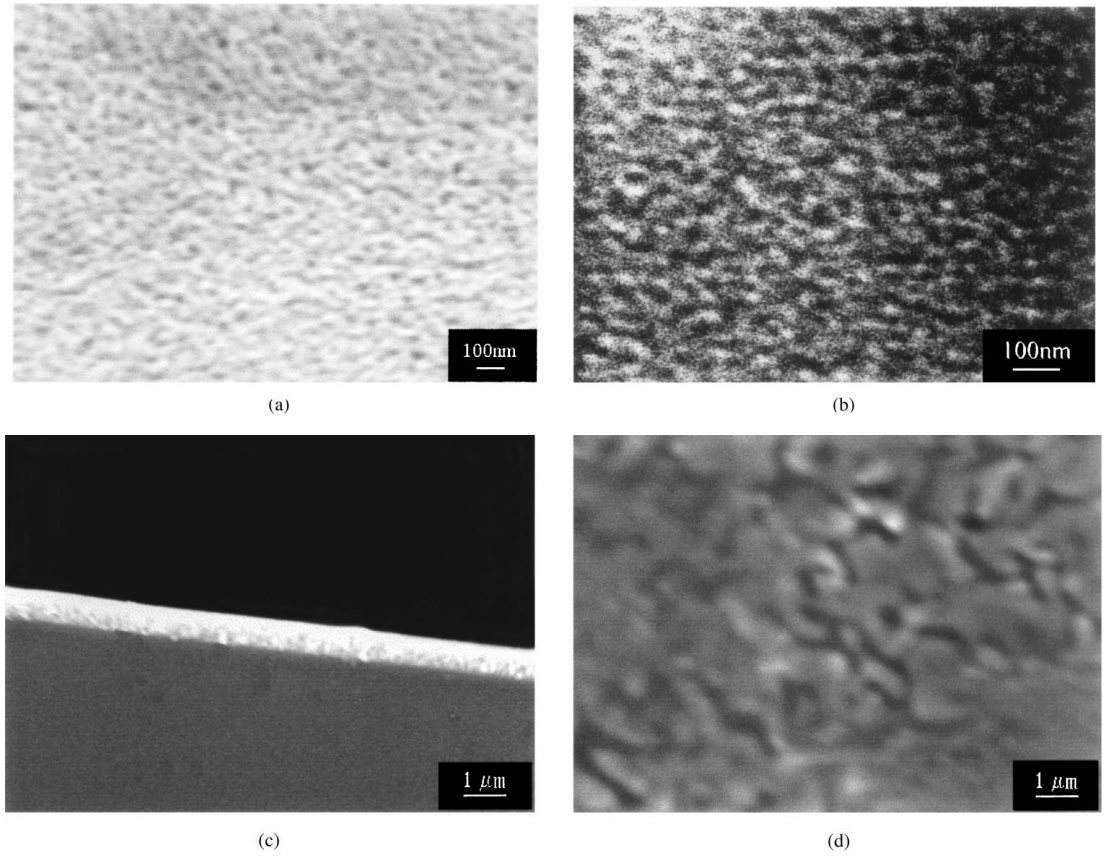

Figure 3 SEM micrographs of the LNO films: (a) surface of the LNO/Si; (b) cross section of the LNO/Si; (c) annealing at 600°C and (d) at 900°C on GC substrates.

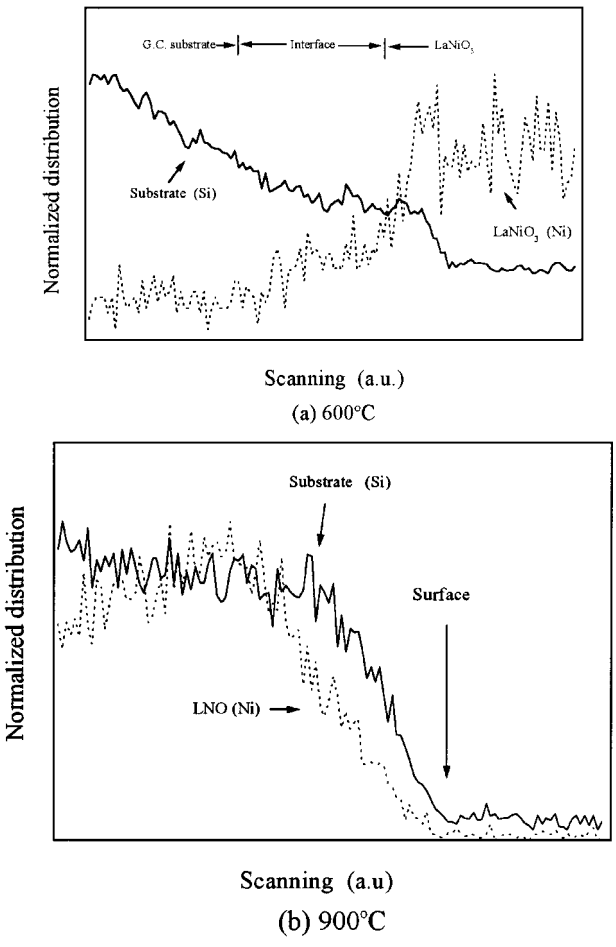

Figure 4 Line scanning of the LNO films annealed (a) at 600°C and (b) 900°C on GC substrates.

remains constant after a certain depth. This is a typical surface feature of the substrate. However, the Ni element in the LNO film displays a canonical distribution, in which the content of the Ni element increases, then reaches a maximum value and finally tends to decrease. This is typical diffusion attribution. It illustrates that, when the film is treated at 900°C, the LNO film diffuses into the substrate. This is the reason why the surface of LNO/GC becomes white.

3.2. Electrical property

Fig. 5 shows the effect of the thermal annealing temperature on the resistivity of the LNO films. The resistivity initially decreased with increasing thermal annealing

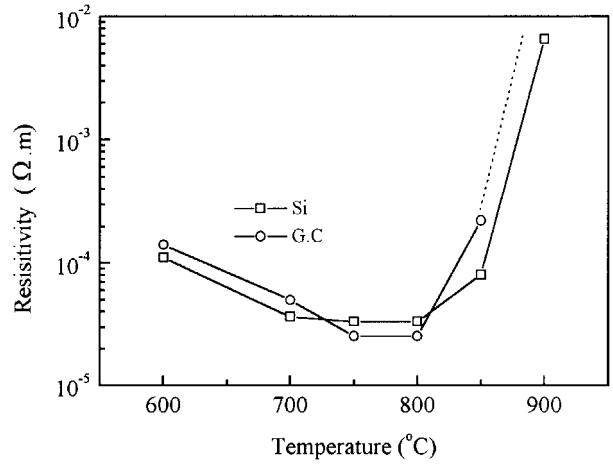

Figure 5 Effect of annealing temperature on resistivity of the LNO films.

temperature up to 800°C due to the improvement in crystallinity of the films, above which the resistivity increased steeply. The LNO films with a resistivity of 2–3 $\times$ 10^{-5} Ω·m were achieved after annealing at 750–800°C for 1 hour in air. On a Si substrate, when the NiO phase appears in the film annealed at high temperature, the valence state of part of the Ni ions in the LNO films changes from Ni^{3+} to Ni^{2+}, that is, $Ni^{3+} + e \rightarrow Ni^{2+}$. The reduction of free electronic numbers in the LNO film causes an increase in the resistivity of the film. Moreover, the resistivity of the NiO as an insulating material is about 3 $\times$ 10^6 Ω·m. The NiO dispersed over the LNO film leads to an increase in the resistivity of the LNO film. Due to the decomposition of the pure LNO at about 825°C (according to JCPDS card of XRD, No. 33-0111), the resisitivity of the film increases greatly after annealing at over 800°C. On a GC substrate, the LNO film diffuses into the substrate with increasing thermal annealing temperature and causes a change in the structure and a decrease in film thickness, which makes the film resistivity increase. The film becomes discontinuous at 900°C, and thus its resistivity undergoes a sharp increase.

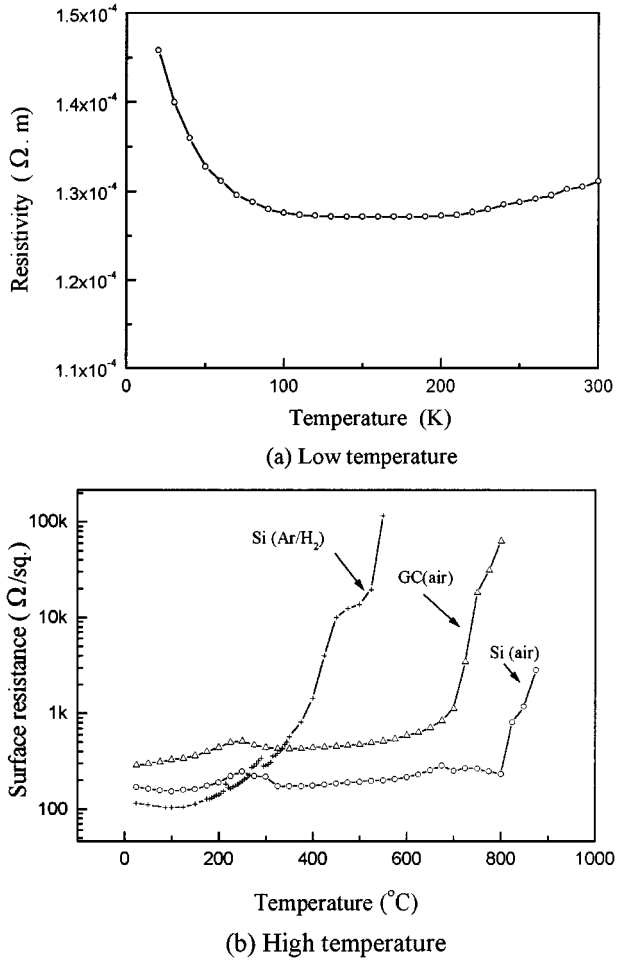

Figure 6 Temperature dependence of resistance in the LNO thin film: (a) low temperature and (b) high temperature.

The temperature dependence of the electrical resistivity was determined by a four-probe method at low temperature and a high precision digital multimeter (R6452, Japan) at high temperature. The results are shown in Fig. 6. With decreasing temperature from room temperature, the resistivity of the LNO film tends to be reduced linearly, showing good metallic behavior. The resistivity of the LNO thin film remains basically constant between100 and 200 K. Its resistivity increases below 100 K.

The resisitivity of the LNO films at high temperature in air was investigated by measuring the surface resistance of the film. The results are presented in Fig. 6b. In the high temperature range, the resistance of the LNO film increases rapidly at 800°C for the Si substrate and at 700°C for the GC substrate. This could be explained by the appearance of the NiO phase and the diffusion of the LNO film into the GC substrate as mentioned above. There is a small peak appearing at about 250°C, which still exists in reactive atmosphere (Ar/H_2). This indicates that the peak does not arise from oxygen absorption but seems to be a phase transition, which is being further investigated.

3.3. Optical property

The LNO film shows a basically flat transmittance spectrum between 345 nm and 760 nm measured (shown in Fig. 7) by a UV-visible recording spectrophotometer (UV-2100, Japan), meaning that the light beam

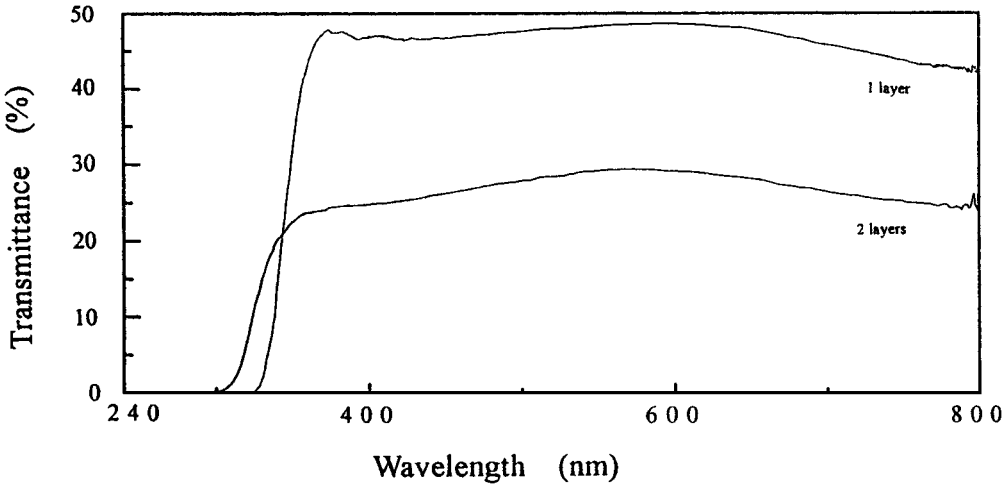

Figure 7 Transmittance spectrum of the LNO/glass.

is transmitted uniformly through glass with the LNO film, which may be used as an optical band pass filter. Moreover, the transmittance of a two-layer film is half that of a one-layer film. Adjusting the thickness of the LNO film can lead to development of a series of filters with different intensities. As the band pass filter, the LNO/glass has obvious advantages of low cost, large area, uniform, and easy adjustment of transmittance.

4. Conclusions

Dense, crack-free and uniform LNO thin films were successfully prepared by an aqueous method on a single crystal of silicon, microcrystalline of GC and amorphous glass substrates. With an increase in thermal annealing temperature, the LNO film on a Si substrate tended to transform from a pseudocubic to a rhombohedral structure along with the formation of an impure phase of NiO. On the other hand, the microstructure of the LNO film on a GC substrate showed no changes with increasing thermal annealing temperature. Instead, the LNO film was found to diffuse into the substrate at a temperature higher than 800°C. Either structure transformation or the diffusion of the film into the substrate led to an increase in the resistivity of the film. As a result, the LNO thin films with a resistivity of 2–3 $\times 10^{-5}$ Ω·m were achieved by thermally annealing at 750–800°C for 1 hour in air on Si and on GC substrates. The film resistance is basically stable in air up to 700°C. Optical measurement shows that the LNO/glass can also be used as a promising material to develop a band pass filter.

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