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Dependence of the properties of compositionally graded $Pb(Zr,Ti)O_3$ ferroelectric films of the bottom electrode

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Abstract

Compositionally graded $Pb(Zr,Ti)O_3$ thin films were prepared on the Pt(1 1 1)/Ti/SiO_2/Si, LNO/Si(1 0 0) and LNO/Pt(1 1 1)/Ti/SiO_2/Si substrates by a modified sol–gel method and rapid heat-treatment. The composition depth profile of a typical up-graded film was determined using a combination of auger electron spectroscopy and Ar-ion etching. The crystallographic orientation and the microstructure of the resulting graded PZT thin films on the different substrates were characterized by XRD. The dielectric and ferroelectric properties of the graded PZT films were discussed. The graded PZT films on LNO/Pt/Ti/SiO_2/Si and LNO/Si(1 0 0) substrates have larger dielectric constant and remnant polarizations compared to that grown on Pt/Ti/SiO_2/Si substrates.
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1. Introduction

Compositionally graded ferroelectric films have exhibited properties not previously observed in conventional ferroelectric materials (uniform or heterostructure). There are many experimental results reported in the literatures about the preparation and characterization of graded thin films [1–3], but these properties have not yet been fully explored, or well interpreted. On the other hand, more and more researches have been concentrated on the effect of the bottom electrode layer to the ferroelectric thin films [4,5]. The bottom electrode layer influences not only the microstructure of ferroelectric films directly, but also the dielectric and ferroelectric properties. Though platinum has been widely used as a typical bottom electrode for PZT, its electrical degradation on account of poor adhesion to Si substrate and polycrystalline structure limits its practical utility. Recently, conductive perovskite oxides such as $YBa_2Cu_3O_{7-x}$ (YBCO), $SrRuO_3$ and IrO_2 have been studied intensively as electrodes. Metallic oxide $LaNiO_3$ (LNO), which is a pseudocubic perovskite with a lattice parameter of 0.384 nm, has also attracted much attention in recent years as a conducting layer for applications in ferroelectric memories [6–8].

Although the electrical conductivity of the LNO films was high enough to act as electrodes, the addition of Pt layers below the LNO bottom electrode and above the LNO top electrode was found to enhance the reproducibility of electrical properties. In this paper, highly oriented conductive LNO thin films were prepared on Si(1 0 0) substrates and Pt/Ti/SiO_2/Si substrates by modified metallorganic decomposition (MOD) using spin-coating technique. Compositionally graded $Pb(Zr,Ti)O_3$ thin films [PZT(80/20)/PZT(52/48)/PZT(20/80)/ different bottom electrode] were prepared by the sol–gel technique on Pt/Ti/SiO_2/Si, LNO/Si and LNO/ Pt/Ti/SiO_2/Si substrates. The effects of these various bottom electrodes on the microstructure and electrical properties of compositionally graded PZT films are reported.

2. Experimental procedure

LNO thin films were prepared by modified metallorganic decomposition on Si(1 0 0) and Pt/Ti/SiO_2/Si substrate, respectively. Lanthanum nitrate [$La(NO_3)_3$] and nickel acetate [$Ni(CH_3COO)_2 \cdot 4H_2O$] were used as the starting materials whereas acetic acid and water were used as the solvents. Nickel acetate was dissolved in acetic acid and equimolar amounts of

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lanthanum nitrate dissolved in distilled water held at room temperature, respectively. Then, the two solutions were mixed together with constant stirring. In order to avoid cracking during heating, formamide was also added to the system. The concentration of the precursor solution was adjusted to 0.3 M by adding or distilling some acetic acid and water. The LNO precursor solution was passed through a 0.22 μm in-line syringe filter directly and spin-coated onto Si(1 0 0) substrates and Pt/Ti/SiO_2/Si substrates at 3000 rpm for 30 s. After each coating, the film was fired at 160 °C for 300 s, then pyrolyzed at 400 °C for 360 s and finally annealed at higher temperatures for 240 s. The process was repeated four times to obtain thicker LNO films. The whole thermal treatment was completed in an RTA furnace.

For fabricating PZT graded thin films, three PZT precursor solutions with varied Zr/Ti molar ratios were synthesized using a modified sol–gel process, in which, the three solid precursors of PZT were prepared first, and then the precursors were dissolved in 2-methoxyethanol (2-MOE) to form the sols for the spin-coating deposition. The three compositions of the solutions are $Pb(Zr_{0.20}Ti_{0.80})O_3$ [PZT(20/80)], $Pb(Zr_{0.52}Ti_{0.48})O_3$ [PZT (52/48)] and $Pb(Zr_{0.80}Ti_{0.20})O_3$ [PZT (80/20)]. The precursor solutions were spin-coated on different bottom electrodes in sequence: first a PZT (20/80) solution, then PZT (52/48) solution, and finally PZT (80/20) solution. In this way, compositionally graded $Pb(Zr,Ti)O_3$ thin films were formed. Each solution was spin-coated three times. After each coating, the film was fired at 130 °C for 200 s, then at 380 °C for 240 s, and pyrolyzed at 460 °C for 240 s. Finally, the graded thin film was annealed at 650 °C for 240 s. The whole thermal treatment was completed in a RTA furnace.

The composition depth profile of the PZT graded thin film was determined using a combination of Auger electron spectroscopy (AES, Model PHI-610/SAM) and Ar-ion etching. The interface structure of the PZT film was investigated by transmission electron microscopy (TEM, Philips CM200-FEG). The crystallographic orientation and the microstructure of the PZT graded thin films on the different bottom electrodes were characterized by X-ray diffraction analysis (XRD, Model D8 advance) using nickel-filtered Cu Kα radiation. The dielectric constant–voltage (q–V) properties of the PZT thin films were measured using a Hewlett-Packard (4284A) precision LCR meter at room temperature. Hysteresis loops were observed at 300 Hz using a Sawyer–Tower circuit (RT66A) at room temperature.

3. Results and discussion

Fig. 1 shows the composition depth profile of the graded film determined using a combination of Auger electron spectroscopy and Ar-ion etching. It is obvious that the contents of Zr and Ti are changing with the depth in the upright direction of the thin film. The content of Ti increases with the etching depth, and Zr decreases with the etching depth. The results confirm that the processing method produces a graded composition change, which is consistent with the expected results.

In addition, the lattice image for the microstructure of PZT graded thin film on the LNO bottom electrode was observed by TEM operated at 200 kV as shown in Fig. 2. The space between crystal face in the TEM pattern is 0.415 nm. It is evident that the crystal face is (0 0 1) of PZT (20/80), which is consistent with that measured by XRD.

To investigate the crystalline nature of the graded thin films, Fig. 3 represents XRD patterns for graded PZT thin films on the

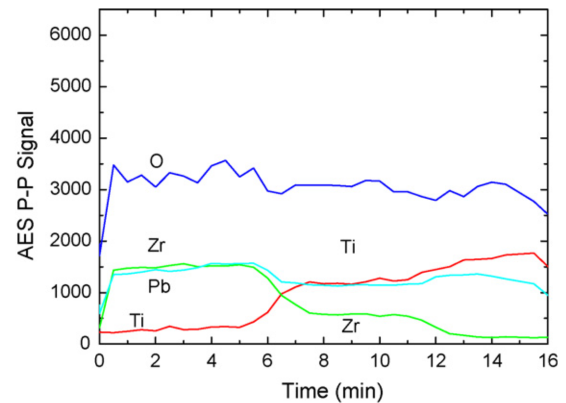

Fig. 1. Thickness distribution of compositions of the graded PZT thin film.

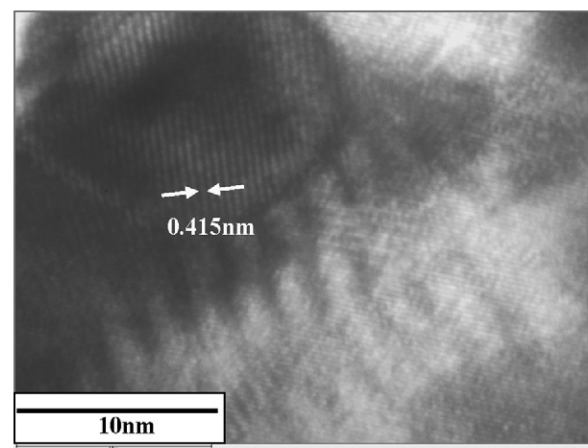

Fig. 2. TEM micrograph of the graded PZT thin film on LNO bottom electrode.

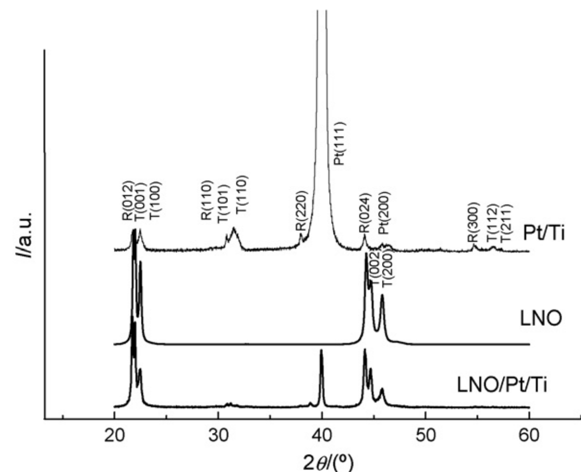

Fig. 3. XRD patterns of the graded PZT thin films on different bottom electrode.

different substrates. The diffraction peaks of the films were all perovskite structured with no pyrochlore phase. The graded PZT thin films deposited on LNO/Si and LNO/Pt/Ti/SiO_2/Si substrates show strong (0 0 1) preferred orientation, respectively, while the films deposited on Pt/Ti/SiO_2/Si substrate shows random orientation. The intensity of PZT films on LNO and LNO/Pt bottom electrodes is several hundred times as large as that of PZT films on the Pt electrode, which resulted from the good crystallographic matching between LNO and PZT films. It can be therefore said that the crystallographic orientation of a graded PZT thin films could be controlled by varying the bottom electrodes. In addition, Fig. 3 shows that the graded thin film possesses diffraction peaks of PZT (80/20) and PZT (20/80) thin films, so the graded thin film is a composite structure of tetragonal and rhombohedral.

The electric properties of the graded thin films were evaluated using a capacitor structure of metal–ferroelectric–metal, onto which the Au (1 mm diameter) top electrode was deposited by sputtering through a mask onto the film surfaces. Fig. 4 displays the dependence of the dielectric constant and dissipation factor as a function of frequency curves of Au/graded film/LNO, Au/graded film/LNO/Pt and Au/graded film/Pt capacitors in the range of 1 kHz to 1 MHz. As shown in Fig. 4A, the graded thin films on the LNO electrode and LNO/Pt electrode have larger capacitance than that on the Pt electrode. The dielectric constants of the graded PZT films on LNO/Si, LNO/Pt/Ti/SiO_2/Si and Pt/Ti/SiO_2/Si substrate were measured to be approximately 255, 276 and 209 at 10 kHz, respectively. This means that Au/graded film/LNO and Au/graded film/LNO/Pt capacitors have good dielectric properties by means of the highly preferred growth.

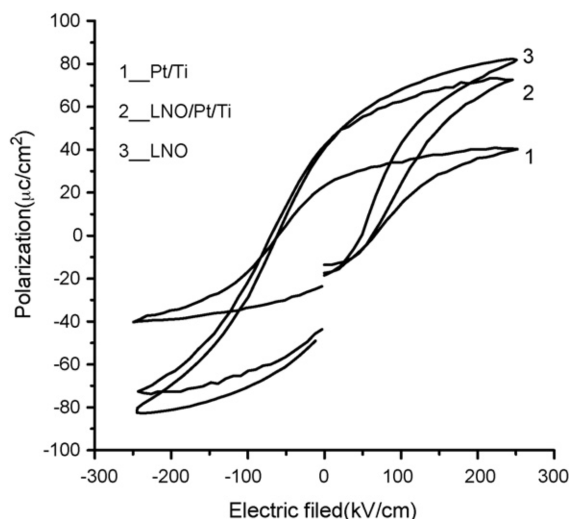

Fig. 5. The hysteresis loops for the graded PZT thin films on different bottom electrode.

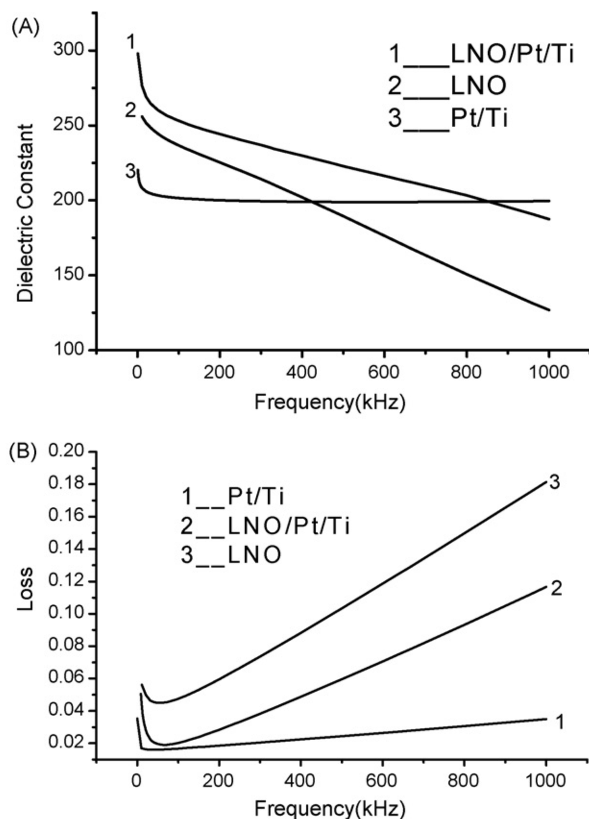

Fig. 4. Frequency dependence of dielectric constant and loss of the graded PZT thin films on different bottom electrode.

Fig. 4B displays the dependence of the dissipation factors as a function of frequency of three capacitors. It is obvious that the graded thin film on the LNO electrode has a slightly larger dissipation factor than the PZT films on the Pt electrode and LNO/Pt electrode. It can be attributed to that the conductivity of LNO film is smaller than Pt electrode. The dissipation factors of the graded PZT films on LNO/Si, LNO/Pt/Ti/SiO_2/Si and Pt/Ti/SiO_2/Si substrate were measured to be approximately 0.046, 0.021 and 0.019 at 10 kHz, respectively.

Fig. 5 shows the hysteresis loops of the graded thin films on the three bottom electrodes. It is obvious that all the graded films showed the polarization reversal. The remnant polarizations (Pr) of the graded films, which are averaged with the positive and negative values, are estimated to be approximately 41, 40 and 23 $\mu C/cm^2$ on the LNO, LNO/PT and Pt electrodes, respectively. It is apparent that the remnant polarizations of the graded PZT films on the LNO and LNO/Pt bottom electrode were higher than on the Pt bottom electrode. It can be attributed to the highly preferred growth on LNO and LNO/Pt substrates too. It could be noted that the approximate coercive field (E_c) value is 58 kV/cm for the graded film on LNO bottom electrode, and 61 kV/cm for LNO/Pt and Pt bottom electrode.

4. Conclusions

LNO thin films were prepared by modified metallorganic decomposition on Si(1 0 0) substrates and Pt/Ti/SiO_2/Si substrates. Compositionally graded PZT thin films were prepared using a modified sol–gel process on the LNO, LNO/Pt and Pt bottom electrodes. The relationship between crystallographic orientation and ferroelectric properties was investigated. It was found that the crystallographic orientation of the film could be controlled only by varying the deposition substrate. As the result of good crystallographic matching between LNO and PZT films, the graded films on LNO or LNO/

Pt bottom electrodes have more epitaxes than that on the Pt electrode. The dielectric and ferroelectric properties of graded thin films were dependent upon the microstructure orientation. The capacitance and remnant polarizations of the graded films on the LNO and LNO/Pt bottom electrodes are higher than that on the Pt electrode.

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