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Preparation and conductive properties of neodymium-doped lanthanum nickelate thin films by chemical solution deposition method

Guangheng Wu, Kaibin Ruan, Tong Liang, Xinman Chen, Dinghua Bao *

State Key Laboratory of Optoelectronic Materials and Technologies, School of Physics and Engineering, Sun Yat-Sen University, Guangzhou, 510275, PR China

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ABSTRACT

Neodymium-doped lanthanum nickelate ($La_{1-x}Nd_xNiO_3$, LNNO) thin films have been prepared on Si substrates by chemical solution deposition method. The effects of annealing temperature and the neodymium concentration on the structural and electrical properties of the thin films have been investigated. X-ray diffraction analysis showed that the LNNO thin films exhibited perovskite structure with (100) preferential orientation. The (100) orientation degree of the thin films changed with neodymium content; however, the resistivity of the thin films was not related to the degree of orientation. Field emission scanning electron microscopy observations confirmed that the films had a smooth surface and uniform thickness. The resistivity of the thin films annealed at 700 °C increased from 1.97 mΩ·cm to 5.35 mΩ·cm, with increasing neodymium doping amount from $LaNiO_3$ to $La_{0.6}Nd_{0.4}NiO_3$.

1. Introduction

Recently, ferroelectric thin films have been widely investigated for various microelectronic device applications, including non-volatile ferroelectric random access memories. These ferroelectric thin films are conventionally prepared on platinized silicon substrates to form a metal–ferroelectric–metal capacitor structure. However, it is well known that platinum (Pt) electrodes often result in electrically shorting the capacitors due to the formation of hillocks induced by large compressive stress [1]. Furthermore, most ferroelectric thin films such as $Pb(Zr,Ti)O_3$ exhibit significant polarization fatigue on Pt electrodes [2,3]. In order to solve these problems, some conductive oxide thin film materials such as RuO_2, IrO_2, $YBa_2Cu_3O_{7-\delta}$, $LaNiO_3$ (LNO), $BaPbO_3$, $SrRuO_3$ and $La_{0.5}Sr_{0.5}CoO_3$ have been investigated as promising alternatives for bottom electrodes of integrated ferroelectric devices. It has been demonstrated that conductive oxide thin films, especially those with perovskite structure, can effectively improve polarization fatigue endurance of the ferroelectric thin films [4–6]. In addition, these conductive oxide thin films used as bottom electrodes can simultaneously act as excellent seeding or buffer layers providing more nucleation sites. Therefore, they can promote perovskite phase formation and growth of subsequently deposited ferroelectric thin films due to their structural compatibility with ferroelectric films [7,8].

Our previous studies have showed that LNO thin film, one of the above-mentioned conductive oxide thin film materials with perovskite structure, can be used as good bottom electrode of ferroelectric thin films [9,10]. Meanwhile, it was also found that, in addition to using as bottom electrode for the fabrication of integrated ferroelectric devices on Si, and using as a seeding layer, promoting perovskite phase formation, LNO thin film can serve another function: suppressing the composition diffusion between ferroelectric film and bottom electrode if there is composition compatibility between them (e.g. the cases of $(Pb,La)TiO_3$ and LNO and of $(Ba,Sr)TiO_3$ and $(Ba,Sr)RuO_3$) [9]. This motivated us to carry out the research on $La_{1-x}Nd_xNiO_3$ (LNNO) thin film which can be used as bottom electrode for La and Nd co-doped bismuth titanate ($Bi_{4-x-y}La_xNd_yTi_3O_{12}$) ferroelectric thin film [11,12]. In addition, it is reasonable to expect that, $La_{1-x}Nd_xNiO_3$ thin film electrode can also mitigate the composition diffusion or decrease interfacial reactions between $Bi_{4-x-y}La_xNd_yTi_3O_{12}$ thin film and $La_{1-x}Nd_xNiO_3$ bottom electrode since both the film and the electrode contain lanthanum, neodymium, and oxygen, they can be seen to be compositionally compatible. Tiwari et al. investigated the electrical transport properties of LNNO ceramics, and good conductive properties were demonstrated clearly [13]. Kumar reported transport

* Corresponding author.
E-mail address: stsbdh@mail.sysu.edu.cn (D. Bao).

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properties of $NdNiO_3$ thin films on $LaAlO_3$ substrates [14]. So far, little work has been done to study LNNO thin films.

In this study, LNNO thin films were prepared on Si substrates by chemical solution deposition method and the effects of annealing temperature and concentration of Nd on the structural and conductive properties of the thin films have been studied.

2. Experimental procedure

For synthesizing the LNNO precursor solutions, lanthanum nitrate ($La(NO_3)_3{\cdot}6H_2O$, 99.9% in purity), neodymium nitrate ($Nd(NO_3)_3{\cdot}6H_2O$, 99.9% in purity), and nickel acetate ($Ni(OAc)_2{\cdot}4H_2O$, 98% in purity) were used as the starting materials, and 2-methoxyethanol was selected as the solvent. Lanthanum nitrate and neodymium nitrate were dissolved in 2-methoxyethanol and stirred at 115 °C for 15 min. Meanwhile, in another beaker, nickel acetate was dissolved in 2-methoxyethanol and stirred at 110 °C for 15 min. These two solutions were mixed after cooled down to 80 °C, and reheated to 115 °C and stirred for 20 min. Then the mixed solution was cooled down to 60 °C and stirred for 2.5 h. Before filtrated, the solution was stirred at room temperature for another 2.5 h. The concentration of the resulting solution was adjusted to 0.2 M.

The solution was spin-coated on (100) oriented p-Si substrates at 3500 rpm for 25 s, then the films obtained were baked at 350 °C for 5 min. The process of spin-coating and baking was repeated for 3 times before a pre-annealing at the temperature of 550 °C for 30 min in air, and then another 3 times of spin-coating and baking process was performed. Finally, the films were annealed at different temperatures in the range from 550 °C to 800 °C for 1 h in air. The thickness of the films obtained was about 300 nm.

The crystal structure of the LNNO films was characterized by X-ray diffraction (XRD, D/MAX 2000 VCP, Rigaku) using Cu K_α radiation with working current and voltage of 30 mA and 40 kV respectively. The morphology of the films was observed using a field emission scanning electron microscopy (JSM-6330F, JEOL Ltd.) with the operating voltage of 15 kV. The resistivity of the films was measured by using a standard four-point-probe technique (SX1934, Baishen Technol. Ltd.) at room temperature.

3. Results and discussion

Fig. 1 shows XRD patterns of LNO thin films annealed at the temperatures from 550 °C to 800 °C. The diffraction peaks related to the pseudocubic perovskite structure of lanthanum nickelate are observed in the patterns of the films annealed above 550 °C. No other

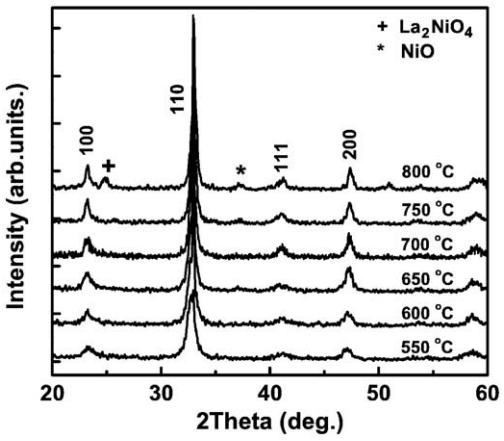

Fig. 1. XRD patterns of LNO thin films annealed at the temperatures from 550 °C to 800 °C.

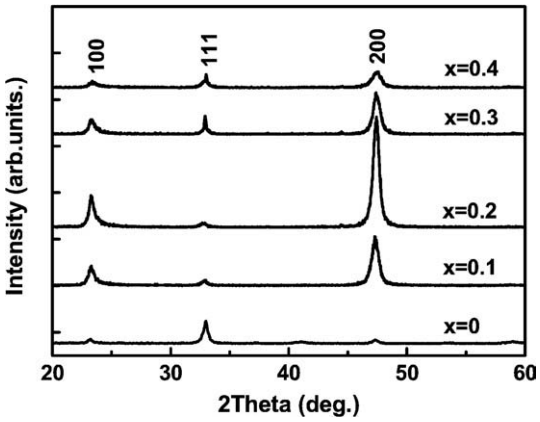

Fig. 2. XRD patterns of $La_{1-x}Nd_xNiO_3$ ($x \le 0.4$) thin films annealed at 700 °C.

peaks were observed except diffraction peaks of Si substrate and LNO thin films even at the annealing temperature of 750 °C. The (110) diffraction peaks are stronger than the others, indicating a randomly oriented growth of the thin films, due to large lattice mismatch between LNO and silicon substrate. With increasing annealing temperature, stronger peaks and decreasing full width at half maximum were observed, indicating better crystallization and larger grain size. When LNO thin film was annealed at 800 °C, there were additional peaks at 24.5°and 36°in the XRD pattern, which have been believed to be the diffraction peaks of La_2NiO_4 and NiO, respectively. This is due to decomposition of lanthanum nickelate at high temperature, which was reported by Miyake and coworkers [15]:

$$2LaNiO_3 \rightarrow La_2NiO_4 + NiO + 0.5O_2$$

Fig. 2 shows XRD patterns of $La_{1-x}Nd_xNiO_3$ ($x \le 0.4$) thin films annealed at 700 °C. All the diffraction peaks can be indexed with the standard data of LNO, implying the substitution of Nd for La without destroying the perovskite structure. With increasing neodymium concentration, all diffraction peaks shift towards higher angles, indicating decreasing lattice parameter of LNNO. This can be attributed to a smaller radius of Nd^{3+} than that of La^{3+}. It is worth noting that, instead of the strongest (110) diffraction peak of XRD patterns for LNO thin films, (200) peaks are the strongest peaks in the XRD patterns of $La_{1-x}Nd_xNiO_3$ ($0.1 \le x \le 0.4$) thin films, suggesting (100) preferentially oriented growth of the films. The (100) oriented growth may be related to lower surface energies of (100)-oriented nuclei of LNNO, and is expected to be used for controlling orientation of subsequent ferroelectric thin films deposited on them if they are used as bottom electrodes [6]. It has been reported that the (100) plane of LNO has the smallest surface energy, and could grow parallel to the substrate surface [16,17]. By comparing the relative intensity of the diffraction peaks, it can be easily observed that $La_{0.8}Nd_{0.2}NiO_3$ thin films have a higher (100) orientation degree than the others. However, further study on the variation of (100) orientation with Nd content is needed.

The surface morphologies of the LNO thin films annealed at different temperatures in the range from 550 °C to 800 °C are shown in Fig. 3. It can be seen that the grain size of the thin films increases with increasing annealing temperature. The grain size of the film annealed at 700 °C is about 100 nm. When the films were annealed at higher temperature, pores appeared in thin films, resulting in roughened surfaces. The similar surface morphology was observed in the LNNO films with different neodymium concentrations. Fig. 4 shows the surface morphologies of LNNO thin films annealed at the temperature of 700 °C. All the thin films with different neodymium concentrations exhibited smooth, uniform, and crack-free surface morphology with