Erbium doped PZT and multilayer structures for pyroelectric applications

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Abstract

Thin films of erbium doped Pb(Zr0.35Ti0.65)O3 (PEZT35) and Pb(Zr0.52Ti0.48)O3 (PEZT52) as well as their multilayer heterostructures PEZT35/PEZT52 were processed on platinized Silicon substrates via solution deposition. The results of microstructure, ferroelectric, dielectric and pyroelectric properties are reported. It is shown that heterostructures can be successfully used to tune the dielectric and pyroelectric properties. The figure of merit for pyroelectric applications calculated for all films are found to be substantially lower than that of modified PZT ceramics because of the higher dielectric constants and loss tangents obtained. The voltage and current responses of the detector elements measured using a modulated laser source and a lock-in amplifier show better results for PEZT35 at low frequencies. A pyrovoltage output amplitude of up to 1 mV could be obtained on unpoled specimens, using platinum top electrodes.

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1. Introduction

Ferroelectrics based on perovskite oxides are known for their pyroelectric properties which make them the materials of choice for low cost infra-red single and array sensors. To date, the most widely used ceramics are LiTaO3 single crystals and modified PZT ceramics [1]. However, the compelling drive for miniaturization and integration of pyroelectric and ferroelectric devices into existent semiconductor technology will lead to an ever increasing demand for ferroelectric thin films. For this purpose, aspects related to materials performance as well as device processing are still to be addressed and thoroughly investigated. With respect to materials performance, the figure of merit given by

\[ F_D = \frac{p}{\epsilon' \sqrt{\tau_0 \tan \delta}} \]  

(1)

where \( p \) is the pyroelectric coefficient, \( \epsilon' \) the specific heat, \( \tau_0 \) the permittivity of vacuum, \( \epsilon' \) the dielectric constant and \( \tan \delta \) the loss tangent, must be optimized. Perovskite thin films based on PZT have been reported to be a good choice [2-4]. Furthermore, low-cost processing of PZT films using solution deposition is well established. However, the high dielectric constant inherent to PZT thin films with interesting pyroelectric properties and the relatively high loss factors related to the disturbed thin film/substrate interfacial layer are still to be overcome. One of the ways to control dielectric properties consists in using thin film heterostructures with different dielectric films in series. A multilayer (ML) structure of a bottom dielectric film with low dielectric constant will control capacity whereas a top film with high pyroelectric coefficient will control the pyroelectric response. To date, only few investigations have been dealing with such heterostructures and their functional properties [5–7]. Ling Sun et al. [5] report on a Pb(Zr0.3Ti0.7)O3/PbTiO3 ML structure where the PbTiO3 (PT) film has been efficiently used to control permittivity of the structure. However, the figure of merit and detector performance could be only slightly improved over those of the monomorph PZT film. In a recent work [6,7] we investigated multilayer structures based on Pb1-x(ZrxTi1-x)O3 (PT) and Pb(ZrxTi1-x)O3 and showed that the figure of merit, though higher than that of the monomorph films, is still substantially lower than that of modified PZT ceramics. In the course of efforts to improve materials performance, thin, erbium doped PZT films (PEZT) have been developed and characterized, and the present work reports on the properties of these PEZT films including those of a heterostructure based on compositions containing different Zr concentrations.
2. Experimental

The stock solutions for PbZr$_{0.35}$Ti$_{0.65}$O$_3$ (referred to as PEZT35) and PbZr$_{0.52}$Ti$_{0.48}$O$_3$ (PEZT52) both containing 0.05 mol Er on Pb sites were prepared from lead(II) acetate trihydrate, erbium(III) acetate hydrate, zirconium(IV) n-propoxide and titanium(IV) isopropoxide. 10 mol of 2-methoxyethanol were used as a solvent. The final solution was stabilized with 3 mol Acetylacetone. Before deposition, the solution was filtered through a 0.2 μm syringe filter. The films were spin-coated on textured (1 1 1) Pt/TiO$_2$/SiO$_2$/Si commercial substrate at 3000 rpm for 30 s, dried on the plate at 340 °C for 10 min after each coating. For the monomorph films, six layers were deposited. An intermediate annealing sequence at 700 °C for 10 min was adopted in order to avoid cracking of the films. The final annealing was conducted at 700 °C for 10 min. For the ML structure, four layers of PEZT35 were first deposited and annealed at 700 °C for 10 min before the PEZT52 layers were processed. Final annealing was conducted at 700 °C for 10 min. Microstructure was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). For electrical characterization capacitors were obtained by sputtering Pt top electrodes of 0.6 mm diameter through a shadow mask. Post top electrode annealing at 400 °C for 15 min was performed. Ferroelectric properties were measured with a commercial ferroelectric testing system (RT6000S, Radiant Technologies) using square pulses modulated with a time of 2 ms and voltage amplitude between 0.5 and 19 V. The Temperature dependence of the dielectric properties were investigated using a computer controlled Agilent 4192A impedance analyzer. Capacitance–dc bias (C–V) curves were obtained at different temperatures between −15 and +15 V using a voltage step of 0.2 V. The experiment involved voltage increase from −15 to +15 V and voltage decrease back to −15 V using the same step. Before testing a suitable ac drive amplitude was chosen by measuring the capacitance vs. ac drive amplitudes from 5 to 500 mV. The capacitance remained constant up to 100 mV and then increased steeply. For a low noise signal, an ac drive amplitude of 50 mV was used. The pyroelectric coefficient was determined from measurements of the remnant polarization as function of temperature in the temperature range from room temperature to 110 °C. For each measurement a fresh capacitor was used. Dynamic measurements of the remnant polarization as function of temperature were performed using the experimental set-up shown in Fig. 1. A near infra-red laser (λ = 680 nm) modulated by a computer controlled function generator serves as radiation source. The lock-in amplifier allows either the current or voltage induced by changes of the film temperature to be measured and displayed on computer screen. The sample may be heated to different temperatures using a heating stage. Using an optical wave guide at 10 mm from the specimen surface, the laser spot was focused on the detector element of interest. The temperature of the sample was continuously recorded.

3. Experimental results

3.1. Microstructure

All thin films show a smooth and featureless surface morphology which indicates a very fine perovskite structure, eventually nanocrystalline, Fig. 2a. The cross-sections show fully compact films with columnar microstructures, Fig. 2b. The XRD diagrams shown in Fig. 3 reveal full crystallization in the perovskite phase. The XRD diagram of the ML structure appears to be almost the superposition of those of the monomorphs (notice the splitting of the peaks) with however higher degree of (1 1 1) orientation. It seems that the constituting monomorphs preserve their individual character in the ML structure, and that long range intermixing did not occur.

3.2. Electrical properties

The ferroelectric hysteresis curves of the ML and monomorph specimens are shown in Fig. 4. For all films, high values of remnant polarization in the vicinity of 20 μC/cm$^2$ were obtained. The coercive field was found to be highest for the tetragonal composition PEZT35 ($E_c = 81.8$ kV/cm) and lowest for PEZT52 ($E_c = 52.7$ kV/cm) with the ML structure ($E_c = 60$ kV/cm) being in between. The ferroelectric properties of the ML film appear therefore to be very similar to those of the monomorph films, although different thickness values are involved.
Fig. 2. Back scattered electron (BSE) micrographs of surface topography (a) and cross-section (b) of the ML thin film.

Fig. 3. X-ray diffraction patterns of PEZT35, PEZT52 and the multilayer PEZT35/PEZT52 structure (ML). The inset shows the splitting of the 100/001 reflection of the ML film.

Fig. 4. Hysteresis loops of the investigated thin films.

Fig. 5. Capacity–dc-bias voltage curves (C–V curves) obtained at different temperatures. The loss tangent tanδ is also shown. The “butterfly” shape of the curves are characteristic for ferroelectric materials and reveal the contribution of domain wall oscillations to the dielectric constant and dielectric loss. Maxima are obtained in the vicinity of the coercive field. With increasing voltage the dielectric constant decreases due to domain growth and decrease in domain wall density. At a dc bias voltage of 2.5 V corresponding to the coercive voltage the dielectric constant amounts to 800 and takes values of approximately 400 at ±15 V. It appears that the C–V curves are quite symmetrical at all temperatures, and that the coercive field is slightly reduced as the temperature increases. Imprints (shifts in ε′ and Ec for forward and reverse bias) reported for thin films with compositional gradients [8] as expected in this ML structure were not found in the present work.

In comparison to the ML film, the monomorph films show similar behavior.

The values obtained of the ferroelectric to paraelectric transition temperatures, Tc, were determined from the temperature dependences of the dielectric constants, and are shown in Table 1. The values of Tc are 390 °C for PEZT35, 375 °C for PEZT52 and 408 °C for the ML film. Because the Tc value of the ML film is expected to lie between those

Fig. 5. C–V curves of the ML film at different temperatures showing dependences of the dielectric constant and loss tangent, tanδ, on applied dc bias voltage.
Dielectric and pyroelectric properties, including the figure of merit $F_p$ of the investigated thin films.

<table>
<thead>
<tr>
<th>Film composition</th>
<th>$T_c$ (°C)</th>
<th>$\varepsilon'$ at 1kHz</th>
<th>$\tan \delta$</th>
<th>$\rho$ (μC/m² K) at 40°C</th>
<th>$F_p = 10^{-6}$ (m²/J)²</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEZT35</td>
<td>390</td>
<td>640</td>
<td>0.02</td>
<td>359</td>
<td>13.5</td>
</tr>
<tr>
<td>PEZT52</td>
<td>375</td>
<td>1010</td>
<td>0.05</td>
<td>324</td>
<td>6.1</td>
</tr>
<tr>
<td>Multilayer</td>
<td>408</td>
<td>845</td>
<td>0.05</td>
<td>340</td>
<td>9.1</td>
</tr>
<tr>
<td>Modified PZT ceramics</td>
<td>290</td>
<td></td>
<td>0.0027</td>
<td>340</td>
<td>58</td>
</tr>
</tbody>
</table>

The values are compared to those of modified PZT ceramics taken from [1].

The increase in $\tan \delta$ observed for PEZT52 may point for a higher contribution from disturbed layers at the electrode/ferroelectric interface [11] which can be considered as a series capacitance (with a low dielectric constant and low impedance) with the bulk ferroelectric. For PEZT35 and the ML films, the $\tan \delta$ is linear in the frequency range investigated which is indicative of a lower contribution from interface polarization in the range of frequencies investigated.

3.3. Pyroelectric properties

The pyroelectric coefficient was obtained from ferroelectric measurements at different temperatures up to 110°C. For each measurement, a new capacitor was used in order to avoid effects due to fatigue and/or electrical degradation. Fig. 8a shows the variation of the remnant polarization as a function of temperature where a parabolic decrease with increasing temperature can be seen.

The generalized pyroelectric coefficient can be written as

$$ p_T = \frac{dD(T)}{dT} $$

(3)

where $\varepsilon$ is the permittivity which also depends on temperature,

$$ P_s = \frac{dP_s}{dT} $$

(4)

Substituting in (4) gives the following equation for the generalized pyroelectric coefficient:

$$ p_T = \frac{dD(T)}{dT} = \varepsilon \frac{d\varepsilon}{dT} + \frac{dE}{dT} + \frac{dP_s}{dT} $$

(5)

since

$$ \frac{dP_s}{dT} = \frac{dP_s}{dT} \frac{dE}{dT} + \frac{dE}{dT} + \frac{dP_s}{dT} $$

(6)

we can write

$$ p_T = \frac{dD(T)}{dT} = \left( \varepsilon + \frac{d\varepsilon}{dT} \right) \frac{dE}{dT} + E \frac{dE}{dT} + \frac{dP_s}{dT} $$

(7)

Assuming that the electric field is constant in the temperature range investigated (this assumption may not hold because the total field which is the sum of the applied and internal fields may not be constant with temperature), and taking $E = 0$ V/cm the pyroelectric coefficient can be written as

$$ p_T = \frac{dP_s}{dT} = \frac{dP_s}{dT} $$

(8)

where $P_s$ is the remnant polarization.
Fig. 7. Dependence of remnant polarization (a) and of the pyroelectric coefficient (b).

From the variation of $P_r$ with temperature shown in Fig. 7a, the pyroelectric coefficient can be obtained, and is shown in Fig. 7b. The pyroelectric coefficient increases with increasing temperature and reaches a maximum of $750 \mu C/(m^2 K)$ in the temperature range between 80 and 90°C. The value of $350 \mu C/(m^2 K)$ obtained at 40°C is very similar to that reported for modified PZT ceramics [1]. In comparison to PEZT52, higher values are obtained at temperatures beyond 40°C. PEZT35 shows a pyroelectric coefficient of $359 \mu C/(m^2 K)$ at 40°C which is similar to the value reported in reference [5] for thin PZT films with Ti:Zr ratio of 65:35.

In Table 1, the figure of merit $F_D$ is calculated for the different films investigated. The results are compared to those of modified PZT ceramics reported in literature [1]. The values obtained are quite low in comparison to modified ceramics because of the high dielectric constants and loss tangents involved. Among the films investigated, PEZT35 shows better figure of merit, more than twice higher than that of the morphotropic phase composition (PEZT52).

The dynamic responses of the different films are illustrated in Fig. 8, where the voltage and current outputs can be seen for unpoled specimens. It should be pointed out that the temperature fluctuations measured at the surface of the detector elements at an incident laser power density of 24 mW/mm² varied between 0.2°C at lower frequencies and 0.1°C at higher ones.

It can be seen that the voltage output of PEZT35 is about four times higher than that of the ML at a frequency of 5 Hz. PEZT52 shows the lowest voltage output (two orders of magnitude lower than for PEZT35. As the frequency increases, the responses of the ML and PEZT35 films are very similar in the frequency range from 20 to 200 Hz. We also notice a quasi-linear decrease (in log-log plot) of the voltage output with frequency for all detectors. Fig. 8b shows the current outputs, where a steady increase of the pyroelectric current can be noticed. For all films current peaks are not obtained in the frequency range investigated which indicates that peak frequencies are beyond 10 kHz. Because the pyroelectric current has a maximum [1] at an angular frequency $\omega$ of $\tau_T^{-1}$, where $\tau_T$ is the thermal time constant, a small $\tau_T$ can be deduced from the present experiments which denotes a high power conduction rate in the film. Considering the voltage output, it can be seen that the voltage starts to decrease at a frequency of approximately 5–7 Hz. This indicates that the electric time constant $\tau_E$ is approximately...
3–4 orders of magnitude higher than $\tau_T$. In bulk elements, however, $\tau_T$ is found to be higher than $\tau_E$. This indicates the preponderance of thermal conduction in the thin film detector response. The necessity of thermal isolation of the detector elements, e.g. via micro-machining, combined with measures to improve thermal absorption at the top surface (the detector elements used in the present work had just metallic Pt-top electrodes) must therefore be addressed in order to improve the responsivity of the detector still more.

4. Conclusions

Erbium doped PEZT35 and PEZT 52 as well as their multilayer heterostructures PEZT35/PEZT52 were processed on platinized silicon substrates via solution deposition. In all cases nanostructured, single phase thin films with columnar grains were obtained. The films were characterized by good ferroelectric properties with high remnant polarization values up to $22 \mu C/cm^2$. The dielectric constants and loss tangents were highest for PEZT52 (1010 and 0.05 at 1 kHz, respectively) and lowest for PEZT35 (630 and 0.02, respectively) while the multilayer film exhibited intermediate values (845 and 0.03, respectively). The pyroelectric coefficient obtained from polarization measurements as function of temperature ranged from $359 \mu C/(m^2 K)$ for PEZT35 to $324 \mu C/(m^2 K)$ for PEZT52 at 40°C. On the basis of these values and the dielectric properties, the figure of merit for pyroelectric applications calculated was highest for PEZT35 and lowest for PEZT52. The values obtained are however substantially lower than that of modified PZT ceramics reported in the literature. This is attributed to the high dielectric constants and loss tangents of the thin films. Dynamic detector performance measured using a modulated laser power source show also higher performance for PEZT35, particularly at frequencies below 20 Hz. Beyond this frequency detector performance of the multilayer structure was very similar or higher. It is thought that the detector performance can be improved by a proper choice of radiation absorbing electrode material and a better thermal isolation.

Acknowledgements

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References