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Crystallization behaviour and phase coexistence at morphotrophic phase boundaries in PZT thin films prepared by sol–gel processing

V. ONTALUS, C. COBIANU
Institute of Microtechnology, P.O. Box 38-160, Bucharest 72 225, Romania
F. VASILIU
Institute for Physics and Technology of Materials, P.O. Box MG-7, R 76900, Bucharest-Magurele, Romania
C. PARLOG
Institute of Physical Chemistry, Splaiul Independentei 202, Bucharest 77208, Romania

$Pb(Zr_{0.53}Ti_{0.47})O_3$ (PZT) thin films, prepared by sol–gel techniques and deposited on to $Si/SiO_2/Ti/Pt$ substrates, have been subjected to thermal annealing in a range of temperatures from 550–800 °C. The crystallization behaviour and phase coexistence (tetragonal and rhombohedral) were studied by X-ray diffraction. According to the values of the {1 1 0} peak intensity and {1 1 0} peak values, the crystallization full-width at half-maximum was more complete at higher temperatures (750, 800 °C). At a fixed Zr/Ti ratio close to the morphotropic phase boundary, the lattice parameters of the two phases changed with the annealing temperature. However, the tetragonality degree had relatively low values and the angular rhombohedral distortion was associated with a narrow angular range. The phase coexistence and the variation of the lattice parameters could be explained by the titanium diffusion through the platinum layer. Thus the formation of a {0 1 1} titanium rich layer at Pt–PZT interface will supply a titanium excess for the nucleation and growth of textured PZT grains.

1. Introduction

Ferroelectric thin films are playing a growing role as basic elements in a variety of solid-state devices, the major interest being in the non-volatile memories and actuators. $Pb(Zr_xTi_{1-x})O_3$ (PZT) films are being extensively studied as one of the most promising materials for these applications.

In recent years, many fabrication techniques have already been used to grow perovskite-type materials such as $Pb(Zr_xTi_{1-x})O_3$ (PZT) thin films. Among them, solution techniques offer a versatile and inexpensive alternative to the physical methods based on vapour phase deposition or r.f. sputtering [1, 2].

In order to obtain the PZT films consistent with their use in I.C. they must have a uniform composition and thickness as well as good structural homogeneity.

Sol–gel processing is one of the most appealing methods for the preparation of PZT and other ferroelectric films. This method enables better control of chemical composition, particle-size distribution and morphology, provides an intimate contact and short diffusion path length between solid reactants and requires relatively low processing temperatures.

The homogeneity of PZT thin films deposited by the sol–gel process on platinum–titanium coated silicon substrates, and the interfacial reactions of the substrate with the ferroelectric thin films at elevated temperatures, are of major concern in device fabrication.

Ternary systems like $Pb(Zr_xTi_{1-x})O_3$ must be carefully studied close to the monotrophic phase boundary (MPB) because crystallization competes with phase separation into binary systems. Although it was often stated that an MPB appears for bulk ceramics at a specific Zr/Ti ratio of about 53/47, [3–6], the coexistence of the two ferroelectric phases (rhombohedral and tetragonal) has been proved to occur in a finite compositional range around the MPB. These compositions have low coercive field strength and significant remnant polarization.

In a recent paper, [7], the influence of zirconium concentration on the lattice parameters of the two phases occurring in $Pb(Zr_xTi_{1-x})O_3$ films prepared by sol–gel and metallo-organic decomposition (MOD) processes, has been studied. The present paper establishes the influence of annealing temperature on the

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crystalline structure of the two coexistent phases in a PZT solid solution with $x = 0.53$. This composition was previously delineated as pertaining to a coexistence range of tetragonal and rhombohedral phases for bulk ceramics [8].

2. Experimental procedure

The lead zirconate titanate precursor solution was prepared using lead acetate trihydrate, zirconium propoxide (70% in propanol), tetraisopropyl titanate and methoxyethanol as solvent.

Lead acetate trihydrate (5% excess to compensate PbO losses during annealing) was dissolved easily in methoxyethanol under heating, and the solution was distilled for the removal of water. The solution was refluxed for complexation and then distilled for the elimination of by-products (alkylacetates). Zirconium propoxide and titanium isopropyl were added and the solution was refluxed and distilled up to 124 °C, several times, until the product eliminated after distillation was pure methoxyethanol as shown by gas chromatography coupled with mass spectrometry.

Finally the sol was diluted to 0.5 M by adding methoxyethanol. The solution was yellow and proved to be stable for at least 12 months.

Prior to deposition, water was added in the solution to start hydrolysis. The solution was stirred for an hour and then filtered with a 0.2 μm syringe filter.

The films were fabricated by spin-casting at 2000 r.p.m. on a photoresist-spinner. For PZT deposition, $Si/SiO_2/Ti/Pt$ sandwiches were used. Substrates were cleaned with trichlorethylene–acetone–methanol. To achieve convenient thickness, multiple depositions were performed with intermediate drying steps of 10 min at 150 °C in ambient atmosphere. For six subsequent depositions, a thickness of 1.2 μm, after the final firing, was determined.

The heat treatments were performed in a quartz furnace tube in an oxygen flow. Specimens were heat treated successively, for 30 min, in a range of temperatures between 550 and 800 °C in steps of 50 °C. It must be noted that a specimen subject to discussion at a certain temperature has been subjected to all thermal treatments performed at lower temperatures.

X-ray diffraction (XRD) analyses were carried out to determine the crystallinity and the crystal structure, the crystallographic orientation, the lattice constants and the grain size for the PZT films. θ–2θ X-ray powder diffraction scans were performed with CuK_α radiation using a computer-controlled URD-6 (Zeiss) diffractometer. The films were scanned in 2θ from 10°–60° with a step size of 0.01° (count time for d spacing 10 s).

3. Results and discussion

The PZT film annealed at 550 °C was still amorphous. The perovskite phase was observed in the films annealed at temperatures of 600–800 °C. PZT films thermally treated above 750 °C developed a $\{110\}$ texture.

The intensities of the peaks in the XRD pattern for the 800 °C sample were used as 100% crystallized intensity values (i.e. I_0) and the fraction of perovskite phase was determined by the ratio I/I_0 of the $\{110\}$ peak intensity, I, of perovskite at a given temperature to that of I_0 specified above. The variation of I/I_0 ratio and full-width at half-maximum (FWHM) of the $\{100\}$ peak is shown in Fig. 1.

Crystallization was more complete at higher temperatures (750 and 800 °C). Thus, an increase of I/I_0 in a ratio 1:3 was registered for the change of annealing temperature from 750 to 800 °C. The value of FWHM $\{110\}$ decreased linearly with the annealing temperature, implying a gradual increase of crystallite size.

The crystallite size evaluated from the FWHM $\{110\}$ peak, assuming no lattice strain, led to a value of about 23 nm for the 800 °C specimen. This value is consistent with those given by other authors for $Pb(Zr_{0.5}Ti_{0.5})O_3$ powders prepared via acetate-based precursor solutions [9] estimated from the $\{111\}$ reflection or for $Pb(Zr_{0.53}Ti_{0.47})O_3$ films fabricated via sol–gel and MOD processes [7] using a $\{100\}$ reflection.

Although we focus on a composition with Zr/Ti = 53/47, close to the MPB, by an accurate scanning in 2θ from 10°–60° with a step size of 0.01°, we have obtained a splitting of the main maxima $\{100\}$, $\{110\}$, $\{200\}$ into triplets which indicates the coexistence of both phases: tetragonal and rhombohedral.

Doublets of type $\{00l\}$, $\{l00\}$, such as $\{001\}_T$, $\{100\}_T$ or $\{002\}_T$, $\{200\}_T$, and $\{h0l\}$, $\{l0h\}$ such as $\{102\}_T$, $\{20\bar{1}\}_T$, and $\{h0l\}$, $\{hl0\}$ such as $\{101\}_T$, $\{110\}_T$, belonging to the tetragonal phase, enclose the homologous rhombohedral line $\{l00\}$ *or* $\{h0l\}$ in their middle forming triplets.

The lattice parameters corresponding to both phases were calculated, using the d spacings associated to the above mentioned lines.

The variation of the lattice parameters a_T, c_T (tetragonal phase) and a_R, α_R (rhombohedral phase) as a function of annealing temperature is presented in Figs 2 and 3. Between 650 and 800 °C, the a_R parameter increased linearly whereas the a_T parameter is relatively constant up to 750 °C but an important increase is observed at 800 °C. The c_T parameter exhibited the opposite behaviour, i.e. after an increase up to 750 °C its value became saturated at 800 °C. The rhombohedral parameter α_R is almost constant.

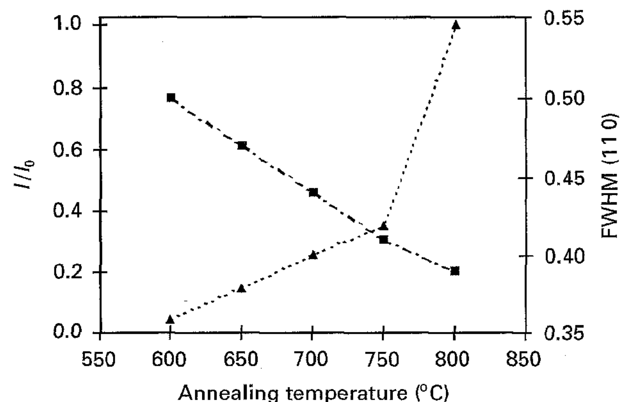

Figure 1 (▲) I/I_0 and (■) FWHM $\{110\}$ of PZT films as a function of the annealing temperature.

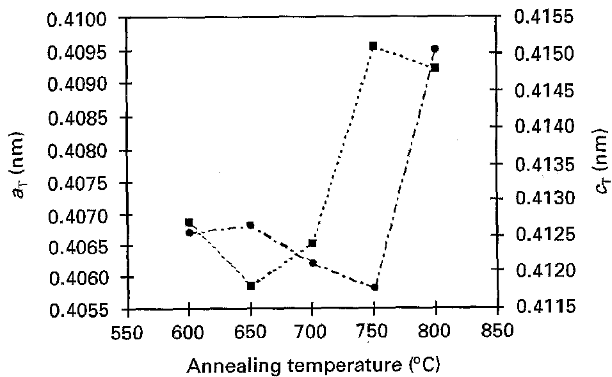

Figure 2 Variation of lattice parameters (●) a_T, (■) c_T for tetragonal phase as a function of annealing temperature.

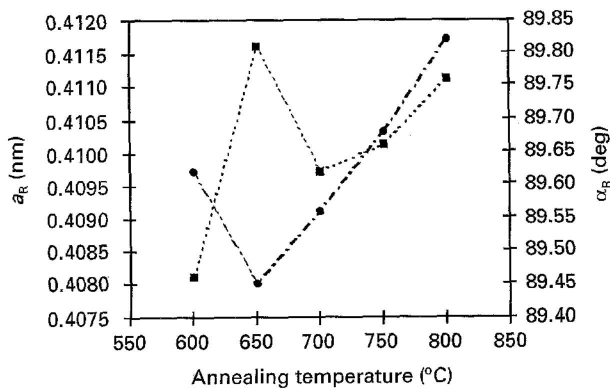

Figure 3 Variation of lattice parameters (●) a_R, (■) α_R for rhombohedral phase as a function of annealing temperature.

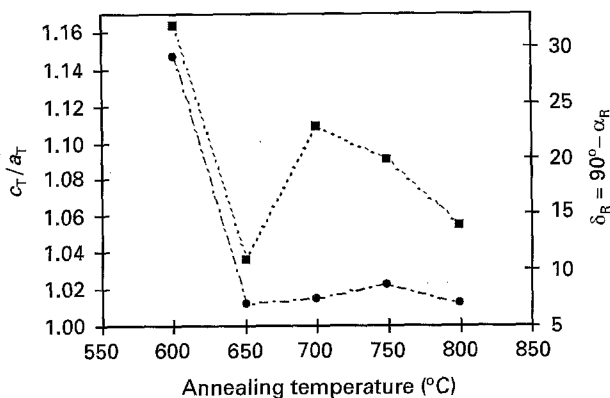

Figure 4 (●) Unit cell tetragonal distortion c_T/a_T and (■) rhombohedral angular distortion $\delta_R = 90° - \alpha_R$ versus annealing temperature for PZT films.

Fig. 4 presents the variation of the distortions from an ideal perovskite cell for the tetragonal and rhombohedral unit cell as a function of the annealing temperature. The axial ratio c_T/a_T, indicating the degree of tetragonality, increases weakly from 1.014 to 1.023 in the 650–750 °C temperature range but decreases to the initial value in the last annealing step (800 °C). The angular rhombohedral distortion $\delta = 90° - \alpha_r$ generally does not exceed 0.5°.

Therefore, for a fixed Zr/Ti ratio close to MPB, the lattice parameters of both phases change with the annealing temperature. Whereas a_R and δ_R are in agreement with reported values [5, 7, 8], the tetragonal c_T and a_T parameters have values which are higher by about 0.7% than the reported values for PZT films and bulk ceramics. This fact could be correlated with the dependence of titanium diffusion rate upon the annealing temperature. It is interesting however, that the tetragonality degree takes relatively low values and the rhombohedral distortion is confined to a narrow angular range.

The phase coexistence in the MPB region as well as the dependence of the lattice parameters on the annealing temperature can be explained by the titanium diffusion through the platinum layer. A {0 1 1} titanium-rich layer is formed at the Pt–PZT interface. The titanium-rich layer supplies titanium in excess for the nucleation of the tetragonal phase with a {0 1 1} texture [10], or {1 1 0} texture [11]. Later, on this interface layer, new PZT grains, having only a {1 1 0} texture were developed, as shown in a previous work [12] and also in our experiments.

At the microscopic level, the titanium and lead concentration and temperature gradients would induce significant deviation from the initially chosen stoichiometry. Thus, the annealing temperature is expected to be an important technological parameter, which through microcompositional fluctuations, determines the width of the phase coexistence range.

4. Conclusion

$Pb(Zr_{0.53}Ti_{0.47})O_3$ thin films prepared by sol–gel techniques and deposited on to $Si/SiO_2/Ti/Pt$ substrate, subjected to thermal annealing in a 550–800 °C temperature range, were apparently single-phase perovskite. A careful X-ray diffraction analysis proved a phase coexistence (tetragonal and rhombohedral) at a fixed Zr/Ti ratio close to MPB. The lattice parameters of both phases changed as a function of annealing temperature, especially in the last treatment step, but the tetragonality degree takes relatively low values and the rhombohedral distortion is confined to a narrow angular range. The annealing temperature is expected to influence the titanium diffusion through the platinum layer, which could play an essential role in the nucleation and growth of PZT films. The significant deviations from the initially chosen stoichiometry (especially for titanium and lead), dependent upon the annealing temperature, could induce an increase of the phase coexistence range width.

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