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Fabrication and characteristics of PZT thick films on Pt/Ti foil substrates for piezoelectric vibrators

Xi-Yun He · Yong Zhang · Ai-Li Ding · Xia Zeng · Ping-Sun Qiu

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Abstract Crack free perovskite $PbZr_{0.53}Ti_{0.47}O_3$ (PZT (53/47)) thick films up to 30 μm were prepared on flexible platinum-coated titanium foil substrates (Pt/Ti) by a metal organic decomposition (MOD) process. The dielectric, ferroelectric and piezoelectric properties of the films were examined and discussed. A well-saturated hysteresis loop of the thick film was present in almost rectangular shape (Pr= 35 μC/cm^2; Ec=32 kV/cm). The efficient piezoelectric coefficient $d_{33,\ f}$ of the thick film is about 448 (1 kHz). PZT piezoelectric vibrators were made in bimorph mode. The displacements of the vibrators were investigated as the functions of the applied electric field and the substrate thickness. Under the same condition, the vibrator made from the thinnest Pt/Ti substrate gives the largest displacement.

Keywords PZT thick films · MOD process · Piezoelectric vibrators

1 Introduction

Lead zirconate titanate ($Pb(Zr_x,Ti_{1-x})O_3$), PZT) ferroelectric films promise a great potential application in micro-electro-mechanical systems (MEMS) for their excellent electromechanical and piezoelectric properties[1–6]. PZT films 1–30 μm thick is particularly suitable for the micro-devices because of the higher force and better sensitivity [7, 8]. Many deposition processes have been proposed to prepare PZT thick films including hydrothermal method, MOD process, 0–3 composite method and screen printing [2, 7–10]. Among the methods, MOD process is particularly suitable to obtain films with high quality, accompanied with the advantages of good control of stoichiometry of films, lower crystalline temperature and low cost. In this study, crack free PZT (53/47) thick films up to 30 μm were prepared by MOD process on the flexible Pt/Ti foil substrates. A one-step firing process with a fast heating rate and high pre-firing temperature was employed to restrain the film from cracking [11]. The structure and electric properties of the films were examined and evaluated. PZT piezoelectric vibrators were fabricated and characterized.

X.-Y. He (✉) · A.-L. Ding · X. Zeng · P.-S. Qiu
State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences,
1295 Ding Xi Road,
Shanghai 200050, China
e-mail: xyhe@mail.sic.ac.cn
e-mail: xiyunhe@hotmail.com

Y. Zhang
Department of Materials Science and Engineering,
Jingdezhen Institute of Ceramics,
Taoyang Road,
333001 Jingdezhen, China

2 Experimental

Pb, Zr, Ti precursor solutions (0.8 M) were prepared from lead acetate trihydrate, zirconium *n*-propoxide, titanium *i*-propoxide and acetic acid as described in the previous report [12]. Flexible titanium foil, coated with a platinum layer (0.4 μm) to avoid the Ti oxidation, are 30, 50, 80 and 100 μm in thickness, respectively. PZT thick films were deposited on the both sides of Pt/Ti substrate by a dip-coating technique. After each dip-coating process, the wet film was preheated at 650 °C for 2 min in air atmosphere by a one-step firing process. The thickness of one layer film is about 600 nm. This step is repeated to obtain a desired film thickness. Finally the multi-layer films were annealed at 700 °C for 0.5 h. The top electrodes of gold (Au) were prepared on the film surfaces by a vacuum evaporation method.

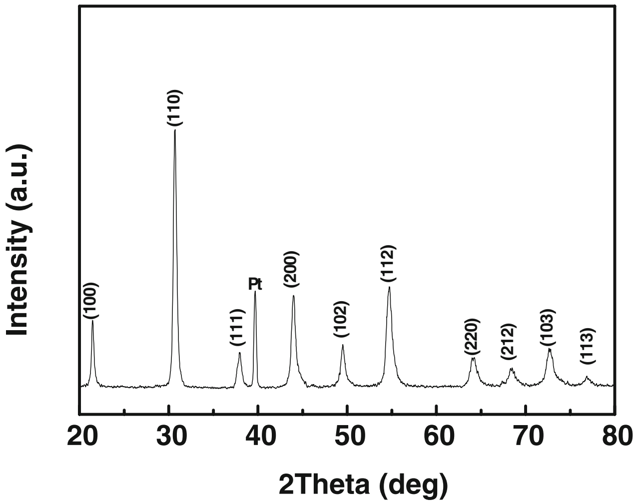


Fig. 1 XRD patterns of the PZT (53/47) thick film on the Pt/Ti foil substrate

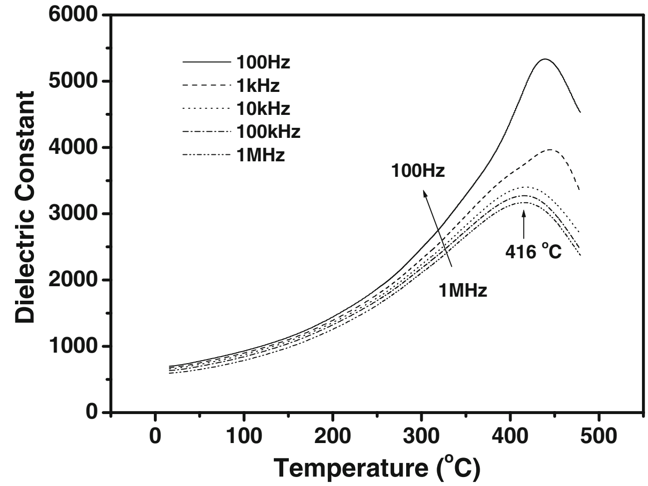


Fig. 3 Temperature dependence of the dielectric constant of the PZT (53/47) thick films

The phase structure of the film was evaluated by the X-ray diffraction (XRD). The film microstructure and film thickness were investigated by a scanning electron microscopy (SEM). The dielectric property of the film was measured by a HP4192 impedance analyzer. Ferroelectric hysteresis loops of the films were examined using a RT-66A ferroelectric tester. The piezoelectric coefficient ($d_{33,\ f}$) was measured using a bimorph-based dilatometer (Hong Kong Technology University). The displacements of the vibrators were measured by a Doppler interferometer.

3 Results and discussions

3.1 Structure and properties of PZT (53/47) thick films

Figure 1 gives the X-ray diffraction patterns of the PZT (53/47) thick film on Pt/Ti (50 μm) substrate. All the peaks indicated that the film was crystallized to the pure polycrystalline perovskite phase with random orientation. The film had a fairly dense microstructure and a smooth and homogenous surface, see Fig. 2. The size of the consisted particle is about 0.2–0.3 μm. The thickness of one side film is 30 μm. The thickness gradient is less than 0.3 μm/mm in the dipping direction. The films adhere to the substrate tightly except a hole observed in the right interface. The formation of the holes was thought to be caused by the greater strains experienced by the platinum when annealed above 500 °C [10].

The temperature dependence of the dielectric constant for the PZT film (30 μm on 50 μm Pt/Ti foil) is shown in Fig. 3. The dielectric constant of the film is 600–800 at the room temperature in the frequency range 100 Hz–1 MHz. It exhibits a little frequency dispersion. The F–P phase transition temperature of the thick film is increased to 416 °C, higher than the Curie temperature of PZT (53/47) bulk ceramics, 368 °C [13]. These phenomena may be resulted from the effect of the substrate clamping and the film internal stress.

The polarization versus electric field (P–E) hysteresis loop of the 24 μm PZT film (on 30 μm Pt/Ti) is presented in Fig. 4.

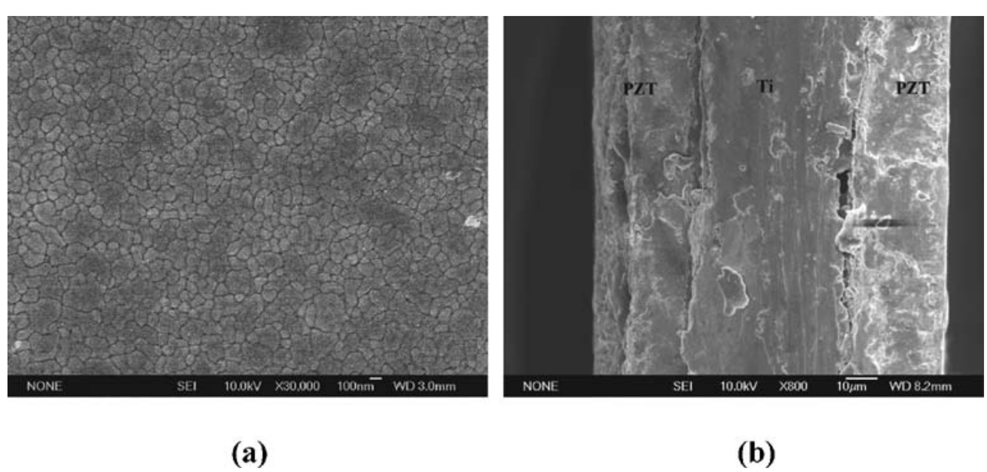


Fig. 2 SEM images of the PZT (53/47) thick film, (**a**) surface; (**b**) cross-section

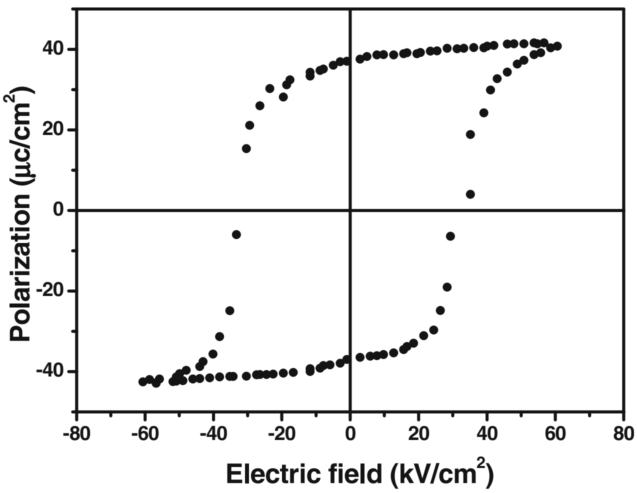


Fig. 4 Ferroelectric hysteresis loop of the PZT (53/47) thick film

It is symmetric and saturated with a perfect rectangular shape. The remnant polarization (Pr) is 35 μC/cm^2, and the corresponding coercive electric field (Ec) is 32 kV/cm.

The piezoelectric coefficient ($d_{33,f}$) of the PZT thick film was measured using a novel bimorph-based dilatometer, which can diminish the effect of the substrate. The value of $d_{33,f}$ of the film (24 μm PZT on 30 μm Pt/Ti foil) is 448–464 pC/N at the 1–100 k frequency range. These values are larger than that of the PZT thick films fabricated by other methods, 50–100 pC/N [14–16]. Values of the $d_{33,f}$ of PZT thick films, which were reported were between 1/4 and 1/3 those of the bulk ceramic [16–18]. The value of $d_{33,f}$ is not only affected by the processing conditions, level of porosity but also by the rigid substrate. The effect of the substrate clamping is to reduce the piezoelectric coefficient and to reduce the degree to which the film can be poled [19, 20]. In this study, the enhanced properties of the film were attributed to the high-density, exact chemical composition (Zr/Ti=52.96/47.04) and the flexible substrates [5]. The measured $d_{33,f}$ demonstrated that the PZT thick films on Pt/Ti substrate by MOD process promise a good application in the piezoelectric micro-devices.

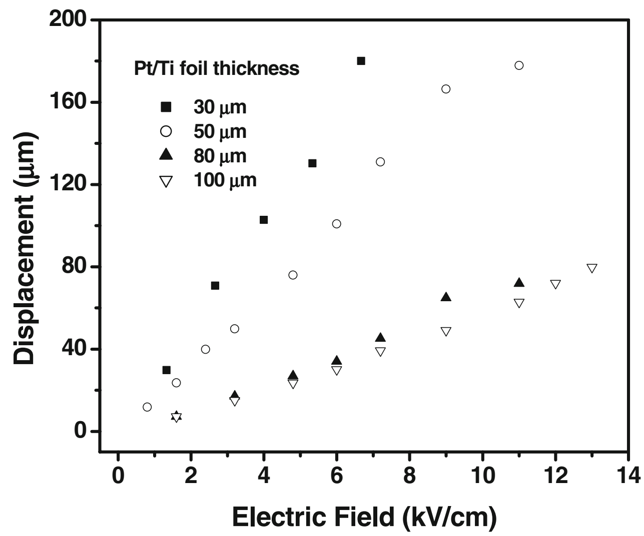


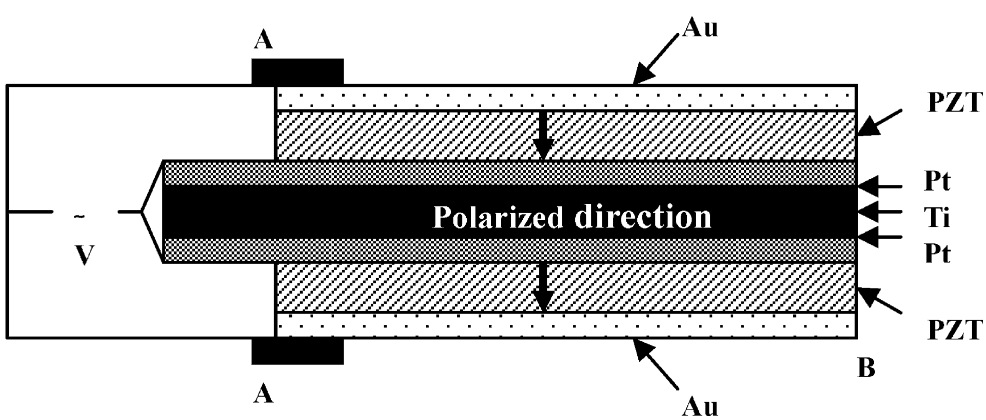
Fig. 6 Displacements as a function of the applied ac electric field (30 Hz)

3.2 Fabrication and characteristics of PZT piezoelectric vibrators

PZT piezoelectric vibrators were made in the bimorph mode by depositing PZT thick films on the both side of Pt/Ti foils, as illustrated in Fig. 5. The vibrators are all 5.0 mm in length, 3.0 mm in width with the deposited PZT films of 30 μm. The thicknesses of Pt/Ti foils are 30, 50, 80 and 100 μm, respectively. The two layer PZT films were polarized in the same direction. One end of the vibrator A was fixed and another end B was free. A sinus-wave electric field was act on the both sides of the PZT thick films in the opposite direction.

The field-induced displacements of the vibrators in an ac electric field of 30 Hz were measured by a Doppler interferometer. Fig. 6 shows the displacements of the free end of the vibrators as a function of the applied electric field. In the lower electric field, all the vibrators give the linear plots, which indicate that the films confirm to the converse piezoelectric effect. The vibrators produce a large

Fig. 5 Schematic of a vibrator made from the PZT thick films on Pt/Ti foil



displacement (>50 μm) in a lower electric field (≤10 kV/cm). However it can be found that in the same electric field the displacement is decreased with the Pt/Ti foil thickness increasing. The effect of substrate clamping on the PZT thick films resulted in this degradation. The vibrator made from the thinnest foil (30 μm) gives the largest displacement, 180 μm.

4 Conclusions

Homogenous and crack free PZT (53/47) thick films up to 30 μm have been prepared from a MOD process on the flexible Pt/Ti foil substrates. The films exhibit excellent ferroelectric and piezoelectric properties. A perfect rectangular P–E loop of the thick film was present; the remnant polarization Pr is 35 $\mu C/cm^2$; the coercive electric field Ec is 32 kV/cm. The estimated piezoelectric coefficient $d_{33,f}$ of the 24 μm PZT film on 30 μm Pt/Ti substrate is 448 pC/N (1 kHz), higher than that of the PZT thick films made by other methods. PZT piezoelectric vibrators with different sizes produced large displacement (>50 μm) in lower electric fields (≤10 kV/cm). The vibrator made from the thinnest Pt/Ti foil present the largest displacement.

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