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Fabrication of low-resistance $LaNi_xO_{3+\delta}$ thin films for ferroelectric device electrodes

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$LaNiO_3$ thin films with different La/Ni ratios were deposited on Si substrates by sol–gel process. The electrical resistivities of $LaNi_xO_{3+\delta}$ films with different La/Ni ratios were measured by four-probe method. $LaNi_{0.95}O_{3+\delta}$ thin film has the lowest resistivity. First-principle calculations show that $LaNi_{0.95}O_{3+\delta}$ has the largest Ni–O–Ni bond angle and the shortest Ni–O bond length, which means $LaNi_{0.95}O_{3+\delta}$ has the strongest metallic property, hence, the electrical resistivity is the lowest. Au/PZT ($PbZr_{0.52}Ti_{0.48}O_3$)/$LaNi_xO_{3+\delta}$ and Au/PZT/Pt ferroelectric capacitors were fabricated to evaluate $LaNi_xO_{3+\delta}$ as a bottom electrode. It is shown that fatigue properties of PZT films can be significantly improved by using $LaNi_xO_{3+\delta}$ instead of Pt as the bottom electrode. The *I-V* test results of PZT films show that $LaNi_{0.95}O_{3+\delta}$ as bottom electrode can reduce the threshold voltages of PZT films, suggesting that La/Ni ratio in $LaNi_xO_{3+\delta}$ has a large influence on the film properties.

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1. Introduction

$LaNiO_3$ (LNO) is an intrinsically conductive oxide material with a perovskite type structure. Due to its electric,[1,2] magnetic[3] and optical[4] properties, LNO has been studied by many researchers as potentially widely-used material. LNO exhibits low resistivity over a wide temperature range,[5–7] which makes it an important candidate for the electrode of ferroelectric devices.[8,9] Since oxygen vacancies in the ferroelectric films can be compensated by LNO in fatigue process, LNO can be used as an oxide electrode to avoid fatigue in ferroelectric films.[10] LNO has been proven to be the suitable electrode to improve the fatigue and aging properties for many different ferroelectrics, such as $PbTiO_3$(PTO), Pb(Zr, Ti)O_3 (PZT), (Pb, La) (Zr, Ti)O_3 (PLZT) and $BaTiO_3$(BTO) films. In addition, LNO also has tremendous potential to be used in developing colossal magneto resistance materials,[11] solid oxide fuel cells[12] and high temperature superconductors.[13,14]

The perovskite structure of LNO is rhombohedrally distorted with a pseudocubic lattice parameter of 0.384 nm (space group $R\bar{3}c$)[15] which matches well with the unit cells of several common superconductors and ferroelectrics, allowing epitaxial growth of these perovskites on LNO substrate. A number of methods have been employed to prepare LNO thin films. In order to get LNO films with good properties on different substrates, physical methods, such as pulsed laser deposition,[16] RF-sputtering[17] and mist plasma evaporation[18] are all good choices, but these methods need complicated techniques and extreme experimental conditions. Some chemical methods such as chemical vapor deposition,[19,20] metallo-organic chemical vapor deposition[21–23] also have the same issues. Compared with these methods, chemical solution deposition like sol–gel process is a simple and versatile alternative for thin film preparation. This process does not require a high vacuum environment and thus provides a fast and low-cost method for producing LNO thin films.[24–26] Moreover, it offers good stoichiometric control for mixed oxides.

In order to obtain LNO films with lower resistivity, researchers have done a lot of experiments to optimize the production process of LNO films. On the other side, in many literature researchers have studied the factors that affect the resistivity of LNO. Several groups have investigated the oxygen content-dependent conductivity for LNO films. With the loss of the O^{2-} content, the metallic $LaNiO_3$ resulted in a semiconducting $LaNiO_{2.75}$ and then an insulating $LaNiO_{2.5}$. Then this MIT (metal-insulator transition) was followed by another insulator to semiconductor transition, as the O^{2-} content was further reduced from 2.5 to 2, responding to the

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semiconducting $LaNiO_2$.[27] The observed behavior was explained based on a model positing that $LaNiO_3$ was a charge-transfer metal,[28,29] whereby the interplay between the bandwidths and the energy gaps of the O 2p and Ni 3d bands determines the conductivity.

LNO film is an important electrode material with low resistivity. Many theses on the study of PZT films with LNO electrode have been carried out because of the much more similarity in lattice parameters, and better ferroelectricity was obtained.[30–32] In those studies, researchers only explored the effect of O content on the performance of LNO thin films, we would like to further investigate the differences in the performance of LNO films with different La/Ni ratios. On the basis of past research, we explored if the La/Ni ratio could affect the resistivity of LNO films. Few literature have mentioned the research in this area. In the present study, $LaNi_xO_{3+\delta}$ thin films with different La/Ni ratios were prepared directly on Si(100) substrates by sol–gel method using spin-coating technique. The range of La/Ni ratio was controlled in a relatively narrow range around 1/1, so that it would not have a fundamental effect on the structure of LNO. The electrical resistivity of $LaNi_xO_{3+\delta}$ was measured by four probe method. We found that $LaNi_xO_{3+\delta}$ thin films had the lowest electric resistivity when the La/Ni ratio was 1:0.95. Then first-principles method was used to calculate the crystal structure and density of states of $LaNi_xO_{3+\delta}$ to demonstrate the mechanism of electrical resistivity change. Although the theoretical calculation of $LaNi_xO_{3+\delta}$ of different La/Ni ratios were based on the crystal cells, the results were equally applicable to films. In the end, the ferroelectric properties and nonlinear current–voltage characteristics of $Pb(Zr_{0.52}Ti_{0.48})O_3$(PZT) films deposited on the $LaNi_xO_{3+\delta}$ film were investigated, PZT films were also deposited on Pt bottom electrode as comparisons. The Au (2-mm diameter) top electrode was deposited by sputtering through a mask onto the PZT film surfaces.

2. Experimental

Sol–gel method was used to prepare LNO films. The sol–gel method has a set of procedures, including preparation of solution, spinning, drying and annealing. Lanthanum nitrate [$La(NO_3)_3\cdot 6H_2O$] and nickel nitrate [$Ni(NO_3)_3\cdot 3H_2O$] were used as starting materials. The starting materials were mixed in a molar ratio of La/Ni = 1/0.8, 1/0.85, 1/0.9, 1/0.95, 1/1, 1/1.1 and 1/1.2 corresponding to LNO of different La/Ni ratios, which were named as $LN_{0.8}O$, $LN_{0.85}O$, $LN_{0.9}O$, $LN_{0.95}O$, LNO, $LN_{1.1}O$ and $LN_{1.2}O$, respectively. The mixed materials were dissolved into 2-methoxyethanol (2-MOE) solvent at room temperature. To avoid cracking during heat treatment and to adjust the viscosity of the solution, an appropriate volume of ethanolamine was added to the system. All chemicals used were analytical reagent. The solutions were stirred at room temperature for 2 h. The concentrations of these solutions were adjusted to 0.2 mol/L by adding an appropriate volume of 2-MOE solvent. The whole sol–gel preparation process was performed at an ambient atmosphere. For $Pb(Zr_{0.52}Ti_{0.48})O_3$ films, the preparation of precursor solution was reported elsewhere.[33]

After the preparation of solution, spinning, drying and annealing are required. The substrates we used were the (100) n-type silicon wafers. The precursor solution was spin-coated onto Si (100) substrates at 4000 r/min for 30 s in air. After each coating, the films were pyrolyzed at 300 °C for 5 min on a hot plate to remove the residual organic compounds. This process was repeated several times to obtain the desired film thickness. The following annealing was carried out at 600, 650, 700 and 750 °C, respectively, for 1 h in a muffle furnace for final crystallization. PZT thin films (about 400 nm) were deposited onto $LaNi_xO_{3+\delta}$ thin films prepared on Si(100) substrates. For comparison, PZT films of equal thickness were deposited on Pt(111)/Ti/SiO_2/Si(100) substrates. The crystallographic characteristics of the $LaNi_xO_{3+\delta}$ films were analyzed by an X-ray diffractometer (XRD, Rigaku D/MAX-2500) with Cu Kα radiation source, and surface morphologies were characterized by field emission scanning electron microscopy (FESEM, ZEISS MERLIN Compact). The resistivity of $LaNi_xO_{3+\delta}$ films was measured using standard four-point-probe technique. The ferroelectric and fatigue properties of PZT films were evaluated using a ferroelectric material parameter tester with a UNI-TUTD2052CL oscilloscope. The remnant polarization P_r and coercive field E_c were determined from the P-E hysteresis loops. The I–V relationship of PZT films was measured using a semiconductor parameter analyzer (Keithley 4200-SCS) with two tungsten microprobes, the detailed testing process was described elsewhere.[34]

3. Results and discussion

3.1. Experimental results

Fig. 1 shows the XRD results for the $LaNi_xO_{3+\delta}$ thin films deposited on Si substrates annealed at 650 °C. It was suggested that the formation of $LaNiO_3$ started at/above 500 °C according to TG/DTA curve,[35] 650 °C is high enough for the formation of $LaNiO_3$. From Fig. 1 we can see that the three main diffraction peaks can be indexed as (110), (200), and (211), respectively. It can be seen that all the films are perovskite. The peaks were indexed as a rhombohedral distorted perovskite structure, space group symmetry $R\bar{3}c$.

The surface morphologies of $LaNi_xO_{3+\delta}$ films are shown in Fig. 2, in which Fig. 2(a–d) correspond to x = 0.8, 0.95, 1 and 1.1 annealed at 650 °C and Fig. 2(e–h) correspond to $LN_{0.95}O$ annealed at 600, 650, 700 and 750 °C. It can be seen that when the annealing temperature is below 750 °C, the surfaces are crack-free with a few pores, which might be due to the volatilization and decomposition of organic compounds during the heat treatment. The size of round-shaped grain is in the range from 50 to 75 nm, when the annealing temperature is 750 °C, there are many cracks in the film, so the annealing temperature was kept below 750 °C. As shown in Fig. 2(a–d), La/Ni ratio has little influence on the morphologies of the films.

Fig. 3 shows a plot of resistivity of the $LaNi_xO_{3+\delta}$ films measured at room temperature as a function of La/Ni ratio annealed at different temperatures. As the La/Ni ratio increased, the corresponding resistivity decreased first and then increased. No matter what the annealing temperature is, the lowest resistivity appears when the La/Ni ratio is 1:0.95. Besides, no matter what the La/Ni ratio is, the higher the annealing temperature, the lower the

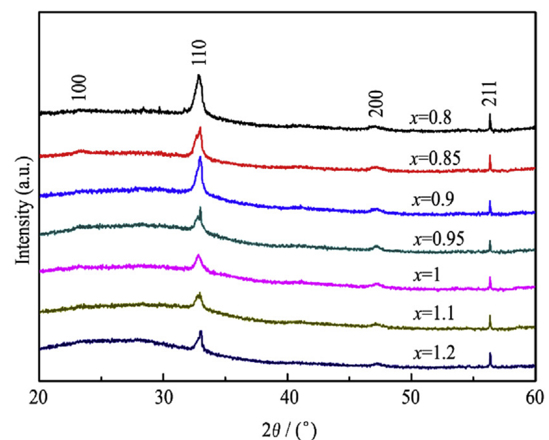

Fig. 1. XRD patterns of $LaNi_xO_{3+\delta}$ films on Si substrates annealed at 650 °C.

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