Available online at www.sciencedirect.com
SCIENCE @ DIRECT®

Journal of the European Ceramic Society 24 (2004) 1633–1636

www.elsevier.com/locate/jeurceramsoc

Structural and photoelectrical properties of Nb-doped PZT thin films deposited by pulsed laser ablation

I. Boerasu[a,*], M. Pereira[a], M.J.M. Gomes[a], B. Watts[b], F. Leccabue[b], P.M. Vilarinho[c]

[a]*Deparment of Physics, CFUM, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal*
[b]*Instituto MASPEC/ CNR, Area delle Scienze 37/A I-443010 Fontanini, Parma, Italy*
[c]*Department of Ceramic and Glass Engineering, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal*

Abstract

Sintered targets of Nb^{5+} doped PZT (65/35) (rhombohedral phase) were used in a pulsed laser deposition process to produce, in a single step, highly oriented ferroelectric thin films onto Pt (111)/TiO_2/SiO_2/Si substrates for electrical applications. The doping influence of 1% mol Nb on the crystalline phase formation and the resulting ferroelectrical and photoelectrical properties of the deposited films were investigated. The characterization was performed using X-ray diffraction, P–E hysteresis loop and photoelectric measurements. Maintaining the same composition PZTN (65/35/1), a comparison with bulk materials and thin films produced by sol-gel technique is also performed. The presented results give some indications about a possible existence of a "dead-layer" in the as-deposited films.

Keywords: Electrical properties; Films; Interfaces; Photoresponse; PZT

---

1. Introduction

In the last three decades, ferroelectric thin films have attracted much attention, since as high-speed non-volatile memories they can substitute conventional semiconductor memories.[1] Mainly one family of ferroelectric materials, based on perovskite crystal structure has been developed. Among the compositions, a widely used one is the lead zirconate titanate (PZT) with the general formula $Pb(Zr_XTi_{1-X})O_3$. In these ferroelectric devices, the fatigue due to the switching polarization during reading-writing steps is considered as the principal drawback for their application in non-volatile memory.[2] Two of the most realistic solutions for fatigue removal proposed till now consist in replacing the PZT by a doped-PZT (i.e. using Nb-doped PZT)[3] or in using the light for nondestructive information readout from the non-volatile memory.[4] Still now, no solution is considered satisfactory. The difficulties are mainly connected to the sandwiched structure Electrode/Ferroelectric/ Electrode with two different interfaces,[5] resulting in the existence of a so-called "dead-layer". The exact nature of this layer is not completely understood since it could be due to interfacial discontinuity, Schottky barriers.[6] Moreover, under illumination, photovoltaic and photoconductive effects have also been reported[7] from these high band gap perovskites (≈3–4 eV). On the other hand, the dead-layer should affect the photoresponse during the non-destructive readout.

The aim of this paper is to investigate the influence of the dead layer on the structural, electrical and photoelectrical properties of a Au/ PZTN/ Pt sandwich structure.

2. Experimental

PZTN (65/35/1) thin film was deposited on Pt(111)-coated Si(100) using an XeCl excimer laser (308 nm) and a ceramic target PZTN (65/35/1) previously produced by the conventional way. More details about the deposition parameters are given elsewhere.[8] The X-ray diffraction (XRD) patterns were recorded with a Philips PW1710 diffractometer using Ni filtered CuK_α radiation in a θ–2θ geometry in the angle range from 20 to 65° with a step of 0.02° and a time constant of 1 s. The unit cell parameters were calculated by adjusting theoretical diffraction planes to the experimental spectra by least-squares method. After the PZTN film growth, thin transparent Au electrodes were deposited onto the

---

* Corresponding author.
E-mail address: iulian@fisica.uminho.pt (I. Boerasu).

0955-2219/03/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0955-2219(03)00403-5

PZTN films. The C–V measurements were performed using a HP 4284A LCR bridge, at 100 kHz and a bias up to 3 V. The P–E curves were measured at 500 kHz, using a modified Sawyer–Tower circuit. Finally, the photoelectric measurements were performed using a computer-controlled set-up consisting of a grating monochromator Spex 270M and 500 W Xe arc lamp as light source. The generated photocurrent was measured with an electrometer Keithley 617.

3. Results and discussion

Fig. 1 shows the XRD pattern for PZTN (65/35/1) produced as thin films by pulsed lased ablation technique. As thin film (thickness of 280 nm), the pattern exhibits several perovskite reflections confirming a polycrystalline single phase mainly oriented along the (111) plane. No pyrochlore phase is detected in the XRD patterns. The cell parameters presented in Table 1 were calculated using the set of diffracting planes imposed by the rhombohedral structure of the PZT (65/35).[9] The (hkl) reflections show an increase of the lattice parameters, i.e. an increase of the volume of the crystal cell, in the case of the as-deposited PZTN thin film (65/35/1) compared to the bulk material. For the films produced by excimer laser, that did not receive post-annealing for stress relaxation, the exaggerated cell expansion implies certainly the existence of an interfacial layer at the ferroelectric/Pt substrate. The existence of this layer also called as "dead layer" was already reported by films grown using different deposition techniques[10] and employing different techniques of investigation.[11] The interfacial layer is supposed to create a tensile stress on the unstressed cell because of a thermal effect and differences in the thermal expansion coefficients between the substrate, interfacial layer and the film.

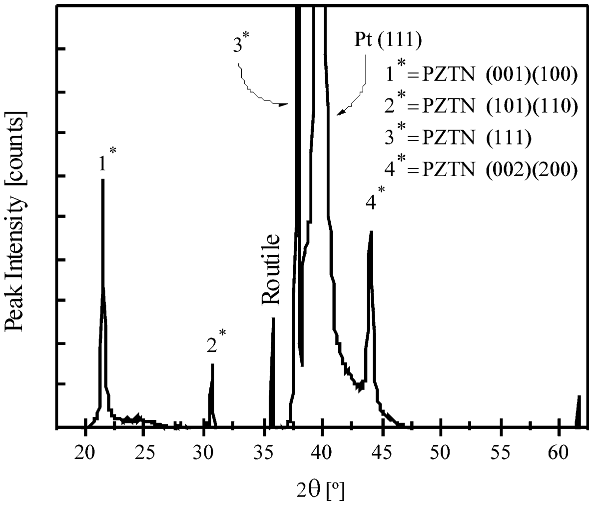

Fig. 1. X-Ray diffraction patterns for PZTN thin film coated on Pt by PLD.

Table 1
Cell parameters (a, α) for PZTN (65/35/1) as thin film and as bulk ceramic

PZTN type	a (Å)	α (°)
XeCl	4.11	89.9
BULK[9]	4.07	89.82

The P–E hysteresis behavior was measured at 500 kHz. The resulting curve is presented in Fig. 2. The hysteresis loop is slightly asymmetric on both polarization and field axes (see Table 2). The polarization asymmetry is characteristic of a ferroelectric with a trapped space charge at an electrode-ferroelectric interface.[4] The asymmetry along electric field is related with an internal electric field mainly generated by the different work function of the metallic electrodes.

The "dead layer", already assumed as stress generator, could act also as a layer of charge accumulation and so, originate a polarization asymmetry. In the case of the coercive field, the asymmetry occurs from the different work functions of the electrodes that generate a built-in bias field (Vbi).

Similarly, the C–V characteristics are presented in Fig. 3. It depicts that the capacitance varies nonlinearly with the applied field, due to the domains switching from one orientation to another and a classical butterfly curve was obtained. The capacitance peak values are different in magnitude, which can be attributed to the different nature of electrodes (Pt and Au). A voltage

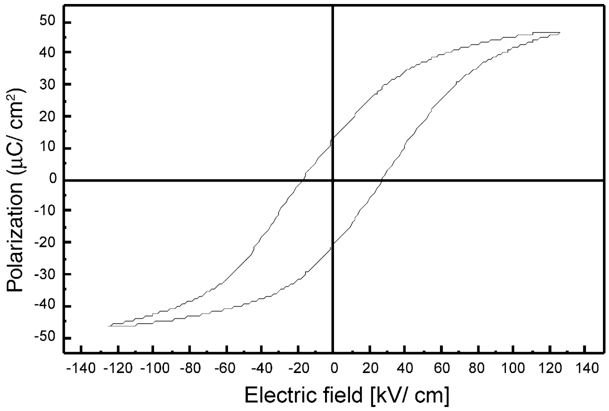

Fig. 2. The polarization versus electric field (P–E) hysteresis loop measured at 500 kHz.

Table 2
The characteristics of the hysteresis loop for the PZTN 65/35/1 thin film deposited on Pt substrate

Item	P_{r+} (μC/cm^2)	P_{r-} (μC/cm^2)	ΔP_r (μC/cm^2)	E_{c+} (kV/cm)	E_{c-} (kV/cm)
Value	17	−25	21	45	−31

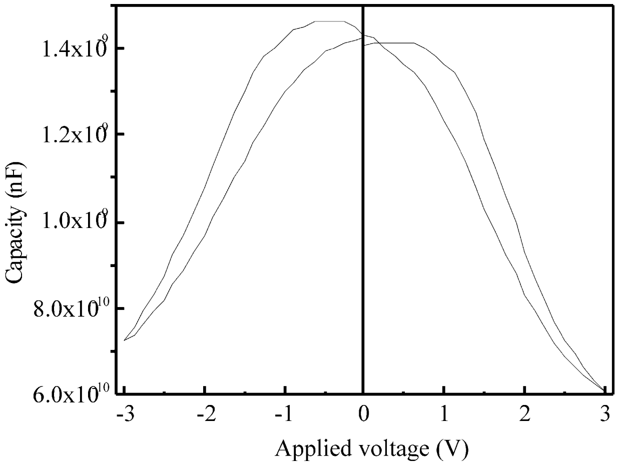

Fig. 3. C–V characteristic for the PZTN 65/35/1 thin film on Pt-coated Si.

offset to the positive side can be seen in C–V characteristic, perhaps due to an internal bias in the film.[4]

The short circuit photocurrent measurement of unpoled PZTN (65/35/1) is shown in Fig. 4. A maximum photoresponse can be seen around 340 nm, which corresponds to an energy of about 3.64 eV. Similar results obtained using PZTN (65/35/1) thin films prepared by sol-gel were reported elsewhere.[12] The threshold wavelength is about 350 nm, giving a rough idea about the band-gap of the ferroelectric PZTN (65/35/1) thin film, i.e. about 3.53 eV. The band gap calculated from this evaluation is in agreement with the one obtained using optical measurements performed in PZTN thin films produced by sol-gel.[13] The produced photocurrent confirms also the non-pyroelectric nature of the signal since the pyroelectric signal is quasi-independent of the wavelength of the light. The photoresponse could be due to bulk photovoltaic effects, localized electronic transitions or transient space charge effects.[14] The spectral distribution behavior can be related with the transmission spectra of PZTN (65/35/1);[8] the photocurrent decreases at low values of the wavelength and is linked to the decrease of the PZTN transmission spectra: the light is mainly absorbed by the PZTN in this region, but, because the absorption length ($1/\alpha = 17.24$ nm at $\lambda = 365$ nm) is smaller than the film thickness ($d = 280$ nm), the light remains near the top electrode.

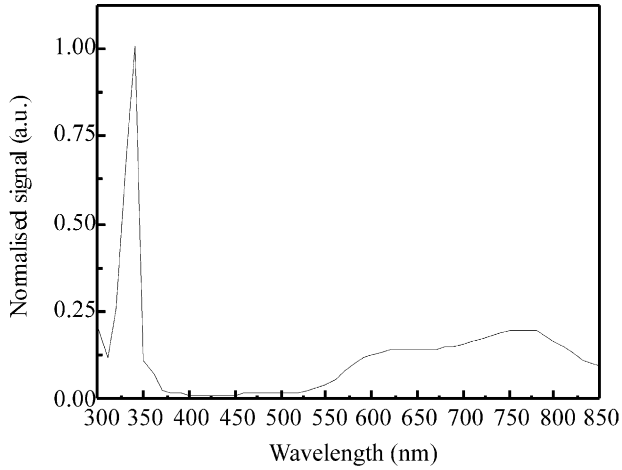

Fig. 4. Spectral distribution of photoconductivity in case of MFM structure with semitransparent top gold electrode.

At high values of wavelength, the light absorption decreases ($\alpha = 0.\ 0098$ nm^{-1} at $\lambda = 810$ nm) and an increase of the photocurrent occurs. Moreover, two broad peaks are present in the photoresponse at high wavelength range ($\lambda = 575$–800 nm). Because of the domed shape of these peaks, their origin could not be assigned to point defects, but to a quasi-continuous distribution of states located in the bandgap, acting as trap centers. At this wavelength range, the non-equilibrium carriers should be generated prior from the bottom electrode through the dead-layer. Then, these states are probably due to the interfacial layer.

4. Summary

In summary, the structural, ferroelectrical and photoconductivity properties of PZTN (65/35/1) thin film deposited by PLD are presented in this paper. The lattice parameters difference between as-deposited PZTN film and bulk material could indicate the presence of an interfacial layer, formed at the bottom electrode interface. Also, the shifted behavior of the P–E hysteresis loop, according to the polarization and the electric field axes was ascribed to the dead-layer. The short circuit photocurrent of unpoled PZTN shows a maximum when the light wavelength is around 340 nm: PZTN (65/35/1) materials seem to have potential applications as UV photoconductive solid detectors. The band gap calculated from photoelectric measurements is calculated as 3.64 eV. The two broad peaks observed in the photoresponse in the range 575–800 nm, could be assigned to the trap states within the forbidden band generated by the interfacial layer.

Acknowledgements

The authors acknowledge FCT-Portugal for financial support under the project POCTI/CTM/12140/1998. I. Boerasu would like to thank FCT for the grant PRAXIS XXI/BD/21539/99.

References

1. Scott, J. F., Limitations on ULSI-FeRAMs. *IEICE Transactions on Electronics*, 1998, **E81-C**, 477.
2. Ricinschi, D., Okuyama, M. and Shimizu, M., Landau theory-based validation of the fatigue mechanism in Sol-Gel and

MOCVD PZT films using the correlated analysis of the hysteresis loop parameters. *Ferroelectrics*, 2002, **269**, 81.

3. Poykko, S. and Chadi, D. J., Dipolar defect model for fatigue in ferroelectric perovskites. *Phys. Rev. Lett.*, 1999, **6**, 1231.
4. Scott, J. F., *Ferroelectric Memories*. Springer-Verlag, Berlin Heidelberg, 2000.
5. Dawber, M. and Scott, J. F., Electrode field penetration: a new interpretation of tunneling currents in Barium Strontium Titanate (BST) thin films. *Ferroelectrics*, 2002, **268**, 35.
6. Sinnamon, L. J., Saad, M. M. and Bowman, R. M., Exploring grain size as a cause for "dead-layer" effects in thin film capacitors. *Appl. Phys. Lett.*, 2002, **81**(4), 703.
7. Thakoor, S., High speed, nondestructive readout from thin-film ferroelectric memory. *Appl. Phys. Lett.*, 1992, **60**(26), 3319.
8. Boerasu, I., Pereira, M., Vasilevskiy, M., Gomes, M. J. M., Watts, B., Leccabue, F. and Vilarinho, P. M., Properties of ferroelectric films based on Nb-modified PZT produced by PLD technique. *Appl. Surf. Sci.*, 2003, **208–209**, 604.
9. Pereira, M., Peixoto, A. G. and Gomes, M. J. M., Effect of Nb doping on the microstructural and electrical properties of the PZT ceramics. *J. Eur. Ceram. Soc.*, 2001, **21**(10–11), 1353.
10. Sreenivas, K., Reaney, I., Maeder, T., Setter, N., Jagadish, C. and Elliman, R. G., Investigation of Pt/Ti bilayer metallization on silicon for ferroelectric thin film integration. *J. Appl. Phys.*, 1994, **75**(1), 232.
11. Madsen, L. D. and Weaver, L., Examination of barrier layers for lead zirconate titanate thin films. *J. Electron. Mater.*, 1992, **21**, 93.
12. Boerasu, I., Pintilie, L., Vasilevskiy, M., Pereira, M. and Gomes, M. J. M., Electrical and photoelectric properties of PZT 65/35 thin films deposited by Sol Gel: Competition between ferroelectric and semiconductor properties. *J. Appl. Phys.*, 2003, **93**(8), 4776.
13. Boerasu, I., Vasilevskiy, M. I., Pereira, M., Costa, M. F. and Gomes, M. J. M., Optical properties of PZT 65/ 35 thin films deposited by Sol-Gel. *Ferroelectrics*, 2002, **268**, 187.
14. Dimos, D., Al-Shareef, H. N., Warren, W. L. and Tuttle, B. A., Photoinduced changes in the fatigue behavior of $SrBi_2Ta_2O_9$ and $Pb(Zr,Ti)O_3$ thin films. *J. Appl. Phys.*, 1996, **80**(3), 1682.