

Structure of PZT thin films deposited on stainless steel and on platinum/silicon substrate

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Pb(Zr_{1-x}Ti_x)O₃ (PZT) thin films were prepared by sol-gel method on stainless steel (SS) and on platinum-coated silicon substrate (Pt/Si). The structure revealed by X-ray diffraction shows strong crystallographic orientation: (110) and (100), respectively. A small amount of pyrochlore phases (Pb₂(Zr,Ti)₂O_{6-δ}) is formed in the films deposited on SS substrate. The crystallite size shows significant differences: $d_{(001)}^{(SS)} = 27.1$ nm, $d_{(h00)}^{(Pt)} = 88$ nm. The tetragonal splitting is $(\Delta c/c)_{(SS)} = 3.55$ % and $(\Delta c/c)_{(Pt)} = 3.32$ %.

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1. Introduction

PbZr_{1-x}Ti_xO₃ thin films are good candidates for microelectro-mechanical systems because they exhibit large piezoelectric coefficients and electro-mechanical coupling coefficients to be used in sensors (acoustic [1], pyroelectric [2], membrane [3]) and in actuators (micro-accelerometers [4] and micro-motors [5]). It is remarkable that the PZT can serve as excellent material with good biocompatibility [6]. Various deposition methods, including sol-gel one [7], have been used to produce ferroelectric PZT films.

Studies on PZT prepared by ceramic method doped by Nb or substituted by other elements (Zr → Mg, Nb) have been performed and the evolution of the microstructure with the sintering temperature was followed [8, 9].

Thin films have been intensely studied but up to day only scattered results have been obtained. While in bulk PZT the ferroelectric properties vary with the Zr/Ti ratio and the maximum values of piezoelectric coefficients, permittivity and polarization are reached near the morphotropic phase boundary [10], in PZT films the influence of crystallographic orientation, film thickness and microstructure on the properties is important so that a definite characterization is still lacking.

In a previous paper we have studied the structural and microstructural properties of porous PZT films. A dielectric constant lower than that in dense film was obtained [11].

In this paper we report the preparation of PZT thin films by sol-gel method on two different substrates (stainless steel and platinum/silicon) and the structural characterization of the films.

2. Experimental

2.1. Preparation of sol-gel PZT films

In order to prepare PBZr_{0.2}Ti_{0.8}O₃ films we used as starting reagents for the synthesis of the precursor solution lead acetate Pb(CH₃COO)₂·3H₂O (Reactivul Bucharest), titanium isopropoxide Ti[OCH(CH₃)₂]₄ (Alfa) and zirconium n-propoxide Zr[OCH₂CH₂CH₃]₄ (Alfa). As solvent there was used 2-methoxyethanol CH₃OCH₂CH₂OH (2ME) (Fluka). An excess of 5 wt% lead acetate trihydrate was added in order to compensate the loss of lead during heat treatment. Dimethylformamide was used as drying agent [12]. The preparation of precursor solution was carried out in an inert atmosphere (N₂). Two types of substrates were used: optically polished stainless steel (SS) and platinum deposited on silicon wafer (Pt/Si).

Precursor solution were thrown on the substrate by spin-coating at 2500 rpm for 60 s. The spin-coating was repeated several times in the following sequence: firstly two layers of PbTiO₃ (PT) solution (with an excess of 10 wt% lead acetate trihydrate) and thereafter 10 layers of PZT solution. After each spin-coating process the film was heated (pyrolysed) for 2 min. at 200 °C and 4 min. at 400 °C in order to eliminate the organic components. A thermal annealing was performed at 650 °C for 30 min after the first two layers stacking, for 15 min., after 7-layer stacking and, finally, the whole film was crystallized in air at 650 °C for 30 min., with a rate of 20°C/min. PZT films of the same composition were deposited on the platinum coated silicon, in identical conditions and subjected to the same heat treatment. All the thermal procedures were performed in normal atmosphere.

2.2. Structural measurements

The films were investigated by X-ray diffraction (XRD) and atomic force microscopy. A TUR M-62 diffractometer provided with a copper target ($\lambda = 1.54178 \text{ \AA}$) was used in the measurements. The X-ray diffraction patterns were recorded by collecting the scattered X-ray quanta at equi-spaced angular position (0.02°) in the range $8-24^\circ$. A reference aluminium plate was used in calibration. The data were processed by computer.

3. Results

The X-ray diffraction patterns of both types of films are shown in Fig. 1. The peak at 20° (θ) (Fig. 1b) originates from the well oriented (111) Pt crystallites on the substrate.

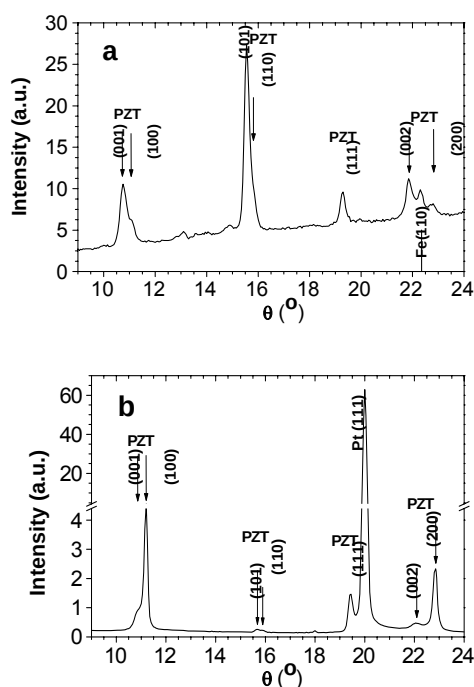


Fig. 1. The X-ray diffraction of PZT films deposited a) on SS; b) on Pt/Si.

The structure of the films corresponds to tetragonal perovskite and this feature is revealed by the splitting of the diffraction lines: (001)/(100), (101)/(110), (002)/(200). The tetragonal splitting was calculated from the position of the twin peaks. For the films deposited on SS substrate $(\Delta c/c)_{(SS)} = 3.55 \%$ (average from (001)/(100) and (002)/(200) lines) while for the film deposited on Pt/Si substrate $(\Delta c/c)_{(Pt)} = 3.32 \%$ (average from (001)/(100) and (002)/(200) lines).

A remarkable feature of the diagrams is related to the intensities of the diffraction lines. In the case of the PZT film deposited on SS substrate the (101) line is very high while (001)/(100) pair and (002)/(200) pair exhibit low intensity. This speaks in favour of a good preferential

orientation of the film crystallites with the plane (101) parallel to the substrate.

For PZT films deposited on Pt/Si the diffraction lines show very low intensities, while the (001)/(100) pair and (002)/(200) pair exhibits high intensities. This fact demonstrates a very good orientation along the (100) crystallographic planes. We have determined the average crystallite size, D , and the internal stress, η , for the direction perpendicular to the (h00) planes, which are oriented along the substrate. The results are:

a) for the film deposited on SS substrate: $\eta_{(001)} = 0.98 \%$ and $D_{(001)} = 27.1 \text{ nm}$

b) for the film deposited on Pt/Si substrate: $\eta_{(h00)} = 1.05 \%$ and $D_{(h00)} = 88.0 \text{ nm}$.

The roughness evaluated from the AFM analysis is higher for the PZT film deposited on SS substrate ($60 \div 100 \text{ nm}$) than for the film deposited on Pt/Si ($3 \div 5 \text{ nm}$). This fact could be explained by excessive growth of large single-crystal particles in PZT film deposited on SS, as deduced from the SEM analysis.

4. Discussion

The sol-gel method [13] has been extensively used for the deposition of PZT films because it allows to get stoichiometric compositions at relatively low crystallization temperatures ($500^\circ - 700^\circ \text{C}$). In case of deposition on metal substrates the crystallization temperature should be low enough to avoid inter-diffusion and reaction between the substrate and film. In order to promote crystallization a seed layer is used. We have deposited two layers of PT (lead titanate) directly on the substrate as a seed for crystallization. The PT has been crystallized by heat treatment (after [14]) before the ten PZT layers were added.

The stainless steel substrate was analysed by X-ray diffraction. The diffraction pattern is shown in Fig. 5. Two phases were revealed: the main ferrite phase ($\alpha\text{-Fe}$) and a minor phase of austenite (Fe_3C). We have calculated the percent of austenite in steel and got 17.4 mol%.

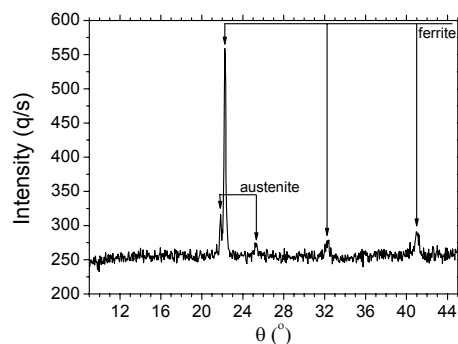


Fig. 5. X-ray diffraction pattern of austenitic steel used as substrate for PZT film.

The Pt/Si substrate consists of (111) oriented platinum crystallites on silicon wafer as evidenced on X-ray diffraction diagram.

A careful analysis of the diffraction pattern of PZT deposited on stainless steel substrate revealed several small peaks due to a very small amount of a second crystallographical phase. The peak situated at $\sim 14.5^\circ$ could be ascribed to the pyrochlore phase, which sometimes appears during PZT preparation at low firing temperatures.

The pyrochlore $\text{Pb}_2(\text{Zr,Ti})_2\text{O}_{6-8}$, a paraelectric phase [15] is formed at temperatures below those of crystallisation in the perovskite phase. The pyrochlore phase, even in small amount, leads to worse ferroelectric properties [16].

In the case of our PZT films the pyrochlore phase does appear only when the substrate is SS (Figure 1a). The presence of pyrochlore reduces the ferroelectric properties: the remanent polarization is reduced and the coercive field is enhanced. The presence of pyrochlore-type phase is indirectly confirmed by the appearance of "rosette" structure in microscopy images on PZT deposited on SS. The Rosette structures contain pyrochlore phase [15]. In the literature is reported that if PZT is supported on stainless steel (coated by SrRuO_3) at 630°C for 1 minute the pyrochlore phase is not visible [13]. Zhou et al [14] have shown that PZT spin-coated on SS and annealed at 550°C for 1 h, no pyrochlore phase was detected by X-ray diffraction. For 0-3 composite samples deposited on SS the pyrochlore phase is still seen for annealing at 550°C but vanishes at annealing temperatures of 650°C .

Pintilie et al. [20] have shown that the electrical and dielectric results on PZT thin films can be explained in the frame of a model which considers the PZT film as a wide-gap semiconductor with Schottky contacts and electrically active traps.

In our study it is remarkable the orientation effect of the substrate on PZT film structure. The (110) orientation is specific to the deposition on SS while (200) orientation is specific to the deposition on Pt/Si. In a previous paper the structure of PZT crystallites is sensitive to external parameters. E. g. high electric field applied perpendicular to PZT bulk pellets (polycrystalline) induces a transition from orthorhombic to tetragonal phase in the composition situated at the morphotropic phase boundary [21]. In the case reported in this paper the substrate strongly influences the structural properties of the PZT film and the orientation effect of the substrate on the PZT crystallites is dominant.

4. Conclusions

The structure of PZT films deposited on SS and Pt/Si and crystallized by specific heat treatment have been investigated. The orientation of PZT crystallites on the SS substrate is (101) and (100) for the film deposited on Pt/Si substrate. The crystallite size and roughness of the films are larger in PZT deposited on the SS than in PZT deposited on Pt/Si substrate.

The SS deposited film contains a minor pyrochlore phase that explains their diminished ferroelectric properties (lower remanent polarization and higher coercive field) if compared to those of the PZT film deposited on Pt/Si substrate.

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