Multilayer ferroelectric thin films for pyroelectric applications

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Abstract

High-quality multiplayer (ML) ferroelectric thin films based on erbium-doped lead titanate $Pb_{1-x}Er_x(2Ti_{1-x}Ta_x)O_3$ (PET) where $x$ = 0.05 and $Pb_{1/2}(Zr_{0.5}Ti_{0.5})O_3$ (PZT) have been processed via chemical solution deposition on textured (111)[PbTiO$_3$/Si] substrates. The dielectric, ferroelectric and pyroelectric properties are being characterised. It is shown that the multilayer film exhibits the relaxor type behaviour found for pure PZFNT, and that its transition temperature of 310 °C at 1 kHz lies between those of PET and PZFNT. The dielectric constant of 520 also lies between those of PET and PZFNT. The ferroelectric properties are considerably improved over those of the monomorph films. An unusually high pyroelectric coefficient of approximately 620 $\mu$C m$^{-2}$ K$^{-1}$ was obtained from measurements of the temperature dependence of the remnant polarisation between 30 and 80 °C. The voltage and current responses measured using a modulated near IR-laser, could be improved by 2–3 orders of magnitude over those of PZFNT. The thermal time constant $\tau_T$ obtained is 3 orders of magnitude lower than the electrical time constant $\tau_E$ and indicates that the high thermal conduction rate in the substrate determines the detector responsivity.

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1. Introduction

Ferroelectrics based on perovskitic oxides are known for their pyroelectric properties which make them the materials of choice for low cost infra-red (IR) single and array sensors. To date, the most widely used ceramics are LiTaO$_3$, (Sr,Ba)Nb$_2$O$_6$ single crystals and modified PZT ceramics [1]. However, the compelling drive for miniaturisation and integration of pyroelectric and ferroelectric devices into existing semiconductor technology will lead to an ever increasing demand for ferroelectric thin films. For example, possibility to fabricate IR image sensor based on pulsed laser deposited BST (barium strontium titanate) thin films was demonstrated by Hashimoto et al. [2]. Fabrication and properties of PZT thin film-based pyroelectric detectors are reported by Ko et al. [3]. For the purpose of development of integrated IR detectors and imaging systems, 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 $F_D$ given by [1]:

$$F_D = \frac{p}{\epsilon c \tan \delta}$$

where $p$ is the pyroelectric coefficient, $\epsilon$ the specific heat, $c_0$ the permittivity of vacuum, $c$ the dielectric constant and $\tan \delta$ the loss tangent, must be optimised. Perovskite thin films based on PZT have been reported to be a good choice [4,5]. 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 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. However, only few investigations have dealt with such heterostructures and their functional properties [6,7]. In a recent work [8], we investigated a multilayer structure based on $Pb_{1/2}(Zr_{0.5}Ti_{0.5})O_3$ (PZT) and showed that the figure of merit, though higher than that of the monomorph films, is still 1 order of magnitude lower than that of modified PZFNT. In the course of efforts to improve the materials performance, thin film heterostructures based on Er-doped lead titanate (PET) and PZFNT have been developed to control the figure of merit for...
pyroelectric applications. The present work deals with processing and characterisation of such heterostructures, including microstructure, electric and pyroelectric properties.

2. Experimental

The precursor solution for PZFNT with the stoichiometry \( \text{Pb}_1\text{Zn}_{0.58}\text{Fe}_{0.2}\text{Nb}_{0.22}\text{Ti}_{0.02}\text{O}_3 \) has been prepared according to the procedure reported in our previous work [9]. For erbium-doped \( \text{PbTiO}_3 \) (PET) the precursor solution was prepared according to the stoichiometry \( \text{Pb}_x\text{Er}_{1-x}\text{Ti}_{1-x/4}\text{O}_3 \) where \( x = 0.05 \). Firstly, lead and erbium acetates were dissolved in 3 mol of acetic acid and refluxed for 3 h at 110\(^\circ\)C to evaporate associated water. Tetraisopropil orthotitanate was stabilised with acetylacetone in a ratio of 1:2 mol. Both parts were then mixed together at room temperature and diluted with 2-methoxyethanol to reach the final concentration of 0.5 mol l\(^{-1}\). The final solutions were filtered through 0.2 \( \mu \)m syringe filter just prior to deposition. The thin films were fabricated by spin-coating on (1 1 1)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. Four layers of PET were first deposited and crystallised for 5 min at 700 \( ^\circ\)C. Subsequently, two layers of PZFNT were deposited and the whole structure was annealed for 20 min at 750 \( ^\circ\)C. The crystalline structure was investigated via X-ray diffraction (Seifert 3000 PTS powder diffractometer, Cu K\(\alpha\) radiation, \( \lambda = 1.5418 \) Å, \( \theta - 2\theta \) scan), and microstructure was observed in the SEM (Philips XL 30). Electrical measurements were conducted on capacitors obtained by sputtering Pt top electrodes with an area of \( 2.8 \times 10^{-3} \) cm\(^2\) through a shadow mask. A post top electrode deposition annealing at 400 \( ^\circ\)C for 15 min was performed in air before measurements. The small signal dielectric properties were characterised using a computer controlled Agilent 4192A impedance analyser at 50 mV drive signal. The leakage current properties (J–V-curves) were investigated at different temperatures using a Keithley 6517A electrometer. Ferroelectric properties were investigated using a commercial system RT6000S (Radiant Technology Inc., USA).

The pyroelectric coefficient was determined from measurements of the remnant polarisation as function of temperature in the temperature range from 22 to 100 \( ^\circ\)C. Dynamic measurements of current and voltage responsivity were performed using the experimental set-up shown in Fig. 1. A laser (\( \lambda = 680 \) nm) modulated by a computer controlled function generator serves as radiation source. Using an optical wave guide at 10 mm from the specimen surface, the laser spot was focused on the capacitor of interest. 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.

3. Results and discussion

3.1. Microstructure

The microstructure of the monomorph PZFNT film was reported elsewhere [9], and shows relatively coarse single-phase perovskite grains with a mean grain size of approximately 200-300 nm, and a (1 1 1) preferential orientation. The monomorph PET film shows randomly oriented fine grains of approximately 100 nm size [10]. The XRD patterns of the PZFNT, PZFNT/PET and PET films are shown in Fig. 2. PZFNT/PET heterostructure consists in fact of the superposition of the patterns of the monomorph films. No second phase pyrochlore was observed which indicates full crystallisation of the film in the perovskite phase. The preferential (1 1 1) texture of the
film can also be noticed which is in agreement with the microstructure of the monomorph films.

The surface morphology of the ML thin film illustrated in Fig. 3a consists in equiaxed, single-phase perovskite fine grains with a mean grain size in the range of 150 nm. No second phase particles were observed. SEM cross-section observations show homogeneous microstructures with no evidence of strata or sharp interface between PET and PZFNT, Fig. 3b. It seems that diffusion processes were taking place during the high-temperature processing of the ML film. Although EDS microanalysis is not well suited for the chemical analysis of thin films because of the high interaction volume involved, the results obtained (not shown) suggest a composition gradient of Ti and Fe perpendicular to the film surface. It appears therefore that the chemistry of the ML film is complex and that probably long range diffusion of ionic species takes place resulting in complex defect chemistry.

3.2. Dielectric properties

The dielectric properties of PZFNT have been reported elsewhere [9], and are summarised in Table 1. PZFNT shows a relaxor type behaviour with a Curie transition temperature of 245 °C at 0.5 kHz and 260 °C at 1 kHz. The small signal dielectric constant (ε') and loss tangent (tan δ) measured at 1 kHz are high and amount to 1400 and 0.04, respectively.

The temperature dependences of the small signal dielectric constant of PET5 thin film and the multilayer structure are shown in Fig. 4. PET5 thin film has demonstrated rather sharp ferroelectric-to-paraelectric phase transition (Fig. 4a). The ML film exhibits a frequency-dependent transition temperature, however at higher temperatures in comparison to PZFNT (Fig. 4b and Table 1), so that the relaxor type behaviour found for PZFNT [9] is still present. At room temperature, the values of tan δ and particularly ε' are reduced (Table 1). Therefore, it is possible to tune the dielectric properties through a proper choice of the film heterostructures. Assuming two capacitors in series with dielectric constants ε'_1 and ε'_2 and thickness d_1 and d_2, the dielectric constant ε'_ML of the multilayer structure with a total thickness d of 600 nm can be calculated through:

$$\varepsilon'_ML = \frac{d_1 \varepsilon'_1 + d_2 \varepsilon'_2}{d_1 + d_2}$$

Assuming d_1 = d_2 = 300 nm, taking values of ε'_1 and ε'_2 of 1400 and 312, respectively, for PZFNT and PET [10] and ignoring interdiffusion phenomena (this assumption is not valid, since EDS analysis suggests diffusion of Fe and Ti ions) the value of ε' calculated is 510 which agrees well with the measured one.

3.3. Ferroelectric properties

The ferroelectric hysteresis loop of the ML film is compared to those of the monomorph films in Fig. 5a. It can be seen that the ML film is characterised by well developed,
Table 1

Summary of dielectric and pyroelectric properties of the investigated films

<table>
<thead>
<tr>
<th>Sample designation</th>
<th>At 1 kHz</th>
<th>ε′</th>
<th>tan δ</th>
<th>Tc (°C)</th>
<th>F0 (×10−6 (mJ⋅F−1)1/2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>312</td>
<td>0.03</td>
<td>416</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PZFNT</td>
<td>1400</td>
<td>0.04</td>
<td>260</td>
<td>120</td>
<td>2.2</td>
</tr>
<tr>
<td>PET/PZFNT</td>
<td>520</td>
<td>0.029</td>
<td>310</td>
<td>620</td>
<td>21.5</td>
</tr>
</tbody>
</table>

3.4. Leakage current properties

The leakage current density, J, as a function of voltage, V, is plotted in Fig. 6 at various temperatures for the ML structure. It can be seen that for negative voltages, the leakage current is very low and lies below 10−11 A, whereas at positive voltages the leakage current density increases exponentially at some threshold voltages which appear to be temperature dependent. This behaviour is very much similar to that of a Schottky diode [13], and implies that the conduction properties in the ML film are strongly influenced by charged defects and internal fields [13].

3.5. Pyroelectric properties

The generalised pyroelectric coefficient can be written as [1]:

\[
\varepsilon' \tan \delta = T \frac{(E^+ + E^-)}{2} = 6.65 \text{ kV cm}^{-1}
\]

Fig. 5b shows the quasi-static ε′ curve obtained using impedance analysis. The butterfly shape is characteristic for ferroelectric materials, and denotes extrinsic contributions to the dielectric constant through domain wall oscillation around some equilibrium position. In the vicinity of the coercive field domain wall density is highest, and leads to highest values of the dielectric constant. As domains grow as a result of the increasing dc bias voltage, the dielectric constant decreases and approaches values of monodomain material, where extrinsic contributions are lowest. The asymmetry along the polarisation axis and built-in internal field \((E^+ + E^-)/2 = 6.65 \text{ kV cm}^{-1}\) towards positive values (negative internal field) can also be seen. These asymmetries have been attributed to different factors including formation of the defect layer (mainly near the bottom electrode). Such layer may contain entrapped charge and at the same time cause partial screening of the field [11]. The value of the built-in field is however rather small (compared, for example, the value of 67.5 kV cm−1 for sol-gel deposited lead titanate thin film, doped with 1 mol% of Er [12]).
where \( D \) is the dielectric displacement which in the case of ferroelectric material is given by:

\[
P_g = \varepsilon E + P_s
\]

where \( \varepsilon \) is the permittivity which also depends on temperature, \( E \) the electric field and \( P_s \) the spontaneous polarisation (also temperature dependent). Substituting in (3) gives the following equation for the generalised pyroelectric coefficient:

\[
p_g = \frac{dD(T)}{dT} = \varepsilon \frac{dE}{dT} + \frac{dP_s}{dT}
\]

since

\[
\frac{dP_s}{dT} = \frac{dP_s}{dE} \frac{dE}{dT}
\]

we can write

\[
p_g = \frac{dD(T)}{dT} = (\varepsilon + \frac{dP_s}{dE}) \frac{dE}{dT} + E \frac{dE}{dT} + \frac{dP_s}{dE}
\]

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\(^{-1} \) the pyroelectric coefficient can be written as:

\[
p_g = \frac{dP_s}{dT} = \frac{dP_s}{dT}
\]

where \( P_s \) is the remnant polarisation. From the variation of \( P_s \) with temperature, the pyroelectric coefficient can be obtained by differentiating the polynomial fit to the \( P_s = f(T) \) curve. The dependence of the remnant polarisation and the pyroelectric coefficient of the unpoled ML film on temperature is plotted in Fig. 7. The measurements have been conducted up to 105°C. Higher temperatures resulted in misshapen hysteresis loops. In comparison to PZFNT, an unusually high pyroelectric coefficient was found for the ML film. In the temperature range from 30 to 80°C, a mean value of \( p \) of 620 \( \mu \)C m\(^{-2} \) K\(^{-1} \) was obtained, and a drastic increase at higher temperatures can be noticed. Such high values have been reported for compositionally graded thin films [14], and may arise from the existence of the internal field mentioned above. In fact, it has been reported that the pyroelectric coefficient is dependent on the applied voltage and may increase to high values for electrical fields anti-parallel to the direction of spontaneous polarisation [15]. The figure of merit \( F_0 \) computed in Table 1 using Eq. (1) and a \( c' \) value of 2.5 MJ m\(^{-3} \) K\(^{-1} \) known for PZT ceramics [1] shows for the ML film a value by a factor of 10 higher than that of PZFNT. However, this value is still lower than that of modified PZT ceramics reported in Ref. [1]. A way to improve \( F_0 \) lies in reducing the dielectric constant and the loss tangent still more.

The dynamic response of the detector is illustrated in Fig. 8, where the voltage and current outputs can be seen for unpoled specimens and different incident laser power densities (measured using an appropriate detector). It should be pointed out that the temperature fluctuations measured at the surface of the detector element at an incident laser power density of 24 mW cm\(^{-2} \) varied between 0.2°C at lower frequencies and 0.1°C at higher ones.

Taking into account that the voltage difference \( \Delta V \) between the upper and lower surfaces of the detector is given by [16]:

\[
\Delta V = \frac{p}{\varepsilon' k} \Delta T
\]

where \( \Delta T \) is the detector thickness and \( \Delta T \) the temperature difference, the pyroelectric coefficient can be calculated, and lies in the range of values obtained from polarisation-temperature measurements. It can be seen that at equivalent incident power densities, e.g. 24 mW mm\(^{-2} \), the voltage output of the ML film is approximately 2–3 orders of magnitude higher than that of PZFNT, depending on frequency, Fig. 8a. 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 PZFNT, a peak is obtained at 7 kHz, whereas the ML film shows a peak frequency higher than 10 kHz.
Because the pyroelectric current has a maximum [1] at an angular frequency \( \omega \approx 1/\tau_T \), 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 10 Hz. This indicates that the electric time constant \( \tau_E \) is approximately 3 orders of magnitude higher than \( \tau_T \). In bulk elements, however, \( \tau_T \) is 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 micromachining, 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

In conclusion, the present work shows that it is possible to tune the dielectric properties of ferroelectric thin films through a proper choice of heterostructures. The figure of merit for pyroelectric applications can be considerably improved via the use of multilayer thin films. A poling of the film is not necessary due to self polarisation, and high output voltages and currents can be achieved despite the transparency of the films and the use of thick platinized Si substrates. In this respect, the response of the film is expected to be improved via the use of micromachined detector elements.

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