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Metal-organic chemical liquid deposited (1 1 0)-preferred $LaNiO_3$ buffer layer for $Pb_{0.97}La_{0.02}(Zr_{0.85}Sn_{0.13}Ti_{0.02})O_3$ antiferroelectric films

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Abstract

Conductive perovskite lanthanum nickelate $LaNiO_3$ (LNO) thin films were fabricated on SiO_2/Si substrates through metal-organic chemical liquid deposition method. The effect of annealing temperature on the orientation and sheet resistance of the LNO films were investigated. XRD patterns showed that the LNO films deposited on SiO_2/Si substrates exhibited preferred-(1 1 0) orientation. The lowest sheet resistance of the LNO thin films, 250 Ω/□ was obtained after being annealed at 650 °C for 1 h. Subsequently, $Pb_{0.97}La_{0.02}(Zr_{0.85}Sn_{0.13}Ti_{0.02})O_3$ (PLZST) antiferroelectric thin films were prepared on the $LaNiO_3$ buffered SiO_2/Si substrates via sol–gel process. And the crystallinity, microstructure and electric properties of the PLZST thin films were studied in details.

Keywords: Antiferroelectric thin films; Electric property; $LaNiO_3$; PLZST

1. Introduction

Since 1990s, antiferroelectric thin films, such as $PbZrO_3$ [1], $(Pb,La)(Zr,Sn,Ti)O_3$ [2] and $(Pb,Nb)(Zr,Sn,Ti)O_3$ [3], have been studied extensively for their potential usage in integrated ferroelectric system due to their remarkable change of polarization and strain, which were caused by phase transformation between antiferroelectric (AFE) and ferroelectric (FE) state under electric field. But ferroelectric and antiferroelectric thin films on Pt or Au bottom electrode often expressed bad properties, such as poor polarization fatigue, because of oxygen deficiency of the perovskite materials [4]. In order to resolve above problem and improve the properties of the antiferroelectric and ferroelectric thin films, conductive perovskite metal oxide thin films, such as $BaPbO_3$, $SrRuO_3$, $YbaCuO_3$, $LaSrMnO_3$, $LaSrCoO_3$ and $LaNiO_3$ (LNO) [5], were introduced as buffer layers to improve electric properties. Zhai et al. [3] had obtained improved electric fatigue PNZST antiferroelectric thin films on LNO buffered Pt/Ti/SiO_2/Si substrates. Except for as bottom electrode, these perovskite oxide thin films have following two functions [6]. One is used as a seed layer, promoting perovskite phase formation at lower temperature for their structural compatibility with antiferroelectric and ferroelectric films. The other is to suppress the composition diffusion between films and substrates.

Among these perovskite-type metal oxides thin films, $LaNiO_3$ was the most potential electrode material for ferroelectric application because of moderate crystal lattice constant (a = 0.384 nm), low receptivity and good metallic conductivity [5]. There were some papers [7,8] on deposition PZT ferroelectric thin films on LNO buffered SiO_2/Si substrates. But up to now antiferroelectric films grown on LNO/SiO_2/Si substrates are not reported. So in this investigation, (1 1 0)-oriented $LaNiO_3$ was fabricated on SiO_2/Si substrates by metal-organic chemical liquid deposition method. Then for the first time using a novel and cheaper tin source, dibutyloxide of tin, as raw material, $Pb_{0.97}La_{0.02}Zr_{0.85}Sn_{0.13}Ti_{0.02}O_3$ (PLZST) antiferroelectric thin films were deposited on the LNO-buffered SiO_2/Si substrates through sol–gel process. And dielectric properties of the PLZST thin films were studied as functions of frequency, electric field and temperature.

2. Experimental procedure

For LNO films, the starting materials were lanthanum acetate [$La(CH_3COO)_3$], and nickel acetate [$Ni(CH_3COO)_3{\cdot}4H_2O$]. The starting materials were mixed with a mole

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ratio of La:Ni = 1:1 and mixed in acetate acid and deion water (CH_3COOH and H_2O with a volume ratio of 5:1) at 105 °C for 1 h. The concentration of the LNO precursor solution was 0.1 M. The solution was spin-coated on SiO_2/Si substrates at 3000 rpm for 20 s. Then the wet films were heat-treated at 450 °C for 20 min. This procedure was repeated 15 times. Finally, the LNO films were annealed at 600, 650, 700 and 750 °C, respectively, to obtain well-crystallized structure. And the final thickness of the LNO layers was about 150 nm.

$Pb_{0.97}La_{0.02}Zr_{0.85}Sn_{0.13}Ti_{0.02}O_3$ (PLZST) antiferroelectric thin films were prepared from raw materials lead acetate trihydrate [$Pb(CH_3COO)_2{\cdot}3H_2O$], lanthanum acetate [$La(CH_3COO)_3$], zirconium propoxide [$Zr(OC_3H_7)_4$], titanium isopropoxide [$Ti[OCH(CH_3)_2]_4$] and dibutyloxide of tin [$(H_9C_4)_2SnO$]. Acetate was selected as a solvent. At first, lead acetate trihydrate, dibutyloxide of tin, lanthanum acetate hydrate and acetic acid were mixed in a ratio according to the predetermined number. In order to compensate Pb loss during annealing and prevent the formation of pyrochloren phase, 10% excess lead was added. The mixed solution was distilled at 110 °C for 1 h to remove water. When the mixed solution was cooled to room temperature zirconium propoxide and titanium isopropoxide were added and mixed for 30 min. During the mixing process distilled water was added in the proportion of 20 moles of distilled water to 1 mole of lead to stabilize the solution. Finally, the solution was adjusted to 0.3 M using the propanol. The addition of propanol lowered the surface tension of the solution and could improve the wettability of the solution. Then PLZST films were grown on LNO buffered SiO_2/Si substrates also by spin-coating method. Each PLZST layer was spin coated at 3000 rpm for 20 s and pyrolyzed at 450 °C for 10 min. The spin coating and heat-treatment were repeated several times to obtain desired thickness. At last the films went through a final anneal at 650 °C for 30 min to form the perovskite phase. The final thickness of the thin films was about 350 nm. Gold pads of 0.50 mm in diameter were coated on the film surface as top electrodes by dc sputtering.

The X-ray diffraction (XRD) patterns of the LNO and PLZST films were obtained using a Bruker D8 advance diffractometer. The sheet resistance of LNO was characterized by a standard four-point-probe technique. The microstructure of the PLZST was examined though scanning electron microscopy (SEM). The field-induced hysteresis loops of the PLZST thin films were measured by a modified Sawyer–Tower circuit. The temperature and field dependent dielectric properties of the antiferroelectric films were measured using an Agilent 4284A *LCR* meter.

3. Results and discussion

XRD patterns of LNO thin films on SiO_2/Si substrates annealed at 600, 650, 700 and 750 °C, respectively, were shown in Fig. 1. It can be seen that LNO thin films exhibited a single perovskite phase with preferred-(1 1 0) orientation. The result is similar to Bao's report [6]. But Wang [5] obtained (1 0 0)-orientated LNO thin films on Si and SiO_2/Si substrates. These may be leaded by the different pyrolysis process. Bao took the

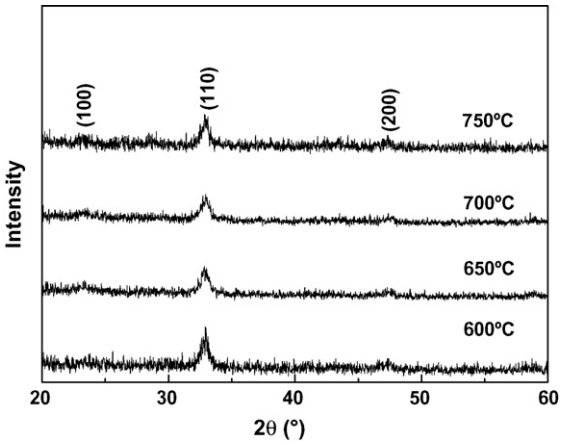

Fig. 1. XRD patterns of LNO thin films grown on SiO_2/Si substrates, annealed at different temperature for 1 h.

similar heat treatment method with our, while Wang adopted a three-steep anneal process. In order to compare the orientation of LNO films annealed under different temperature in details, the (1 1 0)-orientation factor (F) was described by the diffraction intensity ratio of the (1 1 0) peak to the (1 1 0) and (2 0 0) peaks [7]:

$$F = \frac{I_{(110)}}{I_{(200)} + I_{(110)}}$$

It can be found in Fig. 2 that the (1 1 0)-orientation factor declined from 0.777 to 0.680 with the annealing temperature increasing from 550 to 750 °C. This may be explained that higher heat-treatment temperature improved the growth of LNO along (2 0 0)-orientation.

The sheet resistance of the LNO thin films annealed under different temperature were shown in Fig. 2. The minimum sheet resistance value, 250 Ω/□, was obtained after LNO films heat-treated at 650 °C for 1 h, which was very close to the pervious report [4]. Because of its lowest sheet resistance and comparatively higher (1 1 0)-orientation, LNO films grown at 650 °C for 1 h were taken as the buffer layer for fabrication PLZST films.

Fig. 3 shows the X-ray diffraction pattern of the PLZST after being annealed at 650 °C for 30 min with LNO buffer layer,

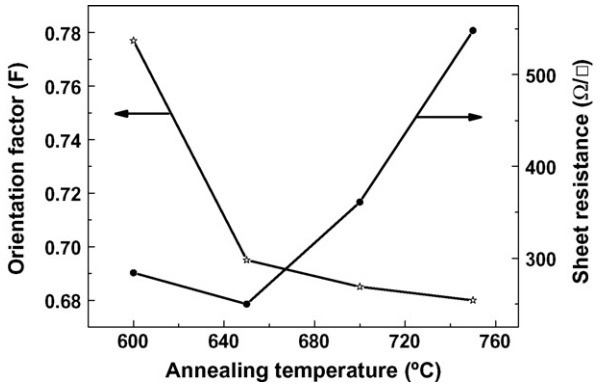

Fig. 2. The XRD peak relatively orientation factor (F) and sheet resistance of the LNO thin films annealed at 600, 650, 700 and 750 °C for 1 h, respectively.

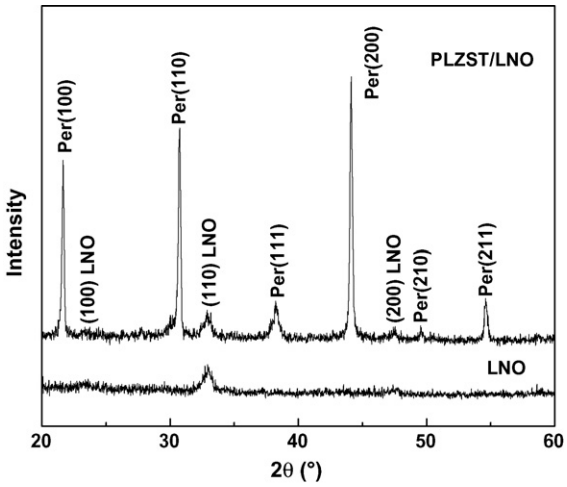

Fig. 3. XRD pattern of PLZST thin films deposited LNO/SiO_2/Si substrates annealed at 650 °C for 30 min.

which displayed a polycrystalline structure and manifested the (1 0 0), (1 1 0), (1 1 1), (2 0 0), (2 1 0) and (2 1 1) peaks. But the diffraction intensity was higher along (1 0 0), (1 1 0) and (2 0 0) directions, which were correspond to the only three appeared peaks in LNO films, as shown in Fig. 1. So it is obviously that the structure of PLZST films was affected heavily by the bottom electrode LNO. In pervious reports, PLZST deposited on Pt/Ti/SiO2/Si substrates directly often needed annealing at 700 °C in order to obtain good perovskite structure. But in present work, PLZST films with LNO buffer layer have been crystallized well after heat-treated at 650 °C for 30 min. Therefore, the LNO buffer layer in present work also mainly took the following two functions. The first was as bottom electrode. The second was to decrease the crystallization temperature.

The scanning electron microscopy (SEM) of the PLZST films with LNO buffer layer was given in Fig. 4. It can be seen that the films were consisted by round light-colored regions and dark regions. And energy-dispersive spectroscopy (EDS) examination revealed that the round light-colored regions were rich in Pb and the dark regions were deficient in Pb. The

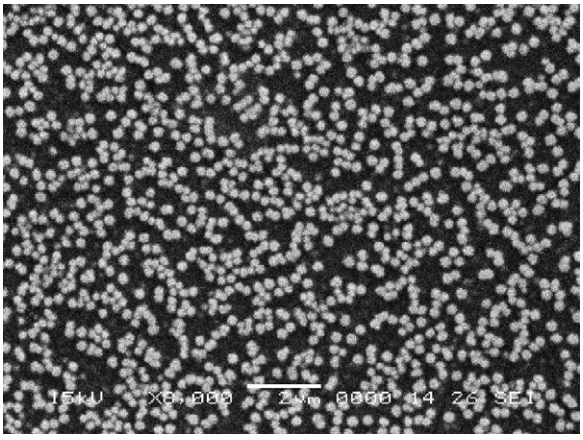

Fig. 4. SEM micrograph of PLZST on LNO/SiO_2/Si substrates annealed at 650 °C for 30 min.

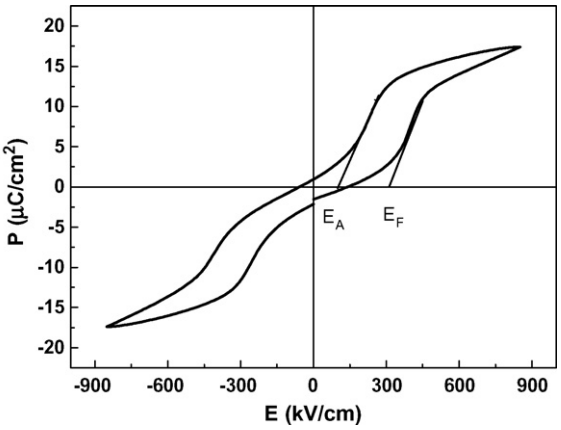

Fig. 5. The hysteresis loops of PLZST thin films grown on LNO/SiO_2/Si substrates.

similar microstructure and results were also gotten by Ebru and Pintilie in PZ and PZT thin films [1]. It was believed that the formation of this kind of structure was duo to the heterogeneous nucleation of the perovskite phase in the films. Ebru thought that the crystallization of the perovskite phase was started at numerous Pb-rich points.

The *P* (polarization)–*E* (electric field) curves of the PLZST films on LNO buffered substrates were given in Fig. 5. The double loops demonstrated the antiferroelectric nature of PLZST thin films and its field-induced transition into the ferroelectric phase. With the electric field adding and monishing, the polarization also showed a gradual increasing and decreasing, indicating a diffused phase switching between AFE and FE phases. Under maximum applied field LNO buffered PLZST films on SiO_2/Si substrates demonstrated a slanted hysteresis loop with diffusing phase switching, and a maximum polarization of 18 μC/cm^2. The switching fields were determined by extrapolating the two steepest sections of the hysteresis loops and obtaining their intersections with the horizontal axis. The forward (AFE-to-FE) phase switching field E_F and backward (FE-to-AFE) phase switching field E_A were 311 and 102 kV/cm, respectively.

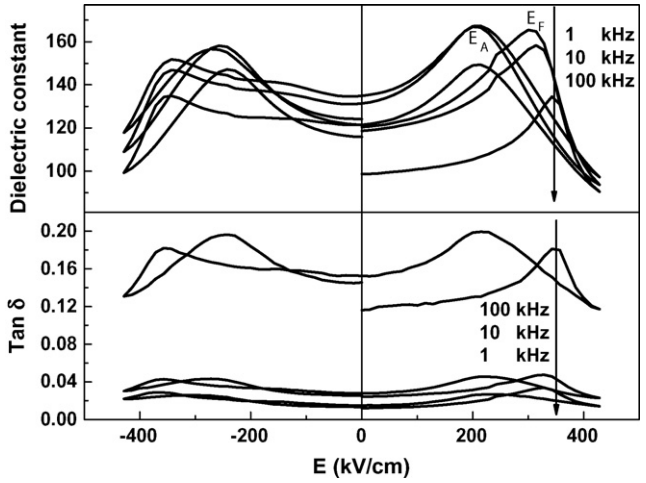

Fig. 6. Dielectric constant and dielectric loss of the PLZST films as a function of dc voltage at 1, 10 and 100 kHz.

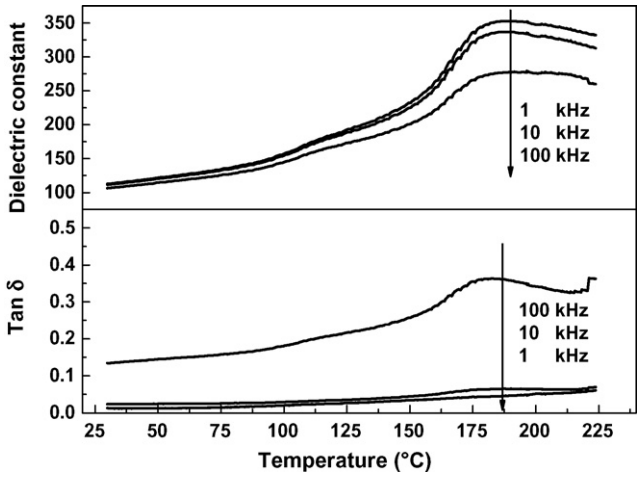

Fig. 7. Temperature dependence of the dielectric constant and dielectric loss of PLZST thin films derived on LNO/SiO_2/Si substrates at 1, 10 and 100 kHz, respectively.

The dielectric constant and dielectric loss of PLZST thin films deposition on the LNO buffered substrates were measured as a function of a slowly varying dc bias applied field at 1, 10 and 100 kHz, respectively. As shown in Fig. 6, with the frequency adding, the dielectric constant of the PLZST films declined slighted, but dielectric loss rose greatly. Ferroelectric films deposited on sol–gel derived LNO electrode on Si and SiO_2/Si directly, often suffered a larger dielectric loss under higher frequency [6]. It was supposed that LNO electrode have larger resistance comparing with Pt electrode and the detailed reason was under study. The magnitude of the phase switching fields of PLZST films can also be determined both from the peaks of the *C–V* curves. Accordingly, the AFE-to-FE transition field was approximately 305 kV/cm and the reverse FE-to-AFE was approximately 206 kV/cm for the thin films on LNO/SiO_2/Si substrates. These results from the *C–V* analysis were not very in close agreement with the *P–E* measurements on the same sample. The different values determined from these two methods may be resulted from measurement mechanism. The *P–E* curves were measured with a triangle wave, while the *C–E* curves were measured with a dc bias plus a weak ac wave.

Fig. 7 shows the dielectric constant and dielectric loss of PLZST films grown on LNO/SiO_2/S substrates, as a function of temperature under the frequency 1, 10 and 100 kHz. It demonstrated the Curie temperature of PLZST with this composition was 185 °C at 1 kHz. It was found that a strong frequency dispersion of dielectric constant existed at higher temperature. It was probably attributed to the space charge effect which usually became significant at high temperatures. This may be also a reason the dielectric loss of the films was larger at 100 kHz, compared with 1 and 10 kHz.

4. Conclusions

Using metal-organic chemical liquid deposition method, conductive $LaNiO_3$ thin films were grown on SiO_2/Si substrates successfully. LNO films exhibited (1 1 0)-preferred perovskite structure with a moderate sheet resistance annealed at different temperature for 1 h. Subsequently, PLZST antiferroelectric thin films were deposited on the LNO buffered SiO_2/Si substrates, which heat-treated at 650 °C for 1 h. The PLZST antiferroelectric displayed a random orientation structure. SEM and EDS analyses demonstrated that the PLZST films were consisted of Pb-rich bright round regions and Pb-deficient regions. The maximum polarization value was 18 μC/cm^2. The temperature dependence dielectric constant the Curie temperature of PLZST composition was 185 °C at 1 kHz.

Acknowledgements

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