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Structural, ferroelectric and optical properties of PZT thin films

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Abstract

We report on the structural, ferroelectric and optical properties of lead zirconate titanate (PZT) thin films (with a molar ratio of Zr:Ti::65:35) deposited by sol–gel technique on ITO-coated corning 7059 glass substrates. A seed layer of $PbTiO_3$ (0.1 μm) was coated by sol–gel on the substrates before depositing PZT. A metal/ferroelectric/metal (MFM) structure was used for electrical property measurements, formed by depositing gold electrodes on top of the film. The films were characterized for *C–V*, *I–V*, *P–E* and optical transmission. Relatively low remnant polarization ($P_r = 3.6\,\mu C/cm^2$) was observed for the films. Value of optical band gap was found to be 3.4 eV. The results are discussed.

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Keywords: PZT; Thin films; Sol–gel; Optical measurements

1. Introduction

Lead zirconate titanate (PZT) thin films have been of great interest for many years for their applications in electronic devices, such as non-volatile memories, infrared sensors, optical shutters, electro-optic devices, modulators, actuators, multi-layer capacitors (MLCs), etc. [1–3]. Recent research has demonstrated that electrodes made from indium tin oxide (ITO) can greatly improve the fatigue behavior of PZT in comparison with platinum electrodes. This is attributed to the ability of ITO to conduct anion vacancies, thereby dissipating space charge buildup at the capacitor–electrode interface. However, platinum has been reported to be a superior substrate by Madsen and

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Weaver [4]. But for the application of the PZT films in electro-optic devices, it is necessary to fabricate films having low optical losses as well as high electro-optic coefficients [3]. It has been reported that the optical loss in a PZT film is caused by the scattering of propagating light on the film surface, which is strongly dependent on the surface roughness of the film [5]. It is reported that the higher the spontaneous polarization and dielectric constant, the higher the linear electro-optic coefficient of material [6]. For high remnant polarization (P_r), internal electric fields developed by charged defects near the electrodes or in the film volume are believed to play an important role in these phenomena [7,8]. Thus, correlated polarization–electric field (P–E), capacitance–voltage (C–V), and current–voltage (I–V) measurements are necessary in order to reveal the presence of space charge regions (SCR) and to elucidate the problem of conduction mechanisms in PZT thin films [9].

A variety of techniques have been employed to fabricate PZT films, such as metallorganic chemical vapor deposition (MOCVD), sputtering, sol–gel and PLD. Among these, sol–gel method is the most popular one because of its low cost and ease of fabrication for the PZT system [10]. In the present work, we report on structural, morphological, ferroelectric and optical properties for sol–gel–grown $Pb(Zr_{0.65}Ti_{0.35})O_3$ films with a seed layer of $PbTiO_3$ (deposited by sol–gel). The usage of a seed layer has been shown to be beneficial by several workers [3,11]. The possible reasons for low remnant polarization have been examined for its electro-optic usage.

2. Experimental details

The sol–gel PZT thin films were prepared using lead acetate tri-hydrate, zirconium-acetyl-acetonate, and titanium-isopropoxide as precursors. Acetic acid and 2-methoxy-ethanol were used as solvents. The molar ratio of Zr/Ti was kept at 65/35 and a 4% excess of the lead precursor was added to the solution to compensate lead loss during heat treatment and to assist crystallization. Commercially available ITO (3000 Å)-coated corning 7059 glass was used as substrate. Seed layers of $PbTiO_3$ (PT) were prepared by the sol–gel technique using the above-mentioned alkoxides (~0.1 μm thickness). A spin coating unit was used for the deposition of all sol–gel films. Substrates held by a vacuum-chuck were rotated at a speed of 2000 rpm for 20 s each. These films were pyrolyzed intermediately at 200 ° for 2 min, twice and finally at 600 °C. The seed layer was coated on all substrates prior to deposition of the PZT layers. The procedure followed for pyrolysis of PZT films was the same as the one in the case of the PT seed layers. After coating the PZT layer, the final crystallization was achieved by annealing at 650 °C, for 2 h in air. The details about the sol–gel technique have also been reported [12,13].

The morphology of the films was characterized using atomic force microscopy (AFM, NT-MDT Solver P47 H) in the resonant mode operating at 350 kHz and 38 nm amplitude. XRD patterns were recorded on a Philips thin film diffractometer (Model PW 3020) using a Cu (K_α) 1.54 Å X-ray in parallel beam geometry. The incident X-ray beam made an angle of 1.5 ° with the sample. A graphite monochromator was used in the secondary optics to minimize the background fluorescence/scattering.

Optical transmission measurement was performed using CARY–5E UV-VIS-NIR spectrophotometer. The thickness of the film was measured from transmittance interference fringes. A sample measurement was also taken by Dektak-3 stylus profilometer after making a physical step by chemical etching and compared with optically measured thickness value. The metal/ferroelectric/metal (MFM) structure was obtained by depositing gold top electrodes of size ~500 μm with the help of shadow mask using cold DC sputtering. It is to be noted that the structure is asymmetric in terms of electrodes, the bottom one being ITO and the top electrode is gold.

Hysteresis loops were recorded using an automatic P–E loop tracer (RT-66A) of Radiant Technologies Inc. The remnant polarization (P_r) and coercive field (E_c) were obtained from the P–E hysteresis loop.

C–V measurements were done using an HP-4294A Impedance Analyser at 100 kHz with an

oscillator level of 100mV and a delay of 2 s was used during measurement. I–V measurements were done using Keithley 428 current amplifier along with SR 830 Lock-in-Amplifier.

3. Results and discussion

An X-ray diffractogram of PZT 65/35 thin film deposited by the sol–gel techniques is shown in Fig. 1. The XRD pattern shows the formation of a single-phase perovskite for PZT thin films. Formation of the unwanted pyrochlore phase was eliminated through a careful selection of deposition parameters. The selection of deposited parameters is based on our past experience of growing PZT thin films and from the literature available in this area. The films deposited were polycrystalline in nature. PZT films (~0.5 μm thick) were deposited on ITO coated corning 7059 glass substrates by sol–gel with ~0.1 μm ($PbTiO_3$) seed layer thickness. The stress in a thin film have always been the matter of considerable concern, on account of the fact that (i) thermal expansion coefficients between glass substrate and PZT film may contribute in inducing a tensile stress in the film and (ii) volume change induced by phase transition. Since the difference in thermal expansion is $\sim 1.0 \times 10^{-6}/^{\circ}C$ and is too less to cause severe cracking. The properties of the films are greatly dependent upon the effects of stress/strain in them. Although the strains in these films have not been studied in this research, it is felt the situation in polycrystalline films may be relatively lower. This is because a polycrystalline system provides for alleviation of stress through relaxation mechanisms, generally found to occur much more slowly in epitaxial films. The volume change may thus be the main reasons for the stress in the films and hence may lead to cracks also. The reason for low P_r may also be attributed to cracks in the films since they are annealed at 650 °C for 2 h. The PZT (Zr/Ti :: 40/60) films annealed more than 10 min show cracks and are reported [3]. But authors have got better results of P_r and clear oriented AFM grain morphology for the PZT (65/35) films on Pt/Si substrates without cracks even after annealing at 650 °C upto 2 h [13]. It is to be noted that authors have used $PbTiO_3$ as seed layer but Kang et al. [3] have used PZT as seed layer.

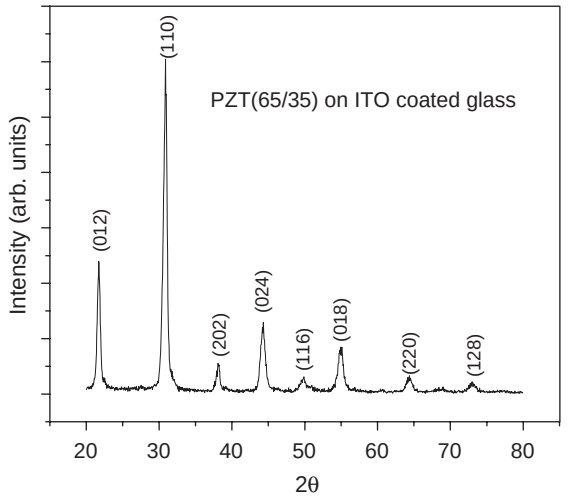

Fig. 1. X-ray diffractogram of PZT 65/35 thin films deposited by sol–gel.

3.1. AFM measurements

The AFM micrographs are shown in Fig. 2. The average surface roughness (R_a) in PZT films deposited on ITO-coated corning 7059 substrates is ~10 nm but three-dimensional (3D) picture of AFM depicts a hazy and clear cracks surface and no oriented growth in the film. Also, the PZT/PT/ITO/corning films surface looks hazy most probably due to the reaction of ITO with PT and PZT as is also seen clearly from the transmittance curves (Fig. 5). This also could be a possible reason for the lowering of remnant polarization apart from cracks in the films. A clear grain size is expected for higher remnant polarization [13].

3.2. I– V measurements

The apparent decrease/change in I–V is mainly due to change in the conductivity nature of the electrode as seen in the optical transmission measurement. The results indicate the current transport through the PZT material due to field enhanced schottkey emission [9]. The results suggests that the two contacts are like back to back schottkey diode with the presence of large

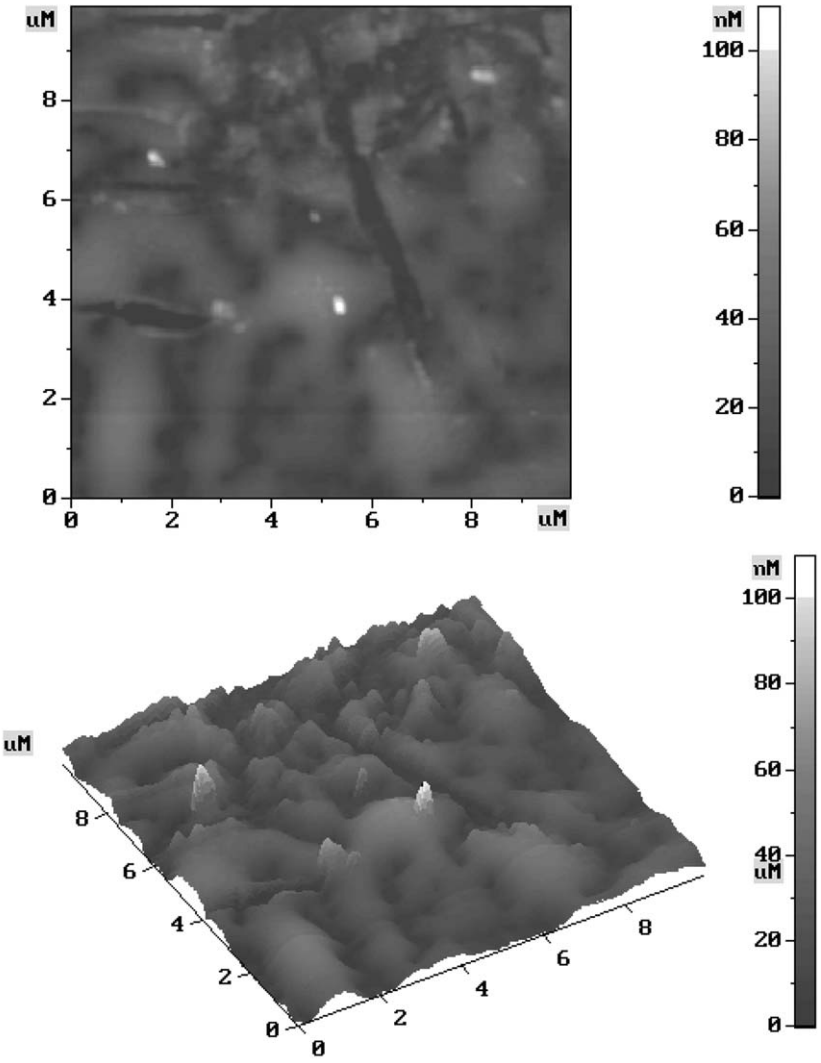

Fig. 2. Atomic force micrograph (plane and 3-D views) of PZT/PT/ITO/corning glass by sol–gel.

space charge region near the metal electrode (Fig. 3a and b). Sample deposited on Pt/Si shows higher conductivity compared to those deposited on ITO-coated glass. The samples deposited on ITO/ glass show shift of minimum current from 0 V. This again suggests accumulation of remnant charge in the material. The remnant charge may be also due to presence of grain boundaries in the deposited materials as seen in AFM image (Fig. 2).

The sample PZT/ITO shows no effect of trap free space-charge-limited current (SCLC) for which the slope $= 2$. Instead, the slope after 5 V is much more than 2 indicating presence of traps in the material [14]. In contrast, the PZT/Pt/Si sample shows SCLC current dependence with a slope of 2 which indicates that it is a trap free material.

3.3. *C–V measurements*

The *C–V* curves for the films are shown in Fig. 4. The higher capacitance graph already

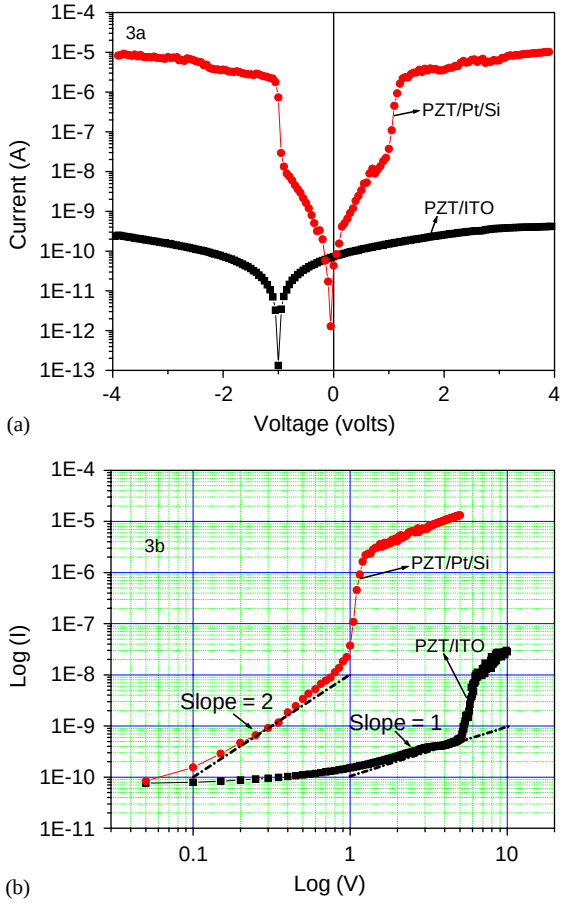

Fig. 3. (a) Current vs. voltage curves, (b) log (current) log (voltage).

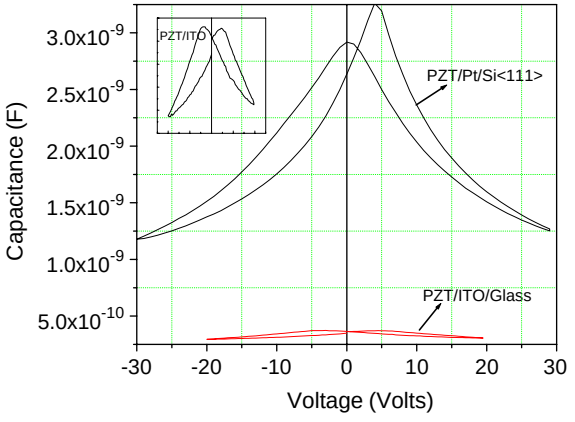

Fig. 4. Capacitance vs. voltage curves.

reported [13] has been shown here for comparison. The inset in the graph shows the clear C–V graph of ITO/PZT film. The gap on Y-axes is mainly due to instrument limitations which gives values only for four cycles. If fifth cycle is done it will give a clear C–V without any gap. The shift of intersection of C–V curve at $Y = 0$ axis is mainly due to space charge regions and DC biasing. The curve has the typical butterfly shape with two maxima that should correspond to the coercive fields. The values of voltages obtained from the two maxima of the C–V curve divided by thickness of the film should be nearly equal to twice the coercive field (E_c) of the P–E curve. A difference in the value may be attributed to the space charge regions, which could develop due to DC biasing in the C–V measurements. However, these capacitance values are much lower than our reported values for the PZT films on Pt/Si substrates [13]. Here again the possible reason for the low values of capacitance may be the electrode/PZT interaction. The C–V behavior of thinner PZT films (thickness <50 nm) can also be understood from the semiconductor physics also. It is known that the depletion layer width (W_d) and junction capacitance (C_j) of a semiconductor/metal junction can be expressed as

$$\text{(a)}\quad W_d = \frac{[2\varepsilon_0\varepsilon_r(V_0 + V)]^{1/2}}{[qN]^{1/2}}$$

and

$$\text{(b)}\quad C_j = \frac{A[q\varepsilon_0\varepsilon_r N]^{1/2}}{[2(V_0 + V)]^{1/2}},$$

where V is the reverse bias voltage, V_0 is the built in potential, N is the carrier concentration and ε_r is the dielectric constant of the material.

Both these equations show the variation of depletion width (W_d) and junction capacitance (C_j) with the applied voltage. While applying a negative DC voltage at the bottom electrode, the space charge becomes less populated (or more depleted) near the PZT/electrode interface and this reduces the overall measured capacitance (b). As the voltage increases to about zero, the space charges become more populated (or less depleted) near both the top and bottom electrodes, thus the junction capacitance reaches a saturated value.

Therefore, a shoulder located near zero voltage is observed. As the voltage further increases to positive values, the maximum capacitance value should occur at the coercive voltage (i.e. ~0.5–1 V for upward voltage sweep) because of polarization switching [15].

3.4. P-E Measurements

Fig. 4 shows the values of remnant polarization ($P_r = 3.6\,\mu C/cm^2$) and coercive field ($E_c = 107\,kV/cm$) for the films grown in this study. The higher P_r value graph already reported [13] has been shown here for comparison. The inset in the graph shows the clear hysteresis of PZT on ITO/glass. The P_r values found in our films are relatively lower than the reported values. Also, the positive value of P_r is greater than the negative value of P_r. The polarization shift has been reported in "graded ferroelectrics" [16]. However, in a homogeneous PZT film the shift may be also due to electrode asymmetry [17]. This may be ascribed to the reaction of PZT/PT with the ITO layer as well as cracks in the films as is evident from the transmission and AFM studies. Tyunina et al. [18] reported values of P_r and E_c as 17 μC/cm^2 and 50 kV/cm, respectively. However, Boerasu et al. reported values of P_r and E_c as 9 μC/cm^2 and 39 kV/cm, respectively, by sol–gel. A higher P_r of 30 μC/cm^2 for higher grain size was reported by Jang sik Lee et al. [19] on account of the larger grain size of the films. The remnant polarization ($2P_r$) of 26 μC/cm^2 (for randomly oriented films) and 46 μC/cm^2 (for films with preferred orientations) were reported by Kang et al. [3]. Authors have also reported growth of PZT films grown on Pt/Si (1 1 1) with a PT seed layer, by sol-gel showed excellent values of $P_r = 56.8\,\mu C/cm^2$ [13].

The dependence of electrical properties on a film thickness, can be explained by a model that incorporates a layer having low ε in series with a normal PZT layer. The origins of the low ε layers have been attributed to the following five possible mechanisms; a non-stoichiometric phase, a chemical reaction with the platinum electrode, space charge layer, stress and the size effects [20]. In the present study, of the aforementioned, it would appear that the space charge, stress and cracks have influence on the films electrical properties. Also, from the AFM data, it may be construed that there is no well-defined grain morphology observed on the surface of the films deposited on ITO-coated glass. This might be on account of the fact that the bottom electrode has seemingly interacted with the overlying PZT films deposited during the process of pyrolysis and subsequent annealing. This re-iterates the well-known fact that the interface between the substrate and the film is detrimental to the films properties. Further, it is has been reported that lead diffuses in ITO even at 550 °C [4]. So, a lead diffusion in ITO could also be one of the reasons for reducing the remnant polarization.

3.5. Optical measurements

Optical transmittance was recorded for the PZT film deposited on ITO-coated glass (Figs. 5, 6). The long wavelength absorption from 1000 to 2500 nm observed for ITO glass is due to the occurrence of plasma resonance around 2500 nm. The transparency begins below the plasma resonance wavelength. It is to be noted that the same absorption is not observed for PZT-coated ITO glass. It is because the carrier concentration of ITO has undergone a major reduction due to reaction of PZT/PT with ITO. Hence, the plasma resonance must have been shifted to much higher

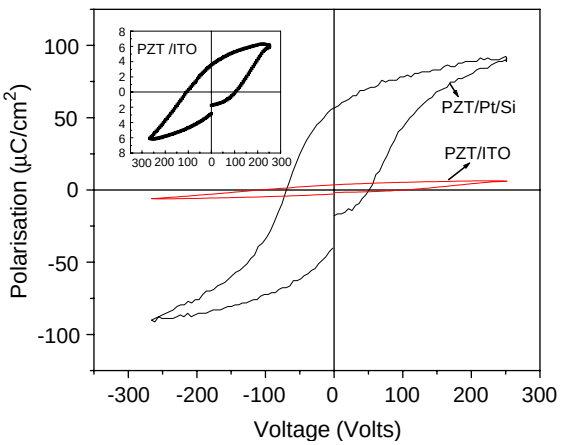

Fig. 5. Polarization vs. electric field hysteresis loop for PZT on ITO-coated glass.

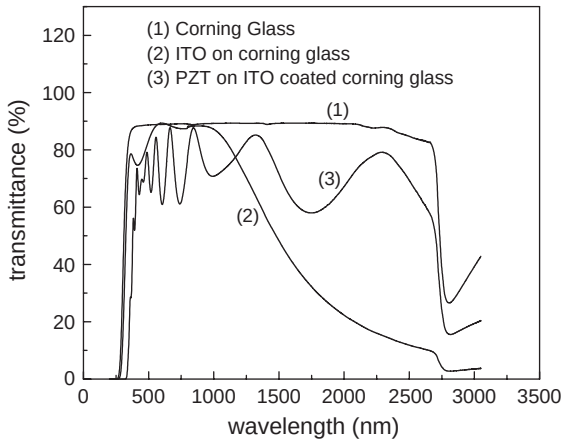

Fig. 6. Transmittance curves for the films.

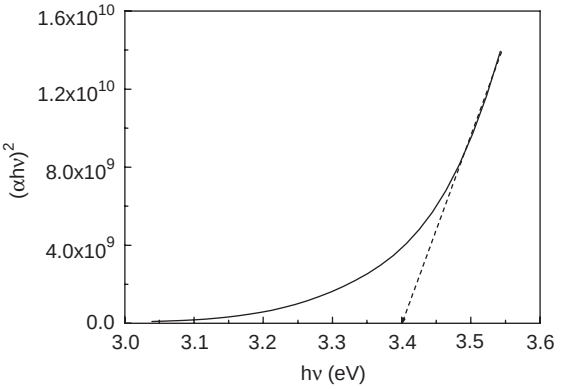

Fig. 7. $(\alpha h\nu)^2$ vs. $h\nu$ plot showing optical band gap.

wavelength. This is the reason for good transparency in the above-mentioned region. This must have serious implication on the performance of ITO electrode. A graph between $(\alpha h\nu)^2$ vs. $h\nu$ was plotted as shown in Fig. 7 and the band gap of the PZT film was estimated as 3.4 eV (α = absorption coefficient , $h\nu$ = incident photon energy). This is in good agreement with a band gap of 3.35 eV reported by Boerasu et al. [9].

4. Conclusions

Structural, morphological, ferroelectric and optical properties of PZT thin films deposited on ITO-coated corning 7059 glass substrates were studied. A significant reason for low remnant polarization (P_r) was observed for PZT thin films deposited on ITO-coated corning glass substrates by sol–gel technique using a seed layer of lead titanate ($PbTiO_3$). A low value of remnant polarization (P_r) was observed in the case of these films. The low value of polarization is mainly due to cracks, ITO/PZT interaction modifying the surface morphology, stress (due to volume change while phase formation) and Pb diffusion in ITO. The transmittance curves of the PZT showed a band gap of 3.4 eV. The AFM picture shows morphology having nanosize surface roughness but unclear grain size indicative of modified PZT/PT/ITO layer structure.

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