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Dielectric and ferroelectric properties of pulsed laser deposited lead zirconate titanate (65/35) thin film

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Abstract

Lead zirconate titanate (PZT) thin films with composition (65/35) were deposited using pulsed laser deposition. A KrF laser with a wavelength of 248 nm, an energy fluence of ~1.2 J/cm^2 with a repetition rate of 5 Hz, and a background pressure of 6 to 13 Pa oxygen was used to deposit the films. A PZT target of 25 mm diameter and 5 mm thickness was prepared by solid-state double sintering ceramic route for laser ablation. The films were deposited at 300 °C (substrate temperature) and thereafter annealed ex-situ at 450 °C for 5 h intermediately and finally at 650 °C for 2 h resulting in single phase polycrystalline PZT with a grain size of ~0.5 μm. A metal/ferroelectric/metal structure was formed by depositing gold electrodes on the film. The Atomic Force Microscope images revealed well-crystallized films with a fine microstructure and an average grain size of ~0.5 μm. The dielectric and ferroelectric properties of the films deposited on Platinum (Pt) coated silicon substrates were studied and the results are discussed. The Polarization vs. Electric field hysteresis measurements showed a well-defined hysteresis loop with a fairly high P_r of 25 μC/cm^2 with a coercive field of 38 kV/cm.

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1. Introduction

Ferroelectric thin films, especially of lead titanate zirconate Pb(Zr$_{0.65}$Ti$_{0.35}$)O$_3$ solid solutions (hereafter PZT) have been of great interest for many years for their applications in electronic devices, such as nonvolatile memories, infrared sensors, optical shutters, modulators, actuators, multilayered capacitors, etc. [1,2]. A variety of techniques have been proposed to fabricate PZT films, such as metallorganic chemical vapor deposition, sputtering, sol–gel, and pulsed laser deposition (PLD). Among them, the pulsed laser ablation is the most popular one because of its easy application to the PZT systems [3]. The method is well developed and can be used to prepare good perovskite films at suitable substrate temperatures. A large number of studies have been dedicated to the investigation of the structural, dielectric, ferroelectric and photoelectric properties of PZT thin films [4–7]. Depending on the target application of the film, the interest was focused on one property or another. For memory applications, the interest was focused on polarization retention, imprint, and fatigue, with the aim to elucidate the mechanisms involved in these phenomena [8]. 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 [9,10]. In the case of memory applications, the requirements include high remnant polarization (P_r) and low coercive field (E_c) allowing operation at low voltages, good square hysteresis loop, short switching times, good retention, and fatigue properties. They correspond to a material with very good ferroelectric properties. In this article, we report structural, dielectric, ferroelectric, and photoelectric properties of laser ablated PZT films with 65/35 value of Zr/Ti ratio. This composition lies in the rhombohedral part of the PbZrO$_3$–PbTiO$_3$ system phase diagram and has been

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Table 1
Deposition parameters for PZT thin films

Substrate	$Pt/Ti/SiO_2/Si\langle 100\rangle$
Target	Pb $(Zr_{0.65}Ti_{0.35})O_3$ ceramic disc (with 10 wt.% excess PbO)
Target diameter	25 mm
Substrate target distance	~50 mm
Substrate (heater) temperature	300 °C
Base vacuum	$\sim 4\times 10^{-4}$ Pa
Deposition vacuum with O_2	~8.93 Pa
Laser energy used	250 mJ/pulse
Repetition rate	5 Hz
Deposition time	40 min
Deposition rate	12 nm/min
Energy fluence	$\sim 1.2\ J/cm^2$
Post deposition ex-situ anneal	450 °C/5 h; 650 °C/2 h
Laser source	KrF excimer, 650 mJ, 25 ns, 10 Hz

less studied than those near the morphotropic phase boundary. The results of our experiments on the dielectric and ferroelectric properties are discussed.

2. Experimental details

A $Pb(Zr0_{0.65}Ti_{0.35})O_3$ target with 10 wt.% excess PbO for laser ablation was prepared by solid state reaction technique using conventional sintering process. The starting materials were AR grade PbO, ZrO_2 and TiO_2 powders. These oxides were mixed in appropriate proportions, ball milled, dried and then calcined at 800° and 850 °C subsequently for 4 h. The resulting calcined powder was uniaxially pelletised using a hydraulic press under a pressure of 20 MPa and then sintered at 1250 °C for 4 h in a lead-rich atmosphere. After sintering, the target was lapped, polished and the density of the target was measured by Archimedes method.

A KrF excimer laser, Lambda Physik Compex 201 (248 nm, 650 mJ, 25 ns) was used to ablate PZT. A low repetition rate of 5 Hz was used for the incident laser beam for deposition of thin films and for better nucleation and growth. Laser pulses with an energy of 250 mJ were focused on to the target rotating at 10 rpm. The distance between the target and the substrate holder inside the vacuum chamber was ~5 cm. The angle of incidence of the laser beam was ~45° from the surface normal. The target was fixed to the programmable target holder inside the PLD chamber. The substrate holder was fitted with a resistive type heater to maintain the substrate temperature to an optimized value of 300 °C (±1 °C). The cleaned platinised substrates ($Pt/Ti/SiO_2/Si\langle 100\rangle$) were clipped to the substrate holder. Oxygen (O_2) was used as reactive gas inside the chamber during deposition. The deposition time was 40 min for all depositions. A metal/ferroelectric/metal (MFM) structure was made by depositing a gold electrode of dia 460 μm and 400 nm thickness by a sputtering unit (Model no. Desk II TSC of Denton Vacuum). PZT target was polished after each deposition. The optimized parameters for the deposition of thin films are shown in Table 1.

The thickness of the thin films were measured by using a surface profilometer (Model DEKTAK-3) after making a physical step by chemical etching. X-ray diffraction (XRD) patterns were recorded on a Philips thin film diffractometer (Model PW 3020) using a $Cu(K_\alpha)$ 1.54 A° 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 fluorescences/scattering. The morphology of the films was characterized using atomic force microscopy (AFM, NT-MDT Solver P47H) in the resonant mode at 350 kHz and 38 nm amplitude. The dielectric constant (ε') as a function of temperature was measured at 100 kHz using an Inductance Capacitance Resistance meter (HP-4284A). Hysteresis loops were recorded using an automatic Polarization–Electric field (*P–E*) loop tracer model RT-66A of Radiant Technologies. P_r and E_c were obtained from the *P–E* hysteresis loop.

3. Results and discussions

3.1. Structural and morphological properties

The experimental density (ρ) of the bulk PZT target was estimated as 7.41 g/cm^3. An X-ray diffractogram of PZT thin film deposited by laser ablation is shown in Fig. 1. The XRD pattern shows the formation of a single perovskite phase for PZT thin film, however, the composition of the PZT in thin film has not been verified and the overlapping ⟨104⟩ peak is not shown. Formation of the unwanted pyrochlore phase was eliminated in the film through a careful selection of deposition parameters. The films deposited were ~0.5 μm thick and polycrystalline in nature with no preferred orientation [11] . The polycrystallinity in the film could be due to lattice mismatch between the PZT and the underlying substrate, due to polycrystalline PZT target and also due to higher deposition rate. The strains in a thin film have always been the matter of considerable concern, on account of the fact that the properties of the films are greatly dependent upon the effects of internal stress. Although the strain in these films have not been studied in this research, it is felt that polycrystalline films show minimal stress compared to that of an epitaxial film. This is because the

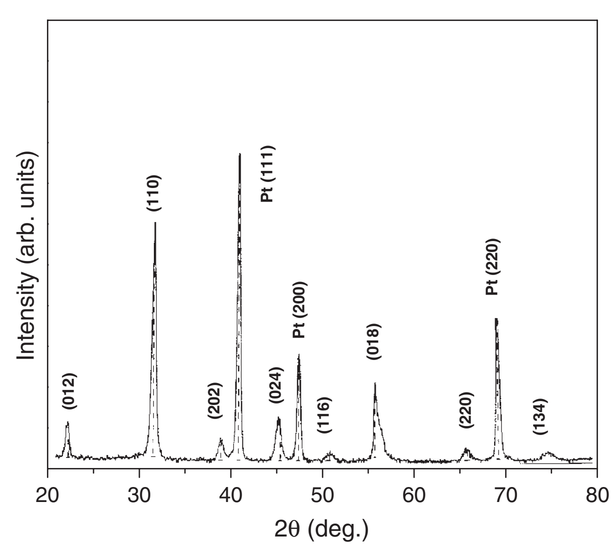

Fig. 1. X-ray diffractogram of PZT 65/35 thin film deposited by PLD.

strain energy density is minimized in a polycrystalline film on account of the presence of grain boundaries which facilitate the alleviation of stresses to a great extent, in a relatively short time [12].

The AFM image revealed well-crystallized films with a very fine microstructure. The films showed an average grain size of ~0.5 μm which is higher than the grain size reported by Tyunina et al. [13]. No significant presence of particulates was observed on the surface of the films, indicating the good quality of films deposited with PLD, a process normally known to have the drawback of having large sized particulates associated with it. The grains were more or less spherical in shape (Fig. 2). A 2-D view of the films surface morphology scanned over an area of 9 μm × 9 μm revealed a surface roughness (r.m.s. roughness) of $R_{\mathrm{r.m.s.}}$ ~ 23 nm. It is to be noted that a large grain size or no grain boundary results in higher remnant polarization and degradation of polarization (such as fatigue and retention) was not observed even with Pt electrodes [14].

3.2. Ferroelectric and electrical properties

3.2.1. P–E measurements

The relatively high values of coercive field compared to bulk PZT may be correlated with the fine-grained microstructure of the films. However, the observed value of remnant polarization (P_r = 25 μC/cm^2) and coercive field (+E_c = 44 kV/cm, −E_c = 42 kV/cm) for the sample shown in Fig. 3 is better than the values reported for the same composition by Tyunina et al. [13] and Boerasu et al. [15]. Here the positive coercive field value is a little higher than the negative coercive field value. This shift in the coercive field value could be attributed to the some internal bias due to different electrode interfaces. Probably different work functions and different densities of interface states might be acting as traps [16]. Tyunina et al. reported values of P_r and E_c as 17 μC/cm^2 and 50 kV/cm, respectively. However, Boerasu et al. reported P_r and E_c as 9 μC/cm^2 and 39 kV/cm, respectively. The improvement in the ferroelectric properties in terms of higher P_r may perhaps be related to the fact that the films in this study have a larger grain size

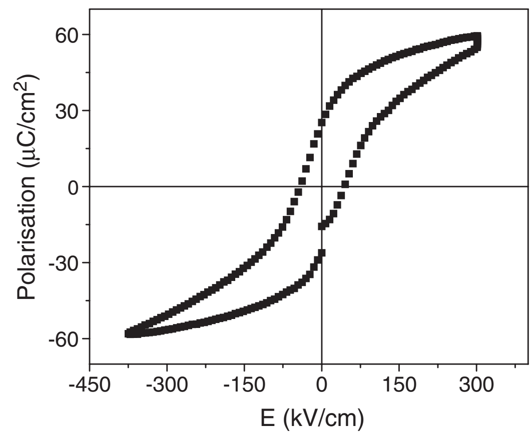

Fig. 3. Polarization vs. Electric field hysteresis loop.

(~0.5 μm) compared to the films by XeCl (λ = 308 nm) ablated ones in which the maximum grain size of the films observed was 0.1 μm. A higher P_r of 30 μC/cm^2 for higher grain size was reported by Lee et al. [14] on account of the larger grain size of the films. Our films may have shown improved results also due to low energy fluence, low repetition rates of laser and the laser source (KrF, 248 nm). It is known that in general, low energy fluence and low repetition rates result in films with good quality and morphological features, with minimal particulates in them. However, the substrate effects, such as clamping cannot be ruled out. A comparison of properties showing substrate effect for the films deposited by sol gel and PLD has been reported by authors [17].

A cursory look at the hysteresis loop (Fig. 3) shows a well-defined, symmetric curve, indicative of the absence of any pinning effects on domain boundary motion on account of defects present in the samples. In addition to the relatively lower stress in polycrystalline films, as mentioned in a preceding paragraph, it may be construed, that domain wall motion in poly-domain grains can relieve applied stress, as was shown previously [18,19].

Dielectric measurements (ε′ and tanδ) at 100 kHz as a function of temperature are shown in Fig. 4. The phase transition temperature (T_c) calculated from dielectric maximum

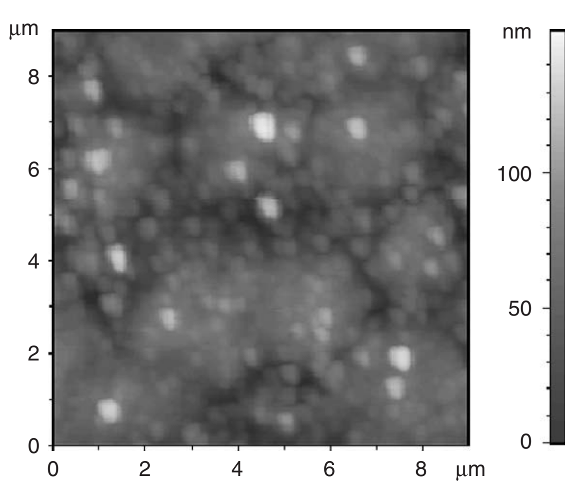

Fig. 2. AFM image of the film (plane view).

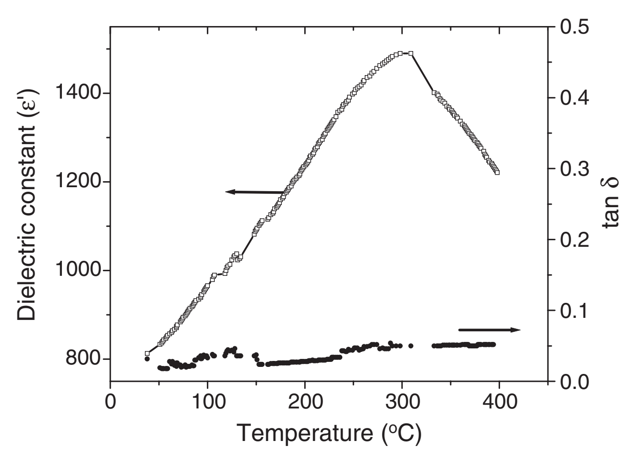

Fig. 4. Variation of dielectric constant (ε′) and loss (tanδ) as a function of temperature at 100 kHz.

is 300 °C. The value of T_c in the film is 25 °C less than that reported in the literature [13], which may be probably due to clamping effect. The dielectric constant (ε') at dielectric maxima was observed as ~1500 which is purely based on our experimental results. However, the dielectric constant (ε') and loss tangent at 100 kHz at room temperature (32 °C) was observed as 812 and 0.026, respectively. The dielectric constant (ε') is more than double from the reported value of Tyunina et al. [13]. The higher values of dielectric constant in the films could be possibly due to higher grain size of the film. It is to be noted that Tyunina et al. [13] have shown a grain size of ~0.1 μm, however, our film's grain size is ~0.5 μm.

4. Conclusions

Single-phase PZT thin films were deposited on the platinised silicon ⟨100⟩ substrates at 300 °C using a KrF excimer laser. The deposition parameters were optimized after several series of depositions. Depositing gold electrode on the films formed a MFM structure, and this structure was used for all electrical measurements. The AFM image shows a grain size of ~0.5 μm with good morphology. The dielectric properties were studied at 100 kHz as a function of temperature. The dielectric and ferroelectric studies showed improved results compared to previously reported ones.

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