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Phase evolution and electrical properties of lead zirconate titanate thin films grown by using a triol sol–gel route

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Abstract

Lead zirconate titanate (PZT) precursor sols were prepared using a triol based sol–gel route. Inorganics salts metal alkoxides lead acetate trihydrate [$Pb(OOCCH_3)_2{\cdot}3H_2O$], titanium (IV) isopropoxide [$Ti(OCH(CH_3)_2)_4$], and zirconium *n*-propoxide [$ZrOC_3H7)_4$] were used as starting materials. Thin films were deposited by spin coating onto $Pt/Ti/SiO_2/Si$ substrates. The samples were pre-heated (pyrolysis) on a calibrated hotplate over the temperature range of 200–400 °C for 10 min then firing at a temperature of 600 °C for 30 min. Randomly-oriented PZT thin films pre-heated at 400 °C for 10 min and annealed at 600 °C for 30 min showed well-defined ferroelectric hysteresis loops with a remanent polarization of 27 $\mu C/cm^2$ and a coercive field of 115 kV/cm. The dielectric constant and dielectric loss of the PZT films were 621 and 0.040, respectively. The microstructures of the thin films are dense, crack-free and homogeneous with fine grains about 15–20 nm in size.

Keywords: A. Sol–gel processes; Films; D. PZT

1. Introduction

During the past four decades, development of high-efficiency piezoelectric materials helped to design and fabricate a number of novel devices for various applications [1]; the use of ferroelectric thin films of $PbZr_xTi_{1-x}O_3$ (PZT) family for a variety device applications including semiconductor nonvolatile memories, piezoelectric microsensors and actuators, pyroelectric detectors and capacitors in dynamic random access memories (DRAMs) has drawn considerable interest [2]. PZT thin films deposited on ($Pt(1\ 1\ 1)/Ti/SiO_2/Si(1\ 0\ 0)$) substrates have been extensively investigated, and led to develop an understanding on the relationships between the microstructure and the properties of the films.

PZT films are sensitive to processing conditions and consequently the properties of PZT films depend on the microstructure and texture of the films. These are determined by the processing characteristic such as pyrolysis, and subsequent heat-treatment temperatures [3] affect the transformation of the pyrochore phase to the perovskite phase. Pyrolysis is an essential step in the sol–gel process whose major object is to remove the organics in the sol. However the pyrolysis conditions also affect the preferential orientation of the film [4].

The present paper investigates the effect of pre-heating temperature on the electrical properties and ferroelectric properties of sol–gel derived PZT films. The pre-heating temperatures were varied from 200 to 400 °C to evaluate the pyrolysis temperature dependence of the texture of the PZT films. The composition of the precursors sol was set at near the morphotropic phase boundary (MPB) in the PZT system. The electrical properties and ferroelectric properties of the PZT films with different pre-heating temperatures were investigated.

2. Experimental procedure

$Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) thin films were prepared by sol–gel methods using various metal organic precursors and solvent systems. The most widely used system is the methoxyethanol route, using commercially $Pt(1\ 1\ 1)/Ti/SiO_2/Si$ substrates with a 1000 Å Pt layer, a 50 Å Ti adhesion, and a thermally grown 3600 Å SiO_2 layer. The precursor solution was prepared from lead acetate trihydrate, titanium diisopropoxide biacetylaceto-

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nate, abbreviated as TIAA, Zr *n*-propoxide, 2,4 pentadione 1,1,1-tris(hydroxymethyl)ethane, abbreviated as THOME, 2-methoxyethanol was used as solvent. Zr *n*-propoxide was mixed with acetylacetone in a dry nitrogen atmosphere. The solution was heated at 90 °C for 2 h, then, cooled, and added to titanium diisopropoxide biacetylacetonate, lead acetate trihydrate and 1,1,1-tris(hydroxymethyl)ethane. The solution was then heated at 70 °C for 4 h to complete the reaction. At the final stage the solution was dilute with 2-methoxyethanol.

The substrates used for film deposition were cut into ~1 cm^2 pieces. Prior to spin coating, the sols were filtered though a 0.2 μm Nylon 66 membrane filter. Sol deposition on the substrate was performed by spin coating at 3000 rpm for 30 s. The films were then pre-heated at 200, 250, 300, 350 and 400 °C, for 10 min before being heated at 600 °C for 30 min.

Phase analysis of the samples was performed by X-rays diffraction (XRD). The surface morphology and cross-sectional microstructure was observed using a field-emission scanning electron microscope (FE-SEM). The electrical properties measurement, the relative permittivity ε_r, and dielectric loss tangent, $\tan\delta$, were measured by using low frequency impedance spectroscopy (HP4192A), at a frequency of 1 kHz. For electric measurement, gold was sputtered using a shadow masking method onto the top surfaces of the film to form top electrodes. The gold electrode area was ~0.80 cm^2. Films at the corner were etched away using a 40% hydrofluorboric acid, HBF_4 solution. The polarization versus electric field (P–E) loop of the specimens was measured using a Radiant Technologies MTI2000 ferroelectrics instrument.

3. Results and discussion

Pre-heating temperatures of 200, 250, 300, 350, and 400 °C were chosen to eliminate the organics from the as-deposited films, and 600 °C was selected as another pre-annealing temperature to establish a preliminary crystal phase of the films. Fig. 1 shows the XRD patterns of PZT films pre-heated at different temperatures. Indexing of XRD peaks was carried out according to the JCPDS file no.73-2022. It was found that other

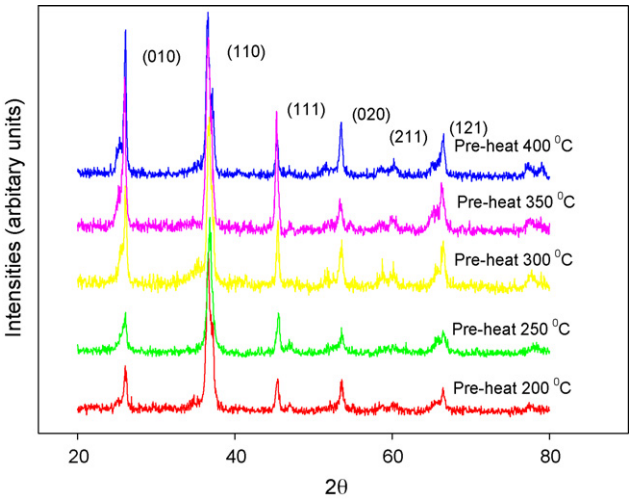

Fig. 1. XRD pattern of PZT thin films pre-heated at different temperatures but annealed at the same temperature of 600 °C.

phase or impurity was not detected by XRD. Our results here are comparable with those reported by Naksata and Milne [5].

Fig. 2 shows scanning electron micrographs (SEM) of the cross section of the PZT thin films annealed at 600 °C after pre-heating at 200 °C (a) and 400 °C (b). The SEM micrographs show that the films are dense, crack-free and homogeneous and contain fine 20–30 nm grains in sample (a) and 10–15 nm grains in sample (b). All the micrographs of the films show larger grain sizes with lower pre-heating temperatures. The film thicknesses are about 200 nm in (a) and 150 nm in (b), in good agreement with the report by Wang et al. [6], who however, employed a modified xerogel process to fabricate their PZT thin films.

The variation of dielectric constant and dielectric loss of the PZT thin films with annealing temperature is shown in Fig. 3. Both the dielectric constant and dielectric loss of the PZT films increase with increasing pre-heating temperature. The dielectric constant of the PZT thin films pre-heated at 200, 250, 300, 350 and 400 °C are 280, 340, 540, 580, and 620 °C, respectively. And the dielectric loss of the films is 0.021,

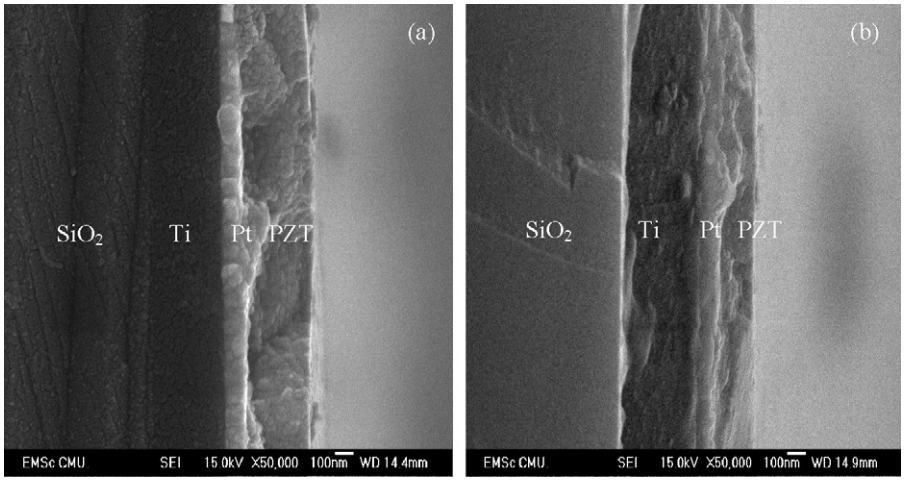

Fig. 2. SEM cross-sectional microstructures of the PZT films (a) pre-heated at 200 °C (b) pre-heated at 400 °C prior to annealing at 600 °C. The substrate is Pt(1 1 1)/Ti/SiO_2/Si(1 0 0).

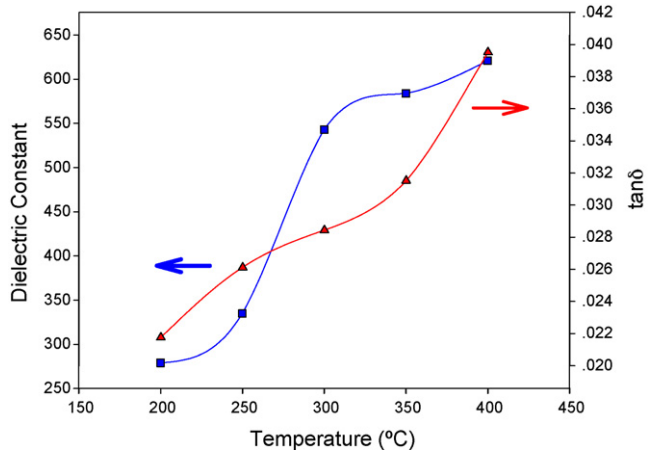

Fig. 3. The dielectric constant and dielectric loss in PZT thin films pre-heated at different temperatures but final heated at 600 °C.

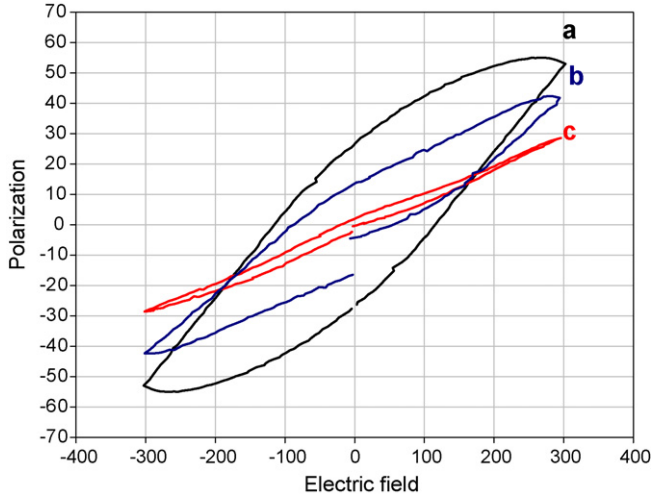

Fig. 4. P–E hysteresis loops of PZT films prepared using pre-heating temperatures of (a) 400 °C, (b) 300 °C and (c) 200 °C.

0.026, 0.028, 0.031 and 0.039, respectively. The increase in dielectric constant of the PZT thin films as a function of pre-heating temperature may be due to the highest perovskite contents [7].

Fig. 4 shows the P–E hysteresis loops of the thin films of various pre-heating temperatures. This sample may not be in a single phase, although the second phase is of such small amount that it cannot be observed in XRD pattern [8]. This very small amount of second phase may distribute in a manner that disrupt the long-range ordering of the polarization vector. The shape of the hysteresis loop varies for the samples with different pre-heat temperatures. It can be seen that the hysteresis loop gets thinner for the samples with lower pre-heat temperatures. The results here indicate that the samples pre-heated at higher temperatures have promising for further developments and applications.

4. Conclusions

Lead zirconate titanate $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) ferroelectric films were successfully fabricated on a Pt/Ti/SiO2/Si substrate using the triol sol–gel method. The films were pre-heated at different temperatures of 200, 250, 300, 350 and 400 °C for 10 min but final heated at 600 °C for 30 min. The film that pre-heated at 400 °C showed the highest perovskite content. These results may be explained by the nucleation and the growth of perovskite phase. In the measurement of P–E hysteresis, dielectric constant and dielectric loss were determined. Dielectric constant (ε_r) and dielectric loss ($\tan\delta$) at 1 kHz, remanent polarization, and coercive field of the films prepared from triol sol–gel and pre-heat at 400 °C were 621, 0.0395, 26.57 μC/cm^2 and 115.42 kV/cm, respectively.

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