Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 30 (2010) 453–457
www.elsevier.com/locate/jeurceramsoc

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

Feng Chen, Jinrong Cheng *, Shenwen Yu, Zhongyan Meng

School of Materials Science and Engineering, Shanghai University, Shanghai, 200072, PR China

Available online 31 May 2009

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 $\mu C/cm^2$, 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-

* Corresponding author at: 149 Yanchang Road, Box 32, Shanghai, 200072, PR China. Tel.: +86 21 56332704; fax: +86 21 56332694.
E-mail address: jrcheng@staff.shu.edu.cn (J. Cheng).

0955-2219/$ – see front matter © 2009 Published by Elsevier Ltd.
doi:10.1016/j.jeurceramsoc.2009.05.007

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:

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

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.

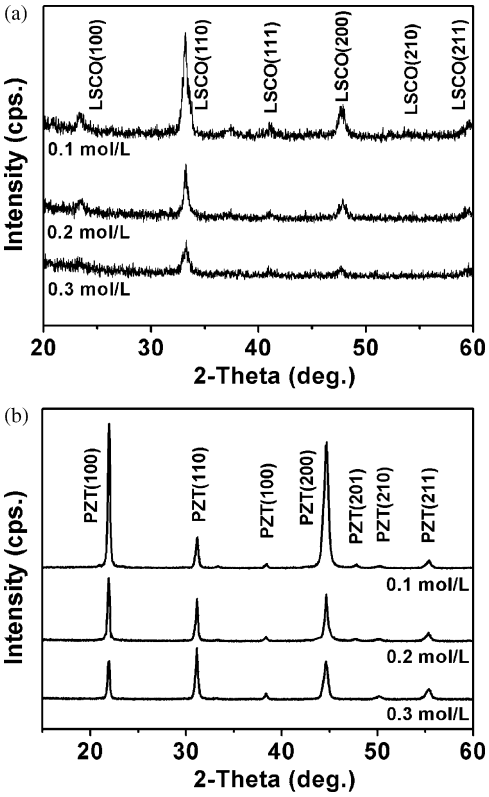

Fig. 1. XRD patterns of (a) the LSCO layers and (b) PZT thin films for different concentrations of LSCO sol.

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