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Microstructure and ferroelectric properties of sol–gel graded PZT (40/52/60) and (60/52/40) thin films

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Abstract

Graded $Pb(Zr_x,Ti_{1-x})O_3$ films with Zr compositions varied across the thickness direction were deposited on $Pt/Ti/SiO_2/Si$ substrate using a conventional spin-coating method. The up- and down-graded PZT films exhibited the perovskite polycrystalline structure. Microstructure investigations of the films showed a dense texture and successive layers of different compositions. The relative permittivities of the up- and down-graded PZT films measured at 1 kHz and room temperature were 1846 and 1019, respectively. Good dielectric and ferroelectric properties as well as the low-temperature processing suggested that the compositionally graded PZT films were promising for memory device applications.

Keywords: Sol–gel method; Ferroelectric; Dielectric; PZT graded films

1. Introduction

Ferroelectric $Pb(Zr_x,Ti_{1-x})O_3$ or PZT films have been regarded to date as the best ferroelectric material for various applications in technology, especially for ferroelectric memories [1]. Polarization-graded ferroelectrics are the new class of ferroelectrics which is distinguished from homogenous ferroelectrics in that the electric dipole moment density varies with position in graded ferroelectrics. These graded ferroelectrics expand the applications and understanding of ferroelectric heterostructures and their related electric properties [2]. Generally, compositional grading is the most common way to introduce a polarization gradient in ferroelectric materials. In this work, the sol–gel method was used to gradually change the Zr content along the thickness direction from one surface to another to achieve graded PZT film of high purity over the large deposition area [3,4]. The films of two types, i.e., up- and down-graded, are systematically investigated their condition parameters such as composition, crystallographic structure and grain size. The dielectric and ferroelectric properties of the films were comparatively reported.

2. Experimental procedure

Compositionally graded PZT films were fabricated using the conventional sol–gel process [5]. The precursor solution of PZT was prepared using tetra-*n* propyl-orthozirconate, tetra-isopropyl-orthotitanate and lead-acetate 3-hydrate as starting materials, and 2-methoxyethanol as a solvent. Lead acetate trihydrate was dissolved in 2-methoxyethanol and mixed for 30 min. The precursor with 10% excess Pb composition was prepared on purpose to compensate for the lead loss during the deposition processing. The solution was distilled until it became white powder with increasing temperature up to 130 °C. 2-Methoxyethanol was then added and refluxed for 3 h. This process was followed by the addition of tetra-*n* propyl-orthozirconate to the lead solution and it was refluxed during 2 h. Finally, tetra-isopropyl-orthotitanate was added to the solution and mixed for more than 12 h. The addition of the tetra-*n* propyl-orthorzirconate in the second step of the reaction and the 2-h refluxing were carried out in order to stabilize the solution and to avoid the formation of the titanium hydroxide [6].

The $Pb(Zr_x,Ti_{1-x})O_3$ solutions were spin-coated onto (1 1 1) $Pt/Ti/SiO_2/Si$ substrates using the following sequences: $x = 40$,

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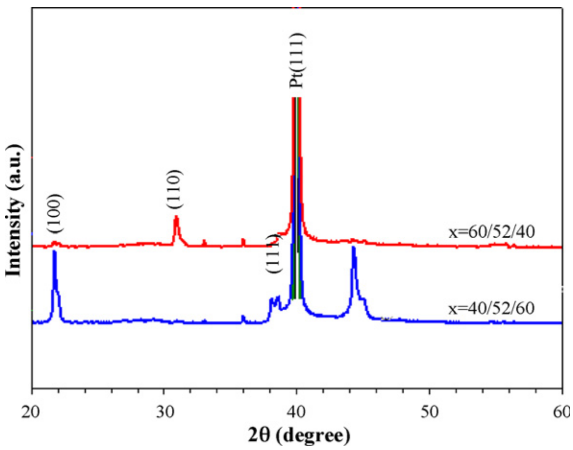

Fig. 1. XRD spectra for 40/52/60 and 60/52/40 $Pb(Zr_x,Ti_{1-x})O_3$ graded thin films.

52 and 60. This was an up-graded PZT film which was noted as PZT 40/52/60. For the down-graded PZT film, the sequence was reversed and the film was noted as PZT 60/52/40. All films were fired at 650 °C for 30 min in a tube furnace by a direct insertion method. The structure of the PZT thin films were analyzed by an X-ray diffractometer (Philips X'pert X-ray diffraction (XRD) system) with Ni filtered Cu Kα radiation. Microstructural analysis was performed by scanning electron microscopy (JEOL 5800 and JEOL2000 FX EM) at 20 kV with a Link AN-10000 EDXS system. To investigate the electrical properties of thin films, top electrodes of Au layer of 0.8 mm in diameter were prepared on the top surface of the graded PZT thin films through a shadow mask in a vacuum evaporation system. The polarization electric-field (*P*–*E*) hysteresis loop was obtained using a ferroelectric test module system (AIXACT TF Analyzer); the input signal was sinusoidal with a frequency of 1 kHz. The relative permittivity (ε_r) and loss tangent measurements were carried out in a frequency range of 10^2 to 10^6 Hz using an HP4284A LCR meter.

3. Results and discussion

All PZT graded structures show typical XRD patterns of perovskite polycrystalline structure without preferred orientation and without pyrochlore phase as shown in Fig. 1. From the XRD data, lattice constants for all films are summarized in Table 1. Fig. 2 illtustrates the surface texture of continuous and fine-grained microstructure without crack of the PZT films. This means that the grain size of the film is independent of the direction of the gradient compositions of the graded structure up- and down-graded of the PZT films. Fig. 3 is a representative cross-sectional SEM images for graded films. The well-defined layers of different *x* values were observed in PZT 40/52/60 film while there was a sign of depletion between $x = 40$ and 52 layers in PZT 60/52/40. This is related to the energy growth during the heat treatment process in the $x = 52$ layer which is very similar to that of $x = 40$ layer [7].

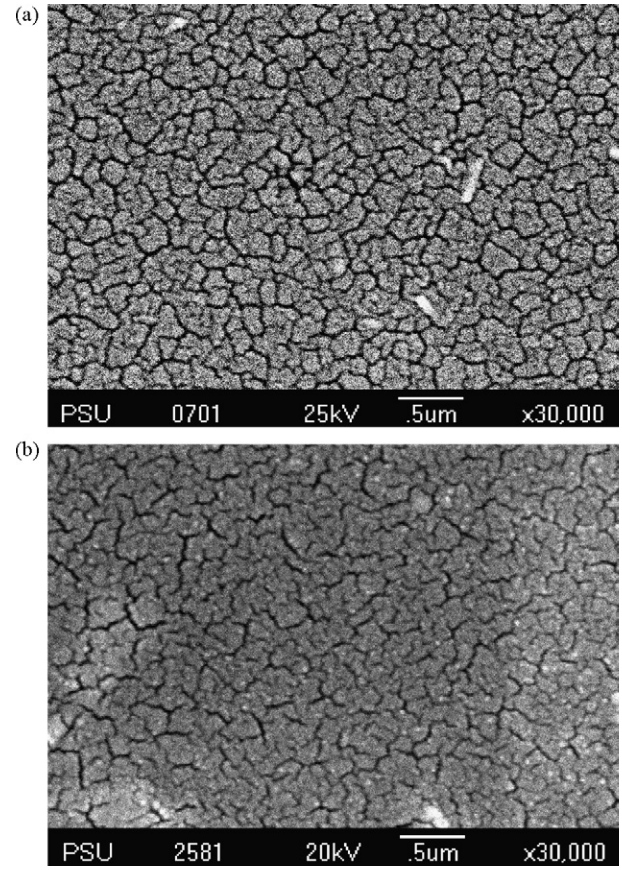

Fig. 2. SEM images for (a) 40/52/60 and (b) 60/52/40 $Pb(Zr_x,Ti_{1-x})O_3$ graded thin films.

Table 1
Lattice parameters summarized for graded PZT ($x = 40/52/60$) films

Sample	Orientation	2Θ	$d_{h\,k\,l}$ extracted	Lattice constants (nm) from (1 1 1) and (2 0 0)
40/52/60	100	21.77	4.0831	$a_t = 4.033$
	111	38.12	2.3611	$c_t = 4.070$
	111	38.57	2.3346	$a_r = 4.087$
	200	44.32	2.0442	
	200	44.87	2.0204	
60/52/40	100	21.77	4.0831	$a_r = 4.088$
	100	22.07	4.0283	$a_t = 4.025$
	111	30.92	2.8925	$c_t = 4.155$

The subscripts t and r refer to tetragonal and rhombohedral, respectively.

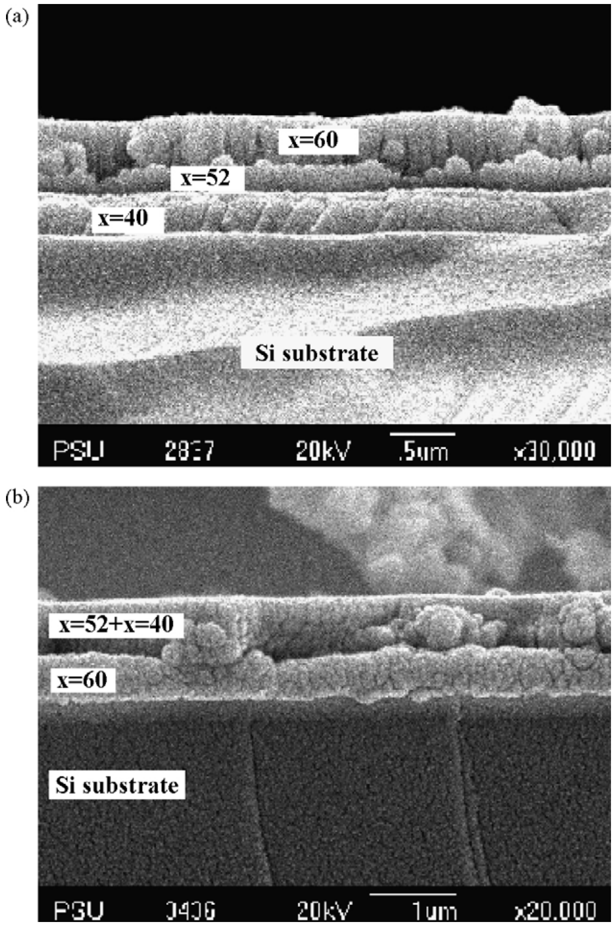

Fig. 3. Cross-sectional SEM images for (a) 40/52/60 and (b) 60/52/40 $Pb(Zr_x,Ti_{1-x})O_3$ graded thin films of average thickness of 1 μm.

Fig. 4 shows the variations of dielectric constants and dielectric loss as a function of frequency at room temperature. In comparison with single compositionally sol–gel PZT film [8], both graded PZT films possessed the relatively high value of dielectric constant and it was a higher value in up-graded PZT. This was related to a uniform stress distribution in the graded ferroelectric film reported elsewhere. [9,10] At 1 kHz,

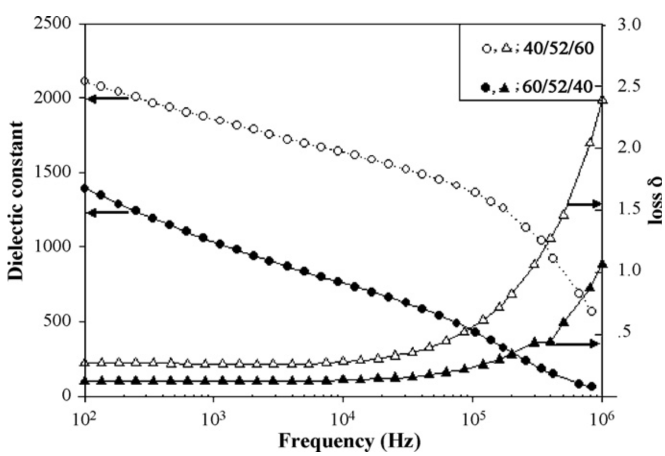

Fig. 4. Variations of the dielectric constant and loss tangent as a function of frequency of PZT graded films.

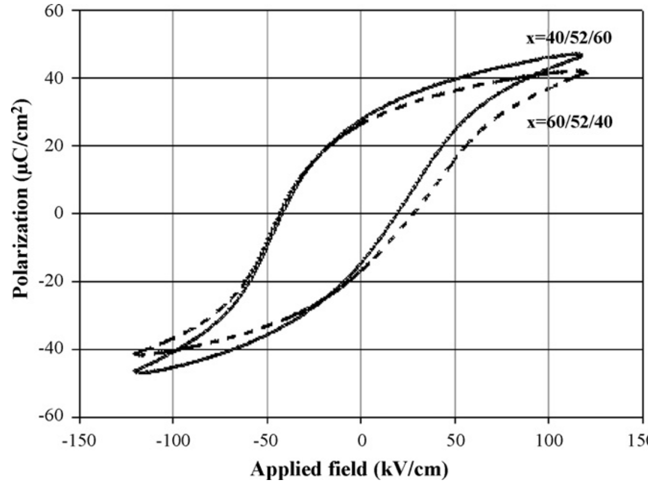

Fig. 5. *P–E* hysteresis loops of PZT graded films.

low-dielectric loss of 0.12–0.26 was found in the films. The high-dielectric loss was clearly obvious at frequencies higher than 10^5 Hz. This was probably because the fact that the graded films contained layers of different lattice parameters (Table 1) in accordance with tetragonal and rhombohedral compositions. Under an applied field with high-operating frequency, various lattice-misfit strains between layers became additionally enhanced, resulting in the high-dielectric loss in graded films [11,12].

Fig. 5 shows the well-defined *P–E* hysteresis loop and the P_r values for the PZT 40/52/60 and PZT 60/52/40 were 46 and 42 μC/cm^2, respectively. The corresponding coercive field values were 67 and 78 kV/cm, respectively. There was no shift of the polarization along the axis. From *C–V* measurement at room temperature (Fig. 6), the curves of both films revealed the expected butterfly shapes and symmetric loops about the zero applied electric field, indicating that the films are in the ferroelectric phase and there was no obvious internal bias field at the interfaces in the graded films. Fig. 6 also shows the thickness effect on the capacitance property of the PZT 40/52/60 films with different thicknesses. Compared to the 1-μm thick film, the 0.3-μm thick film had better dielectric behavior. This is due to the fact

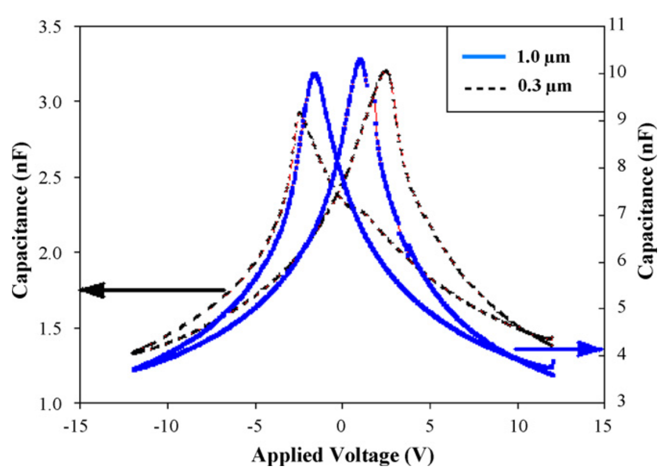

Fig. 6. *C–V* curves for PZT graded films with different thicknesses.

that the capacitance is inverse proportional to the film thickness and capacitance peaks are directly related to the switching of the ferroelectric polarization.

4. Conclusions

Compositionally graded $Pb(Zr_x,Ti_{1-x})O_3$ films of two types, i.e., up-graded 40/52/60 and down-graded 60/52/40, were grown on (1 1 1) $Pt/Ti/SiO_2/Si$ substrate using a conventional spin-coating method. All the PZT films exhibited a perovskite polycrystalline phase. Dense, smooth and pinhole-free surface morphology was obtained for both PZT 40/52/60 and 60/52/40 films. High values of dielectric constant of the graded films were obtained. Small coercive field with good remanent polarization and small coercive field with high-capacitance indicated that the graded PZT films are attractive for memory device applications. Understanding of the formation of various misfit strains and the prevention of the dielectric loss were addressed in further investigation.

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