Microsc Microanal 14 (supp 3), 2008
 doi: 10.1017/S143192760808937X

Microstructure of Compositionally Graded PZT films Grown by Pulsed Laser Deposition

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Ferroelectric films with a composition gradient have attracted much attention because of their large polarization offset present in the hysteresis loops [1-3].
Lead Zirconate Titanate (PZT) films were deposited on $Pt/TiO_2/SiO_2/Si$ substrates by Pulsed Laser Deposition (PLD) technique, using a Nd:YAG laser (Surelite) with a source pulse wavelength of 1064 nm and duration of 5-7 ns delivering an energy of 320 mJ per pulse and a laser fluence energy about 20 J/cm^2. The film growth is performed in O_2 atmosphere (0,40 mbar) while the substrate is heated at 600ºC by a quartz lamp. Starting from ceramic targets based on PZT compositions and containing 5% mol. of excess of PbO to compensate the lead evaporation during heat treatment, three films with different compositions Zr/Ti 55/45, 65/35 and 92/8, and two types of complex structures were produced. These complex structures are in the case of the up-graded structure (UpG), with PZT (92/8) at the bottom, PZT (65/35) on middle and PZT (55/45) on the top, and for down-graded (DoG) one, that order is reversed.

Figure 1 shows the XRD patterns of the PZT films with composition 55/45 and 92/8, as-grown and after conventional thermal annealing in air at 650ºC for 30 min. The perovskite (100), (110), (111) and (200) peaks of rhombohedral phase appear and the films show a preferential orientation along (110) (highest peak). However the selected annealing conditions were not sufficient to eliminate secondary phases like pyrochlore or PbO in the case of PZT 55/45. The layer with composition Zr/Ti 65/35 (the middle layer in the structure) had a similar diffraction spectrum so it is not shown here. For multilayered structures, the (110) peak is in fact a triplet due to the three individual layers that form the structure (Figure 2): Here, the three peaks related with each monolayer, with composition 92/8, 65/35 and 55/45 respectively, are detected in both graded structure. Also, the dielectric study of these multilayer graded structures displays an anomalous behaviour at three different temperatures that corresponds to the three transitions temperatures of different monolayers [4]. Comparing the unit cell parameters of the films with the unit cell parameters of the targets that originated them, a little difference is observed. This confirms the existence of biaxial stress in these films: tensile stress for composition Zr/Ti 55/45 and compressive stress for 65/35 and 92/8 ones.
The surface and cross-section morphology of the films was characterized by Scanning Electron Microscopy (SEM). On the surface image of annealed PZT films, some spherical particles with different sizes are found (figure 3 a).Using Energy Dispersion Spectroscopy (EDS), the composition of these particles was evaluated. The different kinds of grains contain Zirconium, Titanium and Lead with different concentrations in comparison with the target. In figure 4a, the up-graded structure shows on its surface, apart from the spherical particles already refereed, some platelets which composition is mainly PbO, as seen from the EDS spectrum (figure 5, point assigned as 2 in picture)), dispersed in the whole film. These particles are fixed to the thin film by aggregates (size from 200nm to 2000nm) of nanosize grains, forming a homogeneous and porous microstructure.

These platelets, with hexagonal shape, grow from a round aggregate with high titanium and lead content, as show the EDS spectrum presented on figure 5 related to the point assigned as 1.
Because of the low melting point of PT and PbO, the platelet formation mechanism should follow equation (1).

$$PbZr_{0.55}Ti_{0.45\ target} + PbO \xrightarrow{PLD} \{0.45PT + PbO_{dissolved}\} + 0.55ZrO_2 \xrightarrow{650^{o}C} PZT + PbO_{platelets} \qquad (1)$$

For the films with higher Ti concentration (ratio Zr/Ti = 55/45), a low melting point PT phase should include dissolved PbO, before the formation of the PZT phase. Then this mixture should react at high temperature with free ZrO_2 to form PZT and a secondary phase of PbO (platelets).
On the contrary, in the films with low Ti content (ratio Zr/Ti = 92/8), the presence of PbO platelets couldn't be observed because no significant formation of the PT phase occurs during the mechanism of PZT production.
Comparing the SEM micrographs of the surface of PZT monolayers with composition Zr/Ti of 55/45 and 92/8 (figure 3), one could see the presence of some glassy phase on the first. This fact can be related with the formation of PT - PbO mixture that progresses up to the growth of the PZT layer and the platelets found on up-graded structure, with the top layer rich on Ti. The cross-section of all the samples shows a columnar microstructure starting from the Pt layer of the substrate.
The thickness of different single layered films is 720, 720 and 1200 nm for compositions Zr/Ti 55/45, 65/35 and 92/8 respectively. While the thickness values for up-graded and down-graded structures are estimated 780 and 720 nm respectively.
Analyzing the cross-section of the multilayer structures, the three monolayers could roughly be identified (figure 5).This identification is not clearer because the appearance of each monolayer is very similar.

In conclusion, using Pulsed Laser Deposition technique each monolayer could be grown separately and sequentially into a multilayered structure without mixture of the layers.
The structural study had revealed that these PZT films crystallize in a perovskite rhombohedral phase. The calculated unit cell for each individual film indicates the presence of some strain (tensile or compressive) on each monolayer. On the microstructure of the films, SEM observations reveal some spherical particles at the films surface and the formation of some platelets of PbO in the case of films with high Ti concentration.

Acknowledgments

This work was partially supported by the Portuguese Foundation for Science and Technology (FCT) through a Ph.D grant (SFRH/BD/30531/2006) and the Pluriannual Project of Centre of Physics of University of Minho.

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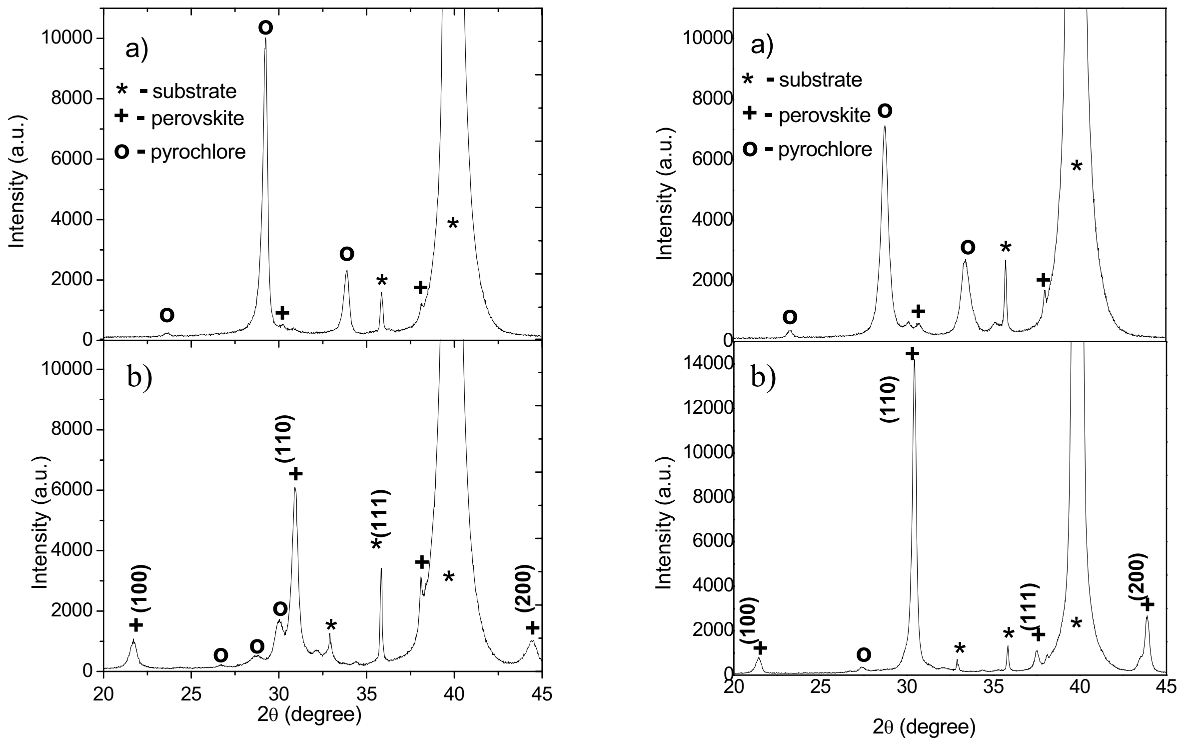

Figure 1. XRD patterns of homogeneous thin films with composition Zr/Ti of 55/45 (left) and Zr/Ti of 92/8 (right) (a) before annealing and (b) after annealing

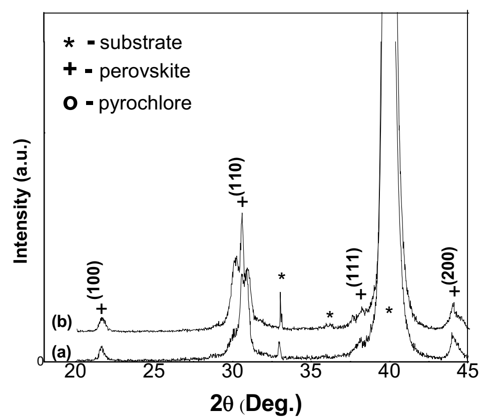

Figure 2. XRD patterns of (a) up-graded and (b) down-graded structures after annealing.

Table I. Lattice parameters and rhombohedral unit cell volume of the three PZT monolayers.

Composition Zr/Ti of PZT layers	Lattice parameter for films		Lattice parameters for targets		Rhombohedral unit cell volume $V = a^3\sqrt{1-3\cos^2\alpha+2\cos^2\alpha}$		$\frac{\Delta V}{V_0}$
	a (Å)	α (º)	α (º)	a (Å)	Films	Targets	
(55/45)	4,084	89,96	89,83	4,062	68,132	67,012	0,017
(65/35)	4,095	90,05	89,77	4,101	68,666	68,976	-0,005
(92/8)	4,121	90,12	89,90	4,143	69,995	71,112	-0,016

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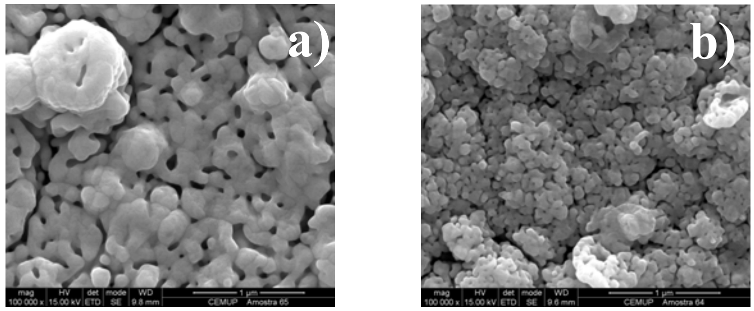

Figure 3. SEM micrographs of monolayer films surface with a) composition Zr/Ti 55/45 and b) composition Zr/Ti 92/8.

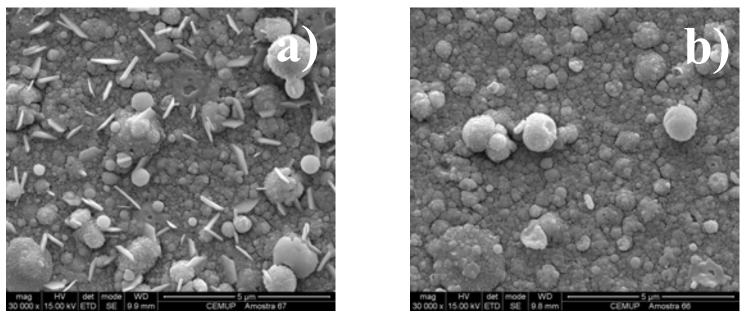

Figure 4. SEM micrographs of multilayer films surface with a) up-graded and b) down-graded structure.

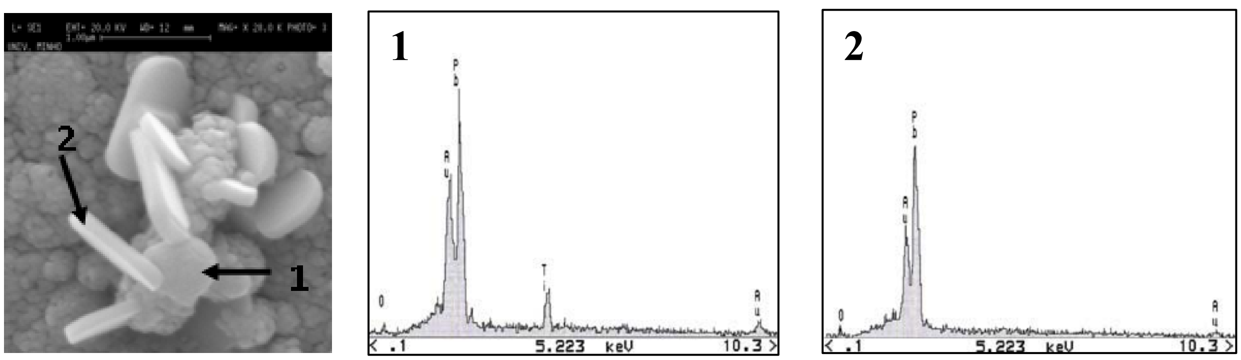

Figure 5. SEM micrographs of some platelets found on up-grade structure and EDS spectra of two distinct zones assigned on SEM image as 1 and 2.

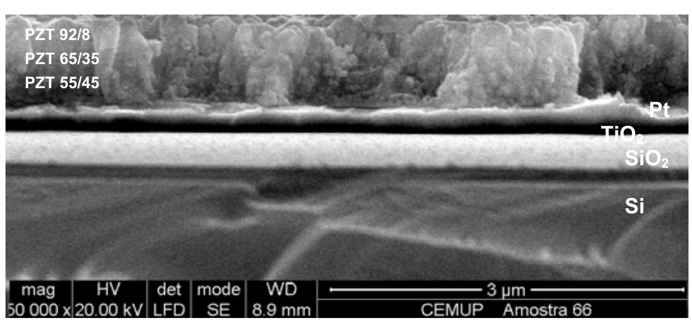

Figure 6. SEM micrograph of down-graded structure cross-section.

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