

## GROWTH AND PROPERTIES OF $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ STEP GRADED-STRUCTURES

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$\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  ( $x = 55, 65, 92$ ), PZT step graded-structure have been deposited by sol-gel technique on Pt-coated Si. Up-graded and down-graded structures has been obtained by changing the Zr/Ti ratio in steps along to the film thickness. Up means that the ratio was increased from the bottom to the top while down means it was decreased. The properties of these films were investigated and compared with those of conventional films with homogeneous composition. It was found that the properties of up and down graded structures are completely different. Up-graded films have better ferroelectric properties than the down-graded ones. Pyroelectric signal could be detected also on as-grown up-graded films, in accordance with the structural results that show a strong (100) orientation in this case. The coercive field of the up-graded film is lower than the values obtained in case of homogeneous films with the same Zr/Ti ratios like those used in the graded structures.

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### 1. Introduction

The concept of “graded ferroelectric structures” was developed at the beginning of 90’s [1,2]. The basic principle of this structures is to have a polarization gradient, that can be induced either by a concentration gradient, by a temperature gradient or by a stress gradient [3-5]. In case of concentration gradient, this can be continuous or is steps. Several interesting properties were reported in case of graded ferroelectric structures (GFS). Among these, the most intriguing is the so-called polarization offset reported by several authors on GFS based on different materials. The phenomena consists in hysteresis loop shift up or down along the polarization axis, depending on the direction of the polarization gradient [6]. Anomalous large pyroelectric coefficients were also reported on graded structures [7,8]. Even devices similar with transistors, called transcapacitors, were proposed based on GFS [9].

Despite the relatively large number of reported experimental data regarding the unusual properties of GFS there is little known about their origin. For example, in case of polarization offset there is not clear yet if it is an intrinsic effect due to polarization gradient (something similar with the occurrence of the built-in potential in p-n semiconductor junctions) or is a measurement artifact (a leakage current asymmetry in a Sawyer-Tower set-up can give such offsets). The proposed models also explain only partly the observed phenomena due to the approximation made (either ideal ferroelectric, with no leakage current, or semiconductor with negligible influence from polarization gradient) [10,11].

The subject of GFS is thus very interesting and offers large possibilities for study. The main problem is to relate the properties of component materials with the overall properties of the structure. Step- graded structures are more suitable for this purpose and the system that offers the easiest way to obtain GFS is  $\text{PbZrO}_3$ -  $\text{PbTiO}_3$ . Just changing the Zr/Ti ratio from one layer to another is possible to

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obtain graded structures. The simplest method for preparation is sol-gel because its chemistry is well developed for the PZT system.

The present work is proposing to analyze and compare the physical properties of step-GFS (up and down graded) with those of the homogeneous layers having same compositions like the component layers of the structure. It will be shown that the structure properties are not a simple summation of the component properties. The different properties of up and down GFS will be discussed in relation with their structure. A qualitative explanation of the results will be presented.

## 2. Experimental

The graded structures were prepared using the sol-gel method. Stock solutions with the following compositions were prepared by a modified Budd method [12]: PZT(92/8); PZT(65/35) and PZT(55/45). The numbers in brackets show the Zr/Ti ratio. The raw materials were: Pb acetate trihydrate, Zr n-butoxide, Ti isopropoxide, and 2-methoxyethanol as solvent. The deposition was then performed by spin-coating on Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/Si substrates. The rotation speed was 2500 cycle/min, and the time was 30 seconds. Two type of structures were realized: the up-graded, with PZT(55/45) at the bottom, PZT(65/35) at the middle, and with PZT(92/8) in the top; the down-graded, in which the order was reversed. For simplicity, the up-graded structure will be named M1 and the down graded M2. After spin-coating the as-deposited layer was subjected to a two stage pyrolysis: first at 200 °C for 2 minutes for solvent evaporation; second at 400 °C for 5 minutes to remove the residues of organic species. The spinning-pyrolysis sequence was repeated three times for each composition. The estimated thickness of the final structure is about 450 nm, with 150 nm for each layer. The final crystallization was performed by conventional thermal annealing at 650 °C, in air, for 30 minutes. Homogeneous films from each composition were also deposited, using the same stock-solutions and the same procedure on the same type of substrates. The thickness of these films was around 150 nm, comparable with the thickness of each composition layer in the structure. Top Pt contacts were deposited by RF magnetron sputtering for electric measurements. The area of the contact was of 0.5 mm<sup>2</sup>.

The structure was investigated by X-ray diffraction using CuK<sub>α</sub> radiation, before top contact deposition. The composition was checked using X-ray Photoelectron Spectroscopy (XPS). The hysteresis loops were recorded using a standard, computer-controlled, Sawyer-Tower circuit. The software does not symmetries the loop, thus the shift along the axes can be observed. The values of the ferroelectric polarization were evaluated knowing the geometry of the samples (top electrode area and thickness) and the value of the reference capacitor. Finally, pyroelectric signal measurements were performed using an experimental set-up composed by: a red He-Ne laser (5 mW nominal power per spot); a mechanical chopper (frequency up 500 Hz); a lock-in amplifier (SR530); an impedance adapter based on a field-effect transistor (FET); power supply for the FET. The ferroelectric films were used as pyroelectric detectors working in the voltage mode [13].

## 3. Results

The XRD spectra obtained in the case of up and down GFS are presented in Fig. 1a. The XRD spectra of the homogeneous film having the same composition as the bottom layer in the two GFS are presented in Fig. 1b. The bottom layer can be considered as the seed layer for the rest of the graded structure. In case of M1 the bottom layer is PZT(55/45). When grown separately, this structure has a dominant (100)/(200) orientation. When used as bottom layer in GFS, it imposes its orientation to the entire stack. This can be observed from the XRD spectra in case of M1. In case of M2 the bottom layer is PZT(92/8). The XRD spectra of the homogeneous layer having this composition shows that the annealing in air is not enough for a complete crystallization of the perovskite phase. The film is a mixture of perovskite, pyrochlor phases, and elementally oxides. When used as bottom layer in GFS, that incomplete crystallization reflects in the structure and properties of M2. The XRD spectra in case of M2 shows much less intense lines, corresponding to a lower crystallization compared with M1. The preferred orientation is (110). Even there are no signs of pyrochlor in the

final XRD spectrum of M2 the presence of this phase in the structure cannot be excluded. A small amount of amorphous pyrochlore can severely affect the ferroelectric properties as will be shown later.

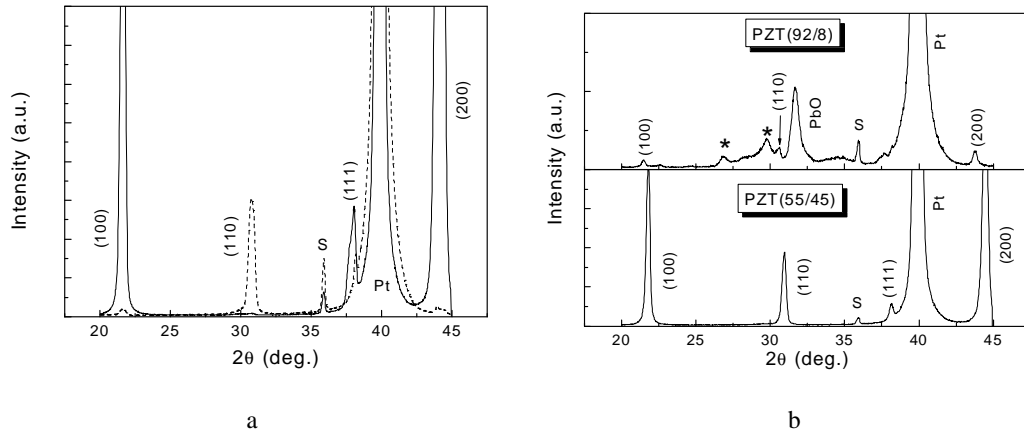


Fig. 1 a) XRD spectra of GFS. Solid line-M1 (up-graded structure). Dash line-M2 (down-graded structure). b) XRD spectra for the homogeneous film having the same composition as the bottom layer in the two GFS. The \* stands for pyrochlore-type phases.

The results of the XPS depth analysis are presented in Fig. 2.

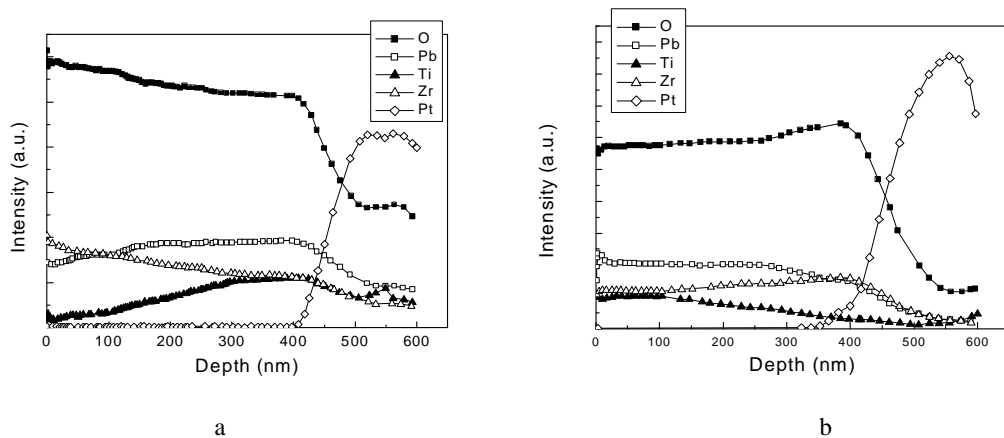


Fig. 2. XPS results in case of up-graded structure (a) and down graded structure (b).

The above results show that there is a variation of the Zr/Ti ratio in the GFS thickness. The ratio decreases in case of M1 and increases in case of M2 from the top surface to the bottom Pt electrode. However, no clear steps can be observed, indicating the existence of 3 separate layers, with different but constant Zr/Ti ratio inside each layer. Both Zr and Ti atomic concentration varies more or less continuously along the film thickness. This is due to the atomic diffusion that takes place during crystallization annealing, leading to a smear of the interfaces between layers. Some variations in the oxygen and lead concentrations can be also observed. In case of M1 the oxygen concentration is higher near surface, while the lead one is lower. In case of M2 the situation is reversed. An interdiffusion layer seems to exist at the interface with the bottom Pt electrode. The increase of both Ti and oxygen concentration beneath the Pt electrode is due to the presence of the  $\text{TiO}_2$  adhesion layer.

The hysteresis loops measured for all the samples are presented in Fig. 3. The values of interest for the remnant polarization and coercive field are given in Table 1. In case of homogeneous layers the hysteresis loops look fairly saturated. The hysteresis loop for M1 is saturated but is

considerably shifted on both axes, while the loop for M2 looks as for a very poor dielectric, with high losses.

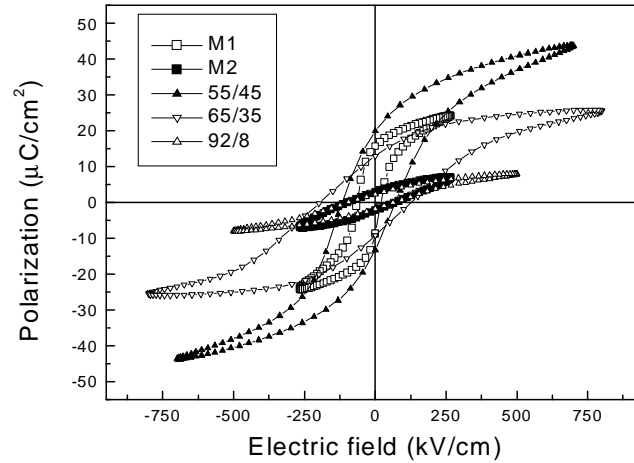


Fig. 3. The hysteresis loops obtained in case of GF structures M1, M2, and in case of homogeneous films having the same compositions like the component layers of the GFS.

Table 1. The determined value for: positive and negative values of remnant polarization and coercive field ( $P_r^+$ ,  $P_r^-$ ,  $E_c^+$ ,  $E_c^-$ ); average values of remnant polarization and coercive field ( $P_r$ ,  $E_c$ ).

Material/Structure	$P_r^+$ ( $\mu\text{C}/\text{cm}^2$ )	$P_r^-$ ( $\mu\text{C}/\text{cm}^2$ )	$E_c^+$ (kV/cm)	$E_c^-$ (kV/cm)	$P_r$ ( $\mu\text{C}/\text{cm}^2$ )	$E_c$ (kV/cm)
PZT(55/45)	19.9	-13.3	71	-117	16.6	94
PZT(65/35)	13	-9.2	127	-195	11.1	161
PZT(92/8)	2.3	-1.8	63	-94	2.05	78.5
M1	15.6	-8.8	19	-65	12.2	42
M2	2.9	-2.3	64	-94	2.6	79

Analysing the values from Table 1 several conclusions can be drawn:

- in all cases the positive remnant polarization is higher than the negative one, while the positive coercive field is lower than the negative one
- the value of remnant polarization decreases with increasing the Zr/Ti ratio, as was expected; however, the coercive field has its maximum value for PZT(65/35)
- the graded structures show very different values for remnant polarization and coercive field
- M1 has the lowest coercive field and a good value of remnant polarization

Some comments regarding the Sawyer-Tower measurement are necessary. The alternative voltage is applied on the series connection of capacitor sample  $C_x$  and reference capacitor  $C_0$ . Because  $C_0 \gg C_x$  it can be assumed that almost all the applied voltage drops on the sample, thus the electric field represented on the Ox axis is the field on the sample. Any shift on the Ox axis is an indication for the presence of built-in fields (dc voltages) that adds to the applied field. The polarization value is computed from the voltage measured on the reference capacitor ( $P = VC_0/A$ , where A is the electrode area and  $VC_0$  is the charge). A shift along the Oy axis means in fact a change in the charge on the sample capacitor. But a change of the charge means a change of the voltage drop across the sample that leads to a shift along the Ox axis. Thus the shifts along the two axes should be related if the cause is a built-in voltage. There will be shift along the Oy axis without shift along the Ox axis only when a built-in charge exists in the sample.

The results of pyroelectric measurements are presented in Fig. 4. The frequency dependence is typical for a pyroelectric signal. It can be observed that the log-log representation becomes a line at high frequencies, indicating that the signal is proportional with  $1/\text{frequency}$ , as predicted by the theory [13].

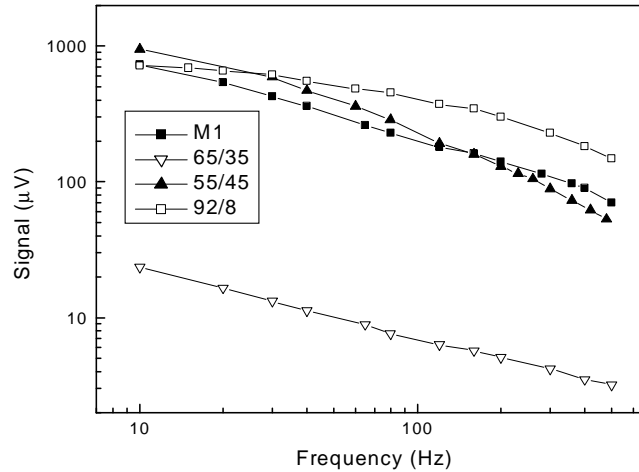


Fig. 4. The frequency dependence of the pyroelectric signal in log-log scale. The top electrode was Pt and the samples were not previously poled.

#### 4. Discussion

Regarding the structure of the GFS it is clear that the growth orientation and the crystallization quality are imposed by the first layer deposited on the bottom Pt electrode. In case of M1 the bottom layer is PZT(55/45), that crystallize with (100)/(200) preferred orientation, thus the entire structure will have the same orientation as seen in Fig. 1a. The XRD lines are sharp and narrow, indicating a good crystallization. In case of M2 the bottom layer is PZT(92/8), that crystallize very poor in air. The fact that the bottom layer is not well crystallized reflects on the entire structure, the intensity of the lines is much smaller than in case of M1, and their width is larger, indicating poor crystallization and smaller size of crystallites. The presence of amorphous pyrochlore phase in M2 cannot be excluded even in the XRD spectra there are not evident signs of its presence. The (110) preferred growth orientation can be due to the presence of PbO in the early stages of crystallization, as is seen from the XRD spectra of PZT(92/8), and according to other reports from literature [14].

The XPS results show that a diffusion of the Zr and Ti atoms takes place during crystallization annealing leading to a quasi-linear variation of the concentrations even the deposition of the graded structure was done layer-by-layer. The diffusion takes place in the region of the interfaces separating the component layers. It would be expected to have regions of constant concentrations in the bulk of the layers and gradual concentration changes in the interface region, but because the layers are thin the region of constant Zr or Ti concentrations is missing. The loss of Pb in the surface layer (PZT(92/8)) in case of M1 suggests the possible presence of a Pb-deficient pyrochlore phase. The same holds for M2 in the bottom layer. The crystallization of the Zr-rich PZT films is much more difficult than in case of Ti-rich films due to the reduced number of nucleation centers for the perovskite phase. A good crystallinity can be achieved only after oxygen annealing. Anyway, the pyrochlore phase cannot be completely removed. In the present case the crystallization annealing was performed only in air, thus some pyrochlore phase can exist in the layer with Zr/Ti ratio of 92/8. The difference is that in case of M1 this layer is at the surface and does not affect the crystallization of the other ones, while in case of M2 this layer is at the bottom and has a critical influence on the crystallization process of the sub-sequent layers. In other words, M1 has a very good perovskite structure, with some pyrochlore phase in the surface layer that does not affect the ferroelectric properties, while the M2 has a less good perovskite structure and contains an important

amount of pyrochlor phase that leads to large losses and low ferroelectric properties as reflected in the hysteresis loop.

The oxygen concentration is also slightly varying in the GFS depth. The oxygen deficit means oxygen vacancies. In case of M1 these are located near the bottom electrode, while in case of M2 they are located near surface. The non-homogeneous distribution of oxygen vacancies suggests the presence of space charge regions (SCR) in the graded structures.

Regarding the hysteresis loops, the fact that the curves are shifted along the field axis means that internal electric fields exist in the samples, both homogeneous films or graded structures. In case of the homogeneous films the internal field can occur due to the un-equivalent electrode interfaces. The bottom interface had suffered a crystallization annealing, while the top interface has not. It is expected, thus, to have a non-homogeneous distribution of defects leading to internal fields. The curves of homogeneous films can be symmetric just by shifting them along the field axis in order to make equal the positive and negative values of the coercive field. The positive and negative values of remnant polarization will become also equal.

The two GFS behaves differently. M2 has poor ferroelectric properties and large leakage that mask the possible existence of internal fields due to concentration gradient and polarization gradient. The hysteresis loop is not saturated, the polarization is small and no pyroelectric signal could be detected due to the poor crystallization and due to the presence of parasitic phases. M1 shows good ferroelectric and pyroelectric properties. The important shift of the hysteresis loop on the field axis implies the presence of an important internal field. This field occurs due to the concentration gradient that induces a polarization gradient. However, the positive and negative values of remnant polarization are still different after making the curve symmetric along the field axis. This fact suggests the presence of a built-in charge besides the built-in potential. This charge is related with the presence of a non-switchable polarization.

## 5. Conclusions

Up and down graded ferroelectric PZT (variable Zr/Ti ratio) structures were prepared by sol-gel. The structural study had revealed that the bottom layer fixes the growth orientation. The best ferroelectric and pyroelectric properties were obtained in case of up-graded structure. That is explained by the fact that the bottom layer in this case is PZT(55/45), a Ti rich composition which crystallize easy and well in the perovskite structure, triggering a good crystallization for the entire structure.

The important shift, along both axes, of the hysteresis loop in case of M1 is explained by the presence of an internal electric field and of a built-in charge.

M1 has a good value of remnant polarization and a low value of the coercive field. The lower coercive field makes this structure attractive for memory applications. On the other hand the presence of the pyroelectric signal makes it interesting for pyroelectric detection of the infrared radiation.

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