Erbium doping effects on solution deposited PbTiO$_3$ thin films

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Erbium doped PbTiO$_3$ (PET) thin films were prepared via a modified sol–gel method on (111) Pt/Ti/SiO$_2$/Si substrates. SEM and XRD investigations showed fully crystallized fine grained perovskite structure achieved after annealing at 700 °C for 5 min. The Er-doped films exhibited (100) preferred orientation, and the lattice tetragonal distortion ($c/a$) was found to decrease from 1.044 for pure PT to 1.036 for PET containing 8 mol% of Er. Dielectric and ferroelectric properties of PET thin films were characterized at room temperature by impedance analysis and hysteresis measurements. It is shown that both small signal dielectric constant and loss tangent as well as ferroelectric properties are specifically affected by Er doping, depending on Er concentration. Based on the results obtained, amphoteric behaviour of Er in lead titanate thin films is suggested.

1 Introduction

Ferroelectric PbTiO$_3$ (PT) based thin films are being considered for use in various functional devices including non-volatile memories [1], IR sensors [2] and micro-electromechanical systems (MEMS) [3]. Doping with Nb, La [4–12] and other elements has been investigated for the purpose of tuning dielectric and ferroelectric properties of the material for specific applications. Unlike bulk samples, the electrical properties of the films are closely related to film thickness and deposition conditions and therefore to microstructure and stress state [4, 5]. In this respect, it has been reported [6] that both remnant polarization and coercive field of (Pb, La)TiO$_3$ thin films decrease as La content increases up to 28 mol%. The dielectric constant was found to be strongly affected by La concentration showing significant increase particularly in the range of doping level from 15 to 28 mol%. Furthermore, A- or B-sites substitution by elements with different ionic radii such as Nb and La was found to noticeably reduce the tetragonal distortion, $c/a$, of tetragonal perovskites like PT [7, 10]. Processing of pure PT ceramics or thin films, which is usually difficult because of the high tetragonal distortion ($c/a = 1.063$ given for bulk ceramic) [13] which leads to the development of cracks while cooling through Curie temperature, may therefore be made more easy via suitable doping. However, along with improved dielectric and ferroelectric properties it has been reported [11, 12] that crystallization kinetics of the films is influenced by donor elements doping. Undesirable second phase such as lead deficient pyrochlore was found more stable in Nb and La doped films.

In the present work we report on sol–gel processing of Er doped PbTiO$_3$ thin films with different doping levels on highly (111) textured Pt/Ti/SiO$_2$/Si substrates. The thin films are characterized in terms of
microstructure, dielectric and ferroelectric properties. The results obtained are compared to those of non-doped PbTiO$_3$ films and discussed in terms of Er doping effects on structure and electrical properties of the films. Based on these results conclusions about the lattice substitution site of Er are inferred.

2 Experimental

Acetic acid and acetylacetone modified sol–gel method was utilized to fabricate PET thin films with different Er content. The flow chart diagram shown in Fig. 1 illustrates the procedure for precursor solution preparation. All the chemical reagents were provided by Fluka Chemicals, Inc., Germany, except erbium acetate that was purchased from Strem Chemicals, Inc., U.S.A. Excess 10 mol% of Pb were added to compensate lead volatility during high temperature treatment. PET precursor solutions were prepared according to the stoichiometry Pb$_{1-x}$Er$_x$Ti$_{1-x/4}$O$_3$ where $x = 0, 0.01, 0.02, 0.05$ and $0.08$ (for simplicity the samples will be denoted as PT, PET1, PET2, PET5, and PET8 in the following). Firstly lead and erbium acetates were dissolved in 3 mol of acetic acid and refluxed for 3 hours at $110^\circ$C to evaporate associated water. Tetraisopropil orthotitanate was stabilized with acetylacetone mixed in ratio 1 : 2 mol. Both parts were then mixed together at room temperature and diluted with 2-methoxyethanol to reach concentration of 0.5 mol/l. The final solutions were filtered through 0.2 µm syringe filter just prior to deposition. PET thin films were fabricated by spin-coating on (111)Pt/Ti/SiO$_2$/Si commercial substrates (Inostek, Seoul, Korea) at 3000 rpm for 30 s. Each coating was dried on a plate at $340^\circ$C for 5 min. For the case of $x = 0.02, 0.05$ and $0.08$ the first layer was annealed at $700^\circ$C for 5 min to reduce the crystallization energy of subsequent layers. A total of 7 coatings were performed. Due to strong cracking effects in PT and PET1 the films were fabricated from solutions with a reduced concentration of 0.4 mol/l and only six coatings were deposited. Furthermore, in order to avoid cracking a different annealing scheme was adopted, consisting of a pre-annealing at $550^\circ$C for 5 min, followed by final annealing at $600^\circ$C for 10 min to achieve crystallization.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Nominal composition and thickness of prepared samples.</th>
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<tbody>
<tr>
<td>sample</td>
<td>composition</td>
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<tr>
<td>PT</td>
<td>Pb$_{1.1}$TiO$_3$</td>
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<tr>
<td>PET1</td>
<td>Pb$<em>{1.099}$Er$</em>{0.01}$Ti$_{0.997}$O$_3$</td>
</tr>
<tr>
<td>PET2</td>
<td>Pb$<em>{1.078}$Er$</em>{0.02}$Ti$_{0.995}$O$_3$</td>
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<tr>
<td>PET5</td>
<td>Pb$<em>{1.045}$Er$</em>{0.05}$Ti$_{0.995}$O$_3$</td>
</tr>
<tr>
<td>PET8</td>
<td>Pb$<em>{1.012}$Er$</em>{0.08}$Ti$_{0.94}$O$_3$</td>
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Microstructure and phase composition of the films were characterized by means of Scanning Electron Microscopy (SEM, Philips) and X-ray diffractometry (XRD, CuKα radiation, θ/2θ scans, λ = 1.5418 Å, Seifert). Film thickness was obtained from SEM cross-section analysis. Nominal composition and thickness of prepared samples are summarized in Table 1. For electrical characterization round Pt electrodes with a diameter of 0.6 mm were sputtered through a shadow mask. Post top electrode deposition annealing was performed at 400 ºC for 10 min in air. Ferroelectric properties of the films were measured with a commercial ferroelectric tester (Radiant Technologies, Inc. RT6000S) using 2 ms square pulses and a voltage amplitude between 0.5 and 19 V. Frequency dependences of the dielectric properties and C–V characteristics were investigated by a computer controlled Agilent 4192 A impedance analyser.

3 Results and discussions

3.1 Microstructure and X-ray diffraction

Back scattered electron (BSE) micrographs of PbTiO₃ are presented in Fig. 2. As can be seen from top-view micrograph (Fig. 2a) very fine, crack-free grain structure with no visible second phase inclusions is obtained after annealing at 600 ºC for 10 min. Cross-section analysis of PT films (Fig. 2b) revealed random grain structure formation. The same features of microstructure were found for 1 mol% doped PET thin film (not shown here). Despite difference in deposition procedure (higher annealing temperature and concentration of the precursor solution) similar fine grained structure is obtained for samples with x = 0.02, 0.05, and 0.08. Top-view SEM micrograph of PET8 thin film is presented in Fig. 3a. Some difference in microstructure may, however, be concluded from the SEM cross-sectional micrograph of Fig. 3b which suggests columnar morphology of the grains. Figure 4 shows XRD patterns of PT, PET1, PET2, PET5, and PET8 films. For all samples no evidence of pyrochlore phase formation was observed. Apart from PET8 where a (001/100) preferred orientation was observed, the thin films are randomly oriented (the XRD-patterns are similar to those obtained for PbTiO₃ powder [14]).

When increasing Er content, the a and c cell parameters determined by least-squares refinement using Celref software [15] gradually increases and decreases respectively. This results in the decrease of the tetragonal distortion c/a (Fig. 5). Such a behaviour is very similar to that reported for PT doped with La [16] and Ca [17] and allows to anticipate the appearance of the composition with the cubic metrics of the unit cell above the content of Er roughly estimated from c/a vs. x plot (Fig. 5) to 15–20 mol%.

3.2 Dielectric properties

Figure 6 presents room temperature small signal dielectric properties (real part of the dielectric constant (ε’)) and loss tangent (tan δ) measured at 1 kHz and plotted vs. Er content. Both ε’ and tan δ increase with Er content from x = 0 to x = 0.02 and then decrease for higher Er concentrations. These results can be explained in terms of a specific behaviour of Er in the PT lattice: systematic investigations of lantha-
nide doped PZT thin films and ceramics were performed by Boyle et al. [18] and Park et al. [19]. Based on the results of structural analysis they claim that Er acts as acceptor in PZT, although investigations involving variable concentrations of Er were not performed. The data of the present work, Fig. 6, rather suggest an amphoteric substitution of Er doping of lead titanate thin films. Furthermore, it is thought that, depending on the concentration, Er can replace Pb and/or Ti in their own sublattices. In small concentrations ($\leq 2$ mol%) it predominantly substitutes A-sites, i.e. acts as a donor, and for higher concentrations it partially substitutes B sites, i.e. it acts as acceptor. In fact donor doping is accompanied by increasing of dielectric constant and $\tan \delta$ [20] as evident from Fig. 6. Yet acceptor doping is compensated by the creation of oxygen vacancies which results in domain wall pinning and consequently decreases $\varepsilon'$ and $\tan \delta$. This leads to intermediate properties with $\varepsilon'$ and $\tan \delta$ decreasing with increasing Er content, yet remaining higher than the values of pure PT. These result show that it is possible to tune the dielectric properties of PT by Er doping. The PET8 film is characterized by noticeably lower loss tangent ($\tan \delta = 0.018$) and dielectric constant ($\varepsilon' = 254$) than the other PET films. Such properties can provide good figure-of-merit for pyroelectric device application (see for example p. 161 in Ref. 2).
It is well known that dielectric properties of ferroelectric materials are chiefly determined by domain wall structure. C–V (or $\varepsilon'$–$E_b$, where $E_b$ external DC bias field) experiments i.e. measurements of dielectric constant of the material under applied DC bias, help to estimate the contribution of domain wall oscillation to dielectric properties. Figure 7a demonstrates typical $\varepsilon'$–$E_b$ curves obtained for a PET2 film.

The hysteretic behaviour is characteristic for ferroelectric materials, and the maxima are reached at an applied bias field in the vicinity of the coercive field of the film ($E_{c+}$ and $E_{c-}$) denote domain walls oscillation contribution to the dielectric constant (extrinsic contributions). Furthermore, the asymmetrical behaviour of the curves concerning the maxima pairs ($\varepsilon_{+}, E_{c+}$) and ($\varepsilon_{-}, E_{c-}$) can also be noticed. Expressing these asymmetries in terms of $\Delta\varepsilon' = \varepsilon_{+} - \varepsilon_{-}$ and $\Delta E_c = E_{c+} - |E_{c-}|$ it can be seen (Fig. 7b) that depending on doping both $\Delta\varepsilon'$ and $\Delta E_c$ first increase with increasing Er and show a maximum at 2% before they decrease to absolute values approaching 0 at 8% Er. This behaviour usually designated as imprint suggests that the presence of built-in fields associated with films of low Er concentration may be responsible for the observed asymmetries. The built-in fields may in turn arise from the existence of a “dead layer” at the interface with the electrodes. This interfacial layer has been made responsible for the thickness dependence of the dielectric properties in many ferroelectric thin films, including PZT [21] and BST [22], although the chemical nature of this layer and its structure are still the subject of controversy. Identical behaviour of C–V characteristics of PZT thin films is reported by Vorotilov et al. [23] who report that entrapped negative charges near bottom electrode – film interface can screen in a certain extent external electrical field and the switching occurs at higher DC bias when the positive bias is applied to bottom electrode. In the present PET films the decrease in $\Delta\varepsilon'$ and $\Delta E_c$ with increasing Er content may be attributed to the charge balancing by Er doping. In this respect increasing Er is to some extent equivalent to...
increasing thickness of the films (which would decrease the contribution of the disturbed layer to overall $C$–$V$-behaviour). However, charge compensation is probably not solely responsible for this behaviour. The stress states of the films which are influenced both by the relief of the tetragonal distortions due to Er doping (see above) and the stresses at the ferroelectric-Pt bottom electrode interface may also contribute to attenuation of the $C$–$V$ curves asymmetry.

3.3 Hysteresis measurements

Figure 8 shows the hysteresis loops of the films with Er content $x = 0, 0.02$, and 0.08 measured at room temperature. While the loop taken for pure PT thin film is strongly misshaped by conductivity, a noticeable improvement of hysteresis loop shape is achieved in the case of doped films. Furthermore, an increase of the remnant polarization of Er doped films over that of pure PT is obtained. Comparison of the ferroelectric properties with increasing Er content shows little change of the remnant polarization but an increase of the coercive field. Although Er decreases the tetragonal distortion $c/a$, a higher polarization is obtained (which is in contradiction to what should be expected). This might be explained by higher domain wall mobility due to donor doping effects of Er. These results agree quite well with those reported by Matsuzaki and Funakubo [7] for Nb doped PbTiO$_3$ films deposited by chemical vapour deposition where a substantial improvement of the ferroelectric properties was revealed despite the decrease in the $c/a$ ratio with increasing Nb content. Figure 8 also shows that at higher Er content, e.g. 8 mol%, the hysteresis loop becomes misshaped due to higher conductivity. Furthermore, the negative value of coercive field obtained from the $P$–$E$ hysteresis ($E_c$) of PET8 thin film was increased over that of PET2 while positive ($E_{c+}$) coercive field did not change (this means that a negative internal bias field is built-up). These results can be explained in terms of acceptor doping effects of Er at higher concentration and/or to limited solubility of Er acceptor ions (for Er contents higher than 2 mol%) giving rise to second phase particles at grain boundaries [24]. High concentration of defects near grain boundaries can inhibit domain walls motion and thus increase the value of coercive field which is consistent with the results of Fig. 8. On the other hand, decreasing the ionic radii of doping element (relative to La) can cause lower solubility of the element in perovskite lattice. For example, Tan et al. [25] report on the precipitation of second phase in PZT ceramics, doped with Dy. In our case doping with Er could also stabilize to some extent pyrochlore phase, yet in small amount (at least out of resolution of X-ray diffractometer and SEM). Such pyrochlore phase can serve effectively as domain pinning centers, increasing the value of coercive field.

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References