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Conductive-perovskite $LaNiO_3$ thin films prepared by using solution process for electrode application

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Abstract: Lanthanum nickel oxide $LaNiO_3$ (LNO) is extensively known as one of typical perovskite-structured materials with metallic conductivity, which is suitable for the electrode application in electronic devices such as transistors or solar cells. Since LNO is a low-cost material and a simple fabrication process, it has been attracted much attention for commercialization. In this paper, we have focused on optimizing the fabrication process of LNO thin films on SiO_2/Si substrate and Al foil by using a solution process. The crystal structure and surface morphology were characterized by using X-ray diffraction and field-emission scanning electron microscopy (FE-SEM), respectively. It was found that the LNO thin films annealed in range of 550-700°C for 30 minutes exhibited a well-formed crystallization and a dense microstructure. According to the SEM cross-sectional observation, the thickness of LNO thin films was estimated about 80 nm. Also, from the four-probe measurement method, the electrical resistivity of LNO thin film annealed at 600°C had a minimum value of 0.42 × 10^{-2} Ωcm, which was possibly comparable to conventional conductive oxides. As a result, the capacitor using $Pb_{1.2}(Zr_{0.4}Ti_{0.6})O_3$ ferroelectric layer annealed at 600°C and LNO bottom electrode provided an interesting ferroelectricity, which included a remnant polarization of 21 μC/cm^2 and a saturated polarization of 35 μC/cm^2. Moreover, the leakage current density was lower than 2 × 10^{-5} A/cm^2.

Keywords: LNO, conductive perovskite, solution process, ferroelectric, PZT.

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1. Introduction

In recent years, conductive thin film with perovskite structure like $LaNiO_3$ (abbreviated as LNO) has been conducted and developed for the potential application of electronic devices [1-3]. Generally, ITO (indium tin oxide) and FTO (fluorine doped tin oxide) were used as a window electrode in optoelectric devices. However, using ITO electrode has a critical limitation owing to the scarcity of indium element on the earth, and the transmission in the near-infrared region, as well as the deflection of FTO structure normally leads to a high leakage current. In addition, the ITO and FTO fabrication processes require a complicated technology and make products expensive. Towards the dramatic development of electrode-fabrication technologies, LNO has been considered due to several benefits. Firstly, LNO is a stable material and a low-cost starting resource, because it only consists of cheap elements such as La and Ni [4,5]. Secondly, LNO plays an important role as a seed for the growth of $Pb_{1.2}(Zr_{0.4}Ti_{0.6})O_3$ (PZT) thin film, because they are similar in perovskite crystal structure. That is, the ferroelectric layer would have the better performances and inherit the electron configuration of LNO layer, which is essential for homologous growth [6-8]. Thirdly, LNO layer is inserted between PZT layer and Al foil to avoid a diffusion of Al into PZT layer during crystallization process, and ensure an adequate contact without formation of Al_2O_3 insulating oxide layer at the bottom electrode of ferroelectric devices [9-11].

In this work, the LNO thin films have been fabricated on SiO_2/Si substrate and Al foil by using a solution process in a viewpoint of simple technique with less-consumed materials and energies. In sequence, we examine systematically on the change of crystal structure, observe surface morphology and cross section, and measure electrical properties, then apply the LNO thin films for the bottom electrode in fabrication of a ferroelectric capacitor. Ferroelectric behavior of PZT thin film has been investigated to get a clear evidence for the use of LNO bottom electrode.

2. Experimental procedures

First of all, SiO_2/Si substrate and Al foil were, in turn, cleaned by using organic solvent and deionized water in combination with ultrasonic cleaner. Next, the LNO precursor solution was uniformly dropped on the surface of SiO_2/Si substrate and Al foil, then spin-coated with a buffer speed of 500 rpm for 6 seconds and a stable speed of 2500 rpm for 30 seconds to create LNO film layer expected. After that, LNO film layer was dried on a hot plate at 150°C for 1 minute, and at 250°C for 5 minutes to promote the LNO film layer from the solution to the gel or amorphous states. One notes that the spin-coated process was repeated for several times, depending on the desirable thickness. Finally, the LNO film layer was crystallized in oxygen atmosphere with a flow rate of 0.2 l/min, at diverse temperatures such as 550-700°C on SiO_2/Si substrate, and 500-650°C on Al foil. Crystal structure and surface morphology of LNO film layer were investigated by using X-ray diffraction system (Bruker D5005, Germany) and scanning electron microscope (NOVA NANOSEM 450, USA). It is a notice that a small-angle scanning was used to characterize crystalline properties of thin films. In order to evaluate potential application of LNO, we fabricated a structure of ferroelectric capacitor as sketched in Fig. 1. In this structure, the PZT film thickness of about 200 nm was formed at the annealing temperature of 600°C under a solution process. The 100-nm thick Pt thin film as a top electrode was deposited by means of a sputtering system (BOC Edward model FL500, England), and the circle dots were patterned with the diameters of 100, 200 and 500 μm via metal masks. Ferroelectric hysteresis loop and leakage-current density of the PZT thin film were characterized by Radiant Precision LC 10 system, USA.

3. Results and discussion

Figures 2 (a) and (b) point out the crystal structure of LNO thin films deposited on SiO_2/Si substrate and Al foil, respectively. The obtained results reveal that the LNO thin films mainly

orient along with (100), (110), (200), and (211) planes when deposited on SiO_2/Si substrate; and (110), (111) and (200) planes when deposited on Al foil. In other words, the LNO thin films fabricated are polycrystalline, which are in contrast with those orientated solely with (h00) on YSZ (100) substrate, according to the previous research [12]. In this study, one can be achieved that the crystallization of LNO thin films has started even below 550°C, when fabricating on SiO_2/Si substrate, but it is around 600°C when fabricating on Al foil. Although the LNO thin film deposited on Al foil has a bit higher crystallization temperature comparing with that on SiO_2/Si substrate, it is almost a single phase of perovskite without any La_2O_3 phase, which basically leads to enhance conductivity of the bottom electrode. The optimum range of annealing temperature between 600°C and 650°C is relatively matched with another report [13], and it is acceptable to avoid any unexpected thermal deformation of Al foil. Herein, we take a note that it is difficult to extract the electrical conductivity of LNO thin film, because the Al foil is conductive, and unable to separate electrical signals between the LNO film layer and the substrate. Therefore, preparing LNO thin film on an insulating substance like SiO_2/Si substrate is necessary for four-probe measurement method. From this point of view, the cross-sectional SEM image of LNO thin film fabricated on SiO_2/Si substrate was conducted as shown in Fig. 3. It is obvious that LNO thin film has not any cracks and porous spaces. Also, the thickness of LNO film layer is determined to be approximately 80 nm. Consequentially, the electrical resistivity could be normalized with the sheet resistance to choose high-quality LNO thin films accompanying XRD results and SEM observation.

The resistivity of LNO thin films versus annealing temperature was studied by using four-probe measurement method, as plotted in Fig. 4. From this figure, we can recognize that the resistivity decreases with increasing the annealing temperature varied from 550°C to 600°C, but it increases with the increase in annealing temperature from 600°C to 700°C. That is, the

annealing temperature of 600ºC for the LNO thin film is optimum to obtain the highest conductivity, corresponding to the minimum resistivity of 0.42 × 10^{-2} Ωcm. Taking into account the structural analysis, the cross section observation and the electrical investigation, it is concluded that LNO film layer on Al foil annealed at 600ºC would be favorable for the bottom electrode application in fabricating ferroelectric capacitors or memories. Using the LNO thin film optimized (crystallized at 600ºC), PZT thin films were stacked on it, by a solution-process method, as drawn in Fig. 1. XRD patterns of PZT thin films annealed at various temperatures of 575ºC, 600ºC and 625ºC for 15 minutes, on the 600ºC LNO bottom electrode, were shown in Fig. 5 (a). One can be seen that the PZT thin films annealed at 600ºC and 625ºC have a single phase of perovskite structure, and polycrystalline orientations such as (100), (110), (111), (200), (210), and (211). Besides, PbO phase is still existed for the PZT thin film annealed at 575ºC, which reduces strongly ferroelectric behavior and enhances unexpected leakage current. Hence, annealing the PZT thin film at 600ºC should be selected to ensure its high-crystalline quality and no deformation of Al foil. Figure 5(b) indicates the surface of PZT thin film on LNO/Al foil annealed at 600ºC, where it behaves a smooth morphology in large scale, and a clear boundary with grain sizes ranged from 10-100 nm (see the inset of Fig. 5(b)), even though growing on a rough surface and flexible substrate like Al foil. It means that Al foil is actually promising to replace traditional Si substrate, reduce production cost and devices weight, but keeping the same film quality.

After sputtering circle dots of Pt with different diameters ranged in 100-500 μm, the ferroelectric property of PZT thin films annealed at 600ºC was evaluated as shown in Fig. 6. As mentioned above, the capacitor structure is Pt/PZT/LNO/Al, whose Al foil is 50 μm in thickness. From Fig. 6(a), it is clearly obtained that the 600ºC PZT thin film possesses a ferroelectric nature, of which the hysteresis loops have a high symmetry, a high remnant polarization of about 21 μC/cm^2, and a saturated polarization of around 35 μC/cm^2.

Comparing to the work reported before, the remnant polarization of PZT thin film on LNO/STO substrate fabricated by an epitaxial method was as high as 30 μC/cm^2, but the hysteresis loops were not saturated, and using an expensive single-crystal substrate [11]. In our case, the remnant polarization obtained is higher than the value of 18.2 μC/cm^2, as reported on LNO/Si substrate [14]. Other groups have also reported that the remnant polarizations were about 19.2 μC/cm^2 and 13.2 μC/cm^2 when the PZT thin films deposited on LNO/poly-Si/titanium nitride (TiN)/SiO_2/Si wafer and LNO/SiO_2/Si substrate, respectively [15,16]. Thus, it should be convinced that the PZT thin film deposited on LNO/Al foil at the annealing temperature of 600ºC possesses high remnant polarization enough for application of ferroelectric devices. This result might come from the high crystallization of both LNO electrode and PZT thin film annealed at the temperature of 600ºC, and the smooth LNO surface, as observed from Fig. 2, Fig. 3 and Fig. 5. As for the optimum ferroelectric capacitor processed at 600ºC, the leakage-current density was determined to be lower than 2 × 10^{-5} A/cm^2, as shown in Fig. 6 (b), corresponding to the voltage less than 10 V, or the electric field less than 500 kV/cm applied on the 200-nm-thick PZT film. This achievement is practically supported to a lower power consumption, while the electric devices operate in a rest or off state.

4. Conclusion

Under a solution process, the 80-nm thick LNO thin film was successfully fabricated on SiO_2/Si substrate or Al foil. XRD patterns show that the LNO thin films formed with a single perovskite phase for annealing temperature over 550ºC. In particular, the preferred orientations of LNO thin films are (100), (110), (200), and (211) for depositing on SiO_2/Si substrate, and (110), (111) and (200) for depositing on Al foil. SEM image evidences the LNO thin film surface at 600ºC having not any cracks. The sheet resistance of LNO thin film was as low as 0.42 × 10^{-2} Ωcm. Using LNO/Al foil as a bottom electrode, the PZT thin film

grown in a single phase with clear grains. As a result, Pt/PZT/LNO/Al ferroelectric capacitor with PZT thin films crystallized at 600ºC gives a remnant polarization of 21 μC/cm^2, and a leakage current density of 2 × 10^{-5} A/cm^2 when the electric field below 500 kV/cm applied. The successful fabrication on Al foil would contribute to reduce the total weight of electronic devices, and open variously the selection of substrates for flexible display panels.

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Figures caption

Figure 1. Sketch of ferroelectric capacitor using LNO as a bottom electrode.

Figure 2. XRD patterns of LNO thin films deposited on: (a) SiO_2/Si substrate and (b) Al foil annealed at different temperatures.

Figure 3. Cross-sectional SEM image of LNO thin film annealed at 600ºC, fabricated on SiO_2/Si substrate.

Figure 4. Dependence of resistivity on annealing temperature for $LaNiO_3$ thin films fabricated on SiO_2/Si substrates.

Figure 5. (a) XRD patterns and (b) top-view SEM image of PZT thin films fabricated on LNO/Al foil.

Figure 6. (a) Hysteresis loops and (b) leakage current characteristic of ferroelectric capacitor with Pt/PZT/LNO/Al foil structure.

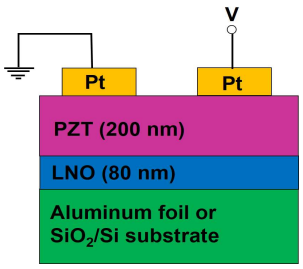

Figure 1

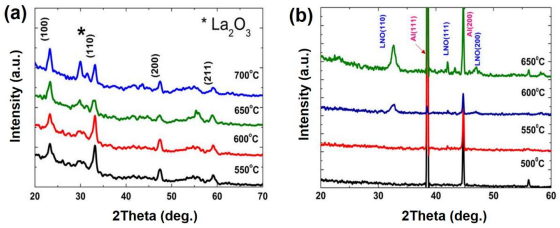

Figure 2

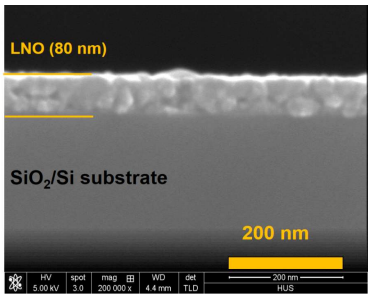

Figure 3

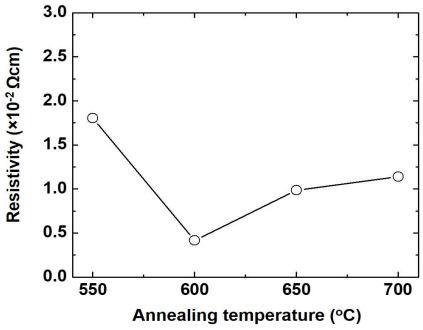

Figure 4

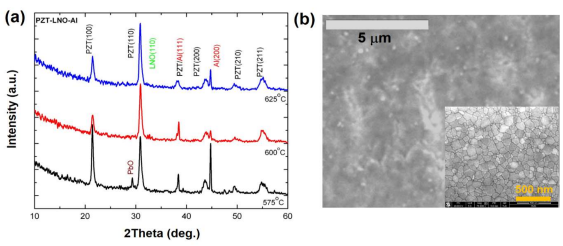

Figure 5

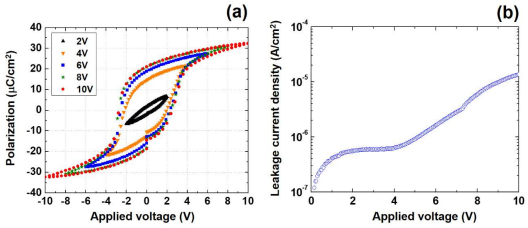

Figure 6