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# Electrical and optical properties of PZT ferroelectric films fabricated by the PVP-assisted sol-gel method

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**Abstract** Lead zirconate titanate (PZT) films were deposited on platinized silicon substrates by spin coating using organic macromolecule polyvinylpyrrolidone (PVP) as an additive, which has the hybrid effects, was dispersed uniformly into the sol-gel precursor solution of PZT. The films were coated by spin-coating and then annealed at a proper temperature by repaid thermal processing. PZT ferroelectric films were polycrystalline and perovskite phase structure. The Coercive Field and remnant polarization of the PZT films annealed at 600 °C were 91 kV/cm and 19 μC/cm$^2$ respectively. The fatigue resistance properties were improved and the polarization value decreased only 8% of the initial polarization at $10^8$ cycles. The optical properties were measured by spectrophotometer and the band energy was calculated about 3.59eV.

**Keywords** PZT · PVP · Fatigue · Ferroelectrics · Optical

## 1 Introduction

Lead Zirconate Titanate ($PbZr_xTi_{1-x}O_3$ or PZT) films are potentially important materials for a variety of devices such as high-density capacitors integrated on dynamic random access memories (DRAMs), ferroelectric memories, infrared pyroelectric sensors and in other integrated technologies [1, 2]. Among all the methods of preparing PZT films, the sol-gel process is widely applied because of its good reproducibility, acceptable processing temperatures and low cost. However, conventional sol-gel coating normally allows crack-free films only less than 0.1 mm in thickness; thicker films undergo cracking and/or delamination on gel-to-ceramic film conversion [3].

In recent years, a new method to fabricate the thicker, dense $BaTiO_3$ and PZT films was used by incorporating polyvinylpyrrolidone (PVP) in precursor solutions to increase the thickness of coating films [4]. The thickness of one-step fabrication films is over one micrometer. However, reports about the ferroelectric and optical properties of the PZT films fabricated from the PVP assisted processing is still few.

The present paper mainly describes the electrical and optical properties of PZT ferroelectric films prepared by PVP-assisted sol-gel method. The fatigue properties and the transmittance properties were investigated as well as the microstructure of the films were mentioned.

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## 2 Experimental

The precursor solution was prepared to give a nominal stoichiometry of $Pb(Zr_{0.52}Ti_{0.48})O_3$. For the synthesis of PZT sols, tetrabutyl titanate [$Ti(OC_4H_9)_4$], lead acetate trihydrate [$Pb(CH_3COO)_2 \cdot 3H_2O$] and tetrabutyl zirconate [$Zr(OC_4H_9)_4$] were used as starting materials. Ethylene glycol monoethyl ether ($HOCH_2CH_2OC_2H_5$) was used as solvent. PVP powders with an average molecular weight of 30,000 (K30) were dissolved in the solvent and acted as the chelating agent. The molar ratio of PVP to PZT was 1:1, where moles of PVP represent those of the monomer (polymerizing repeating unit) of PVP. The solution was stirred at 85 °C for 2 h to obtain the stabilized yellow sols and the concentration was 0.5 mol/l.

The PZT films were deposited on the Pt(111)/Ti/$SiO_2$/Si (100) substrates by spin coating process. The substrates were prepared by sputtering and pre-annealed at 600 °C for 30 min to release the stress. Precursor solution was spun on the substrate at 3,500 rpm for 30 s. The coated substrates were baked at 400°C for 10 min on the hotplate before next deposition. Four deposition cycles were repeated to prepare thicker films. The films were annealed at 600°C for 20 min to form the perovskite phase by repaid thermal processing.

The film crystallization behavior and surface morphology observations were carried out using X-ray diffractometer (CuKα, Rigaku D/max-2400) and by taping mode atomic force microscopy (AFM: nanoscope, Veeco) respectively. For electrical measurement, 1-mm-diameter upper electrodes of Au were fabricated by direct current sputtering using a mask. The dielectric properties were measured on films in a metal-ferroelectric-metal (MFM) configuration, with a HP4192A precision LCR meter (Hewlett-Packard). The P-E hysteresis loop measurements and fatigue properties were carried out with a TF Analyzer2000 standardized ferroelectric test system (Germany, AixACCT Systems). The transmittance properties were measured by UV/VIS/NIR spectrophotometer (JASCO V-570) and the optical band gap energy was calculated.

## 3 Results and discussions

### 3.1 Crystalline structure and microstructure

Figure 1 shows the XRD pattern of PZT films on Pt/Ti/$SiO_2$/Si(100) substrates annealed at 600 °C for 20 min by rapid thermal processing. As observed in Fig. 1, the films showed perovskite structure and were polycrystalline with no evidence of preferential orientation. The relative weak peak intensity and broader phenomena indicated that the size of crystal was small.

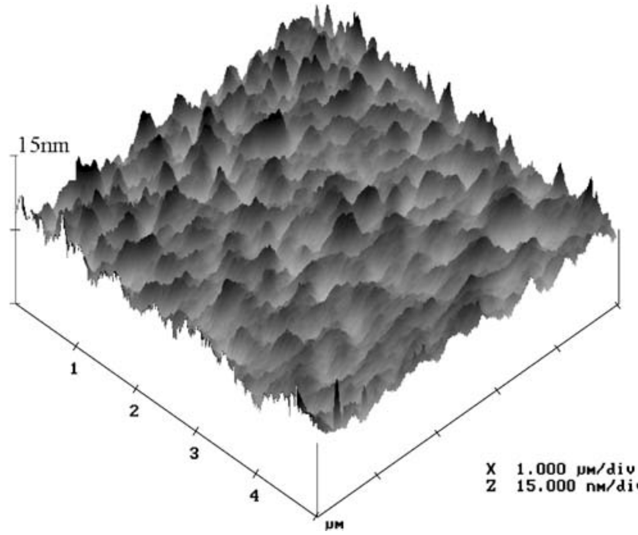

**Fig. 2** AFM image of the PZT film surface

Atomic force microscopy (AFM) was used to obtain an accurate analysis of the sample surface and the quantification of very important parameters such as roughness and grain size. The scan rate was 1.485 Hz and the number of lines was 512. The roughness of surface film was characterized by the $r_{ms}$, which was defined as the root mean square roughness. Figure 2 shows the AFM image on the surface of PZT films annealed at 600 °C for 10 min. The surface structure of PZT films was compact without crack and smoothly. The $r_{ms}$ of 5×5 μm area was measured about 2 nm. The grain size of the film surface was about 200 nm.

Figure 3 is the cross-sectional scanning electron microscopy (SEM) micrograph of PZT film. The film contains four layers and the total thickness is about 1 μm. Columnar

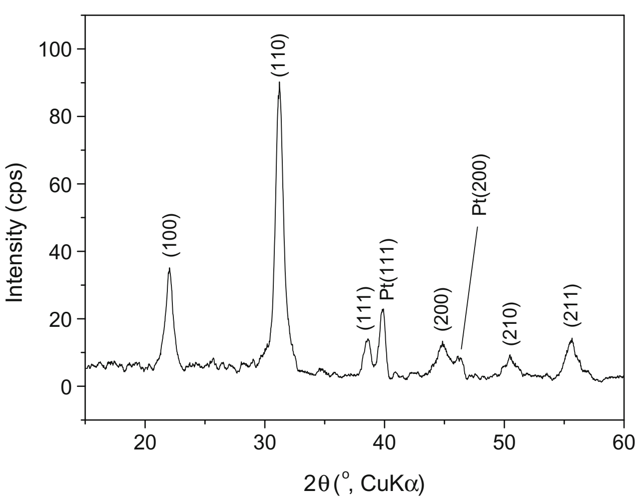

**Fig. 1** XRD patterns of PZT films on Pt/Ti/$SiO_2$/Si(100) substrates

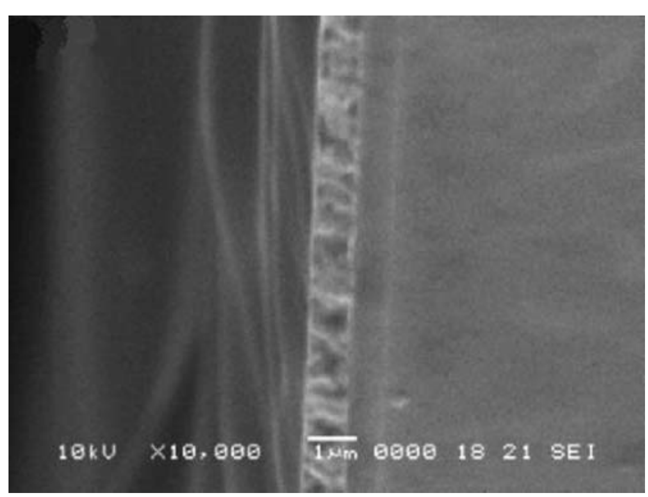

**Fig. 3** Cross-sectional SEM micrograph of the PZT films

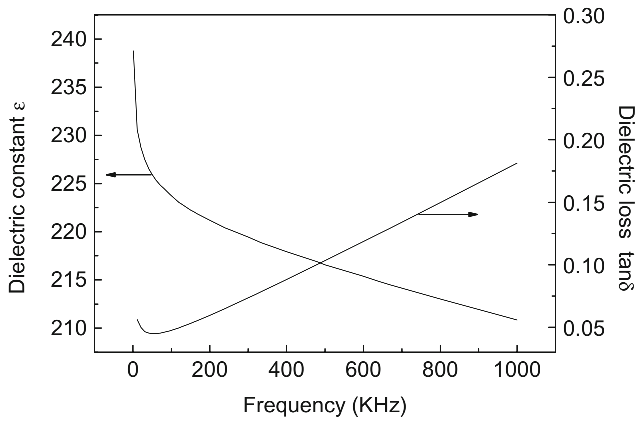


Fig. 4 Dielectric properties of PZT films with Au/PZT/Pt capacitor

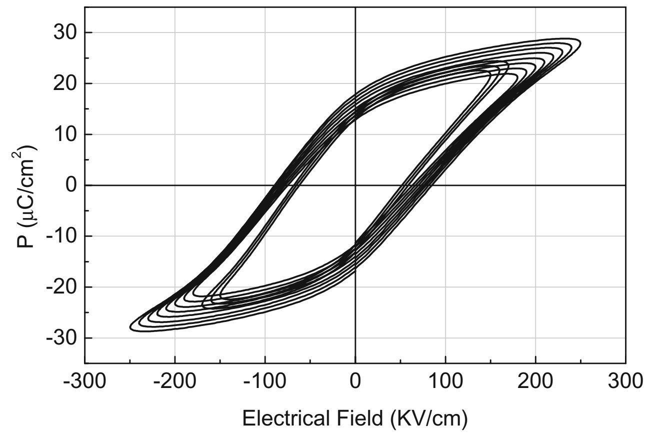


Fig. 6 Fatigue properties of PZT ferroelectric films

crystal growth perpendicular to the substrate can be observed. The SEM images show that the film is dense and crack-free.

### 3.2 Electrical properties

Figure 4 shows dielectric constant and dielectric loss versus frequency for PZT films. The dielectric constant of the films decreased approximately 12.5% with the increase of applied frequency from 1 kHz to 1 MHz. The dielectric loss of 1 μm-thick PZT film at 100 kHz was 0.05 and the dielectric constant was calculated as 223. The relatively lower dielectric constant measured in this work could be due to the small grain of the film [5].

Figure 5 shows the typical P-E hysteresis loop of PZT films with Au/PZT/Pt configuration measured by TF Analyzer2000 standardized ferroelectric test system. The coercive field ($E_c$) and the remnant polarization ($P_r$) of PZT films annealed at 600 °C were 91 kV/cm and 19 μC/cm$^2$ respectively. The large coercive field was contributed to the stress effects originated from the mismatch between the films and substrates and the grain size effects of the films. The relative lower values of polarization were due to the size effects while the grain size was small in the films [6].

Square and bipolar pulses of ±5 V at 100 Hz were applied to the MFM capacitors to study their fatigue characteristics of PZT films using TFA2000 system. Figure 6 shows polarization and coercive field ($E_c$) versus the number of cycles for PZT films. The polarization value of PZT films decreased only 8% of the initial polarization at 10$^8$ cycles while the $E_c$ value increased about 15%. The characteristics of fatigue resistance were increased accompanying with the well organized microstructure [7]. This is also clear from the fact that there is little difference in the hysteresis properties of the capacitors before and after the fatigue test as also shown in Fig. 6. It can be noted that PVP-assisted processing offer significant fatigue reduction compared to conventional processing.

### 3.3 Optical analysis

The optical transmittance characteristics of the PZT films on fused silica substrate were measured and shown in

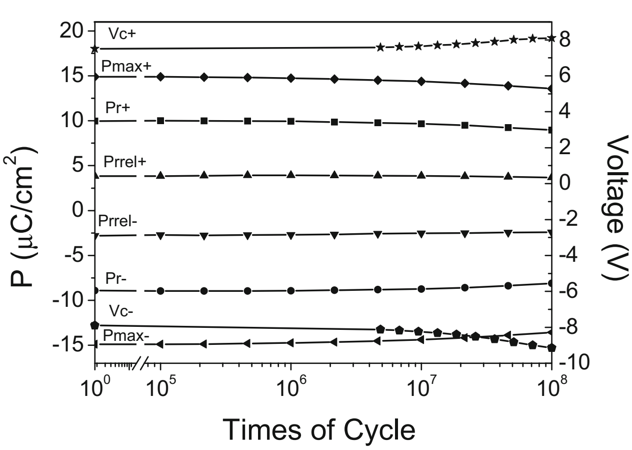


Fig. 5 P-E hysteresis loop of Au/PZT/Pt configuration

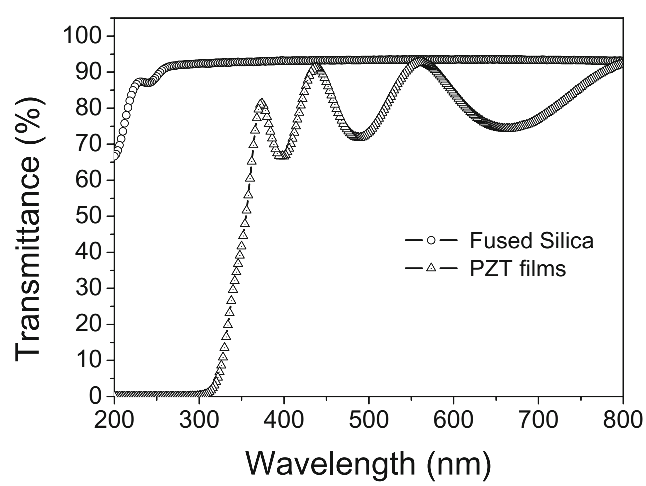


Fig. 7 Transmittance characteristics of PZT films on fused silica substrate

Fig. 7. The absorption edge is about 336 nm. From the Panda's results reported in the literature [8], the improved crystallinity leads to increased transmittance of the film. The transmittance characteristics indicated that the PZT films were well crystalline with small grain size, which confirmed with the results of XRD shown in Fig. 1.

The optical band gap energy of PZT films was deduced from the spectral dependence of the absorption constant $\alpha(\lambda)$by applying the Tauc relation [9]

$$\alpha h\upsilon = \text{const.} \times \left(h\upsilon - E_{\text{g}}\right)^{\frac{1}{r}} \quad (1)$$

where $r$=2 for a direct allowed transition. The absorption $\alpha(\lambda)$was determined from each transmittance spectrum using an extrema (or minima) envelope method, described in detail elsewhere [10]. $\alpha(\lambda)$ is given as

$$a(\lambda) = -ln(T)/d \quad (2)$$

in which $T$ is transmittance and d is the film thickness. The optical band gap was determined by extrapolating the linear portion of the plot to $(\alpha h\upsilon)^2 = 0$, and the value was calculated as 3.59 eV. This was in agreement with the experimental results of composition-dependent band gap measurements of PZT films reported in the literature [11].

## 4 Conclusions

Lead zirconate titanate (PZT) films were fabricated by spin-coating using organic macromolecule polyvinylpyrrolidone (PVP) as an additive, which has the hybrid effects, was dispersed uniformly into the sol-gel precursor solution of PZT. The films were annealed at 600°C by repaid thermal processing. PZT ferroelectric films were polycrystalline and perovskite phase structure. The dielectric constant and dielectric loss were 232 and 0.05 respectively at 100 kHz. The coercive field and remnant polarization of the PZT films were 91 kV/cm and 19 μC/cm$^2$ respectively. The fatigue resistance properties were increased and the polarization value decreased only 8% of the initial polarization at $10^8$ cycles. The optical properties were measured by spectrophotometer and the band energy was calculated about 3.59 eV. The transmittance characteristics indicated that the film was well crystalline with small grain size.

All the results show that PVP-assisted sol-gel processing is a promising method for preparing PZT ferroelectric and piezoelectric films to apply for the DRAMs, FeRAM and other integrated devices.

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