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Processing and characterization of PZFNT and PZFNT/PET thin films for pyroelectric applications

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Abstract

High quality ferroelectric thin films with the stoichiometry $Pb(Zr_{0.58}Fe_{0.2}Nb_{0.2}Ti_{0.02})O_3$ + 10% PbO excess (PZFNT) have been processed via chemical solution deposition (CSD) on textured (111)Pt/Ti/SiO_2/Si substrates. The dielectric and pyroelectric properties are characterized. It is shown that the pyroelectric properties of PZFNT, including voltage response using a modulated IR-laser are quite low due to a low figure of merit. These properties are substantially improved using bimorph films of Er-doped $PbTiO_3$ and PZFNT.

Keywords: Bimorph films; Dielectric properties; Ferroelectric properties; Perovskites; Sensors

1. Introduction

Ferroelectric thin films are being considered for many applications including micro-electromechanical systems (MEMS), different types of storage information devices, infrared sensors etc.[1–3] Particularly $PbTiO_3$–$PbZrO_3$ based family of ferroelectric materials exhibit unique ferroelectric, piezoelectric and pyroelectric properties that make them attractive for such applications.

In the present work we report on the properties of solution deposited PZT thin films modified with Fe^{3+} and Nb^{5+} (PZFNT). PZFNT in a bulk form is known as a pyroelectric material with a good figure of merit and used for infrared sensor applications.[4] In view of the increasing tendency for integration and miniaturization of ferroelectric devices,[5] it appears necessary to investigate thin films with respect to their processing and properties. The aim of the present work is to show that the CSD method can be successfully applied for the processing of high quality thin PZFNT films with controlled microstructure and properties. Furthermore, it is shown that the dielectric and pyroelectric properties can be tuned by using heterostructures based on Er doped lead titanate (PET)and PZFNT to control the figure of merit for pyroelectric applications.

2. Experimental

The precursor solution for PZFNT with the stoichiometry $Pb(Zr_{0.58}Fe_{0.2}Nb_{0.2}Ti_{0.02})O_3$ + 10% PbO excess has been prepared according to the procedure reported in our previous work.[6] For erbium doped $PbTiO_3$ (PET) the precursor solutions was prepared according to the stoichiometry $Pb_{1-x}Er_xTi_{1-x/4}O_3$ + 10% PbO excess where $x = 0.05$. Firstly lead and erbium acetates were dissolved in 3 mol of acetic acid and refluxed for 3 h at 110 °C to evaporate associated water. Tetraisopropil orthotitanate was stabilized 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. The final solutions were filtered through 0.2 μm syringe filter just prior to deposition.

The 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 °C for 5 min. For PZFNT three layers were deposited and crystallized at 750 °C for 20 min. Before annealing an extra layer of PbO was deposited

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on top to compensate for PbO evaporation. To prepare PbO precursor, lead acetate was dissolved in 2-methoxyethanol. Concentration of PbO precursor was 0.2 mol/l. For the bimorph structure, four layers of PET were first deposited and crystallized 5 min at 700 °C. Subsequently, two layers of PZFNT were deposited and the whole structure was annealed 20 min at 750 °C.

The crystalline structure was investigated by X-Ray diffraction (Seifert 3000 PTS powder diffractometer, CuK_α radiation, $\lambda = 5418$ Å). Microstructure was observed in the SEM (Philips XL 30). Electrical measurements were conducted on capacitors obtained by sputtering of Pt top electrodes with an area of 2.8×10^{-3} cm^2 through a shadow mask. A post top electrode deposition annealing at 400 °C for 15 min was performed before measurements. The small signal dielectric properties were characterized using a computer controlled Agilent 4192A impedance analyser at 50 mV drive signal. Ferroelectric properties were investigated using a commercial system RT6000S (Radiant Technology Inc., USA).

The pyroelectric coefficient was determined from measurements of the remnant polarization as function of temperature in the temperature range from 22 to 60 °C. Dynamic measurements of current and voltage response 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.

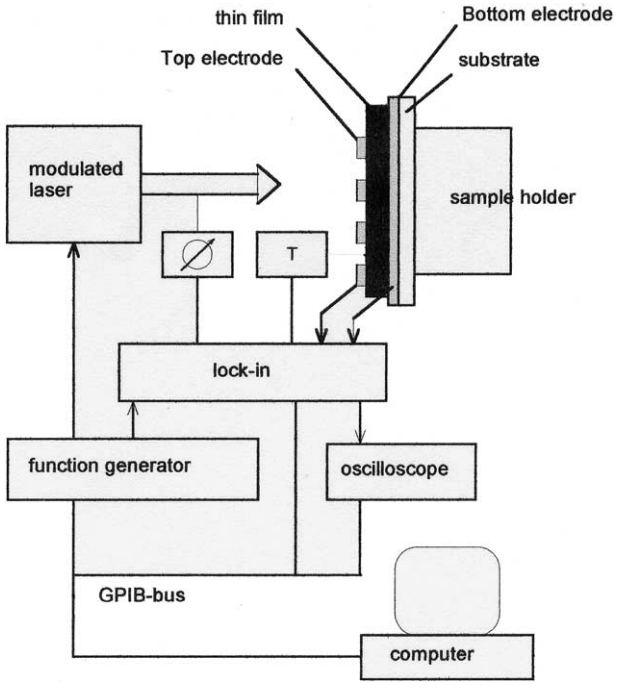

Fig. 1. Schematic drawing of the experimental set-up for dynamic pyroelectric measurements.

3. Results and discussion

The microstructure of the PZFNT thin films is shown in Fig. 2a. It consists of single phased perovskite fine grains. XRD analysis shows a (111) preferred orientation.[6] For PET, the microstructure consists of randomly oriented nano-crystalline perovskite grains with a c/a ratio of 1.0409, substantially lower than that of pure PT (1.0438). In Fig. 2b, the microstructure of the bimorph film is illustrated. A very fine microstructure is obtained, and no second phase particles were observed. SEM

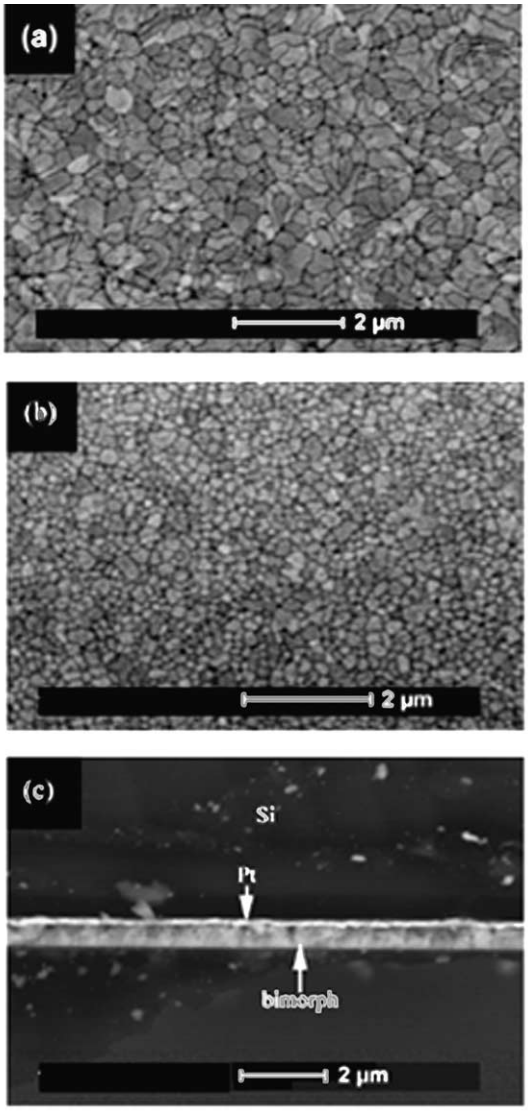

Fig. 2. Back scattered electron (BSE) micrographs of (a) surface topography of PZFNT and (b) PZFNT/PET films; (c) shows a cross section micrograph of PZFNT/PET.

cross section observations show homogeneous microstructures with no evidence of strata or sharp interface between PET and PZFNT (Fig. 2c). It seems that diffusion processes were taking place during the processing of the bimorph film, and EDS microanalysis shows in fact that interdiffusion of Fe and Ti ions has occurred, with, however, a composition gradient perpendicular to the interface.

The dielectric properties of PZFNT have been reported elsewhere, and are summarized in Table 1. PZFNT shows a relaxor type behaviour with a ferroelectric-paraelectric transition temperature of 245 °C at 0.5 kHz and 260 °C at 1 kHz. The small signal dielectric constant (ε′) and loss tangent (tanδ) measured at 1 kHz are high and amount to 1400 and 0.04 respectively. Regarding the pyroelectric coefficient, a value of 120 $\mu C.m^{-2}.K^{-1}$ was obtained in the temperature range from room temperature to 60 °C. These properties lead to a low figure of merit (F_D) which can be expressed as follows:[7]

$$F_D = \frac{p}{c'\sqrt{\varepsilon_0 \varepsilon' \tan\delta}} \quad (1)$$

where ε_0 is the permittivity of vacuum, P the pyroelectric coefficient and c' the specific heat. Taking for c' the value of 2.5 $MJ.m^{-3}.K^{-1}$ known for PZT ceramics,[7] The value of F_D obtained is substantially lower than that reported for modified bulk PZT ceramics.[7]

The temperature dependence of the dielectric constant of the bimorph structure shown in Fig. 3 still exhibit a frequency dependent transition temperature, however at higher temperatures in comparison to PZFNT. The relaxor type behaviour found for PZFNT is still present.

The values of tanδ 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′ of the bimorph structure with a total thickness d of 600 nm can be calculated through:

$$\frac{d}{\varepsilon'} = \frac{d_1}{\varepsilon'_1} + \frac{d_2}{\varepsilon'_2} \quad (2)$$

Assuming $d_1 = d_2 = 300$ nm, taking values of ε'_1 and ε'_2 of 1400 and 312 respectively for PZFNT and PET[8] and ignoring interdiffusion phenomena (although some diffusion takes place according to EDS analysis) the value of ε′ calculated is 510 which agrees well with the measured one.

The ferroelectric hysteresis properties of the monomorph and bimorph films are compared in Fig. 4. It can be seen that the bimorph film is characterized by better ferroelectric properties with a well shaped hysteresis loop, higher remnant polarization and a coercive filed higher than that of PZFNT but lower than that of PET. It can also be seen that a small internal field towards negative values is present ($E_c^+ + E_c^- = -11$kV/cm) which can be attributed to chemical gradients observed perpendicular to the substrate surface.

The pyroelectric coefficient obtained from polarization measurements as function of temperature in the temperature range from 22 to 60 °C was found to be

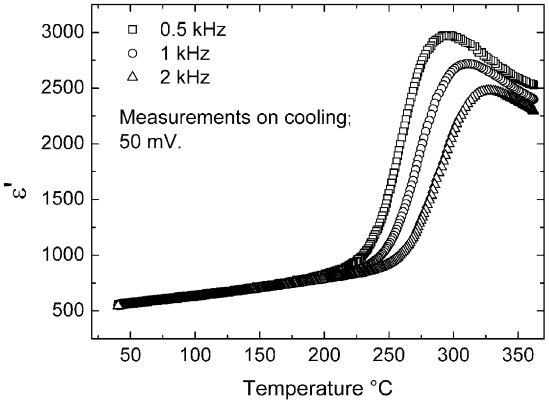

Fig. 3. Temperature dependence of the dielectric constant, ε′, at different frequencies.

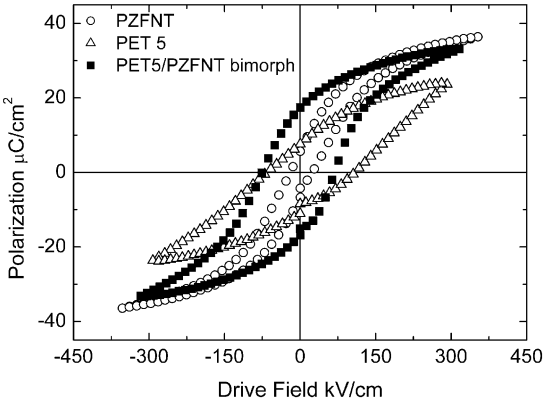

Fig. 4. Hysteresis loops of PZFNT, PET and PZFNT/PET films.

Table 1
Summary of the properties of the investigated films

Film composition	ε′ at 1kHz	tanδ	T_C°C at 1 kHz	$p(\mu C.m^{-2}.K^{-1})$	$F_D \times 10^{-6}$ $(m^3J^{-1})^{1/2}$
PZFNT	1400	0.04	260	120	2.2
PET/PZFNT	520	0.029	310	680	23.5

unusually high with a value of 680 $\mu C.m^{-2}.K^{-1}$. Such high values have been reported for compositionally graded thin films,[9] 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 antiparallel to the direction of spontaneous polarization.[10]

The dynamic response of the detector is illustrated in Fig. 5, 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 42 mW/mm^2 were from 0.2 °C at lower frequencies to 0.1 °C at higher ones. It can be seen that at equivalent incident power densities, e.g. 42 mW/mm^2, the voltage output of the bimorph film is approximately two to three orders of magnitude higher than that of PZFNT, depending on frequency. We also notice a quasi-linear decrease (in log–log plot) of the voltage output with frequency for all detectors. Fig. 5b shows the current outputs where in the frequency range from 5 to 1000 Hz practically no frequency dispersion of the current of the bimorph film can be seen, whereas a steady increase of the pyroelectric current of the PZFNT film can be noticed.

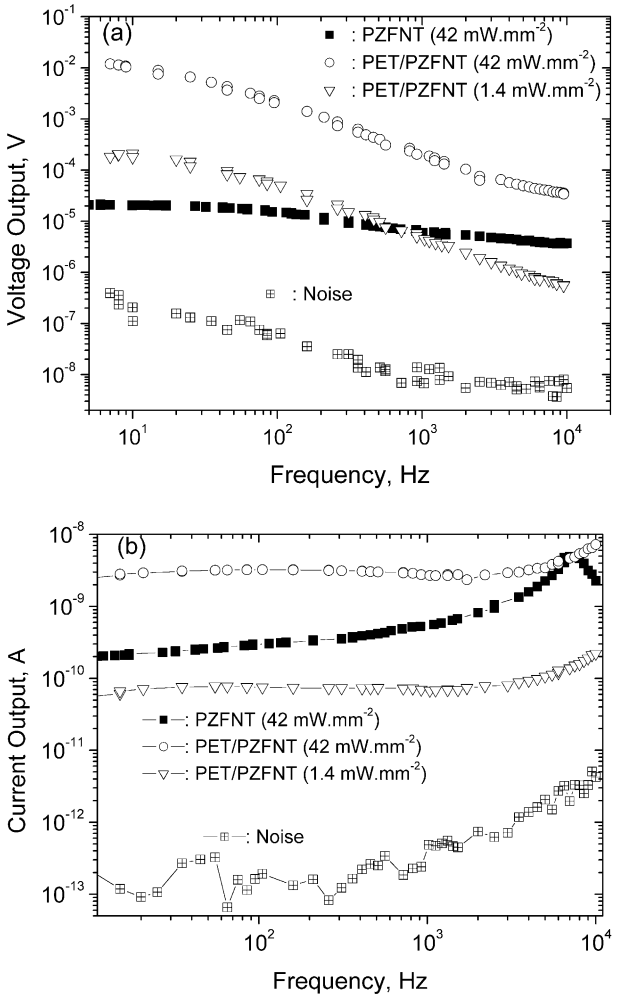

Fig. 5. Dynamic pyroelectric response of PZFNT and PZFNT/PET films. (a) Voltage response and (b) current response for different incident laser power densities.

4. Conclusions

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 bimorph thin films. A poling of the film is not necessary due to self polarization, and high output voltages and currents can be achieved despite the transparency of the films and the use of thick Si substrates. In this respect, the response of the film is expected to be improved via the use of micro-machined detector elements.

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