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Pulsed laser deposition of barium metaplumbate thin films for ferroelectric capacitors

A.I. Mardare[1,a], C.C. Mardare[1], J.R.A. Fernandes[1,2], P.M. Vilarinho[3], and E. Joanni[1,2]

[1] INESC-Porto, Unidade de Optoelectrónica e Sistemas Electrónicos, 4169-007 Porto, Portugal
[2] Universidade de Trás-os-Montes e Alto Douro, Departamento de Física, 5001-911 Vila Real, Portugal
[3] Universidade de Aveiro, Departamento de Engenharia Cerâmica e do Vidro, 3810-193, Aveiro, Portugal

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Abstract. Barium metaplumbate thin films were deposited *in situ* by pulsed laser deposition on $Si/SiO_2/Ti/Pt$ substrates with a high deposition rate. The temperatures used ranged between 400 °C and 700 °C. As the deposition temperature was increased, the films assumed a strong (222) preferential orientation. This orientation of the electrodes was reflected on the PZT films, having a very big influence on their ferroelectric behavior. The PZT films made over BPO deposited at high temperature presented high values of remanent polarization (43 $\mu C/cm^2$) but indications of high leakage currents could be observed in the hysteresis loops. By using BPO bottom electrodes, a 30% improvement in the fatigue behavior of PZT capacitors when compared with the normal platinum electrodes was observed.

PACS. 68.55.Jk Structure and morphology; thickness; crystalline orientation and texture – 77.80.Dj Domain structure; hysteresis – 81.15.Fg Laser deposition

1 Introduction

Barium metaplumbate $BaPbO_3$ (abbreviated as BPO) is a useful material for many applications. The most important ones are ceramic electrodes, sintered resistors, conductive pastes, anticorrosion pigments, etc. Around 1970s Shannon and Bierstedt [1] found that BPO ceramics have an orthorhombic perovskite structure. BPO exhibits metallic conduction behavior, with a very low resistivity and positive temperature coefficient. Ikushima and Hayakawa [2] explained these phenomena as being due to oxygen vacancies while Shannon and Bierstedt considered the filled d bands of Pb^{4+} were the real reason.

Electrical and stability characteristics of BPO were studied in bulk ceramics by Yu-Hung Hsieh and Shen-Li Fu [3]. The study of BPO thin films is important because of the possible applications in ferroelectric devices. In this area, lead zirconate titanate (PZT) thin films are intensively studied as promising candidates for use in capacitors for ferroelectric random access memories due to their nonvolatility and fast switching speed; however, the gradual decrease of the switching polarization of ferroelectric capacitors with the number of switching cycles, when Pt electrodes are used, still limits their application [4]. This fatigue phenomenon is assumed to be due to electromigration of charged defects and/or domain wall pinning [5].

Many efforts have been focused on retaining long term reliability of ferroelectric capacitors by finding optimal oxide electrode materials or modifying the standard ferroelectric composition by adding dopants. Hybrid electrodes for ferroelectric capacitors using RuO_2, $La_{1-x}Sr_xCoO_3$, $LaNiO_3$ and other oxides associated with platinum have been proposed [6–8]. While Pt/PZT/Pt capacitors have low leakage and relatively good dielectric breakdown properties, they suffer from severe polarization fatigue problems upon repeated switching. On the other hand, oxide/PZT/oxide heterostructures have excellent resistance to polarization fatigue, but they usually have large leakage currents and are more susceptible to dielectric breakdown. RuO_2 electrodes, for example, exhibit large and variable leakage currents (10^{-4}–10^{-3} A/cm^2 at 1 V) [9]. Despite the good fatigue performance of PZT capacitors using $La_{1-x}Sr_xCoO_3$ top and bottom electrodes, their remanent polarization is lower than that of Pt/PZT/Pt capacitors and they require high temperatures for heat treatment [10]. A few results have been reported on PZT films deposited over BPO made by magnetron sputtering [11], but the pyrochlore phase was always present in the PZT films, even after heat treatments made at 700 °C. Pure perovskite PZT films deposited over BPO can be achieved by laser ablation as recently reported [12].

In the present work BPO films were deposited on $Si/SiO_2/Ti/Pt$ substrates by pulsed laser deposition technique for being used as bottom electrodes in PZT capacitors for ferroelectric random access memories. The

[a] e-mail: andrei@hobbit.fc.up.pt

perovskite nature of the BPO electrodes has the potential to improve the fatigue of the capacitors and can be used to influence the orientation of the PZT due to the close matching of the lattice parameters. Lead and barium ions diffusing in the PZT layer during heat treatment are not expected to significantly degrade the ferroelectric properties.

2 Experimental details

For obtaining SiO_2 on Si, the Si substrates were heated at 950 °C for 72 h in wet O_2 flow. Ti and Pt films were deposited using the RF sputtering technique in Ar; the sputtering chamber had a base pressure of 10^{-6} mbar. Ti films 20 nm thick were deposited at room temperature using an RF power of 150 W and a deposition pressure of 10^{-2} mbar. The Pt films 200 nm thick were sputtered at 500 °C with the same RF power and the same deposition pressure.

The targets for laser ablation, BPO and PZT (Zr/Ti ratio = 52/48), were 1.5 cm diameter dense ceramic disks. The ceramic powders were prepared by the conventional mixed oxide method. For the BPO targets, stoichiometric proportions of barium carbonate and lead oxide were mixed and calcined at 700 °C for 2 hour, to obtain the pure BPO phase. For the PZT (52/48) targets, stoichiometric proportions of lead carbonate, zirconium and titanium oxide were mixed and calcined at 900 °C for 1 hour, to form the pure PZT phase. Fine BPO and PZT powders (<5 μm) were obtained after milling for several hours in a planetary mill. Circular pellets were prepared by uniaxially pressing at 200 MPa. In order to obtain dense BPO and PZT ceramics, the BPO samples were sintered in air between 800 °C and 1000 °C for 2 hours in the presence of BPO packing powder; the PZT samples were sintered at 1250 °C for 2 hours, with a O_2 flux and in the presence of lead zirconate packing powder.

BPO films with different deposition conditions were made. The base pressure of the PLD chamber was 10^{-9} mbar. Before depositing each film the chamber was evacuated until at least 10^{-7} mbar. The films were deposited in an O_2 atmosphere with a pressure of 1×10^{-1} mbar. The BPO was heated *in situ* at temperatures ranging from 400 °C to 700 °C. For the deposition, a KrF laser with energy of 100 mJ for a 10 Hz repetition rate and a fluence of 1.4 J/cm^2 was used. The distance between target and substrate was 4 cm and the deposition time was 15 minutes. Under these conditions the thickness of the films was 600 nm.

Without breaking the vacuum in the PLD chamber, the BPO target was replaced with a PZT target and 600 nm films of PZT were deposited on top of BPO with a deposition pressure of 2×10^{-2} mbar in O_2. All the PZT depositions were carried out at room temperature. The energy of the laser was 300 mJ for a 10 Hz repetition rate and the deposition time was 30 minutes with a target-substrate distance of 4 cm. The crystallization of PZT was achieved with a heat treatment at 675 °C for 15 minutes in O_2 flow. Aluminum top electrodes were deposited by thermal evaporation using a shadow mask at a pressure of 10^{-6} mbar.

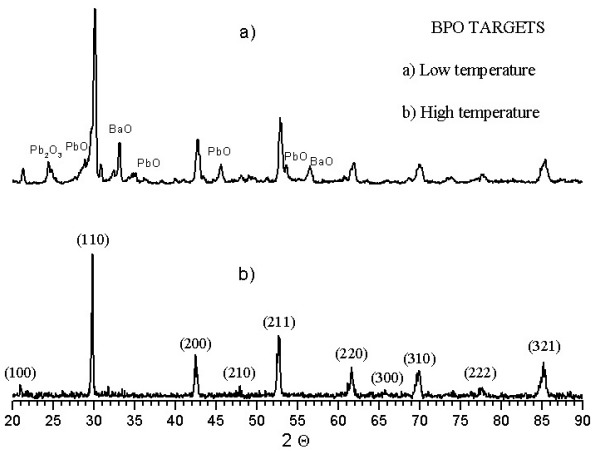


Fig. 1. X-ray diffraction pattern of the BPO targets sintered below (a) and at (b) 1000 °C.

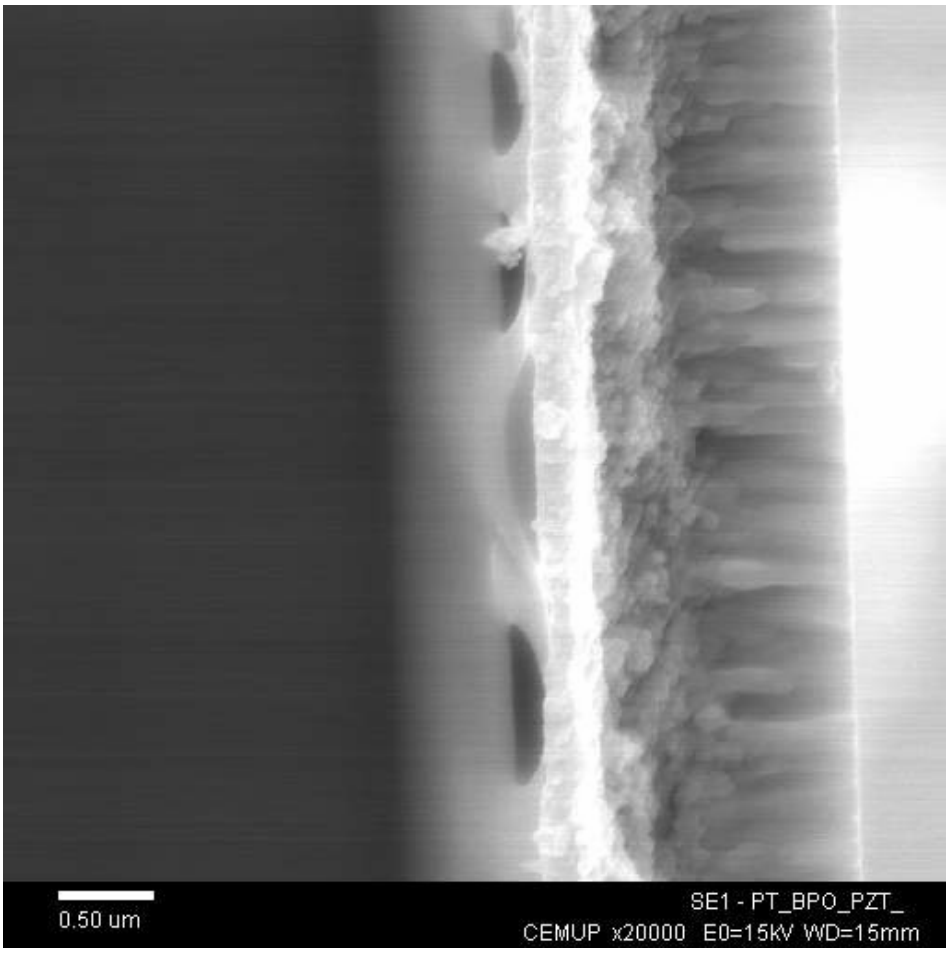
The thickness of the films was measured with a contact profilometer (Dektak II A) and they were structurally analyzed using optical and scanning electron microscopy (JEOL JSM-6301F) and X-ray diffraction (Siemens D5000). A system composed of an amplifier, a function generator (HP 8116A), an oscilloscope (LeCroy 9310M) and a computer running a LabView program was used for recording the hysteresis loops and the fatigue behavior of the capacitors.

3 Results and discussion

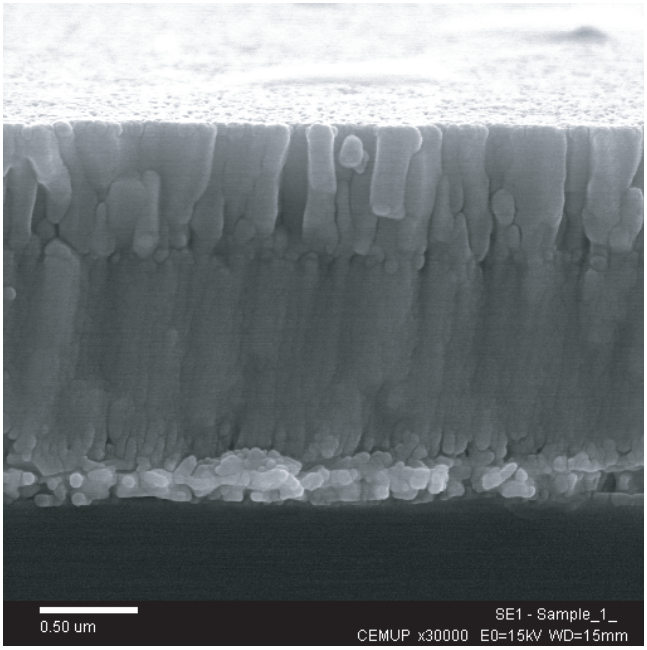
For the deposition of BPO films with stable properties it is important to use fully reacted targets sintered at high temperature. Figure 1 shows X-ray diffraction patterns for BPO targets sintered at 800 °C and 1000 °C. One can see from the diffractograms that the target sintered at low temperature has residual barium and lead oxide peaks. Films made from this target were highly hygroscopic and in less than one minute the presence of a reacted layer could be observed on the surface.

The X-ray diffractogram of the BPO target sintered at 1000 °C shows only the peaks from BPO and the films made from this target were immune to the atmospheric moisture. BPO films made from this target are black, smooth, uniform and no reactions could be detected, even after long term air exposure.

Figure 2 shows the cross sections of PZT films deposited over BPO made at different temperatures. The scanning electron micrograph in Figure 2a shows that the BPO film deposited at 450 °C consists of small grains. On the other hand in Figure 2b one can see that when deposited at a higher temperature the BPO layer (600 °C) consists of small grains near the platinum, assuming a



(a)



(b)

Fig. 2. Cross section of BPO films deposited at (a) 450 °C, (b) 600 °C with the PZT layer on top.

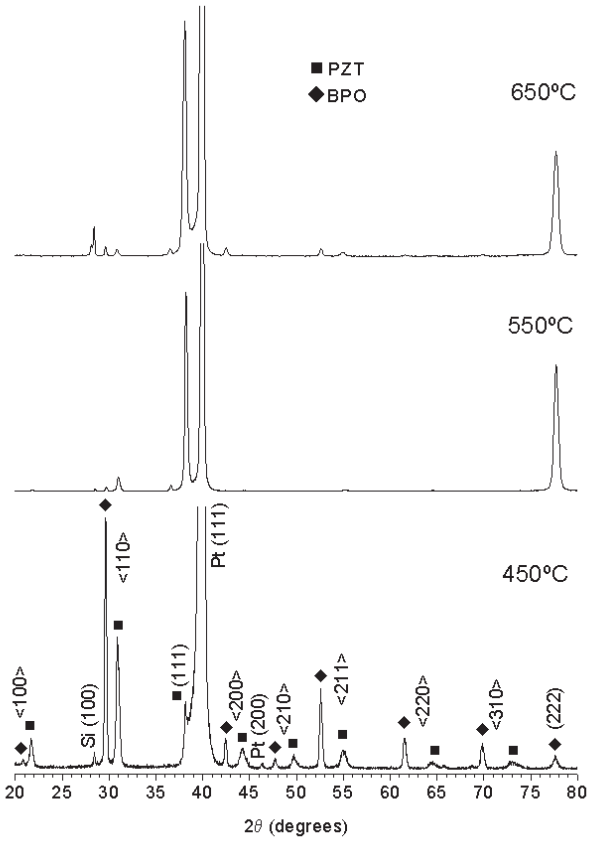


Fig. 3. X-ray diffraction patterns for the PZT crystallized over BPO made at 450 °C, 550 °C and 650 °C.

columnar structure once it is about 100 nm thick. The interface between BPO and PZT is sharper, but a small granular layer can be observed. The PZT has a dense columnar structure and a smooth surface.

The orientation of the BPO and PZT films after crystallization of the PZT at 675 °C was analyzed using X-Ray Diffraction Method (Fig. 3). In the graph the families of planes are shown in brackets, and one can see that the peaks for BPO and PZT appear in pairs and their intensities are similar. Another important feature of the films made by laser ablation is the absence of peaks from pyrochlore, in contrast with the results reported by Luo and Wu on films made by sputtering [11]. Figure 3 shows the results of the X-ray diffraction patterns for the PZT crystallized over BPO made at 450 °C, 550 °C and 650 °C.

At 400 °C the BPO film is amorphous. The first crystalline peaks appeared in the BPO films deposited at 450 °C and one can see clearly from the graph that at this relatively low temperature the BPO is polycrystalline without any preferential orientation and the PZT follows the same trend. When the deposition temperature for BPO is increased (up to 700 °C), the film is strongly oriented in the (222) direction and the PZT assumes the BPO orientation, indicating that the BPO is functioning as a template layer for the nucleation and growth of the PZT.

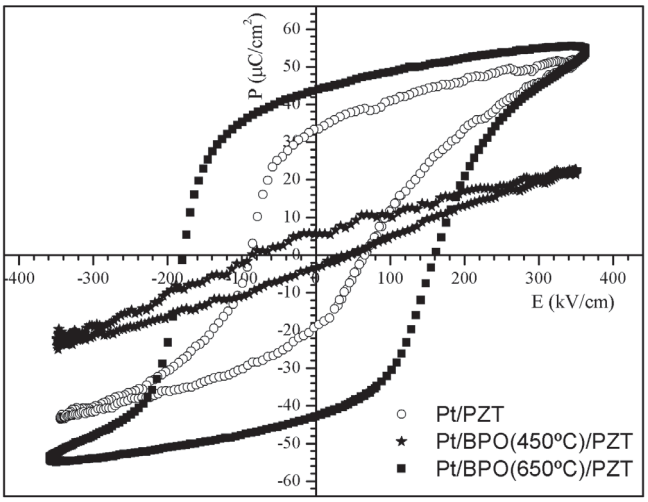


Fig. 4. Hysteresis loops for PZT films deposited over Pt and BPO electrodes deposited at different temperatures.

This indicates that the PZT films have an epitaxial relationship with BPO.

At low BPO deposition temperatures the mismatch of the BPO and Pt lattice parameters (0.426 nm for BPO and 0.392 nm for Pt) favors the polycrystalline growth of the BPO. With the increase in the deposition temperature for BPO the films assume a strong (111) orientation due to the bigger thermal expansion coefficient of Pt with a consequent decrease in lattice strain for BPO.

The different orientations of the PZT films influenced by the BPO layers had a big effect on the ferroelectric behavior of the capacitors. In Figure 4 are plotted the hysteresis loops for the films deposited over BPO electrodes made at 450 °C and 650 °C. A PZT film deposited over platinum and heat treated under the same conditions is shown for comparison.

The loop for the BPO made at 450 °C shows almost inexistent ferroelectric behavior for the PZT film due to the incipient crystallization and random orientation of both BPO and PZT layers as shown in Figures 2 and 3. With the increase of the deposition temperature for BPO, the ferroelectric behavior is steadily improved and at 650 °C the remanent polarization is around 43 μC/cm^2. Comparing with the hysteresis loop measured for the PZT deposited directly over platinum and crystallized using the same conditions, one can observe that for the PZT films deposited over BPO the coercive field is sensitively increased and the loop is not saturated, indicating the existence of high leakage currents.

The high coercive field can be explained by the relatively high resistivity of the BPO films. The best previously reported value of resistivity for BPO thin films made by sputtering using targets with different excess lead oxide contents and Ar:O_2 ratios was 1.4×10^{-3} Ω cm [11]. Because the resistivity of the films deposited by PLD was higher by two orders of magnitude and the films were 600 nm thick, the result was a decrease in the electric field effectively applied to the PZT.

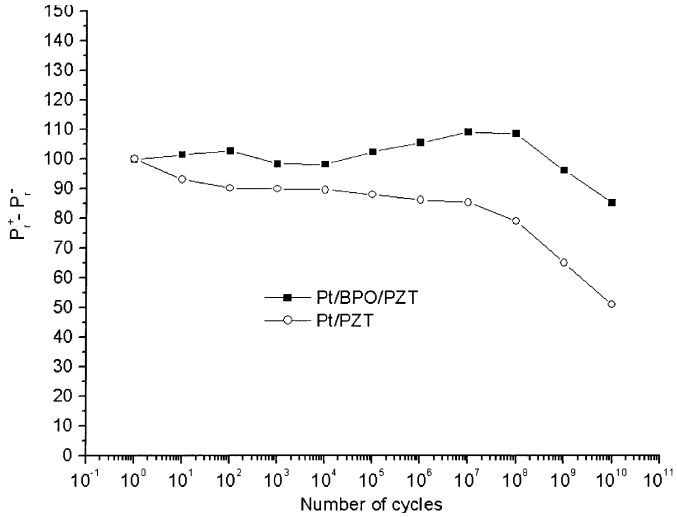


Fig. 5. Ferroelectric fatigue for PZT films made over Pt and BPO and crystallized under the same conditions.

Figure 5 shows a comparison between the fatigue behaviors of PZT films deposited directly on platinum and over BPO made at high temperature (650 °C).

The films deposited over BPO show a marked improvement in the fatigue behavior of the PZT, with only a 20% decrease in the difference between the positive and negative values of remanent polarizations, whereas the film made over platinum lost around 50% for 10^{10} switching cycles of a 200 kV/cm applied field. The improvement of the fatigue behavior can be explained by the inhibition of the oxygen vacancy accumulation at the PZT/electrode interface due to the use of the oxide electrodes.

4 Conclusions

In summary, barium metaplumbate thin films were deposited by laser ablation with a high deposition rate. Films made at low temperature were composed of small randomly oriented grains. When the deposition temperature was increased, a columnar structure was favored and the films assumed a (222) preferential orientation. This orientation of the electrodes was reflected on the PZT films, having a very big influence on their ferroelectric behavior. The PZT films made over BPO deposited at high temperature presented high values of remanent polarization (43 μC/cm^2) but indications of high leakage currents could be observed in the hysteresis loops. The low conductivity of the BPO films was responsible for the decrease of the effective field applied to the PZT with a consequent increase in the coercive field. By using BPO bottom electrodes, substantial improvement in the fatigue behavior of PZT capacitors when compared with the normal platinum electrodes was observed due to the suppression of oxygen vacancies near the PZT/BPO interface. Work is now under way for optimizing the conductivity of the BPO films made by PLD using targets with different excess lead contents and different partial oxygen pressures during deposition.

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