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Structural and electrical properties of $Pb(Zr_{0.53}Ti_{0.47})O_3$ films prepared on $La_{0.5}Sr_{0.5}CoO_3$ coated Si substrates

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Abstract

$PbZr_{0.53}Ti_{0.47}O_3$ (PZT) thin films with thickness of 0.9 μm were prepared on $La_{0.5}Sr_{0.5}CoO_3$ (LSCO) coated Si substrates. Both PZT and LSCO were prepared by the sol–gel method. The concentration of LSCO sol was varied from 0.3 to 0.1 mol/L, which could modify the preferential orientation of PZT thin films and consequently affect the dielectric and ferroelectric properties. The LSCO electrode layers derived from lower sol concentration of 0.1 mol/L have much more densified structure, which facilitates the formation of (1 0 0) textured PZT films with smooth and compact columnar grains. PZT thin films prepared on the optimized LSCO films exhibit the enhanced dielectric constant and remnant polarization of 980 and 20 μC/cm^2, respectively.

Keywords: A. Sol–gel processes; B. X-ray methods; C. Dielectric properties; C. Ferroelectric properties; D. PZT

1. Introduction

Lead zirconate titanate (PZT) films with composition near the morphotropic phase boundary have attracted great attention for the possibility of using them in many applications such as non-volatile ferroelectric memory and microelectromechanical systems due to their large remanent polarization and piezoelectric coefficient. Conventionally, Pt was widely used as the bottom or top electrode for ferroelectric thin films. However, PZT films were found to present strong polarization fatigue upon using simple metallic electrodes, which was attributed to mobile oxygen vacancies and Schottky depletion regions due to work function mismatch at the interfaces.[1] Recently, much effort has been devoted to developing perovskite-type metallic oxides as electrodes to obtain a perennial reliability of ferroelectric thin films. $La_{0.5}Sr_{0.5}CoO_3$ (LSCO) is a promising candidate for electrode due to a low electrical resistivity of about 90 μΩ cm at room temperature as well as the (pseudo-) cubic perovskite structure with $a = 3.83$ Å.[2] The similarities in crystal structure and lattice constant between electrodes and ferroelectric thin films offer the potential for improved electrical properties.[3]

For a practical intention, epitaxial or well-textured PZT films are preferable, which is mainly because epitaxial or well-textured PZT films can hold predominant integrative performance, and produce a larger remnant polarization in the appropriate direction.[4] So far, the growth of epitaxial PZT films with LSCO electrodes has been reported on single crystal substrates such as $LaAlO_3$,[5] $SrTiO_3$,[6,7] yttrium-stabilized zirconia,[6] etc. using physical process such as rf-sputtering and pulsed laser deposition. However, since Si is the essential material of semiconductor industry which is closely related to microelectronic devices, the growth of well-textured PZT on Si substrate is of timely interest. On the other hand, sol–gel processing is a very attractive method for preparing perovskite-type thin films with precise composition control and good reproducibility.[2] To our knowledge, few works have been reported on the successful preparation of the (1 0 0) oriented PZT films grown on Si substrates with LSCO electrodes by a sol–gel route. The objective of this work was to prepare (1 0 0) oriented PZT films on the Si substrate by adjusting the concentration of LSCO sol.

2. Experimental procedure

The LSCO sol was prepared from the starting materials: $La(NO_3)_3{\cdot}6H_2O$, $Sr(NO_3)_2$ and $Co(CH_3COO)_2{\cdot}4H_2O$, which were mixed with a molar ratio of La:Sr:Co = 1:1:2 and dis-

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solved into the mixed solvents of heated glacial acetic acid and deionized water to obtain LSCO sol of 0.1, 0.2 and 0.3 mol/L, respectively. The molar ratio of acetic acid and deionized water was 1:2. A 7 wt.% polyvinyl alcohol (PVA) was added to the system to stabilize the solution. PZT precursors with 0.5 mol/L molarity and excess lead of 20 at.% were synthesized by dissolving lead acetate, zirconium isopropoxide and titanium tetrobutoxide into the 2-methoxyethanol solvent. The precursors were modified to form the polymeric solution by addition of acetic acid and deionized water.

Firstly, the LSCO sol of 0.1, 0.2 and 0.3 mol/L was separately spin-coated on the Si substrates at 4000 rpm for 30 s, and then heat-treated in flowing oxygen at 550 °C for 90 s. This process was repeated 21, 10 and 7 times for the LSCO sol of 0.1, 0.2 and 0.3 mol/L, respectively, to achieve the thicknesses of LSCO films of about 230 nm. The total LSCO layer was annealed at 700 °C for 10 min in flowing oxygen. Then, PZT thin films with thickness of 900 nm were deposited on the top of LSCO. The as-deposited PZT films were annealed by the rapid thermal annealing at 650 °C for 30 min in air.

The phase structure of LSCO and PZT thin films were characterized by X-ray diffraction (XRD, SHIMADZU). The morphologies of the surface and cross-sectional PZT thin films were observed by the field emission scanning electron microscopy (FE-SEM, LEO1530VP, Germany). To investigate the electrical properties, the top electrodes of gold (Au) with diameter of 0.4 mm were evaporated on the PZT films through a shadow mask. The dielectric properties of the PZT films were measured using an HP4294A impedance analyzer. The leakage current was examined by the Keithley 4200 system. The ferroelectric properties were measured by using the ferroelectric measurement system (Radiant, RT6000 HVS).

3. Results and discussion

X-ray diffraction patterns of the LSCO films on Si and the PZT films on the LSCO coated Si substrates are shown in Fig. 1. According to Fig. 1(a), LSCO films for different sol concentrations are identified to be pseudocubic perovskite crystal structures with the (1 1 0) preferred orientation. By comparison of the intensity of the major diffraction peaks, it can be deduced that the crystallinity of the LSCO films is enhanced with decreasing the LSCO sol concentration. As revealed from Fig. 1(b), PZT thin films annealed at 650 °C exhibit a good crystalline quality and a pure perovskite phase with no evidence of secondary phase formation. It is evident that the crystal orientation of the PZT films is strongly dependent on LSCO micro- and crystal structure. This is demonstrated by the orientation factor using the formula:

$$\alpha_{100} = \frac{I(1\ 0 0)}{I(1 0 0) + I(1 1 0) + I(1 1 1)}. \qquad (1)$$

where I is the integrated intensity of the corresponding diffraction peaks.[8] The (1 0 0) intensity ratio increases from 0.26 to 0.8 as the concentration of LSCO sol decreases from 0.3 to 0.1 mol/L. It is worthwhile to note that (1 0 0) oriented PZT thin films were successfully prepared on (1 1 0) oriented LSCO electrode layers and the lower concentration of LSCO sol facilitates the growth of the (1 0 0) oriented PZT films.

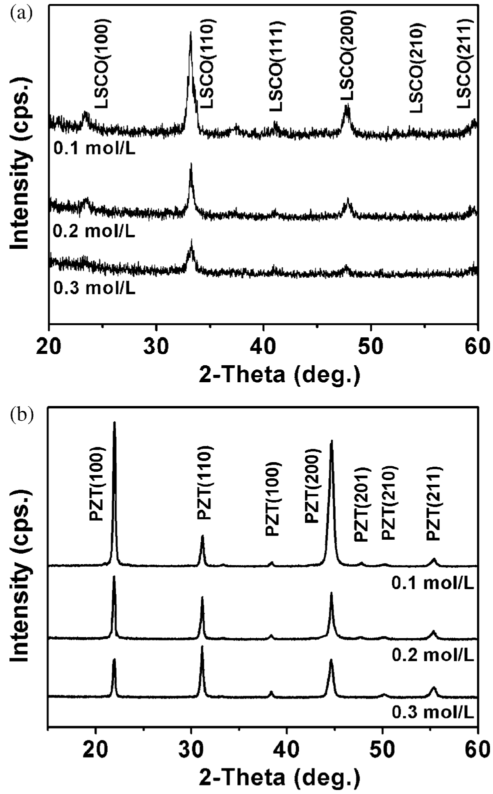

Fig. 1. XRD patterns of (a) the LSCO layers and (b) PZT thin films for different concentrations of LSCO sol.

The corresponding surface and cross-sectional images for PZT thin films fabricated on LSCO coated Si substrates for various LSCO sol concentrations were examined by SEM, as illustrated in Fig. 2. The PZT films possess a well crystallized, compact and crack-free microstructure with grain size of 100–200 nm. As the concentration of LSCO sol decreases, increase in grain size of the PZT films is observed. A columnar texture throughout the film thickness can be distinguished for the PZT films for LSCO of 0.1 mol/L. Meanwhile, the LSCO electrode layers derived from lower sol concentration of 0.1 mol/L have much more densified structure.

In our case, the LSCO solution concentration is optimized to 0.1 mol/L for growing the (1 0 0) textured PZT films. For the LSCO sol of lower concentration, the decomposition products can be efficiently burned off during pyrolysis, without significant embedded impurities. Thus, the more homogeneous single LSCO layer can be obtained. When the subsequent layer is spin-coated over the prior pyrolyzed layer, it is able to cover the pores and defects left behind by the burn-off of the organic addenda. Thus fully dense and well crystallized LSCO films were obtained after the subsequent annealing process, as evidenced by the XRD and SEM studies. When the PZT films are spin-coated on the top of LSCO, it is obvious that not only the surface energy of LSCO films but also the interface energy between the crystallites of LSCO and PZT can play a role in the self-textured growth.[9] Those grains with low surface energies will grow faster

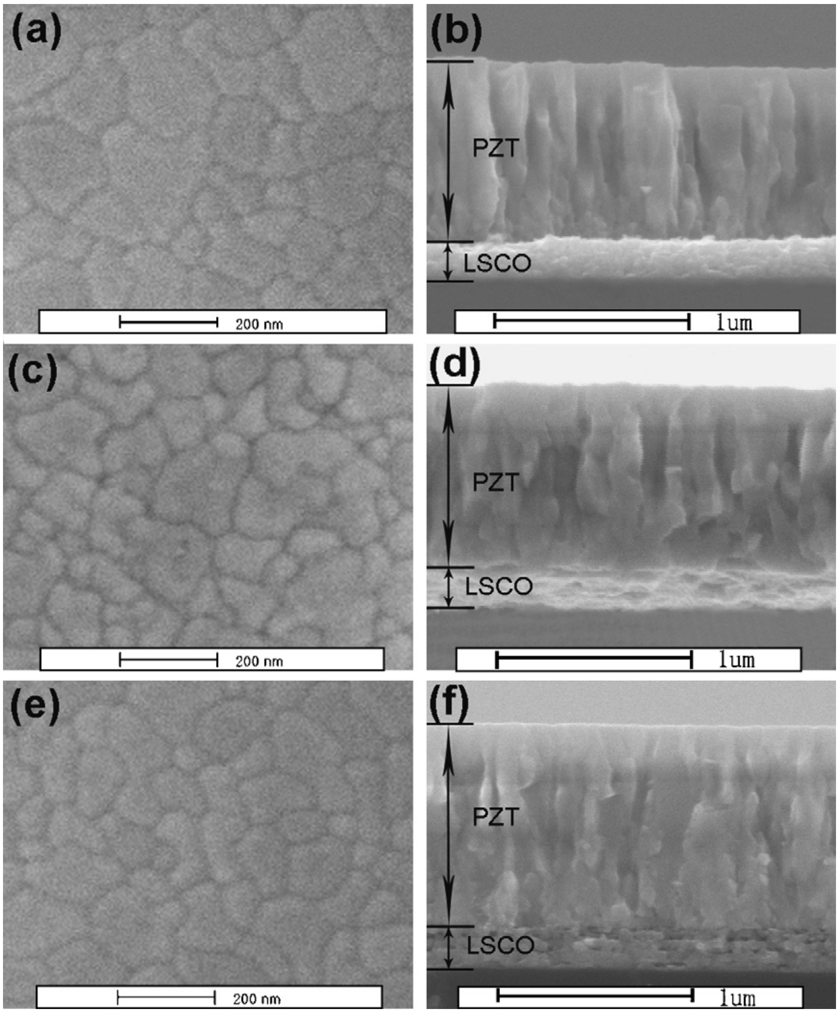

Fig. 2. SEM images of the surface and cross-sectional PZT thin films for different concentrations of LSCO sol: (a) and (b) 0.1, (c) and (d) 0.2, (e) and (f) 0.3 mol/L.

than other grains. Once grains with the preferred texture have obturated all other grains, resulting in the uniform surface texture, the rate of grain size evolution will diminish and columnar grain structures with parallel boundaries can be evolved.[10] The interface energy between the LSCO and PZT layers can also affect the orientation of PZT thin films. LSCO films derived from LSCO sol of 0.1 mol/L have good orientation and crystallinity, which will mitigate the interface energy between the PZT films and LSCO films. As a result, the texture of PZT films becomes predominantly (1 0 0), which is mainly because the (1 0 0) orientation grains with lowest nucleation energy is easy to grow.[11]

On the other hand, the lower nucleation energy barrier facilitates the formation of the rounded crystal cluster with larger grain size at the early stage of crystallization, which could be the origin of the columnar perovskite grains in the fully crystallized films.[12]

The room temperature relative permittivity (ε_r) and loss tangent ($\tan\delta$) of PZT thin films for various LSCO sol concentrations as a function of measured frequency (*f*) is given in Fig. 3. The dielectric constant increases and the dielectric loss decreases with decreasing concentration of LSCO sol. The PZT films for LSCO sol of 0.1 mol/L have relatively high ε_r and low $\tan\delta$ of about 980 and 0.046, respectively, at 10^3 Hz. Such improvement in dielectric constant of PZT thin films is believed due to the effect of increased grain size inducing fewer grain boundaries.[13] The increase in grain size not only enhances the dipole density but also decreases the amount of low dielectric constant grain boundaries, inducing fewer grain boundary defects per unit volume. The lower dielectric loss may be caused

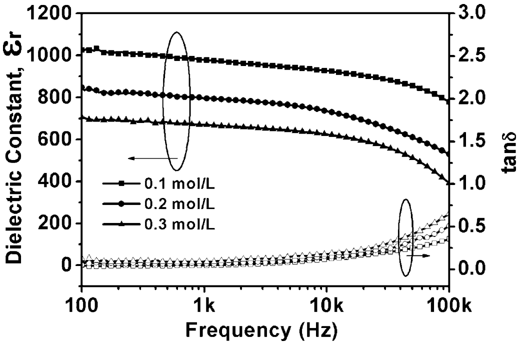

Fig. 3. Dielectric constant and $\tan\delta$ as a function of frequency of PZT thin films for different concentrations of LSCO sol.

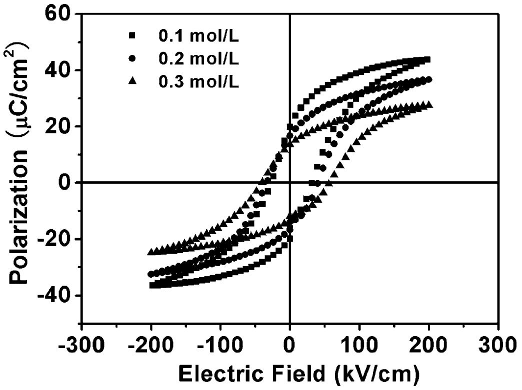

Fig. 4. *P–E* loop of PZT thin films for different concentrations of LSCO sol.

by slight interactions between the dielectric material and the bottom electrode during crystallization period as well as superior film quality during the initial stages of nucleation and growth process. The ε_r of the PZT films for LSCO sol of 0.1 mol/L decreases the most gently with the frequency up to 100 kHz, exhibiting the smallest dispersion. This indicates that the film has excellent homogeneity in absence of internal interfacial barriers, such as surface pyrochlore phases or electrode/film interfaces. At low frequencies, the $\tan\delta$ of all the samples is virtually in the similar range, changing slightly with frequency, indicating that the concentration of the space charges in the interfacial layer between PZT/LSCO is very small. It can be concluded that the nature of LSCO layers has a direct impact on the dielectric properties of PZT films.

Fig. 4 displays the polarization–electric field (*P–E*) loops of PZT thin films for various LSCO sol concentrations. Switchable ferroelectric properties are presented for the PZT films prepared on the LSCO coated Si substrates. The remnant polarization (Pr) increases and the coercive field (Ec) decreases with decreasing the concentration of LSCO sol. The (1 0 0) textured PZT thin films for LSCO sol of 0.1 mol/L reflect excellent ferroelectric behavior as indicated by well shaped loops with Pr and Ec of about 20 μC/cm² and 31 kV/cm, respectively. The larger remnant polarization and saturation polarization may be attributed to the denser structure, preferred orientation and larger grain size of the PZT films. It is notable that a larger remnant polarization can be expected in epitaxial or preferential oriented ferroelectric films compared to that in films with random texture.[4] This is mainly because that crystallization is highly oriented, normally vertical to the surface of the films in epitaxial or preferential oriented ferroelectric films, providing a stronger polarization direction. Such a highly oriented structure tends to form a concentrated polarization which results in higher dielectric constant.

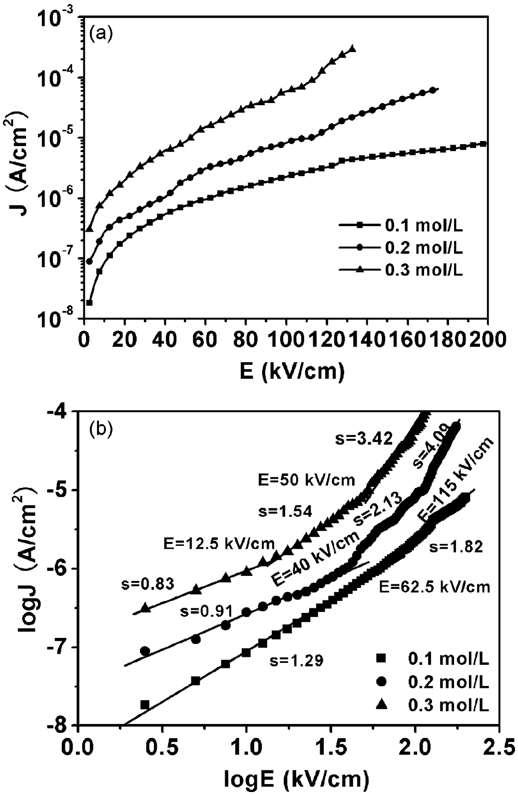

Fig. 5. Leakage current density of PZT thin films for different concentrations of LSCO sol: (a) *J–E* curves and (b) log *J*–log *E* curves.

Fig. 5 reveals the leakage current density *J* as a function of applied field *E* for PZT with different LSCO sol concentration. It can be clearly seen from Fig. 5(a) that the leakage current density *J* of PZT thin films is considerably reduced with decreasing the concentration of LSCO sol. The value of current density is 2.28×10^{-6} A/cm² for PZT thin films for LSCO sol of 0.1 mol/L at a field of 100 kV/cm, nearly one order of magnitude lower than that (5.92×10^{-5} A/cm²) of PZT for LSCO sol of 0.3 mol/L under the same field. From the double logarithm plot of current density *J* versus applied field *E*, as shown in Fig. 5(b), we can quickly gain insight into the nature of the leakage mechanism. At low electric field, the slopes of all the samples are around 1, indicating occurrence of Ohmic conduction, which is because thermal excitations of trapped electrons from one trap site to another dominating the transport in the films.[14] As the applied field is increased further, the density of free electrons due to carrier injection becomes greater than the density of thermally stimulated free electrons. As observed, LSCO electrode layers derived from sol concentration of 0.3 mol/L have residual porosity which might have lots of carrier traps. As to the PZT films for LSCO sol of 0.3 and 0.2 mol/L, the slopes are 1.5 and 2.1, respectively, indicating that the current density follows the SCL current law (which is a modified Child's law). Finally, the slopes become 3.4 and 4.1 after SCL current law, which could be due to the combined effects of SCL and other field-induced conduction mechanism. Commonly, the leakage current originates from the scattering of charge carriers, the charge carrier detrapping rate and the migration of oxygen vacancies.[15] Hence, under a relatively high field, the migration of oxygen vacancies near the cathode would induce a larger leakage current. It is worth noting that the log *J*–log *E* of the PZT films for LSCO sol of 0.1 mol/L is very smooth, exhibiting no distinct segment with increased slopes, indicating that space charge-limited current (SCLC) have less impact on the leakage current behavior. This is mainly because the much denser LSCO electrode layers suppress the oxygen vacancies, resulting in the minimization of mobile charge carriers in the film and subsequently ameliorate the leakage current characteristics.

4. Conclusions

The PZT films grown on silicon substrates with LSCO electrodes have been successfully prepared by a sol–gel route. It is noteworthy to mention that PZT thin films for LSCO sol of 0.1 mol/L exhibit (1 0 0) orientation with increased grain size and dense columnar structure, which is considered to be associated with the minimization of surface and interface energies. The PZT films for LSCO sol of 0.1 mol/L reveal the higher dielectric constants, larger remnant polarization and lower leakage current, which may be attributed to the larger grain size, preferred orientation and the denser LSCO electrode layers. It is demonstrated that PZT films prepared on LSCO/Si substrates possess superior dielectric and ferroelectric properties, suitable for device applications.

Acknowledgments

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