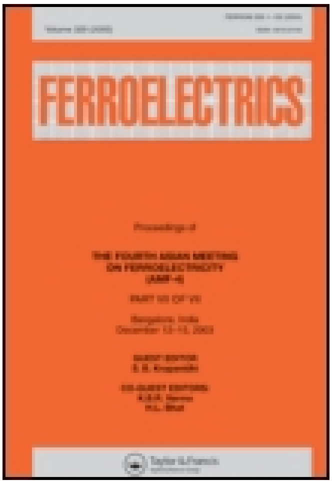

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Effect of Thickness on Microstructure and Electrical Properties of PZT Films Prepared by a Modified Sol-Gel Method

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A modified sol-gel multiple coating and annealing process was developed to prepare lead zirconate titanate $PbZr_{0.5}Ti_{0.5}O_3$(PZT) thin films with various thickness on Pt(111)/Ti/SiO_2/Si(100) substrates. The PZT films with thickness 280, 560 and 810 nm underwent one, two and three annealing cycles, respectively, which consisted of 5 coating layers, 10 coating layers and 15 coating layers. Surface morphology and phase structure of the thin films were studied by SEM and XRD, respectively. The relationship between the thickness, namely different annealing cycles, and degree of texture was investigated. The dielectric constant increases with increasing film thickness. The dielectric constant and dielectric loss of PZT films as functions of applied field and frequency had also been examined and discussed.

Keywords PZT thin film; sol-gel; thickness; orientation; electrical property

1. Introduction

There has been increasing interest in ferroelectric lead zirconate titanate (PZT) thin films for applications in nonvolatile memories and MEMS devices because of their excellent piezoelectric, dielectric, and pyroelectric properties [1]. The properties of PZT thin films are most dependent on composition ratio, bottom electrodes, thickness and annealing conditions. A variety of techniques have been adopted to fabricate PZT thin films [2–5]. Sol-gel technique is considered attractive due to its large deposition area, easy composition control and low cost. Usually, in conventional sol-gel method, PZT thin films with different thickness are obtained by varying spin RPMs, concentration of precursor solutions or coating layers. We report a modified sol-gel multiple coating and annealing process where strong textured thin films were prepared with the increasing of PZT film thickness. The effect of thickness on

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the microstructure, crystallization behavior and the dielectric properties of the PZT films were discussed.

2. Experiments Procedure

A PZT precursor solution (Zr/Ti = 50/50) was prepared using lead acetate trihydrate, zirconium nitrate pentahydrate, and titanium tetrobutoxide. 2-methoxyethanol and acetylacetone were used as the solvent and the chemical modifier, respectively. The coating solution of PZT films was deposited onto Pt(111)/Ti/SiO_2/Si(100) substrates by spin-coating at 4000 rpm for 30 s. After each spin-coating process, the wet PZT thin film was baked at 200°C on a hot plate for 5 min. A five-coated PZT thin film was obtained by repeating the coating and baking process for five times. Then the first annealing cycle was produced by annealing the five-coated PZT film at 600°C for 30 min by rapid thermal annealing (RTA) process. Five times spin-coating and pre-baking, one time post-annealing composed a so-called coating and annealing cycle. PZT thin films with three different thickness were received by repeating the coating and annealing cycle for one, two and three times, respectively.

The phases and crystal orientations of PZT films with different thickness were examined by X-ray diffraction (XRD-6000, SHIMADZU, Japan). The thickness of the PZT films was measured using a Microfigure Measuring Instrument (Surfcorder ET4000M, Kosaka Laboratory Ltd., Japan). The surface morphology of the PZT films was observed using a Scanning Electron Microscope (XL30, Philips). The dielectric constant and dielectric loss of PZT films as functions of applied field and frequency were measured using an impedance analyzer (HP4194A, Hewlett-Packard).

3. Results and Discussions

3.1 Phase Crystallization and Microstructure

Figure 1 shows the XRD patterns of $Pb(Zr_{0.5}Ti_{0.5})O_3$ thin films with various annealing cycles of (a) one, (b) two, and (c) three, which have the thickness of 280 (5 layers), 560

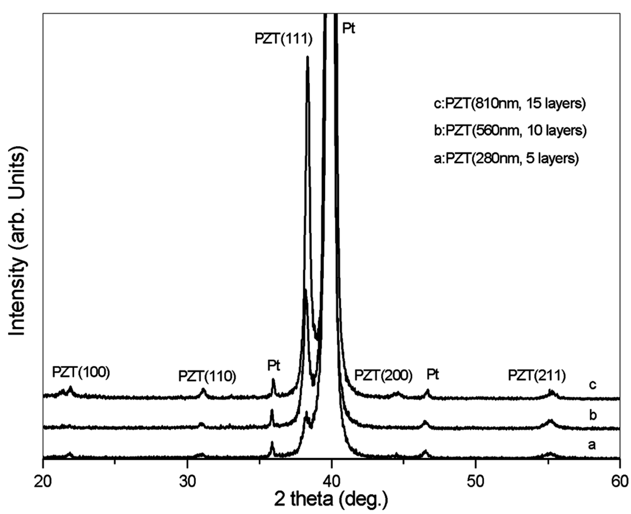
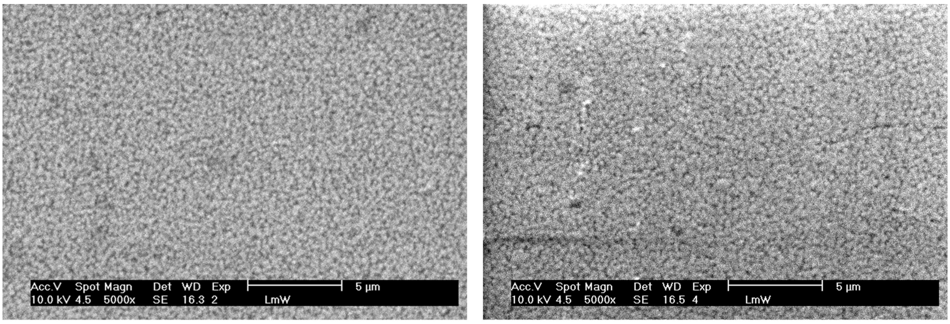


Figure 1. XRD patterns of PZT films with various annealing cycles of (a) one, (b) two, and (c) three.



(a) (b)

Figure 2. SEM image of the surface morphology of the PZT films with (a) five and (b) fifteen layers.

(10 layers) and 810 nm (15 layers), respectively. X-ray diffraction reveals that all the PZT films consist of the perovskite phase with no detectable pyrochlore phase and exhibit highly (111) preferred orientation. It has been reported that the lattice parameter of intermetallic compound (Pt_3Ti) formed on $Pt/Ti/SiO_2/Si$ substrate matches closely that of PZT (111) [6]. Therefore, PZT (111) nucleates directly on Pt due to lattice matching. As the film thickness increase, the (111) diffraction peak of PZT films become much stronger and shaper. However, the relative intensity of other diffraction peaks such as (110) and (211) has little difference with the increase of film thickness.

The surface micrographs (Fig. 2) of PZT films reveal that the films with different thickness are dense and crack-free. The average grain size of the PZT films is about 200~250 nm. No dependence of grain size on film thickness is evident in the SEM photographs, which may result from the fact that the spin coating time (five times in our experiment) is fixed in each crystallization annealing process, even though the PZT films have the different thickness.

3.2 Dielectric Properties

All the films exhibit butterfly-type capacitance hysteresis loops, which can be attributed to ferroelectricity of PZT films. Figure 3 shows the C-V characteristics of PZT film (810 nm, 15 layers) at 1 kHz under different applied voltage levels. Switching voltages are independent of the applied voltage from 7.5 to 10.5 V and are about −2 and 2.5 V, respectively. From the C-V curves, it is observed that the centers of the hysteresis loops are not located at 0V, but shift to the positive bias voltage. This is very likely due to the existence of the internal bias field at electrode-film interface, which may be induced by the different thermal history of the top and bottom electrodes.

Figure 4(a) shows the dielectric constant—electric field characteristics of PZT films with different thickness. The P-E hysteresis loops of PZT films in Fig. 4(b) were measured as a function of the applied field from 80 to 150 kV/cm using the TF Analyzer 2000 on FE mode at a frequency of 100 Hz. It is observed that the 810 nm thick PZT film possesses higher dielectric constant than that of 560 nm thick PZT film. The PZT film with small thickness shows the relatively slow increase and decrease of permittivity. These features are similar to the P-E hysteresis loops in Fig. 4(b), which exhibit a faster switching process for the PZT film with 15 layers coating.

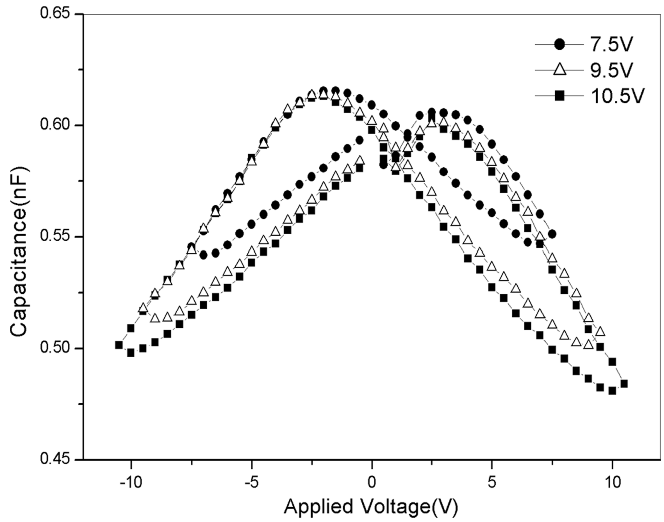


Figure 3. C-V characteristics of PZT (810 nm, 15 layers) film under different applied voltage levels.

As shown in Fig. 5(a), the relative dielectric constants are 311,484 and 652 for the PZT films at 1 kHz with one, two, and three annealing cycles, respectively. Dielectric constants have slight decrease with increasing frequency and increase obviously with the increase of PZT film thickness. The presence of the low permittivity layers between the PZT film and two electrodes have substantial influence on the dielectric response of ferroelectric thin films [7]. The thickness-dependent permittivity can be explained by the mechanism that the influence on the whole permittivity of thin film tends to decrease as the film thickness increases [8].

As shown in Fig. 5(b), dielectric loss decreases with increasing frequency for the film undergoing one annealing cycle. However, besides the decreasing tendency, both the peaks of dielectric loss in PZT films undergoing two and three annealing cycles were found at

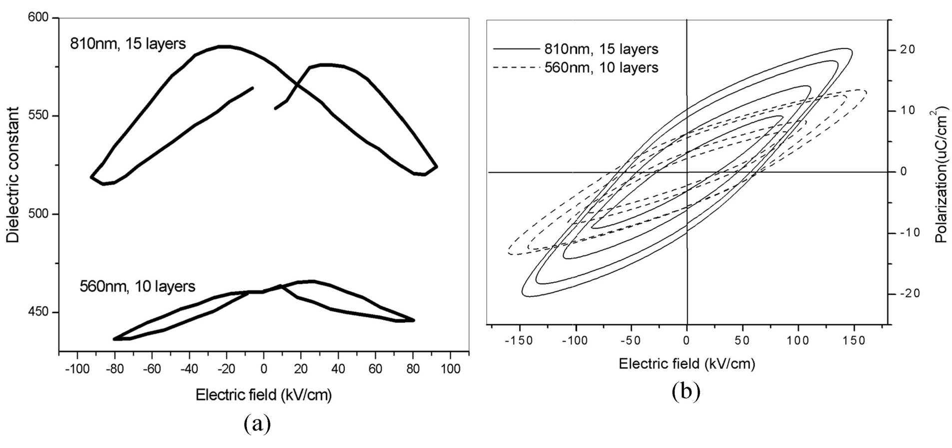


Figure 4. Dielectric constant (a) and polarization (b) of PZT thin films with thickness of 810 nm and 560 nm as a function of electric field.

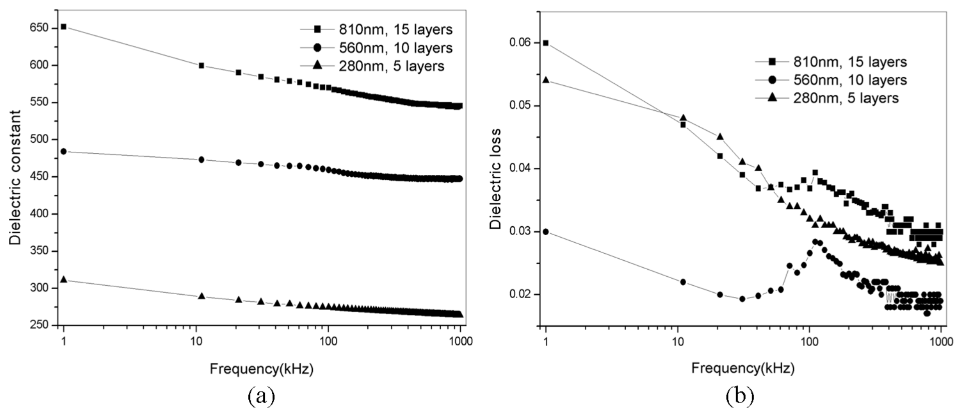


Figure 5. Variation of the dielectric constant(a) and the dielectric loss(b) of PZT films with various thickness as a function of frequency.

the same frequency of 120 kHz. This indicated an evidence of the relaxor behavior of PZT films fabricated more than one annealing cycle, which may be due to the presence of passive layers at PZT-PZT interfaces formed by multiple annealing processes.

4. Conclusion

Highly (111) oriented $PbZr_{0.5}Ti_{0.5}O_3$ thin films with various thicknesses were prepared on Pt/Ti/SiO_2/Si substrate by a multiple coating and multiple annealing sol-gel method. Using the modified technique, PZT thin films show a dense grain structure and consist of identical grain size regardless of the film thickness. The dielectric constant increases with increasing film thickness. It is concluded that highly textured PZT films with desired thickness and dielectric properties can be obtained by optimizing the coating layers and annealing cycles.

Acknowledgments

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