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The effect of crystallographic orientation and solution aging on the electrical properties of sol–gel derived $Pb(Zr_{0.45}Ti_{0.55})O_3$ thin films

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Abstract

Lead zirconate titanate—$Pb(Zr_{0.45}Ti_{0.55})O_3$ thin films are grown on $Pt_{\langle 1\,1\,1\rangle}/Ti/SiO_2/Si_{\langle 1\,0\,0\rangle}$ substrates by a sol–gel method with $\langle 1\,0\,0\rangle/\langle 0\,0\,1\rangle$ and $\langle 1\,1\,1\rangle$ preferred orientations. Film orientation was controlled mainly by the annealing process and temperature. Films with $\langle 1\,0\,0\rangle/\langle 0\,0\,1\rangle$ orientation consist of a uniform microstructure with micron size grains, whereas films with $\langle 1\,1\,1\rangle$ orientation contain sub-micron grains. The electrical properties were influenced markedly by the microstructure and orientation of the films. The $\langle 1\,1\,1\rangle$ oriented films exhibit a square-like hysteresis loop with remnant polarization (P_r) reaching 46 $\mu C/cm^2$ under 550 kV/cm, whereas $\langle 1\,0\,0\rangle/\langle 0\,0\,1\rangle$ oriented films have a P_r of 20 $\mu C/cm^2$ with more slim hysteresis curves. Aging of the precursor solutions resulted in films growing with $\langle 1\,0\,0\rangle/\langle 0\,0\,1\rangle$ texture and displaying inferior electrical properties.

Keywords: A. Sol–gel processes; C. Ferroelectric properties; D. PZT; Thin films

1. Introduction

Ferroelectric thin films, such as lead zirconate titanate—$Pb(Zr_xTi_{1-x})O_3$ (PZT), are attracting a great deal of attention for their application in non-volatile memories, pyroelectric sensor arrays and microelectromechanical devices. The main properties expected from a ferroelectric random access memory (FRAM) device are large remnant polarization and polarization reversibility under an applied field. On the other hand, polarization in the capacitor of a dynamic random access memory (DRAM) is not reversed but instead, biased in one polarity. It is therefore essential to have a large dielectric constant for higher integration of DRAM [1].

Since ferroelectric materials have polar axes in certain crystallographic directions, one approach to improve the performance of such devices is to utilize the anisotropic properties of the crystal. It has not been possible, to this date, to texture bulk PZT ceramics with a composition close to the morphotropic phase boundary. However, PZT thin films with preferred orientation are achievable through the use of appropriate substrates [2], oriented conductive oxide electrodes [3], seeding layers [4,5], modified adhesion layers between the Pt bottom electrode and the silicon substrate [6], or through control of the processing conditions [1,7]. The influence of preferred orientation on the electrical properties of the PZT films has been investigated by several researchers [1–7], however the issue has not been fully resolved yet. Most of the reports indicate significant variation in the electrical properties as a result of orientation difference [1,2,4–6], whereas several reports point to orientation independent properties [3] or properties without any significant correlation with the orientation [7].

In this paper, the preparation of lead zirconate titanate thin films by sol–gel process is reported. Our main aim in this study was to investigate and discuss the effect of annealing conditions on the microstructure and crystallographic orientation of the PZT thin films. Electrical characteristics are evaluated and

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discussed in relation to film texture. Aging of the precursor solution and its influence on the structure and properties of the films have also been investigated.

2. Experimental procedure

The PZT thin films were obtained by using a sol–gel method. Lead zirconate and lead titanate precursor solutions with 15 mol% Pb excess were prepared separately to obtain the final PZT solution with various Zr/Ti ratios. Lead acetate trihydrate, zirconium *n*-butoxide and titanium tetraisopropoxide were used as starting materials. 2-Methoxyethanol was utilized as the main solvent and the concentration of the final precursor solution was adjusted to 0.2 M. Lead acetate was mixed and dissolved in 2-methoxyethanol at 80 °C. This lead acetate solution was then dehydrated at 120 °C. Zirconium *n*-butoxide and titanium tetraisopropoxide solutions in 2-methoxyethanol were prepared separately at room temperature and then dehydrated at 120 °C. Lead acetate precursor solution was prepared as two separate solutions and then zirconium and titanium precursor solutions were added into these lead acetate solutions separately. The lead zirconate and lead titanate precursor solutions obtained from these mixtures were then dehydrated further at 120 °C. These separate precursor solutions were mixed in the desired Zr/Ti ratio and final dehydration of the PZT precursor solution was done at 120 °C and then solution was cooled to room temperature. The results presented in this paper are based on the PZT precursor solutions with Zr/Ti = 45/55 composition.

The substrate used in this study is $Pt_{\langle 1\,1\,1\rangle}/Ti/SiO_2/Si_{\langle 1\,0\,0\rangle}$ prepared by RF magnetron sputtering a 5 nm Ti adhesion layer on $SiO_2/Si_{\langle 1\,0\,0\rangle}$ and a 200 nm ⟨1 1 1⟩ oriented Pt electrode layer on top of the Ti layer using an $Ar/O_2 = 90/10$ sputtering gas. The solution deposition on $Pt_{\langle 1\,1\,1\rangle}/Ti/SiO_2/Si_{\langle 1\,0\,0\rangle}$ substrate was performed by spin-coating process at 600 rpm for 6 s and 3000 rpm 70 s. The coatings were dried at 250 °C for 5 min and then pyrolyzed at 400 °C for 5 min. The films were prepared as five layers (~180 nm). Two different methods were investigated for the crystallization and annealing of the films. The first method (named *single annealing*) involves the final annealing of the amorphous films in a single step after coating and pyrolysis of five layers. The annealing process was carried out in a tube furnace for 1 h at two different temperatures (600–650 °C) under air atmosphere by instantly putting the samples into the furnace. In the second method (named *multi-annealing*), after coating and pyrolysis of each layer, an intermediate annealing was applied for 10 min at the desired temperature. After obtaining the five-layer thick films, a final annealing was applied at the same temperature for 1 h in a tube furnace under air atmosphere. An experimental flow chart is shown in Fig. 1.

The crystallinity and phase formation of the PZT thin films was examined using a Philips XPert X-ray diffractometer (XRD) with Cu Kα radiation. Chemical analyses of the films were done with Philips MagiX X-ray fluorescence spectrometer (XRF). Microstructural properties of the films were observed using a JEOL JSM-6301F field emission scanning electron microscope (FESEM). Platinum top electrodes with 100, 200 and 400 μm diameter and 200 nm thickness were deposited on the surface of the films by RF magnetron sputtering using a shadow mask. Electrical properties were measured using an AixACCT-TF 2000 ferroelectric tester.

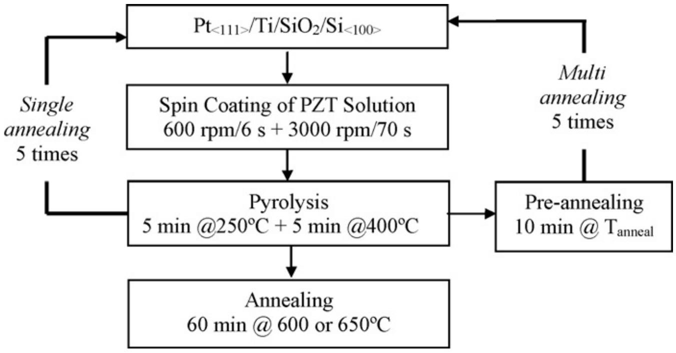


Fig. 1. Process flow chart for sol–gel derived PZT thin films.

3. Results and discussion

3.1. Phase analysis and microstructure

The phase analysis of the thin films obtained by the single and multi-annealing processes is presented in Fig. 2. In the evaluation of the results, integrated intensity ratio, i.e., $I_{(h\,k\,l)}/(I_{(1\,0\,0)} + I_{(1\,1\,1)})$ was used to express the texture fraction for the ⟨1 0 0⟩/⟨0 0 1⟩ or ⟨1 1 1⟩ preferred orientation of the films. The results are given in Table 1. From Fig. 2 and Table 1, single annealing process was found to yield 60% ⟨1 0 0⟩/⟨0 0 1⟩ texture at 600 °C and over 95% ⟨1 1 1⟩ texture at 650 °C for films prepared from fresh precursor solutions. Multi-annealing

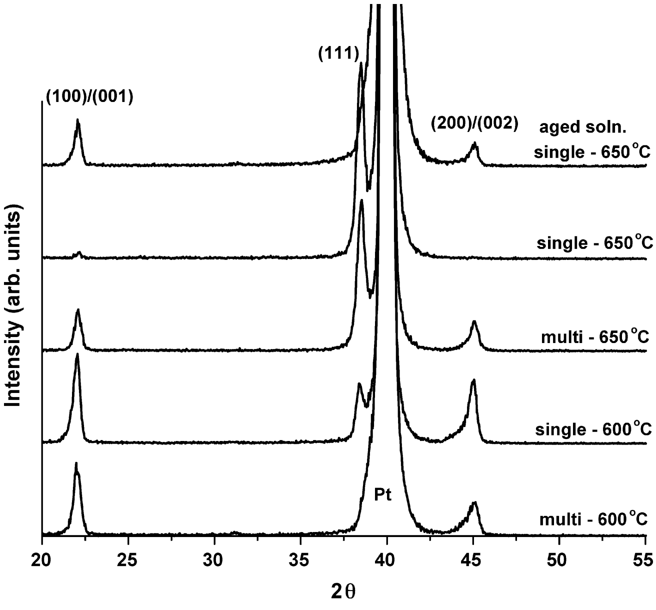


Fig. 2. X-ray diffraction patterns of PZT thin films prepared by single or multi-annealing steps. The perovskite peaks belonging to the tetragonal PZT structure are indexed with *h k l* indices, Pt denotes the (1 1 1) peak of the platinum bottom electrode.

Table 1
Properties of PZT thin films produced under various annealing conditions

	Annealing temperature (°C)				
	600 Multi-fresh[a]	600 Single fresh[a]	650 Multi-fresh[a]	650 Single fresh[a]	650 Single aged[a]
Excess Pb (after annealing) (%)[b]	9	11	5	6	11
Preferred orientation	100% ⟨1 0 0⟩/⟨0 0 1⟩	60% ⟨1 0 0⟩/⟨0 0 1⟩	80% ⟨1 1 1⟩	95% ⟨1 1 1⟩	100% ⟨1 0 0⟩/⟨0 0 1⟩
Grain size	1.3–1.8 μm	1.0–1.5 μm	195–240 nm	150–180 nm	0.5–1.0 μm
P_r (μC/cm^2)[c]	20	30	36	46	32
P_{max} (μC/cm^2)[c]	73	63	60	72	63
E_c (kV/cm)[c]	66	65	108	77	83
Dielectric constant, ε_r	980	950	700	1000	970

[a] Annealing type.

[b] Excess Pb ratio in the precursor solution was 15%.

[c] Measured under 550 kV/cm applied field.

process, on the other hand, was found to result in 100% ⟨1 0 0⟩/⟨0 0 1⟩ texture at 600 °C and 80% ⟨1 1 1⟩ texture at 650 °C for fresh solutions. These results indicate that lower annealing temperature leads to a ⟨1 0 0⟩/⟨0 0 1⟩ dominant orientation, whereas higher temperature results in a ⟨1 1 1⟩ dominant orientation.

The preferred orientation of PZT thin films is mainly governed by substrate orientation or properties of the substrate–film interface, such as presence of buffer or seeding layers. The substrate used in this study is $Pt_{\langle 1\,1\,1\rangle}/Ti/SiO_2/Si_{\langle 1\,0\,0\rangle}$ prepared by sputtering 5 nm Ti adhesion layer on $SiO_2/Si_{\langle 1\,0\,0\rangle}$ and 200 nm fully ⟨1 1 1⟩ oriented Pt electrode layer on top of the Ti layer using a mixed sputtering gas ($Ar/O_2 = 90/10$). It was suggested in the literature [7] that close lattice matching between $Pt_{\langle 1\,1\,1\rangle}$ and $PZT_{\langle 1\,1\,1\rangle}$ leads to nucleation and growth of ⟨1 1 1⟩ oriented PZT. Additionally, Huang et al. [8] proved that formation of a metastable Pt_3Pb intermetallic phase promotes ⟨1 1 1⟩ orientation at much lower crystallization temperatures due to much better lattice match between the ⟨1 1 1⟩ oriented PZT and ⟨1 1 1⟩ oriented Pt_3Pb compared to that of Pt. On the other hand, formation of ⟨0 0 1⟩ oriented PbO microcrystallites in the presence of excess Pb [9] or directly coating a PbO seeding layer underneath the PZT thin film [10] were reported to facilitate growth of ⟨1 0 0⟩/⟨0 0 1⟩ oriented PZT thin films due to the good lattice matching with $PbO_{\langle 0\,0\,1\rangle}$.

In this study, the change of orientation from ⟨1 0 0⟩/⟨0 0 1⟩ to ⟨1 1 1⟩ in both the single and multi-annealing processes is believed to be related to the Pb content of the films. As given in Table 1, increasing annealing temperature resulted in increased lead loss. The precursor solution was prepared with 15 mol% excess Pb, and at 600 °C annealing temperature, it would be conceivable to have a PbO phase formation that would lead to ⟨1 0 0⟩/⟨0 0 1⟩ textured films. The critical influence of lead content on the orientation of perovskite films have also been observed previously by Shimizu et al. [11] and the mechanism of PbO on film orientation and growth have been discussed in details by Muralt et al. [12]. A very thin layer of PbO formed on the surface in the presence of excess Pb reduces the surface energy and promotes nucleation and growth of (1 0 0) oriented perovskite film. However, at annealing temperatures of 650 °C and above there is an increased lead loss due to increasing volatility of Pb with increasing temperature. Decrease of Pb content as a result of increased temperature, in turn, may prevent complete coverage of the surface with PbO. In the absence of such a low energy surface and at high heating rates used in our study, nucleation and growth of the films is controlled by the kinetics of the reaction. As a result, the films tend to grow with ⟨1 1 1⟩ texture, following the orientation of the platinum substrate due to the lattice matching between the crystal structures.

When the two annealing processes are compared, the single annealing process was found to yield higher crystallinity at both annealing temperatures, as indicated by the relative intensity of XRD peaks in Fig. 2. Single annealing also resulted in a higher degree of ⟨1 1 1⟩ texture at both temperatures, whereas the multi-annealed films still retained a certain degree of ⟨1 0 0⟩/⟨0 0 1⟩ orientation at 650 °C. Similar results were reported by Aoki et al. [13] in the literature for multi-annealing process. This result seems to contradict the reasoning presented in the previous paragraph for the relation of film texture with Pb content. In the multi-annealing process, the films go through a longer thermal cycle due to the intermediate annealing steps, and as a result, they have slightly higher Pb loss (Table 1). However, we think that the persistence of the ⟨1 0 0⟩/⟨0 0 1⟩ orientation in the multi-annealed films is due to the interrupted growth process that occurs in this process. Since an intermediate annealing is employed after deposition and pyrolysis of each layer (Fig. 1), the upper layers may not fully duplicate the texture of the underlying layer. As the number of layers increase, some of the texture information from the bottom layer will be lost and the new layers will nucleate and grow as if they are on a partially random surface. This may lead to a partial ⟨1 0 0⟩/⟨0 0 1⟩ orientation, because this is the self-textured growth direction. Due to the minimum surface energy of flat-faceted surfaces, growth in the ⟨1 0 0⟩/⟨0 0 1⟩ direction is thermodynamically favoured compared to ⟨1 1 1⟩ direction [14].

The microstructural features of PZT thin films which were fabricated by the two different annealing methods and at various temperatures were examined with scanning electron microscopy (SEM). The cross-sectional SEM micrographs indicate the film thickness to be ∼180 nm as shown in

Fig. 3. The surface and cross-sectional micrographs presented in Fig. 3 showed that the annealing temperature and associated film orientation have a significant influence on the microstructure and the grain size of the films. The PZT films prepared at 600 °C using both the single and multi-annealing process have an order of magnitude larger grains compared to the films prepared at 650 °C (Table 1). The cross-sectional micrographs clearly show that all the films have columnar grains with no indication of a sub-granular structure. Increasing annealing temperature normally causes further grain growth. However, in the case of this study, there is also a change in the film orientation with increasing temperature. The large difference observed in the grain size of the films and the smaller size observed at higher temperature, contrary to the expectation, is attributed to the change in the preferred orientation of the films with increasing temperature. The nucleation and growth rate in $\langle 1\,0\,0\rangle/\langle 0\,0\,1\rangle$ and $\langle 1\,1\,1\rangle$ directions in a crystal lattice are different from each other. It is therefore expected that there will be a variation in the grain size and morphology in the films with different orientations. From Fig. 3, the smaller grain size of the $\langle 1\,1\,1\rangle$ oriented films indicate a higher nucleation density and, therefore, a lower activation energy for nucleation compared to $\langle 1\,0\,0\rangle/\langle 0\,0\,1\rangle$ oriented films. Comparison of the influence of the type of annealing process on the microstructure, on the other hand, points to a grain growth as a result of the multi-annealing process. This is due to the longer annealing time that the films undergo in the multi-annealing case.

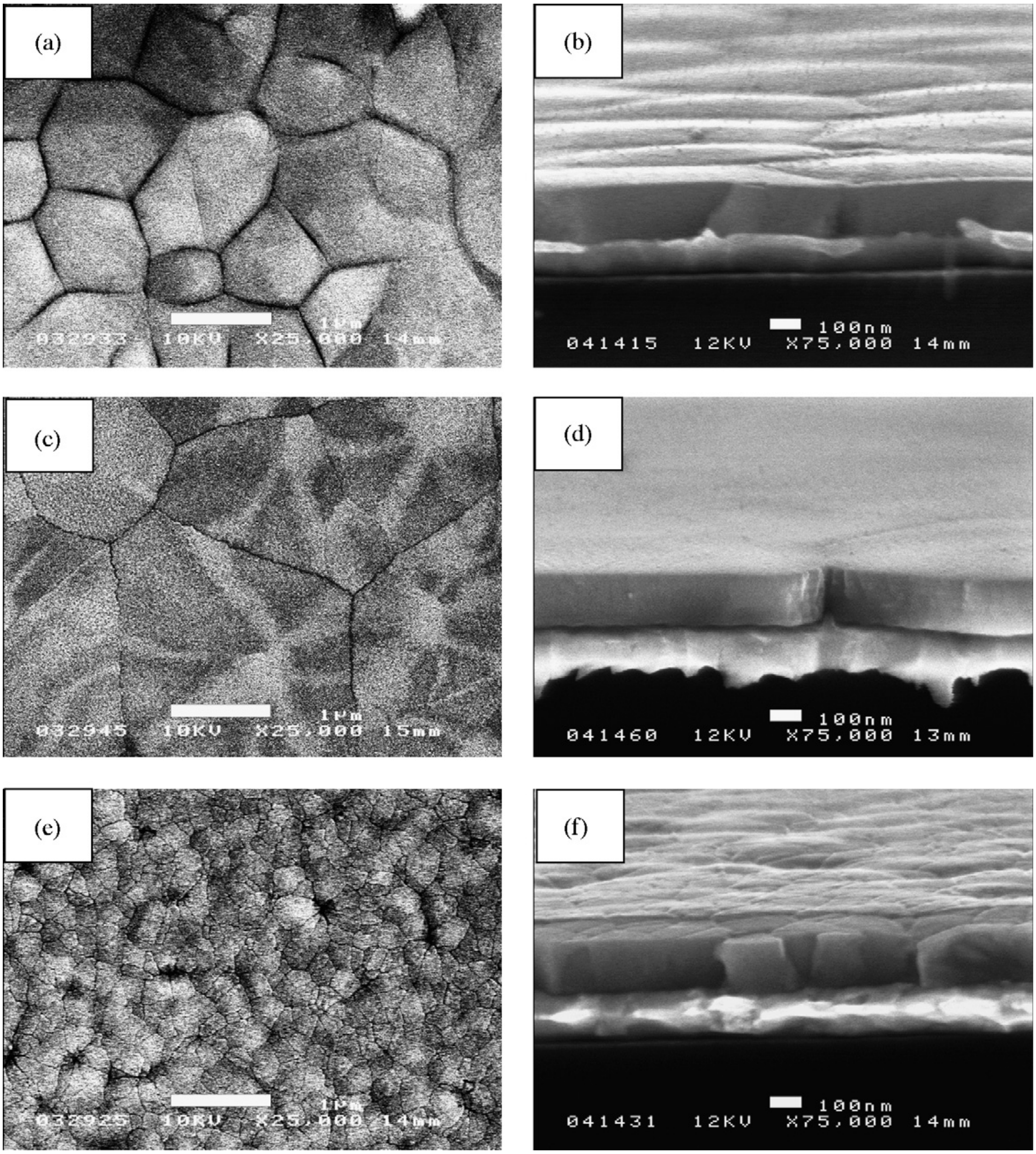


Fig. 3. Scanning electron micrographs of the PZT thin films obtained by: (a and b) single annealing at 600 °C; (c and d) multi-annealing at 600 °C; (e and f) single annealing at 650 °C; (g and h) multi-annealing at 650 °C; (i and j) single annealing at 650 °C from aged precursor solution.

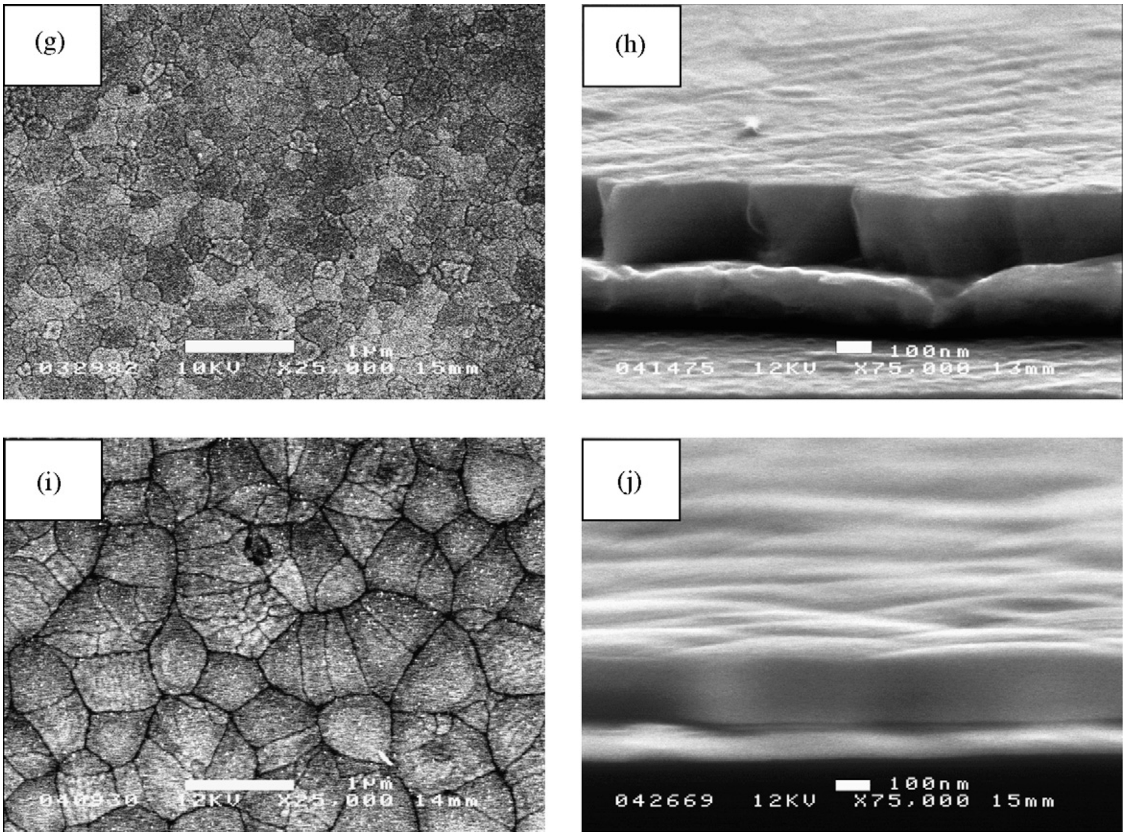


Fig. 3. (*Continued*).

3.2. Electrical properties

The change in film orientation and microstructure as a result of annealing type and temperature is expected to reflect on the electrical properties. For example, grain size in ferroelectrics has a strong relationship with domain size and switching behaviour [15]. However, from processing point of view, it is usually very difficult, if not impossible, to change one material parameter (grain size or orientation) and keep the others constant so that the effect of only one parameter can be investigated. As explained in the previous section, the drastic change in the microstructure and especially in grain size in our study is accompanied by a change in film orientation. Therefore, it would not be possible to comment on the direct effect of microstructure on the electrical properties. As a result, we focused our discussion of the electrical properties mostly on the effect of preferred orientation. In Fig. 4(a), *P–E* curves for the films annealed at 600 °C using single and multi-annealing process were compared. The polarization curve of the multi-annealed films has inclined domain reversal segments. Whereas, single annealed films have a more square-like polarization curve with more abrupt domain reversal compared to the previous one. The remnant polarization (P_r) of the single annealed films are higher compared to multi-annealed ones (Table 1). Fig. 4(b) shows the polarization hysteresis curves for films annealed at 650 °C. In this case, both of the annealing processes resulted in square-like hysteresis loops and abrupt domain reversal with single annealing having larger P_r but lower E_c values compared to the multi-annealed ones (Table 1). Fig. 5 shows change of $2P_r$ with respect to applied electric field. This figure concurs with the above findings, indicating a well-saturated polarization and an abrupt domain reversal at lower field levels for especially the films that were annealed at 650 °C. Films annealed at 600 °C, on the other hand, have lower polarization values and reach saturation at higher field levels. The magnitude of polarizations follow the order of increasing $\langle 1\ 1\ 1 \rangle$ preferred orientation in the films, where purely $\langle 1\ 0\ 0 \rangle / \langle 0\ 0\ 1 \rangle$ oriented films having the lowest and purely $\langle 1\ 1\ 1 \rangle$ oriented films having the highest polarization values.

From microstructural point of view, smaller grains with sub-micron sizes may have a higher domain wall density, which in turn results in higher extrinsic contribution on the electrical properties [15]. As a result, films with smaller grains, i.e., films annealed at 650 °C using either one of the annealing process, may be expected to display better properties. But on the other hand, smaller grains may lead to higher stresses inside the grain, absence of 90° domain walls and decreased domain mobility [15,16]. Therefore, the effect of grain size on the polarization switching and ferroelectric properties is of a complex nature with competing effects. It requires further investigation where grain size is the only changing parameter.

The results of the *P–E* measurements can be explained qualitatively, in a more straight forward manner, with the preferred orientation of the films using a simplified domain structure. In this study, the PZT films are prepared with a Zr/Ti ratio of 45/55 and this composition was confirmed by XRF

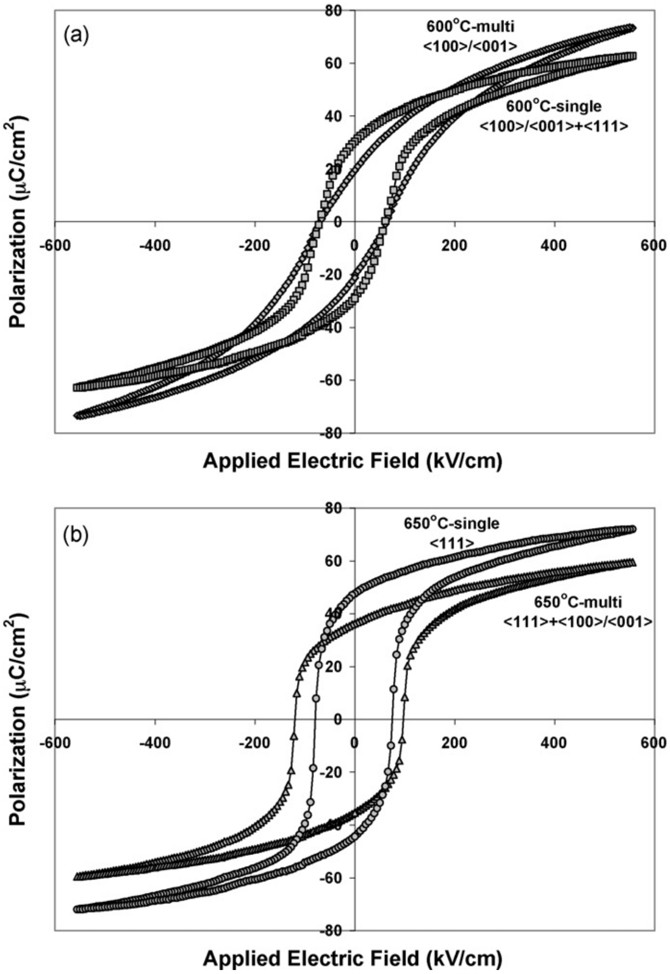


Fig. 4. Polarization vs. hysteresis loops of PZT thin films annealed at: (a) 600 °C and (b) 650 °C.

analysis. Therefore, these films are in the tetragonal region of the PZT phase diagram. Fig. 6 illustrates the possible spontaneous polarization directions in ⟨1 0 0⟩/⟨0 0 1⟩ and ⟨1 1 1⟩ oriented films with tetragonal structure. The electric field is applied normal to the film, i.e., along "*z*" direction in the ⟨1 0 0⟩/⟨0 0 1⟩ oriented films and along the body diagonal in the ⟨1 1 1⟩ oriented films. In the ⟨1 0 0⟩/⟨0 0 1⟩ textured films, the polarization direction 1 is along the applied field direction and direction 6 is its reverse equivalent. Both of them are perpendicular to the film plane. The directions 2, 3, 4 and 5 are perpendicular to the field direction and lie within the film plane. When the field direction is reversed from upward to downward, domains along direction 1 will be reversed first since they are aligned parallel to the field direction. However, domains along 2, 3, 4 and 5 are aligned perpendicular to the field direction. They, therefore, require 90° domain switching, which necessitate higher electric fields and possibly compressive stresses in the films parallel to the film surface due to small lattice mismatches with the substrate. Thus, the domain reversal segments of the *P*–*E* hysteresis curves in purely ⟨1 0 0⟩/⟨0 0 1⟩ oriented films would be inclined and they will have lower remnant polarization.

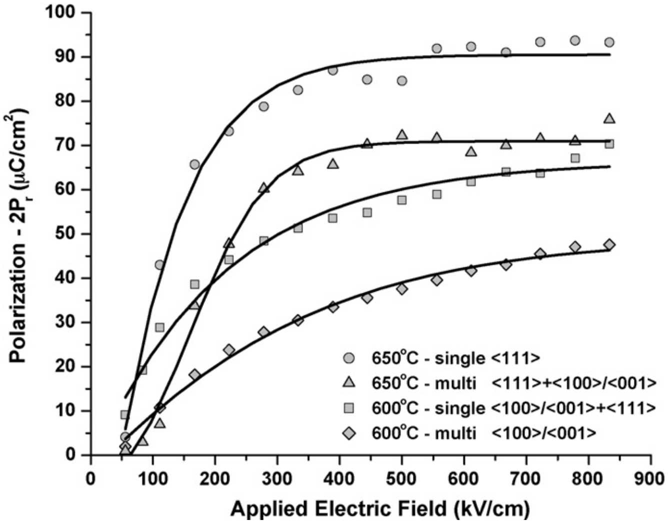
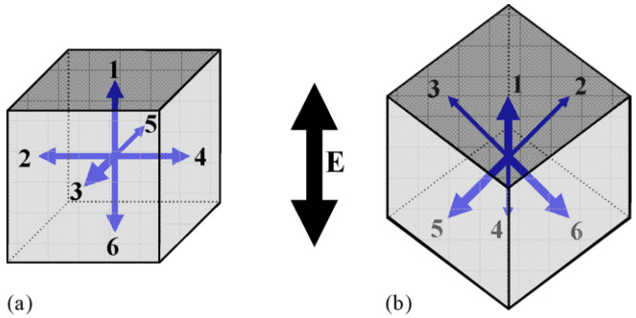


Fig. 5. Change of remnant polarization of PZT thin films with respect to applied field.

In the purely ⟨1 1 1⟩ textured films, on the other hand, the polarization directions 1, 2 and 3 are equivalent and are 54.7° away from the applied field direction. Polarization directions 4, 5 and 6 are reverse equivalents of the first three. Therefore, remnant polarization of ⟨1 1 1⟩ textured films are expected to be higher than the ⟨1 0 0⟩/⟨0 0 1⟩ ones. Additionally, when the electric field direction is reversed from upward to downward, the domains along 1, 2 and 3 will be switched simultaneously to 4, 5 and 6, creating an abrupt change in the domain reversal segment of the *P*–*E* hysteresis curves and leading to more square-like shape. Films with mixed orientation will display a mixed behaviour with primary orientation dominating the shape and P_r values of the hysteresis curves. The results presented in Figs. 4 and 5 confirm these theoretical expectations.

Fig. 7 shows the dielectric constant versus electric field curves of the PZT films calculated from the *C*–*V* measurements. It is clearly seen from these curves that increasing ⟨1 1 1⟩ texture in the films causes sharper changes in the peak points of the dielectric constant due to the abrupt domain reversal, in accordance with the *P*–*E* hysteresis loops. The leakage current of the PZT films is given in Fig. 8. The measured values for ⟨1 0 0⟩/⟨0 0 1⟩ and ⟨1 1 1⟩ textured films were found to vary



(a) (b)

Fig. 6. Possible spontaneous polarization directions for textured PZT films with a tetragonal structure: (a) ⟨1 0 0⟩/⟨0 0 1⟩ and (b) ⟨1 1 1⟩.

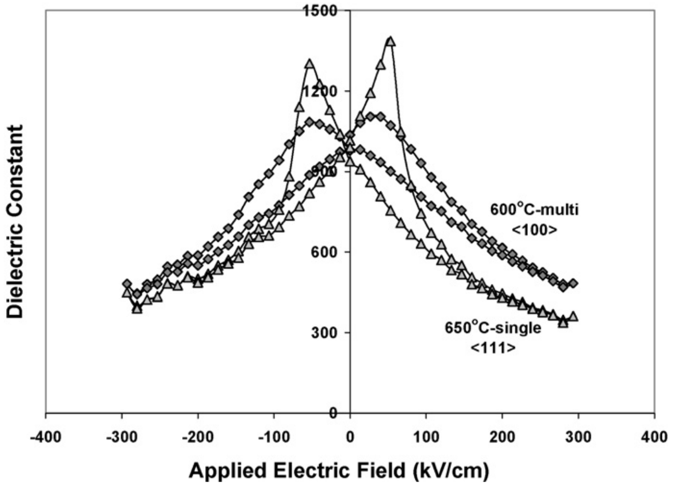


Fig. 7. Dielectric constant–electric field behaviour of PZT thin films with ⟨1 0 0⟩/⟨0 0 1⟩ and ⟨1 1 1⟩ preferred orientation.

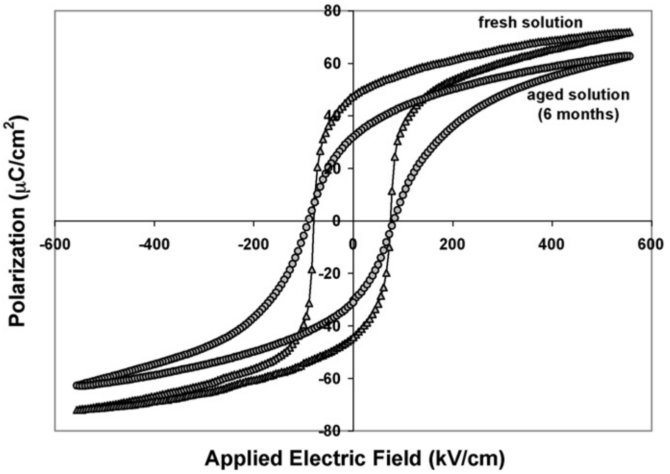


Fig. 9. Polarization vs. hysteresis loops of PZT thin films prepared from fresh and 6 months aged solutions by single annealing at 650 °C.

within two orders of magnitude of each other with peak values less than 10^{-4} A/cm^2. The higher leakage current values observed in the ⟨1 1 1⟩ textured films were attributed to the smaller grain size, i.e., larger number of grain boundaries, observed in these films.

All of the results presented and discussed up to this point have been obtained from films prepared from fresh precursor solutions. However, when the precursor solution was aged for 6 months and reused in film preparation, the remnant and maximum polarization of the films were found to decrease markedly. Fig. 9 gives a comparison of the *P–E* hysteresis loops of PZT thin films prepared from fresh and 6 months aged precursor solutions by the single annealing process at 650 °C. The shape of the *P–E* hysteresis loop of the films prepared from the aged precursor solution was found to have more inclined domain reversal segments. The X-ray diffraction analysis of these films indicate that the crystallographic orientation of the films have changed from ⟨1 1 1⟩ to ⟨1 0 0⟩/⟨0 0 1⟩ and the crystallinity was lower as a result of using aged solutions (Fig. 2 and Table 1). Zhang et al.'s studies [17] on aging of precursor solutions and their effects on the physical properties of PZT thin films indicate that the particles in PZT precursor solutions assume a chain-like shape and the size of these particles increases with aging time. The particle size in PZT precursor sols was found to have a direct effect on the orientation of the thin films and the pyrochlore to perovskite phase transformation properties. Aging of $PbZrO_3$ precursor solutions was also reported to lead to phase separation and a segregation of Pb [14]. This, then, was reported to result in the formation of pyrochlore-like second phases and a tendency to nucleate and grow films with a ⟨1 0 0⟩/⟨0 0 1⟩ preferred orientation. Similarly, Kushida et al. [18] studied the change of orientation of $PbTiO_3$ thin films and found that solution aging promotes growth of films with ⟨1 0 0⟩ orientation. This was attributed to the increase in the molecular weight and particle size and the chain-like shape of the particles in the solution. These chain-like particles are then more easily aligned during the spin-coating process, resulting in a ⟨1 0 0⟩ orientation. In the light of these reports and our results in this study, the films we prepared from aged PZT precursor solutions were also found to have a tendency to grow with ⟨1 0 0⟩/⟨0 0 1⟩ preferred orientation. As shown in Fig. 3(i and j), the microstructure of the films consists of large (0.5–1 μm) columnar grains, which is similar to the ⟨1 0 0⟩/⟨0 0 1⟩ oriented ones prepared from fresh solutions. The shape of the *P–E* loop and properties given in Table 1 are similar to the ⟨1 0 0⟩/⟨0 0 1⟩ oriented films prepared at lower temperatures and are, therefore, believed to be due to the change in orientation.

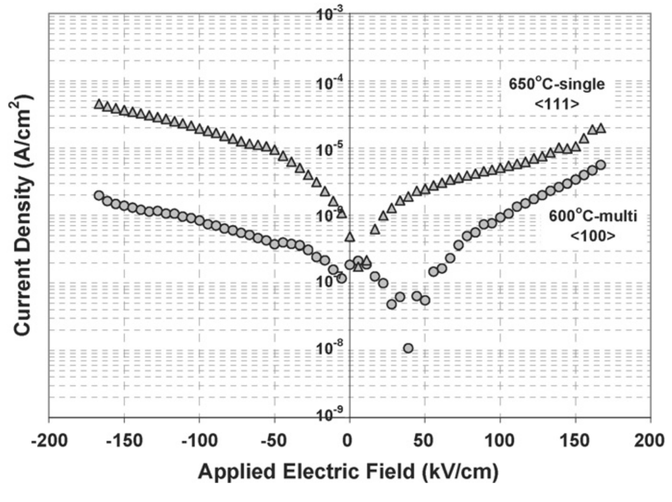


Fig. 8. Leakage current–electric field behaviour of PZT thin films with ⟨1 0 0⟩/⟨0 0 1⟩ and ⟨1 1 1⟩ preferred orientation.

4. Conclusions

In this study, lead zirconate titanate—$Pb(Zr_{0.45}Ti_{0.55})O_3$ thin films were prepared by sol–gel method. The crystallographic orientation, microstructure and electrical properties of the films were controlled by annealing process and temperature. Purely ⟨1 0 0⟩/⟨0 0 1⟩ textured films were prepared by using a multi-annealing process at 600 °C, whereas pure ⟨1 1 1⟩ orientation was obtained by using a single annealing process at 650 °C. Thin films with higher ⟨1 0 0⟩/⟨0 0 1⟩ texture were found to contain an order of magnitude larger grains compared to ⟨1 1 1⟩ oriented ones. All of the films yielded well-saturated *P–E* hysteresis loops; however, higher values of remnant polarization, as well as, more square-like hysteresis curves and abrupt domain reversal were obtained from the films with higher ratio of ⟨1 1 1⟩ texture. The observed remnant polarization for ⟨1 0 0⟩/⟨0 0 1⟩ and ⟨1 1 1⟩ textured films were 20 and 46 μC/cm^2, respectively, under 550 kV/cm applied field. The dielectric constant of the films was calculated to be between 700 and 1000. The combined effects of microstructure and orientation on the observed dielectric and hysteresis characteristics were discussed. Aging of the precursor solution was found to lead to a change in preferred orientation and decrease in the electrical properties.

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