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Damping properties of epoxy-based composite embedded with sol–gel-derived $Pb(Zr_{0.53}Ti_{0.47})O_3$ thin film with different thicknesses

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Abstract. **$Pb(Zr_{0.53}Ti_{0.47})O_3$ (PZT) thin films were prepared on Pt/Ti/SiO_2/Si substrate by sol–gel method. The effect of film thickness on microstructure, ferroelectric and dielectric properties was investigated. The single-phase PZT films were obtained with different thicknesses. PZT films with a thickness of 190–440 nm had better dielectric and ferroelectric properties. The epoxy/PZT film/epoxy sandwiched composites were prepared. The thickness of PZT films influenced their damping properties of the composites, and the epoxy-based composites embedded with 310 nm-thick PZT films had the largest damping loss factor of 0·915.**

Keywords. **$Pb(Zr_{0.53}Ti_{0.47})O_3$ thin film; sol–gel method; film thickness; damping property; epoxy-based composite.**

1. Introduction

Vibrations can result in equipment damage and production accidents, and shorten the service life of materials. Damping materials have an ability to dissipate the vibration energy, and they have been widely used in the fields of aerospace, marine, aircrafts, automobiles, etc (Alghamdi and Dasgupta 2000; Cai *et al* 2006; Anthony *et al* 2009). Piezoelectric materials are a class of useful damping materials, with which the vibration energy is changed into electric energy due to the piezoelectric effect and the electric energy is dissipated as thermal energy through an external electric resistance (Sun and Huang 2001; Edery-Azulay and Abramovich 2006; Erturk *et al* 2008). But the piezoelectric damping materials are generally brittle, fragile and hard. In order to improve their properties, Newnham *et al* (1978) prepared the piezoelectric composite composed of piezoelectric materials and polymers. The piezoelectric composite overcomes the weakness that properties of polymers heavily depend on the temperature and frequency, and avoids the disadvantage of piezoelectric materials, and preserves the advantages of the two materials. There are many studies reported on the damping properties of epoxy-based composites with piezoelectric particles or fibres (Shields *et al* 1998; Chan *et al* 2003; Ray 2006; Tanimoto 2007; Liu *et al* 2008; Ma and Wang 2009). $Pb(Zr_{0.53}Ti_{0.47})O_3$ (PZT) is a typical piezoelectric material which has been widely used in the piezoelectric composites (Lin and Ermanni 2004; Li *et al* 2006; Wang *et al* 2009). However, for these composites, the piezoelectric phase was dispersed in the epoxy resin. In our previous work, the piezoelectric PZT films were embedded in the composites and the piezoelectric phase was kept as a whole (Fu *et al* 2011; Guo *et al* 2012). The damping properties of composites were improved with improving ferroelectric properties of PZT films. The ferroelectric properties of PZT films were also influenced by the film thickness.

In this study, PZT thin films were prepared on Pt/Ti/SiO_2/Si substrates by sol–gel method, and then the film was embedded in the epoxy resin. The effect of PZT film's thickness on microstructure, ferroelectric and dielectric properties of PZT thin films, and the damping properties of epoxy/PZT composites were investigated.

2. Experimental

$Pb(CH_3COO)_2$, $Zr(NO_3)_4$ and $Ti(OC_4H_9)_4$ were used as the source materials for Pb^{2+}, Zr^{4+} and Ti^{4+} ions, respectively. The solvents were 2-methoxyethanol and acetylacetone. All chemical agents used were of analytic purity. The desired amounts of $Pb(CH_3COO)_2$ (with 10 mol% excess), $Zr(NO_3)_4$ and $Ti(OC_4H_9)_4$ corresponding to $Pb(Zr_{0.53}Ti_{0.47})O_3$ composition were dissolved in 2-methoxyethanol and acetylacetone, respectively. After they were fully dissolved, these solutions were mixed together to obtain 0·3 mol/L PZT precursor. The PZT thin films were coated on Pt/Ti/SiO_2/Si substrates by a spin coater at 3000 r/min for 30 s, and then the as-coated films were heated at 350 °C for 10 min. The above process was repeated for several times to obtain films

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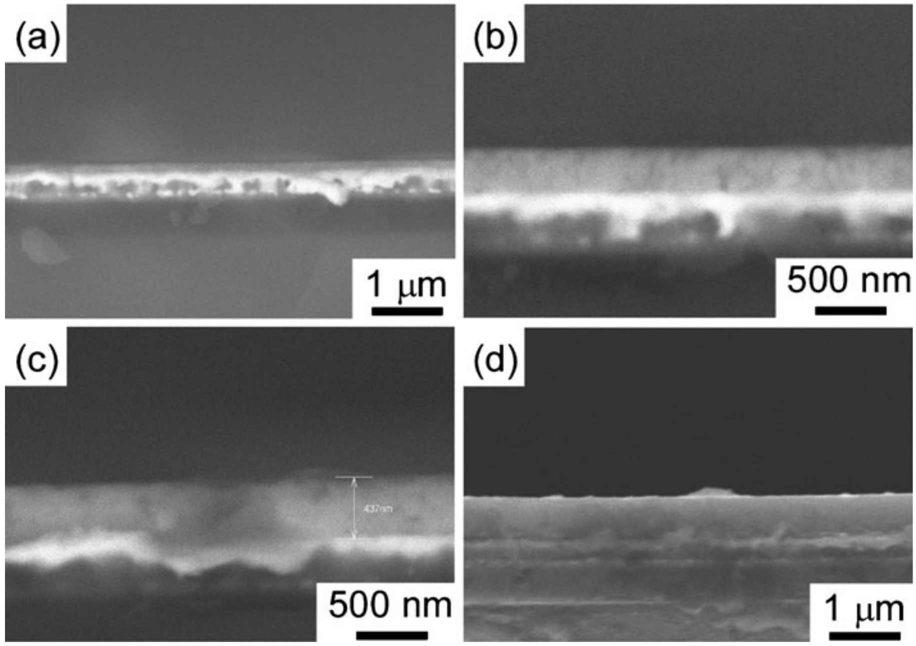

Figure 1. Typical cross-section morphologies of PZT films: (a) 2 layers, (b) 6 layers, (c) 8 layers and (d) 10 layers.

of desired thickness. Finally, the films were annealed at 700 °C for 90 min in air atmosphere. PZT thin film with substrate was sandwiched between two epoxy resin layers, and polyethylene polyamine was added as a curing agent. Finally, $15 \times 5 \times 2$ mm^3 composite specimens were cured at room temperature for 24 h and 80 °C for 2 h. The details of preparation were reported elsewhere (Guo *et al* 2012).

The crystal structure of PZT films was analysed by an X-ray diffractometer (XRD, Rigaku D/Max-IIIA) with CuKα radiation. The scanning rate was 4°/min. The surface morphologies were observed by a field emission scanning electron microscope (FESEM, JEOL JSM-7500F). Top electrode with Au, the area of $1{\cdot}0 \times 10^{-3}$ cm^2, was sputtered using a shadow mask. The ferroelectric properties were measured by radiant precision workstation ferroelectric tester system, and the dielectric properties were measured by an Agilent HP4294A precision impedance analyser at room temperature. Damping properties were evaluated by a dynamic mechanical analyser (J Diamond-DMA) in tension mode at a frequency of 1 Hz, with a heating rate of 2 °C/min from 20 to 180 °C.

3. Results and discussion

The thickness of PZT films was observed according to the cross-sectional morphologies as shown in figure 1. In this study, one coating cycle means 1 layer. The thicknesses of PZT films with 2, 4, 6, 8 and 10 layers were about 120, 190, 310, 440 and 630 nm, respectively which indicated that the 1-layer thickness was 50–60 nm. Figure 2 displays XRD results of PZT films with different thicknesses. The 120 nm-thick

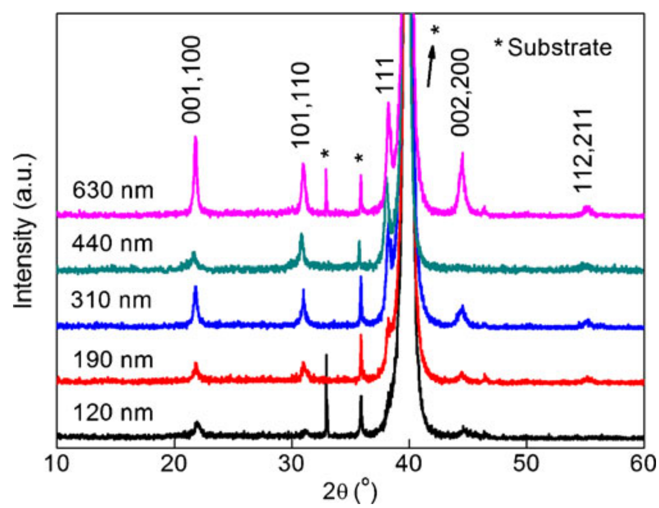

Figure 2. XRD patterns of PZT films with different thicknesses.

PZT film showed weak peaks. With increasing film thickness, the intensity of peaks became stronger.

Figure 3 depicts the polarization–electric field (P–E) hysteresis loops of PZT films under an applied E of 320 kV/cm. All PZT films had well loops. With increasing film thickness from 120 to 440 nm, the variation of remnant polarization ($2P_r$) and coercive electric field ($2E_c$) was small. But for the 630 nm-thick PZT film, $2P_r$ decreased and $2E_c$ increased abruptly. The 310 nm-thick PZT film showed better ferroelectric property with $2P_r$ of 50 μC/cm^2 and $2E_c$ of 155 kV/cm.

The dielectric properties of PZT films as a function of frequency ranging from 40 Hz to 1 MHz are depicted in

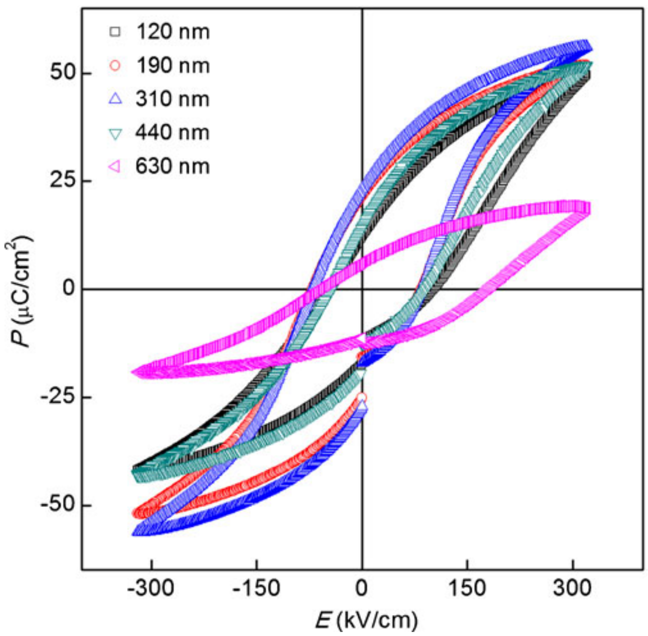

Figure 3. *P–E* hysteresis loops of PZT films with different thicknesses.

figures 4(a) and (b). With increasing frequency, both dielectric constant (ε_r) and dielectric loss (tan δ) decreased abruptly at $40^{-6} \times 10^5$ Hz, and decreased slightly at 6×10^5–1×10^6 Hz. For the ferroelectric films, ε_r was mainly attributed to the intrinsic ferroelectric polarization at high frequency (Guo *et al* 2009). The dependence of film thickness on ε_r and tan δ at 1 MHz is shown in figure 4(c). With increasing film thickness, tan δ increased, and ε_r increased to the maximum of 569 at 310 nm and then decreased. The 310 nm-thick PZT film had better dielectric property with ε_r of 569 and tan δ of 0·032 at 1 MHz.

Damping loss factor is an important parameter to represent the damping capacity of the materials that expresses an ability of converting the mechanical energy into heat energy when the material is subjected to an external loading. Figure 5 shows dependence of temperature on damping loss factor of epoxy/PZT film/epoxy sandwiched composites. In the vicinity of the glass transition temperature (T_g) of the composites, with variation of the film thickness, the peaks shifted. As shown in figure 5(b), with increasing film thickness, the temperatures of peak (T_p) in the curves showed increased tendency, and the top damping loss factor increased to a maximum of 0·915 at 310 nm and then decreased. In

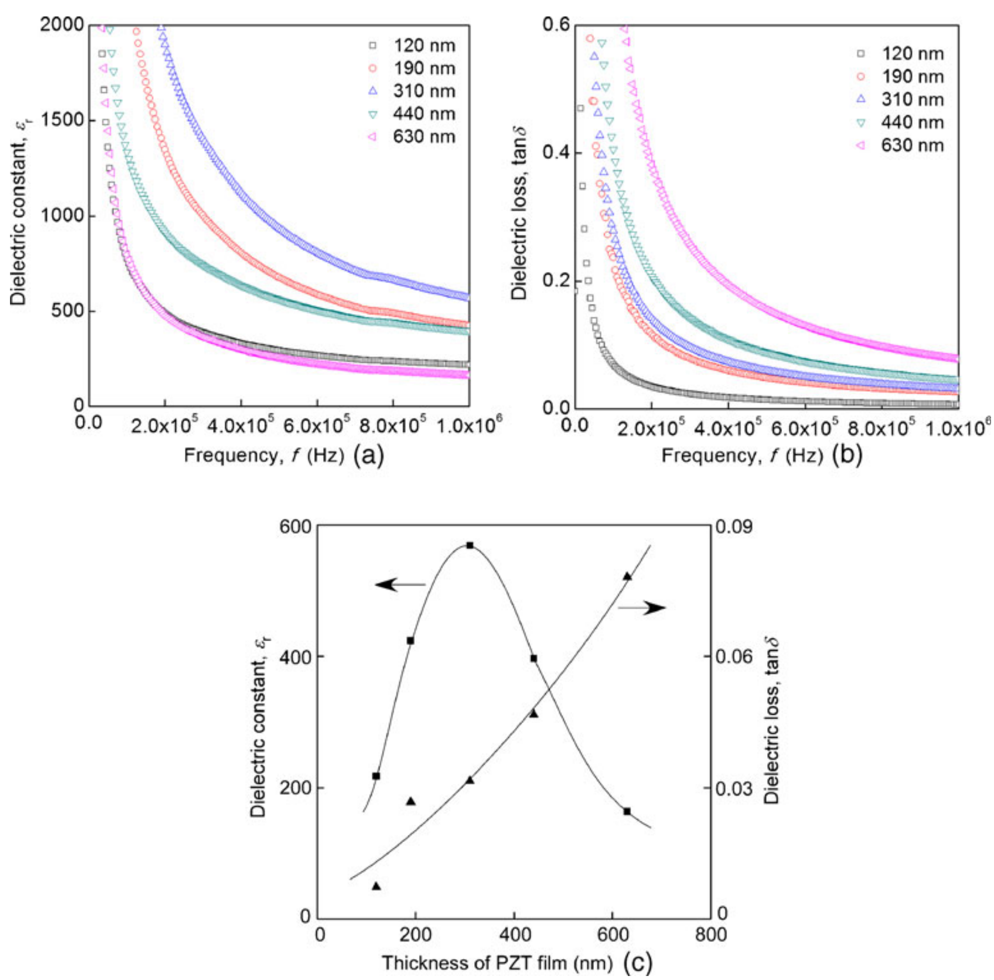

Figure 4. Dielectric properties of PZT films with different thicknesses: (a) ε_r, (b) tan δ and (c) dependence of film thickness on ε_r and tan δ at 1 MHz.

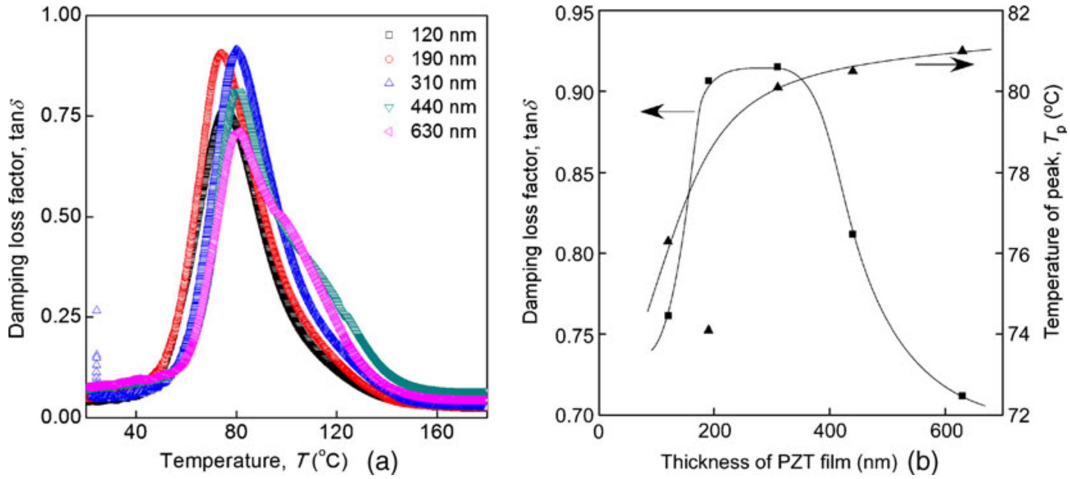

Figure 5. Damping properties of epoxy/PZT film/epoxy sandwiched composites: (a) dependence of temperature on damping loss factor and (b) influence of film thickness on top damping loss factor and T_p.

these systems, other components were almost the same, and only PZT films were different. The variation of damping loss factor was attributed to piezo-damping effect because of PZT films.

There were two possible reasons to explain the variation of ferroelectric, dielectric and damping properties. One was the crystallization of PZT phase. In this study, the crystallization was improved with increasing film thickness, which helped to improve the ferroelectric and dielectric properties. Another was the stress and interfacial trouble due to the sol–gel method. It was well known that the spin-coating process had to be repeated many times to obtain the desired film thickness. With increasing film thickness, the stress became large, and interfacial defects increased, which resulted in poor dielectric and ferroelectric properties. The variation of ferroelectric and dielectric properties was caused by competition of the two processes. In this study, the 630 nm-thick PZT film had a poor surface morphology and awful properties. For the PZT films, the variation of piezoelectric properties were monotonically corresponding to those of ε_r and polarization (Kholkin *et al* 2001), so the PZT films with a thickness of 190–310 nm also had better piezoelectric properties. Then epoxy-based composites embedded with PZT films with a thickness of 190–310 nm had larger damping loss factor.

4. Conclusions

PZT thin films were prepared on Pt/Ti/SiO_2/Si substrate by sol–gel method. The single-phase PZT films were obtained with different thicknesses. PZT films with a thickness of 190–440 nm had better dielectric and ferroelectric properties. The thickness of PZT films influenced the damping property of the composites, and the epoxy-based composites embedded with 310 nm-thick PZT films had the largest damping loss factor of 0·915, which indicated that the PZT films had potential application to damping composites.

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