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Effect of dopants on ferroelectric and piezoelectric properties of lead zirconate titanate thin films on Si substrates

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Abstract

Lead zirconate titanate $Pb(Zr_{0.52}Ti_{0.48})O_3$ (undoped PZT) and doped PZT thin films with thickness of about 500 nm were grown on $Pt/Ti/SiO_2/Si$ substrates by pulsed laser deposition (PLD). In this study, 1.0 mol% Nb-doping (at Zr/Ti site) as donor, 1.0 mol% Fe-doping (at Zr/Ti) as acceptor and 10 mol% Ba-doping (at Pb site) as isovalence were used. The effects of the introduction of these dopants on the ferroelectric and piezoelectric properties were investigated and compared to the undoped PZT film. A noticeable improvement of the dielectric constant (ε) and effective piezoelectric coefficient ($d_{33,f}$) are obtained. The maximum values of these parameters vary from 1280 and 126 pm/V for undoped PZT film to 1520 and 164 pm/V for Nb-doped PZT film. The largest remnant polarization (P_r) and coercive field (E_c) are obtained for Fe-doped PZT film, equal to 22.6 μC/cm^2 and 35.3 kV/cm, as compared to 17.3 μC/cm^2 and 31.2 kV/cm respectively for undoped PZT film. The Ba-doping decreases the dielectric constant but enhances the breakdown field of the film, reaching 800 kV/cm while it was only 660 kV/cm for undoped PZT film. The crystalline structure of Ba-doped film has a dominating (110) orientation instead of (100) in case of undoped, Nb-, and Fe-doped PZT films. The obtained results are important for the applications of doped PZT films in piezoMEMS devices.

Keywords: Piezoelectric thin films; Doping; Breakdown field; Pulsed laser deposition

1. Introduction

Lead zirconate titanate $Pb(Zr,Ti)O_3$ (PZT) is an important ceramic material with excellent dielectric and piezoelectric properties. In particular, these properties are remarkably high values in the morphotropic phase boundary (MPB, Zr/Ti = 52/48) region. PZT thin films, besides in nonvolatile memory applications, in recent years also gained considerable attention as potential candidate materials for piezoelectric MEMS devices [1–5]. MEMS sensor and actuator applications require a high dielectric constant and piezoelectric coefficient, as well as a high breakdown voltage; while low electrical loss is desired for ultrasonic applications. The broad range of possible isomorphism in the perovskite structure of ABO_3 ceramics like PZT enables the introduction of dopants with different valences into both the A positions (Pb-site) and B positions (Zr/Ti-site) of the compound. Therefore, PZT doping provides an opportunity to control electro-physical parameters that may give improved ferroelectric-properties of the material. In fact, these properties can be adjusted by doping PZT films with donors (Nb^{5+} [6,7], Sb^{5+} [8]) or acceptors (Fe^{3+} [9,10], Mn^{3+} [11]) occupying the B-site, and isovalences (Ba^{2+} [12], Sr^{2+} [13]) on the A-site.

The effect of dopants on the properties of PZT thin films was studied. It was shown that a concentration of 1.0–2.0 mol % Nb^{5+} increases the remnant polarization and piezoelectric coefficient in PZT thin films [6,14,15], whereas Fe^{3+} dopant decreases the dielectric constant and piezoelectric coefficient

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with increasing dopant level [9,10]. Moreover, donor and acceptor doped PZT thin films were found to exhibit asymmetrical polarization hysteresis loops, related to the role of oxygen vacancies and space charges in these doped PZT thin films. With the Fe-doped PZT films, the change in the domain contribution by introduction of acceptor species in PZT films is induced by an increase of the oxygen vacancies density. The oxygen vacancies in addition to cations can form complex dipolar defects such as $Fe^{3+}-V_O$ complexes or $V''_{Pb}-V_O$ complexes that exist in perovskite oxides [16]. It is possible that Fe^{3+} can bind oxygen vacancies in the unit cells containing substitutional Fe [17,18]. According to Dawber et al. [19], mobile charged defects such as oxygen vacancies are easily accumulated near the film–electrode interfaces, because the mobility of the oxygen vacancies is larger than that of lead that results in formation of interfacial layers under an external field [20,21]. All these kind of defects can block the movement of domains and pin them in a partial or total way [22]. In addition, since many defect–dipole complexes exist in the Fe-doped PZT, thin films involving oxygen vacancies can result in shifts of hysteresis loops. The substitution of donor dopants, such as Nb^{5+}, in PZT films can reduce the concentration of oxygen vacancies, and as a result, the domain wall motion and then the polarization are enhanced [23]. Moreover, a study on the polarization properties of Nb-doped PZT thin films by Haccart et al. [14] described that the internal bias field (the shift of the hysteresis loop along the electric field axis) increased with the Nb concentration. This is because of the presence of the dipolar defects, such as V''_{Pb}–Nb_{Ti}, which can be aligned within the bulk of the film [14].

Recently, many papers have been studied to understand the effect of doping on the properties of PZT films. Most of the reports are based on sol–gel-derived doped PZT films [6,10,18,22–26]. Although sol–gel processes have been successfully used for many years, there remain tremendous challenges, such as defects (cracks and delamination), which effect the properties of PZT films. The sol–gel PZT films often consist of multiple coating in which each coating ranges from 15 to 100 nm in thickness [27], and the corresponding crack-free area is about 1 mm^2 [28,29]. The cracks are so densely populated and then the crack-free area is decreased with increasing number of coating layers (the sol–gel PZT film becomes virtually useless with film thickness exceeding 1 μm, as the crack-free area is so tiny [27]). In the piezoelectric thin film devices, such as membrane actuators and cantilevers, the obtained uniform and homogeneous PZT films with thickness of 0.75–1.00 μm and over a large area (2 cm^2) are required [30]. Using the pulsed laser deposition (PLD) technique, these required PZT films can be easily fabricated [31].

In this study, the effect of doping on the properties of PZT thin films, which was fabricated by PLD, has been investigated. The dopant optimum concentrations of 1.0 mol% Nb^{5+} as donor and 1.0 mol% Fe^{3+} as acceptor (both at Zr^{4+}/Ti^{4+} site) were selected relying on the reported works. Moreover, the PZT thin film with 10 mol% Ba^{2+} (at Pb^{2+} site) as isovalence has also studied. The crystalline structure, ferroelectric and piezoelectric properties have been measured and analyzed. In addition, the thin film structure suitable for the requirement of specific applications has also suggested.

2. Experiment

All the $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT), $Pb(Zr_{0.52}Ti_{0.48})_{0.99}Nb_{0.01}O_3$ (1.0 mol% Nb-doped, PNZT), $Pb(Zr_{0.52}Ti_{0.48})_{0.99}Fe_{0.01}O_3$ (1.0 mol% Fe-doped, PFZT), and $Pb_{0.9}Ba_{0.1}(Zr_{0.52}Ti_{0.48})O_3$ (10 mol% Ba-doped, PBZT) thin films used in this study were deposited on Pt/Ti/SiO_2/Si substrates using a PLD method. No additional perovskite seed layer on top of Pt was used. The thickness of all PZT films is about 500 nm. A detailed fabrication procedure of PZT thin films is described in an earlier publication [32].

The crystalline structures of the undoped and doped PZT thin films were analyzed by high-resolution X-ray diffraction (XRD: Bruker D8 Discover) with a Cu-Kα cathode in a Bragg–Brentano geometry.

For the electrical measurements, Pt top-electrodes (200 × 200 μm^2 in size) were sputter deposited and patterned by a lift-off technique. The bottom electrode was exposed by wet-chemical etching of the PZT using a mixed solution of HF, HNO_3, and HCl. The polarization hysteresis (*P–E*) loop measurements were performed using the ferroelectric mode of the aixACCT TF-2000 Analyzer. The *P–E* loops were measured with an applied *ac*-electric field of ± 200 kV/cm at 1 kHz frequency at room temperature. A Süss MicroTech PM300 manual probe-station equipped with a Keithley 4200 Semiconductor characterization system was used for the capacitance measurement. The capacitance–electric field (*C–E*) curves were measured using a slowly sweeping *dc*-electric field of ± 200 kV/cm and a 1 kHz *ac*-electric field of 4 kV/cm. The dielectric constants were calculated from these corresponding *C–E* curves.

The effective piezoelectric coefficient ($d_{33,f}$) of the piezoelectric thin-film capacitors was measured using a Polytech MSA-400 scanning laser Doppler vibrometer (LDV) method with a precision below 1 pm, by applying a sinusoidal 8 kHz *ac*-voltage of 3 V (or 6 V_{p-p} peak-to-peak) to the piezoelectric capacitor.

3. Results and discussion

The crystalline structures of undoped and doped PZT thin films are deduced from the θ–2θ scans shown in Fig. 1. All films have crystallized corresponding to the perovskite structure and no other phases due to doping are observed. The (100) preferred orientation is dominant for the undoped as well as Nb- and Fe-doped PZT thin films, while the (110) orientation becomes more evident in the Ba-doped PZT thin film. The mixture of orientations is a consequence of the Pt coated substrate. The in-plane orientation of the crystallites in the film is random, as can be followed from phi-scans (ϕ-scans) on similar films (not shown here).

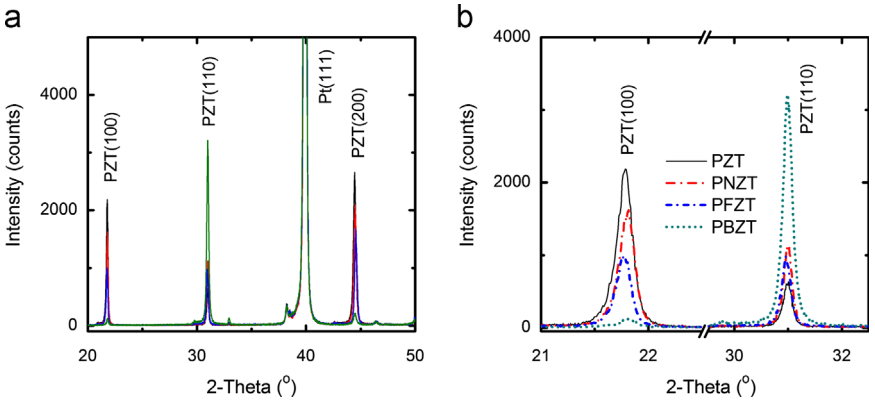

Fig. 1. XRD patterns of the PZT, PNZT, PFZT and PBZT thin films: (a) full scale and (b) zoom scales of (100) and (110) peaks.

Fig. 2 shows the initial polarization (P–E) hysteresis loops for the doped and undoped PZT films. The PZT, PNZT and PFZT films have the same shape, but the PFZT has a larger remnant polarization (P_r) and coercive field (E_c). The PBZT has clearly more slanted P–E loop. This may be a consequence of the preferred (110) orientation in PBZT thin films, as shown in Fig. 1. In comparison with sol–gel doped PZT films with large polarization asymmetry [10,24,26], a much smaller (slight) asymmetry on the electric field axis of P–E loops in doped PLD–PZT films is observed. This may be due to the difference in work function of the top and bottom Pt electrodes caused by different heat treatments [33]. On the other hand, the polarization asymmetry due to the doping effect may not be induced in our PLD–PZT thin films. The polarization asymmetry in doped PZT thin films will be discussed in the next study for both textured films (sol–gel and PLD doped PZT films grown on Pt/Ti/SiO_2/Si substrates) and epitaxial films (PLD doped PZT films grown on (110)$SrRuO_3$/YSZ/Si, (001) $SrRuO_3$/$SrTiO_3$/Si and (001)$SrRuO_3$/$SrTiO_3$ substrates).

In Fig. 3 the dielectric constant–electric field curves are shown, and the dielectric constant (ε at zero field) and dielectric loss ($\tan\delta$) values are given in Table 1. Table 1 also gives the values of the effective piezoelectric coefficient ($d_{33,f}$). The PNZT thin film has the highest dielectric constant ($\varepsilon = 1520$) (and slightly increased dielectric loss) and effective piezoelectric coefficient ($d_{33,f} = 164$ pm/V). The improvement of the piezoelectric property in PNZT thin film is explained by a reduction in the oxygen vacancy concentration, as Nb doping enhances the oxygen density [23]. The improved oxygen density has a strong effect in increasing the domain reorientation and therefore the piezoelectric effect. In general, the lack of accurate chemical control in PZT materials during annealing at crystallization temperature could cause PbO loss and result in the formation of lead and oxygen vacancies according to the following equation [23]:

$$Pb_{Pb} + O_O \underset{evaporation}{\Longrightarrow} V''_{Pb} + V_O \quad (1)$$

Nb^{5+} ion is considered as donor doping to replace B-site (Zr^{4+}/Ti^{4+}) atoms, providing improved oxygen content via the reaction

$$Nb_2O_5 + V_O \underset{2TiO_2}{\Longrightarrow} 2Nb_{Ti} + 5O_O \quad (2)$$

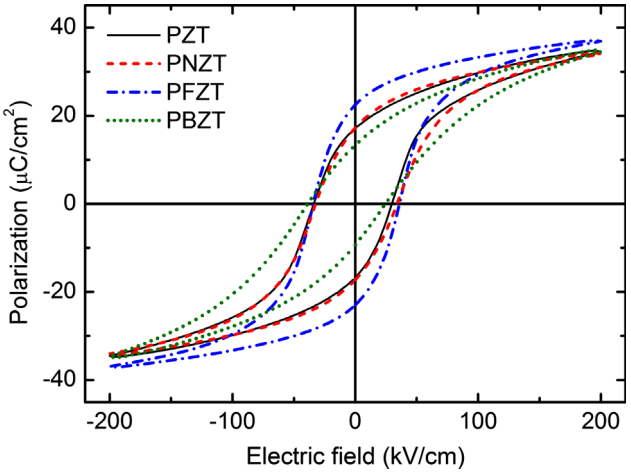

Fig. 2. P–E loops of the undoped and doped PZT thin films.

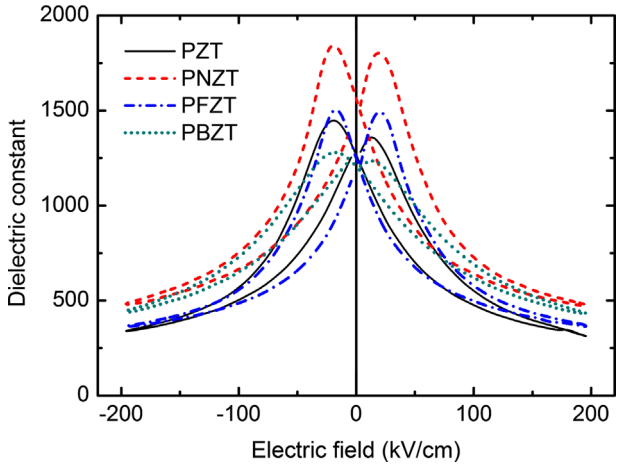

Fig. 3. Dielectric constant–electric field curves of the undoped and doped PZT thin films.

This property makes PNZT thin film, with high piezoelectric coefficient and dielectric constant, suitable for applications

Table 1
Ferroelectric and piezoelectric properties of the undoped and doped PZT thin films.

Sample	Orientation ratio of (100)/(110)[a]	P_r (μC/cm^2)	E_c (kV/cm)	ε	tan δ	Breakdown field (kV/cm)	$d_{33,f}$ (pm/V)
PZT	7.5/1.0	17.32 ± 0.28	31.22 ± 0.58	1280 ± 18	0.071 ± 0.005	660 ± 24	126 ± 5
PNZT	3.3/1.0	17.08 ± 0.32	32.80 ± 0.48	1520 ± 21	0.122 ± 0.006	560 ± 18	164 ± 6
PFZT	2.8/1.0	22.64 ± 0.30	35.34 ± 0.66	1215 ± 18	0.043 ± 0.004	620 ± 22	104 ± 4
PBZT	0.1/1.0	11.52 ± 0.18	31.56 ± 0.62	1205 ± 22	0.092 ± 0.005	800 ± 25	120 ± 4

[a]Ratio of peak areas of [(100)+(200)] to peak area of (110).

requiring high piezoelectric responses such as sensors and actuators.

For the PFZT thin films a significant decrease in piezoelectric coefficient was observed, whereas for both PFZT and PBZT the dielectric constant was somewhat reduced. In PFZT thin films, Fe^{3+} ion is considered as acceptor doping to replace B-site (Zr^{4+}/Ti^{4+}) atoms, creating oxygen vacancies during the annealing process, due to the reaction with the arising Pb-vacancies, according to the reaction mechanism.

$$Fe_2O_3 + V''_{Pb} \underset{2TiO_2}{\Longrightarrow} 2Fe_{Ti} + 3/2O_2 \quad (3)$$

As a result, domain wall motion in PFZT thin film caused by an external electric field becomes harder due to the increase in coercive field. This goes together with a decrease in dielectric constant and dielectric loss. Altogether, this makes PFZT ideal for rugged applications such as ultrasonic motors, and transformers. Ultrasonic motors, for instance, demand a high mechanical quality factor (Q-factor) as well as a low dielectric loss (tan δ), in order to minimize heat generation and maximize displacement [34,35].

Fig. 4 shows the device current as a function of increasing applied field. It can be seen that the PBZT thin film shows significantly higher breakdown field than the other devices (see also Table 1). This was explained by the observation that smaller and more tightly bonded grains with homogeneous microstructure are obtained with increasing Ba-doping concentration [36]. The Ba doping concentrates near the grain boundaries, reduce the mobility of ions at the grain boundary [36]. As a result, the reduction in leakage current and the enhancement in breakdown voltage are observed. Therefore, PBZT thin film may be preferentially used in piezoelectric MEMS accelerometers, in which the output sensitivity varies proportionally to the applied voltage and moreover, the output-noise density decreases as the applied voltage increased. Hence the signal-to-noise ratio improves at higher applied voltage.

The change of the remnant polarization as a function of number of P–E loop cycling in undoped and doped PZT thin films is shown in Fig. 5. The P_r of undoped PZT film decreases on increasing the number of switching cycles. At about 10^8 cycles, the remnant polarization saturates at about 70% of the initial value. This decrease of remnant polarization in ferroelectric thin films (commonly named fatigue) with an increase in the number of switching cycles has been studied extensively. Most of the studies indicate two mechanisms: (i) suppression of domain switching, and (ii) accumulation of oxygen vacancies upon cycling. Both mechanisms occur near the ferroelectric film–electrode interfaces.

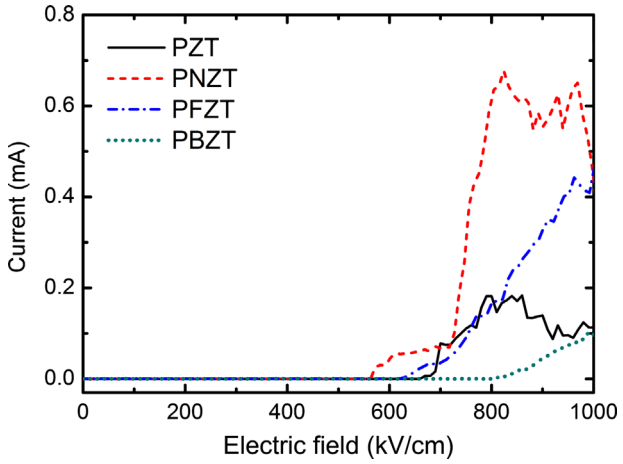

Fig. 4. Current–electric field characteristics of the undoped and doped PZT thin films.

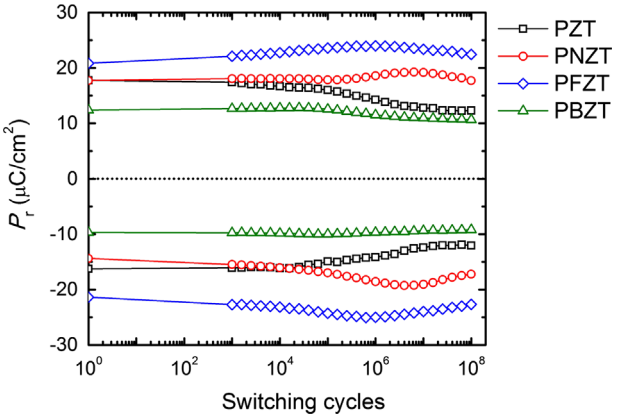

Fig. 5. Polarization–switching characteristics of the undoped and doped PZT thin films.

The suppression of domain switching is related to the pinning of the domain wall in the ferroelectric films [37,38] or the inhibition of the near-interfacial nucleation of the opposite domain switching by trapped charge [39–42].

Improvement of the ferroelectric switching performance is observed in the doped PZT thin films. Doping with donor (Nb^{5+}) cations reduces the oxygen vacancy density and thus the dipolar defect concentration [14]. As a result, the domain wall motion or on the other hand the polarization is enhanced

in PNZT thin film. In the case of the PFZT thin film, acceptor doping introduces oxygen vacancies, which segregate to the grain boundaries and then the motion of domain walls is reduced. Under the application of electric field, oxygen vacancies are transported toward film/electrode interface. As a result, the domain wall is easier to move in the bulk of the film, and then the polarization is also improved in PFZT thin film.

4. Conclusions

In this work, the ferroelectric and piezoelectric properties of undoped and doped PZT thin films on Pt/Ti/SiO_2/Si substrates using the PLD technique intended for piezoMEMS devices applications have been investigated. Optimized doping concentrations, as reported in literature, were used. The experimental results are compared to literature values, and the main observations and differences are:

- The donor type 1.0 mol% Nb doping into PZT thin film results in an increased dielectric constant and piezoelectric coefficient making it useful for actuation and sensing applications. It is supposed that the Nb doping reduces the oxygen vacancy density due to Pb loss during fabrication at high deposition temperatures.
- The acceptor type 1.0 mol% Fe-doped PZT thin film has lower dielectric constant and dielectric loss considered suitable for ultrasonic applications.
- Finally, PZT thin film with the isovalence 10 mol% Ba-doping shows the highest breakdown voltage, making it a good candidate for accelerator applications.

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