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Influence of oxygen flow on crystallization and morphology of PLZT thin films

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Abstract

PLZT thin films were prepared by a dip coating process using Pechini's method, also known as polymeric precursor method. The PLZT solution was obtained from a mixture of the individual cation solutions and the process to prepare each solution is based on metallic citrate polymerization. The viscosity of the PLZT solution was adjusted at 40 cP while the ionic concentration was adjusted at 0.1 M. PLZT solutions were deposited on silicon (100) and platinum coated silicon (100) substrates with withdrawal speed at 5 mm/min. The coated substrates were thermally treated with a heating rate of 1 °C/min up to 300 °C and 5 °C/min up to 650 °C in order to obtain homogeneous and cracks free films. The influence of oxygen flow on crystallization and morphology of PLZT (9/65/35) thin film is discussed. © 2002 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

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1. Introduction

Much attention has been given to the application of ferroelectric thin films, such as $PbTiO_3$, $Pb(Zr,Ti)O_3$ (PZT), and $(Pb,La)(Zr,Ti)O_3$ (PLZT), in dynamic random access memories (DRAM) and in nonvolatile ferroelectric memories (FRAM) [1–4]. Conventionally, polycrystalline ferroelectric thin films were grown on Pt-coated Si substrates. It was observed that the interaction which occured on film/Pt interfaces degraded the film performance substantially [5–6].

Due to the high temperatures required for the formation of the ferroelectric perovskite phase, the production of PLZT thin film has not proved easy and, at present, a wide range of thin films synthesis techniques, such as MOCVD, sol-gel, RF magnetron, ion beam sputtering and laser ablation are subject to intensive research [7]. Solution-based methods have been widely used to prepare thin oxide films [8,9]. The most frequently method used in the preparation of the solution can be grouped into two categories: (1) the sol-gel process and (2) metallorganic decomposition. There are essentially three different kinds of sol-gel processes such as: colloidal sol-gel process, derivation of inorganic polymeric gels from organometallic compounds and gel routes involving formation of an organic polymeric complex (polymeric precursor method). The polymeric precursor method can be divided into two groups [10]. The first is in situ polymerization of organometallic monomers and the second involves the preparation of a viscous solution system containing metal ions, polymers and a solvent.

This viscous solution can be easily converted into a thermoplastic gel at high polymer concentrations. The in situ polymeric precursors method has been extensively used to obtain ceramic powders with small particle size and homogeneous monophase system [11,12]. This method was originally developed by Pechini [13] and is based on the chelation of a metallic cation by a carboxylic acid, such as citric acid, and further polymerization promoted by the addition of ethylene glycol and consequent polyesterification. However, this method has not been much used to obtain thin films. Liu and Wang reported the deposition of $La_{1-z}Sr_zCo_{1-y}Fe_yO_{3-y}$ on dense or porous substrates using the polymeric precursors method [14]. They obtained nonporous and uniform crack-free film with 400 nm of

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thickness with a single dip. According to Liu and Wang the most important parameter is the citric acid/metal ratio in controlling the deposition process.

An intrinsic problem of the solution-based methods is the large volume change that takes place when the liquid solution transforms into the thin solid inorganic oxide film. This change of volume can cause cracking in the film during the pyrolysis and sintering process. In general, the appearance of cracks is lower in thinner films. The main reason for this is that in the thinner coatings the adhesion on the interface, film–substrate, is higher and lateral shrinkage of film is suppressed. When the critical value of the thickness of films is reached, the cracks could not be avoided. To obtain crack-free films it is necessary to control the parameters including characteristics of the solution such as: viscosity and ionic concentration, substrate-film adhesion, heating conditions, atmosphere, substrate and withdrawal speed. The differences between the thermal expansion coefficients of the film and the substrate have also influenced this behavior [15].

It has been reported that the crystallization process is affected by variables such as composition (Zr/Ti ratio), substrate, annealing temperature, atmosphere, drying condition [16–21]. It was noticed that the oxygen atmosphere has a prominent influence on the crystallization process of PLZT.

The crystallization process developed at a lower temperature results in Ti-rich PLZT compositions and at higher temperatures results in Zr-rich PLZT compositions [22]. Films annealed at higher temperatures can lead to a secondary phase Pb-deficient, Pb (Ti, Zr)$_3$O$_7$. Higher temperatures also favor the interfacial reactions with silicon-based substrates. Much effort has been expended on the processing of PLZT to eliminate the undesirable phase on the composition of thin films. Thus, the control of atmosphere and temperature are critical factors in the development of single-phase perovskite material. The effect of oxygen atmosphere on the crystallization of the PLZT phase is to prevent the volatility of PbO, control the stoichiometry and improve the electric properties of the film [23]. Besides that, the use of higher atmosphere flows was found to affect the microstructure of the films decreasing the grain size and increasing the content of perovskite phase [24].

In general, the choice of substrate depends on the intended application. To investigate the integration of PLZT materials in semiconductor-based-devices, a silicon substrate is used [25].

Having in mind that PLZT (X/65/35) with La content in the interval of 8–10 mol% shows characteristics as high transparency and relaxor behavior, the main objective of this work is to verify the effect of oxygen flow on crystallization and morphology of PLZT (9/65/35) thin films deposited by a dip coating process using a polymeric solution [26].

2. Experimental procedure

The composition of PLZT used in this study was 9/65/35 with formula $Pb_{0.91}La_{0.09}(Zr_{0.65}Ti_{0.35})O_3$. Zirconium *n*-propoxide (Aldrich), titanium isopropoxide (Hulls AG), hydrated lanthanum carbonate (Aldrich) and lead acetate (Merck) were used as raw materials. The precursor solutions of zirconium, titanium, lanthanum and lead were prepared by adding the raw materials in ethylene glycol and citric acid with heating and stirring. Appropriate quantities of Zr, Ti, Pb and La solutions were mixed and homogeneized by stirring at 90 °C. The viscosity of the solution was adjusted at 40 cP by the addition of water and measured by Brookfield viscosimeter. To obtain homogeneous and crack-free films the PLZT solution was deposited by a dip coating process, controlling the withdrawal speed of substrate from the solution at 5 mm/min. The heating rate used was at 1 °C/min up to 300 °C and 5 °C/min up to 650 °C. PLZT films obtained from polymeric solution were deposited on silicon (100) and platinum coated silicon (100) substrates and pre-annealed at 90 °C in a hot plate for polyesterification, elimination of water and excess of ethylene glycol. Films with 1, 2 and 3 layers were prepared with each layer annealed at 650 °C. To study the effect of oxygen atmosphere on the crystallization, the films were annealed in static oxygen atmosphere and dynamic oxygen flow of 20, 40 and 60 cm^3/min.

Phase analysis of the films were performed at room temperature using a X-ray diffractometer (Siemens D-5000). The morphology of the annealed films was studied using scanning electron microscopy (Topcon SM-300). The PLZT film surfaces were analyzed without any cover or special preparation by incidence of secondary electrons while the thickness was measured from the transversal section. In the last case back scattering electrons were used. The thickness results obtained from SEM represent an average value of three measurements. The standard deviation for each value of thickness measured is ±4%. The roughness and grain size were measured by atomic force microscopy (Nanoscope IIIa).

3. Results and discussion

It is well known that the properties of material are significantly affected by the crystallographic orientation of thin film which is controlled by the orientation of the underlying layer, film thickness and atmosphere flow. In general, it is known that PZT and PLZT films deposited on silicon and platinum coated silicon substrates have (111) preferential orientation because in this plane the interatomic distances of the material and substrate are very close [27].

The X-ray diffraction data obtained from 1, 2 and 3 layers of PLZT thin films deposited on silicon (100)

substrates and annealed at 650 °C for 3 h in static oxygen atmosphere and dynamic oxygen flow are shown in Fig. 1. The peaks located at $2\theta = 22$, 31.3, 38 and 44.78° corresponds to polycrystalline PLZT phase for films annealed in static oxygen atmosphere (Fig. 1a). It was also observed an increase of peak intensities with the increase of film thickness. The pyrochlore phase was only observed for films with three layers [Fig. 1a curve (c)]. This indicates that for films deposited on silicon (100) substrates and annealed in static oxygen atmosphere the presence of pyrochlore phase is related to the amount of PLZT deposited on the substrate surface (Table 1). It can also be concluded that the static oxygen atmosphere favored the crystallization of polycrystalline PLZT phase.

Films annealed in dynamic oxygen atmosphere showed preferential orientation on the direction (111) and (200) of PLZT phase, as well a presence of small amount of pyrochlore phase (Fig. 1b–d). Evidently, the presence of pyrochlore phase is independent of number of layers. The pyrochlore phase was formed as a result of PbO evaporation during the annealing. Otherwise, because the grains of pyrochlore phase were quite smaller compared to the grains of PLZT (~60 nm), it was very difficult to identify those grains by scanning electron microscopy (Fig. 3). This phenomenon was also noticed for sintered PZN ceramics obtained by polymeric precursor process and results in the relatively small pyrochlore grains compared to PLZT [28]. Thus, the appearance of pyrochlore phase can be avoided decreasing the temperature of thermal treatment [26].

The obtained results suggest that the oxygen atmosphere flow during annealing has a strong influence on the formation of PLZT crystalline phase. The oxygen flow promotes the decomposition of the organic material caused by an exothermic reaction favouring the crystallization from substrate surface. Independently of the number of deposited layers, the presence of oxygen favored the crystallization of PLZT phase with preferential orientation on directions (111) and (200), (Fig. 1b–d) besides the presence of small amounts of pyrochlore phase. On the other hand, the preferential

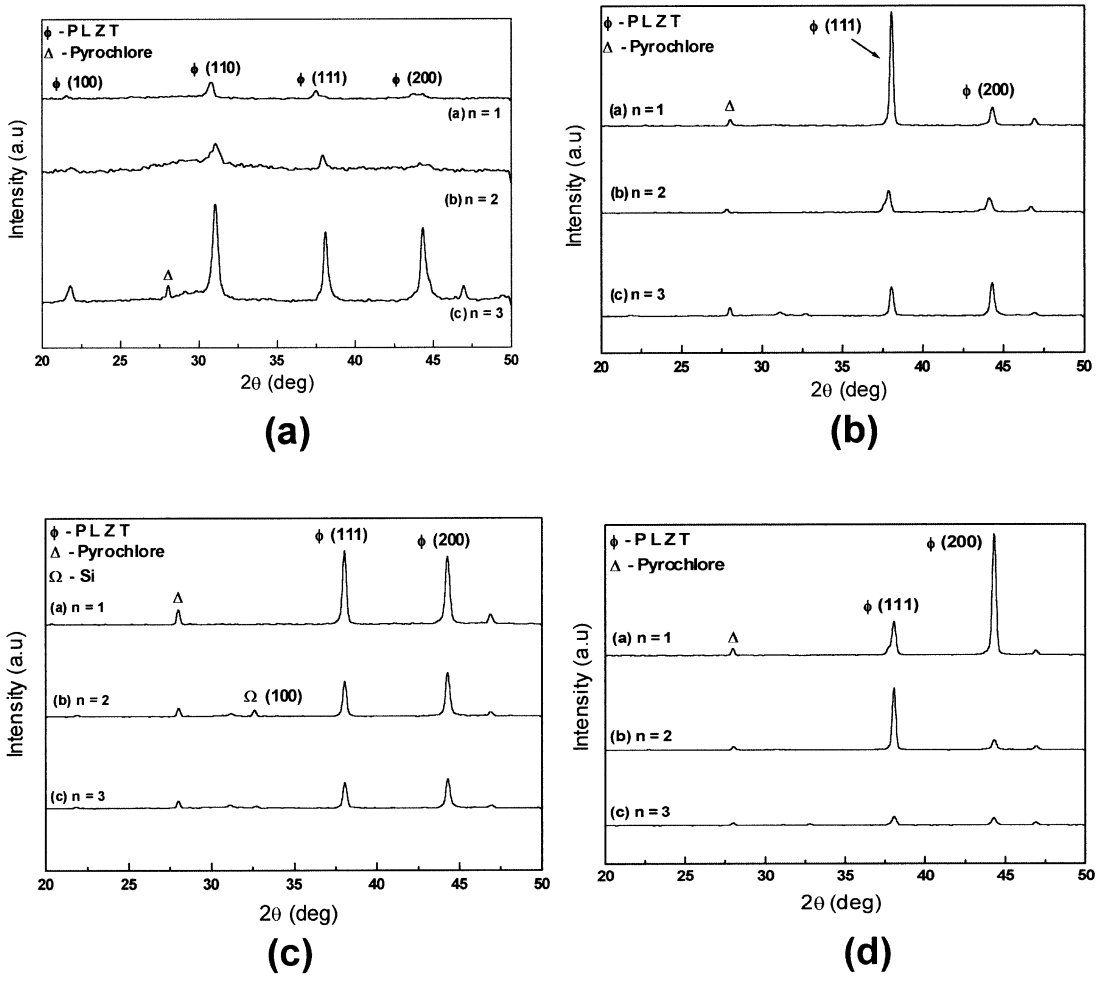

Fig. 1. X-ray pattern of PLZT thin films ($\eta = 40$ cP) deposited on silicon substrate (100) in different number of layers and annealed at 650 °C for 3 h with oxygen flow atmosphere of: (a) static oxygen flow, (b) 20 cm^3/min, (c) 40 cm^3/min and (d) 60 cm^3/min.

orientation is more evident for the PLZT films with one layer than for two or three layers (Fig. 1b–d). These results indicate that the crystallization process starts from the surface of substrate which possess oriented planes with lower energy for the crystallization of PLZT phase. It can also be observed that the increase of oxygen flow changes the preferential orientation in the direction (111)–(200). The decomposition of organic material is accelerated and the crystallization process starts from the surface of film which does not possess oriented planes. Consequently, the crystallization of PLZT films is not influenced by substrate with oriented planes. The formation of pyrochlore phase observed for 1, 2 and 3 layers resulted from the volatilization of lead-oxide accelerated by the oxygen flow.

Table 1
Thickness vs number of layers (oxygen flow of 60 cm^3/min)

Number of layers	Substrate	Atmosphere	Thickness (nm)
1	Si (100)	Static	90
2	Si (100)	Static	150
3	Si (100)	Static	195
1	Si (100)	Dynamic oxygen	75
2	Si (100)	Dynamic oxygen	100
3	Si (100)	Dynamic oxygen	165
1	Si/Ti/Pt (100)	Static	95
2	Si/Ti/Pt (100)	Static	107
3	Si/Ti/Pt (100)	Static	125
1	Si/Ti/Pt (100)	Dynamic oxygen	83
2	Si/Ti/Pt (100)	Dynamic oxygen	102
3	Si/Ti/Pt (100)	Dynamic oxygen	126

The X-ray diffraction data obtained from 1, 2 and 3 layers of PLZT thin films deposited on platinum coated silicon (100) substrates and annealed at 650 °C for 3 h in static oxygen flow and dynamic oxygen flow are shown in Fig. 2. Characteristic peak for platinum coated silicon (100) substrates was observed in the range of $38° < 2\theta < 41°$.

The peak related to polycrystalline PLZT phase at $2\theta = 31.3°$ was observed for films annealed in static oxygen and dynamic oxygen, Fig. 2a–d. Films with three layers annealed in oxygen atmosphere showed the

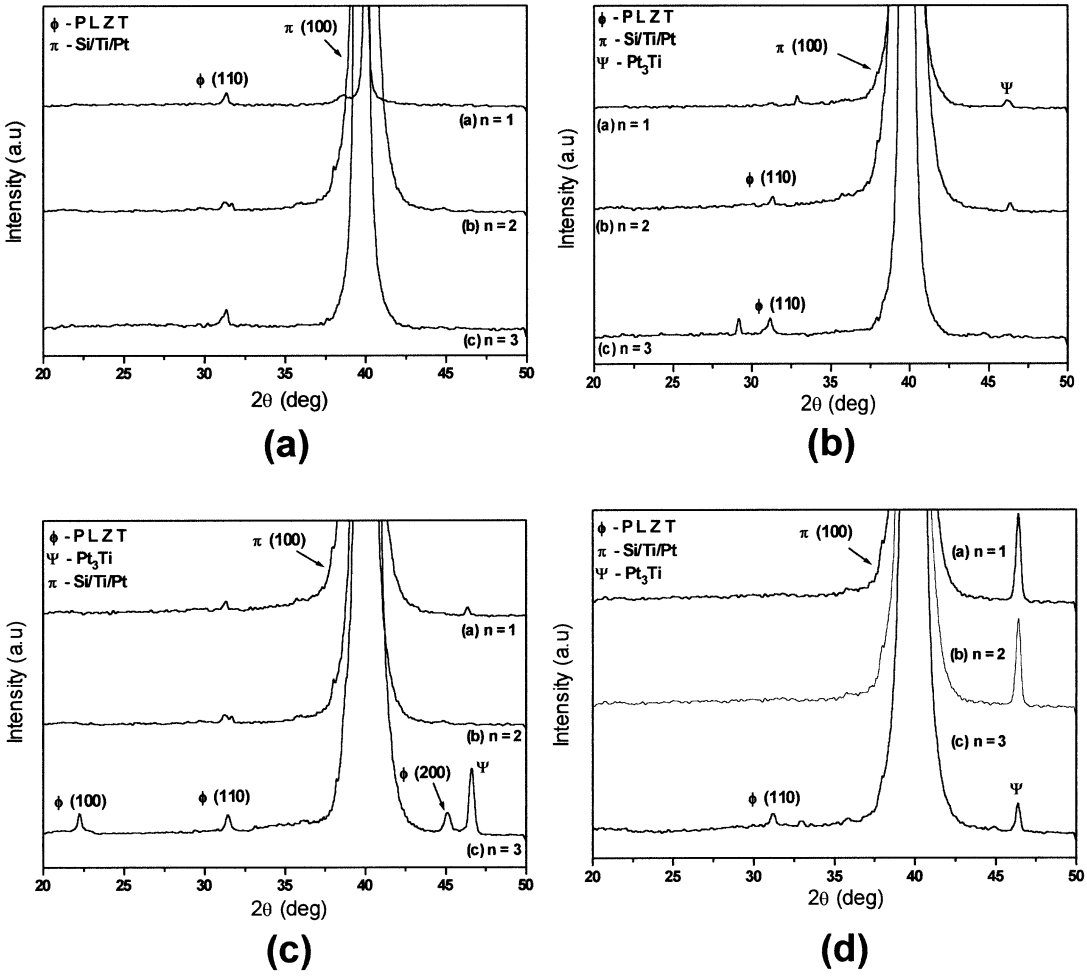

Fig. 2. X-ray pattern of PLZT thin films ($\eta = 40$ cP) deposited on platinum coated silicon substrate (100) in different number of layers and annealed at 650 °C for 3 h with oxygen flow atmosphere of: (a) static oxygen flow, (b) 20 cm^3/min, (c) 40 cm^3/min and (d) 60 cm^3/min.

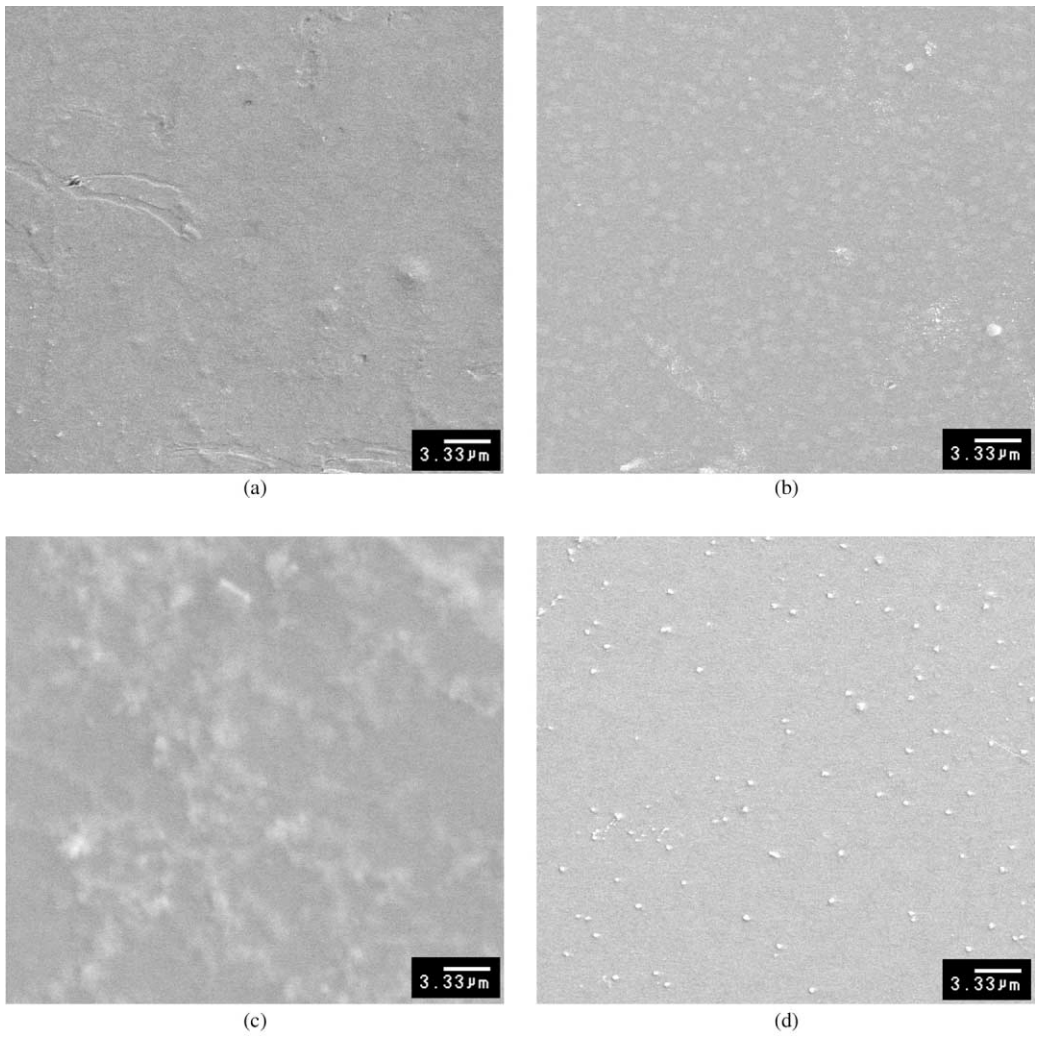

Fig. 3. SEM micrographs of PLZT film surfaces ($\eta = 40$ cP) deposited on silicon (100) and platinum coated silicon (100) substrates with speed of 5 mm/min, heating rate of 5 °C/min and annealed at 650 °C for 3 h at different atmospheres: (a) static oxygen flow, (b) oxygen flow of 60 cm^3/min, (c) static oxygen flow and (d) oxygen flow of 60 cm^3/min.

main peaks of PLZT phase at $2\theta = 22$ and 44.78° [Fig. 2b–d curve (c)]. A peak at $2\theta = 46°$ pointed to a reaction between platinum and titanium resulting in an intermetallic Pt_3Ti phase. This phase is favored in a dynamic oxygen atmosphere [Fig. 2b–d curve (a) and (c)]. It can be noticed (Fig. 2b–d) that the presence of secondary phase Pt_3Ti formed in the interface PLZT-film inhibits the PLZT growth in some preferential orientation [26].

The morphology of film surfaces obtained for three layers deposited on silicon (100) and platinum coated silicon (100) substrates annealed at 650 °C for 3 h are shown in Fig. 3. The surfaces of films deposited on silicon (100) substrate are homogeneous and uniform, (Fig. 3a and b).

Crack-free thin films were obtained on platinum coated silicon (100) substrate. Otherwise, it can be noticed other phases on the surface of films (Fig. 4a and b). These defects were apparently caused by differences in thermal properties (thermal expansion coefficient and heat capacity) of platinum (9×10^{-6} °C^{-1} and 0.1338 J/g°C) and PLZT film (5.6×10^{-6} °C^{-1} and 0.1045 J/g°C) and due to a reaction between platinum and titanium resulting in an intermetallic Pt_3Ti phase which is favored in oxygen atmosphere. These differences lead to a higher volatilization rate of organic materials and of the species with low vaporization temperature, like PbO. Contrary to that, for the silicon (100) substrate the thermal expansion coefficient and heat capacity (3×10^{-6} °C^{-1} and 0.0711 J/g°C) are lower than for PLZT film. Thus, it is able to form a homogeneous and regular surface of films.

The influence of oxygen flow on grain size and roughness of films obtained on silicon (100) and platinum coated silicon (100) substrates are shown in the Table 2 and Fig. 4. It was observed that independently of substrate used, films annealed in dynamic oxygen atmosphere show a more homogeneous surface compared

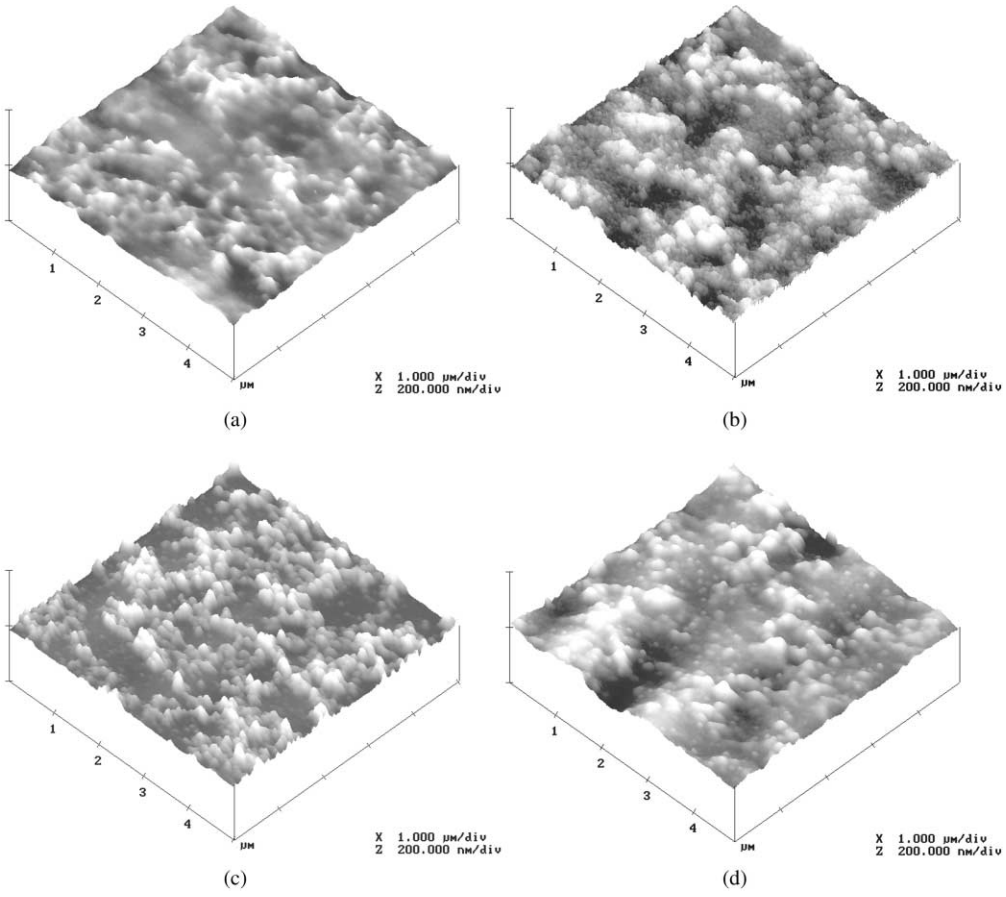

Fig. 4. AFM results of PLZT ($\eta = 40$ cP) films deposited on silicon (100) and platinum coated silicon (100) substrates with speed of 5 mm/min, heating rate of 5 °C/min and annealed at 650 °C for 3 h at different atmospheres: (a) static oxygen flow, (b) oxygen flow of 60 cm^3/min, (c) static oxygen flow, (d) oxygen flow of 60 cm^3/min.

Table 2
Grain size and roughness in dependence of oxygen flow

Substrate	Oxygen flow (cm^3/min)	Average grain size (nm)	Roughness (nm)
Si/Ti/Pt (100)	Static	107	5.6
Si/Ti/Pt (100)	20	31	0.7
Si/Ti/Pt (100)	40	44	1.5
Si/Ti/Pt (100)	60	70	4.5
Si (100)	Static	32	2.4
Si (100)	20	42	0.6
Si (100)	40	51	1.1
Si (100)	60	53	2.9

to the films annealed in static oxygen. This is due to the small thickness obtained for the films thermally treated in oxygen atmosphere favouring the redistribution of grains during annealing.

It was also observed that independently of the used substrate, the grain growth and roughness of the material increased with the increase of oxygen flow during the annealing. It can also be noticed that higher oxygen flow promotes the increase of the grain growth which results in a higher roughness. Having in mind that the control of roughness and grain size are important parameters for application of PLZT as electrooptic material, the deeper knowledge regarding the influence of atmosphere on the microstructure and crystallinity of PLZT thin films could obviously result in better quality of those films.

4. Conclusions

The PLZT thin films were obtained by organic citrate solutions deposited by dip coating on Si (100) and Si/Ti/Pt (100) substrates. It can be concluded that the static oxygen atmosphere favored the crystallization of polycrystalline PLZT phase while the dynamic oxygen atmosphere caused the preferential orientation on the direction (111) and (200) of PLZT phase.

The morphology of film surfaces deposited on silicon (100) are homogeneous and uniform while on platinum coated silicon (100) substrates the presence of other phases was caused by differences in thermal properties of PLZT and substrate.

The oxygen flow influences on the grain size and roughness of the PLZT thin films. Higher oxygen flows promotes an increase of the grain growth and roughness.

The most convenient condition for the preparation of PLZT thin films with lower roughness and larger grain size is using oxygen flow of 40 cm^3/min.

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