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Orientation control and electrical properties of PZT/LNO capacitor through chemical solution deposition

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Abstract

This paper describes the deposition of PZT/lanthanum nickel oxide (LNO) electrode thin-film capacitor on a Si(1 0 0) substrate with a chemical solution deposition (CSD). Highly (1 0 0)-oriented LNO film with a perovskite structure was deposited by annealing at 700 °C from a precursor solution of $La(NO_3)_3$ and $Ni(CH_3COO)_2$. In addition, highly (1 0 0)&(0 0 1)-oriented PZT/LNO capacitor was deposited on LNO/Si substrate by annealing at 600 °C, showing $P_r = 18\ \mu C/cm^2$ and $E_c = 36\ kV/cm$. Furthermore, the resultant PZT/LNO thin-film capacitor exhibited no fatigue up to 10^8 switching cycles.

Keywords: Sol–gel processes; PZT; Lanthanum nickel oxide; Films; Ferroelectric properties

1. Introduction

Ferroelectric thin films of $Pb(Zr_xTi_{1-x})O_3$ (PZT) have attracted much attention for their wide applications for memories and micro-electro-mechanical-systems (MEMS). Previous reports have indicated that the use of a metal electrode resulted in the serious fatigue of the PZT thin films at a relatively short number of switching cycles.[1] Origins and mechanisms of fatigue are still controversial. On the contrary, conductive metal oxide such as $SrRuO_3$ (SRO),[2,3] $YBa_2Cu_3O_{7-X}$,[4] IrO_2,[5] RuO_2,[6] $LaNiO_3$ (LNO),[7] and $La_{0.5}Sr_{0.5}CoO_3$ (LSCO)[8] were found to be effective candidates to improve the fatigue properity for PZT thin films. All these materials show electrical conductivity of a few hundred μΩ cm. In addition, the selection of an electrode material will determine the orientation and the properties of the resultant ferroelectric thin-film capacitors. The deposition of the lattice-matched hetero-structures of PZT/oxide electrode thin-film capacitors can be expected to improve the electrical properties, especially for the fatigue property. Perovskite-type oxide electrode such as SRO and LNO are promising candidates because of their similar lattice parameters (the lattice parameters for a PZT of a morphotropic phase boundary: $a = 4.036$ Å, $c = 4.146$ Å and the lattice parameters for a LNO of a pseudo-cubic symmetry: $a = 3.84$ Å). Therefore, LNO is mentioned as a candidate for oxide electrode for the PZT thin films, which shows a lattice matching with a PZT.

In our previous work,[9] LNO thin film with relatively good conductivity and preferred orientation has been prepared by the CSD, and the PZT/LNO capacitor with ferroelectric property was also deposited by a CSD. However, the CSD-derived PZT/LNO capacitor shows inferior electrical properties because of the relatively high dielectric loss and low conductivity. Therefore, in this paper, we focused on the optimization of the processing parameters to deposit the high quality LNO thin film with high conductivity and preferred orientation as well as the PZT/LNO capacitor on a Si(1 0 0) substrate by CSD.

2. Experimental procedure

LNO and PZT thin films were deposited through a CSD. $La(NO_3)_3$ and $Ni(CH_3COO)_2$ were used as raw materials for the LNO precursor and 2-methoxyethanol and 2-aminoethanol mixed solution or ethanol was used as a solvent. Details for precursor preparation are described elsewhere.[9] The ethanol was used to prepare the LNO precursor solution, from which the removal of the residual organics was easier by the pre-annealing,

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leading to the LNO thin film with high conductivity and low loss. The LNO thin films were deposited on Si(1 0 0) substrate by spin coating. The as-deposited LNO thin film was dried at 150 °C for 10 min to remove residual organics, pre-annealed at 350 °C for 10 min and then finally annealed up to 700 °C for 5 min with a rapid thermal annealing in an oxygen atmosphere to effectively remove the residual organics in the precursor film. The starting reagents for the preparation of PZT precursor solution of 0.6 M were a lead acetate, titanium *iso*-propoxide and zirconium *n*-propoxide. Experimental details were described elsewhere.[10] The zirconium to titanium ratio in the PZT precursor solutions were controlled to a MPB condition (53/47). The as-deposited PZT thin film was dried at 110 °C for 10 min to remove residual organics, pre-annealed at 420 °C for 10 min and then finally annealed at 600 °C for 5 min with a rapid thermal annealing in an electric furnace.

The crystalline phases developed in the films were examined by X-ray diffraction (XRD) with Cu Kα radiation. Microstructure of the films was observed by a scanning electron microscope (SEM). Resistivity of the films was measured by a four-point probe resistivity measurement. The dielectric behavior of the capacitor was measured using a LCR meter. Ferroelectricity (P-E hysteresis loop) and the fatigue property were measured using a ferroelectric thin film test system (Radiant Technologies Inc., RT6000S).

3. Results and discussion

3.1. Effect of solvent and annealing atmosphere on orientation and properties of LNO thin film

In our previous paper, perovskite-type LNO thin film and PZT/LNO capacitor were deposited on a Si wafer. However, the ferroelectricity of the resulting PZT/LNO capacitor was not so good because of the film quality of the LNO electrode. Therefore, we tried to improve the film quality of the LNO thin film by changing the solvent for the precursor solution and the annealing atmosphere. Fig. 1 shows the XRD patterns for the resultant LNO thin films from different precursor solutions with different solvent. As a result, perovskite-type LNO thin films with preferred orientation has been deposited above 600 °C. In the case of LNO thin film from a precursor solution of ethanol, the resultant film exhibited no preferred orientation even at 700 °C. On the other hand, the LNO thin film annealed at 700 °C exhibited preferred orientation. The orientation mechanism is not clear yet. However, this result indicated that the film orientation of the LNO electrode depended upon the molecular structure of the precursor solution. Fig. 2 shows the change in the electrical conductivity of the resulting LNO thin films with annealing temperature. The conductivity of the resultant LNO films increased with increasing annealing temperature because of the crystallinity and the microstructure were improved with increasing temperature, and reached about 1.0×10^{-3} Ω cm at 700 °C, showing the good microstructure and crystallinity. In addition, the conductivity of the LNO thin films from the precursor solution of ethanol solvent was higher if the annealing temperature was lower than 600 °C. Higher conductivity for the

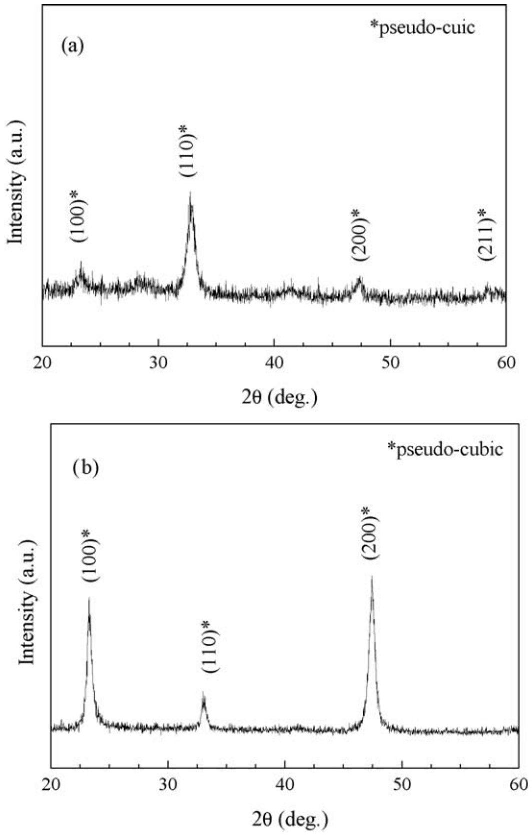

Fig. 1. XRD patterns for the LNO thin films from different precursor solution with different solvent of (a) ethanol and (b) 2-methoxyethanol and 2-aminoethanol mixed solvent, respectively.

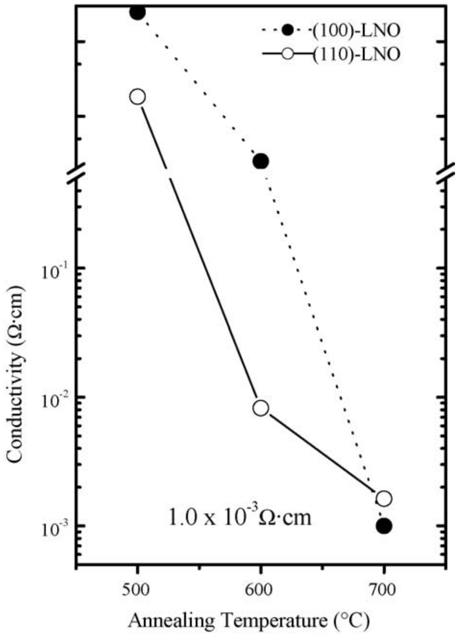

Fig. 2. The electrical conductivity for the LNO thin films with different orientation and annealing temperatures.

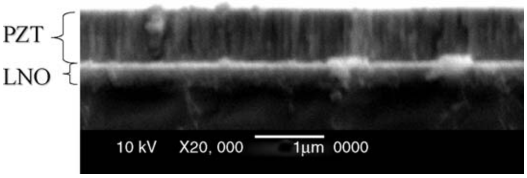

Fig. 3. Cross sectional SEM image of the PZT/LNO thin-film capacitor. Thickness of the PZT and LNO layer are about 700 nm and 250 nm, respectively.

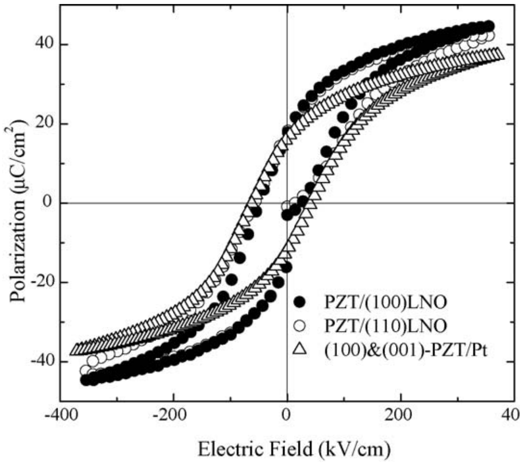

Fig. 5. Ferroelectric property for the resultant PZT/LNO capacitors with different orientations, together with the PZT/Pt capacitor with preferred orientation. Gold thin film was deposited for the top electrode.

(1 0 0)-oriented LNO film annealed at 700 °C may be ascribed to the film orientation and the annealing atmosphere, because the preferred orientation results in the columnar microstructure which permits the oxygen gas diffusion easier to remove the residual organics during annealing.

3.2. Deposition of PZT/LNO thin-film capacitor and its electrical properties

It was demonstrated that the CSD-derived LNO thin film with a preferred orientation and the high conductivity was successfully deposited by optimizing the processing parameters. Therefore, in this paper, PZT thin film with a MPB composition was deposited on the highly (1 0 0)-oriented LNO thin film. Fig. 3 shows the SEM image of the resultant PZT/LNO capacitor. From this figure, it was found that the resultant PZT/LNO capacitor also exhibited columnar and dense microstructure. In addition, PZT thin film on a (1 0 0)-oriented LNO/Si substrate exhibited high degree of (1 0 0)-orientation of 96% as shown in Fig. 4. Therefore, this PZT/LNO capacitor is expected to show good electrical properties.

Fig. 5 shows the ferroelectric P-E hysteresis loops for the resultant PZT/LNO thin-film capacitors with and without preferred orientation, together with that of the (1 0 0)&(0 0 1)-oriented PZT/Pt capacitor. This figure indicated that the LNO electrode improved the ferroelectric property of the resultant PZT thin films on the LNO/Si wafer and, therefore, the remanent and saturated polarization of the resulting PZT films were larger than that of the (1 0 0)&(0 0 1)-oriented PZT thin film on the commonly used substrate of a Pt/Ti/SiO$_2$/Si. In addition, coercive field of the resulting PZT films was also reduced by using the LNO electrode because of the better contact of the interface between electrode and the ferroelectric PZT thin film. The remanent and saturated polarization for the PZT/LNO capacitors with and without preferred orientation were $P_\mathrm{r} = 18\ \mu\mathrm{C/cm}^2$ and $18\ \mu\mathrm{C/cm}^2$, and $P_\mathrm{s} = 44\ \mu\mathrm{C/cm}^2$ and $42\ \mu\mathrm{C/cm}^2$, respectively. The coercive field for the PZT/LNO capacitors with and without preferred orientation were 36 kV/cm and 50 kV/cm, respectively.

Dielectric constant for these PZT/LNO thin film-capacitors with and without preferred orientation at 1 kHz were about 900 and 700, respectively (Fig. 6). On the other hand, dielectric constant for the PZT thin film on a Pt/Ti/SiO$_2$/Si substrate was about 1150, which was higher than that of the PZT film on the LNO thin film with a preferred orientation, suggesting the higher *c*-axis orientation of the PZT thin film on the (1 0 0)-oriented LNO thin film. This result demonstrated that the (1 0 0)-oriented LNO thin film can act as not only a electrode but also a seeding layer for the

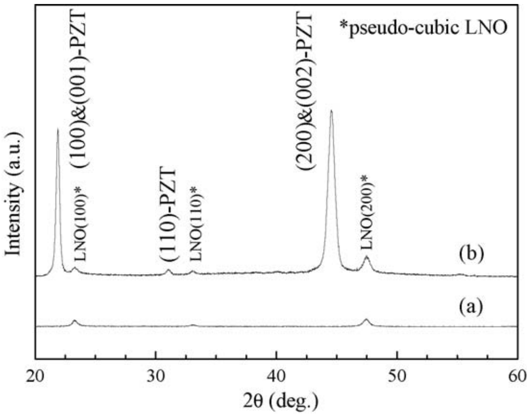

Fig. 4. XRD patterns for (a) LNO thin film annealed at 700 °C and (b) PZT/LNO thin-film capacitor.

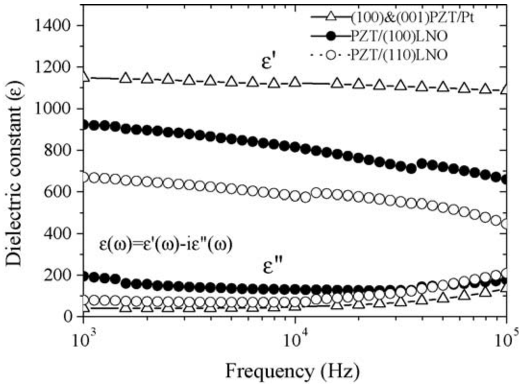

Fig. 6. Dielectric behavior for the resultant PZT/LNO capacitors with different orientations, together with the PZT/Pt capacitor with preferred orientation. Gold thin film was deposited for the top electrode.

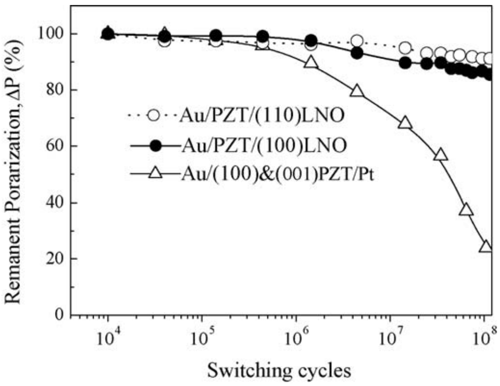

Fig. 7. Fatigue characteristics for the PZT/LNO capacitors with different orientations, together with the PZT/Pt capacitor with preferred orientation.

c-axis orientation of the ferroelectric PZT thin film because of the better lattice matching. In addition, these PZT/LNO capacitors exhibited no fatigue up to 10^8 switching cycles (Fig. 7), in contrast to the PZT thin film on a Pt/Ti/SiO_2/Si substrate. These results indicated that the LNO thin films were suitable for the thin-film electrode of the PZT thin films.

4. Conclusion

In conclusion, we have successfully deposited PZT/LNO thin-film capacitors with and without preferred orientation by a CSD. The film orientation of the LNO thin film and the PZT/LNO capacitors could be effectively controlled by optimizing the processing parameters for the LNO thin film deposition. These PZT/LNO thin-film capacitors with and without preferred orientation exhibited better ferroelectricities and excellent fatigue property compared with that of the (1 0 0)&(0 0 1)-oriented PZT/Pt capacitor on a Si substrate. These results indicated that the thin-film oxide electrode was essential for the lead-based ferroelectric thin-film capacitors.

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