Effects of annealing on the crystallization and roughness of PLZT thin films

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Abstract

Lead lanthanum zirconate titanate (PLZT) thin films with stoichiometry \(9/65/35\) were prepared by a dip-coating process using a polymeric organic solution. The solution viscosity was adjusted in the range of 15–56 cP. Silicon (100) substrates were previously cleaned and then immersed in the solution. The withdrawal speed of substrate from the solution was adjusted within a range of 5 to 20 mm/min. The coated substrates were thermally treated in the 450–700°C temperature range. Surface roughness and crystallization of these films are strongly dependent on the annealing conditions. Infrared and X-ray diffraction data for PLZT powders heat-treated at 650°C for 3 h show that the material is free of carbonate phases and crystalline. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Lead-based ferroelectric thin films such as \(\text{Pb}_{1-x}\text{La}_x(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3\) have attracted much attention due to their great potential for application as pyroelectric detectors, piezoelectric vibrators, electrooptic devices and non-volatile random access memories [1,2]. Due to the high dielectric constant, these materials can be used in the future for (ICs), but for this they need to fulfill several requirements.

The basic requirements for high dielectric constant materials are low leakage currents to provide long retention time and good fatigue properties for long time reliability. The preparation of lead lanthanum zirconate titanate (PLZT) thin films on Si substrate are, however, extremely difficult due to the frequent formation of the pyrochlore phase [3] and Pb-deficient secondary phases [4]. Polycrystalline ferroelectric thin films are conventionally grown on a Pt-coated Si substrate, however, the high-angle grain boundaries in ferroelectric thin films and the non-ideal interfaces between the ferroelectric layer and metal deteriorate the device performance, causing aging and fatigue [5,6].

PLZT thin films have been produced by several different techniques, such as sputtering, laser ablation, metalorganic chemical vapor deposition (MOCVD), chemical solution deposition (CSD) and sol-gel [7–11]. One of the methods recently used to obtain thin films is the, ‘polymeric organic solution’ based on Pechini’s method. Thin films of \((\text{LiNbO}_3, \text{SrTiO}_3\) and \(\text{SrBi}_2\text{Nb}_2\text{O}_9\)) obtained from Pechini’s method have good morphologies and structural characteristics, which are very important for optical properties [12–14]. This method has also been used to obtain PLZT powders with good stoichiometry control and high surface area [15]. Considering that PLZT (X/65/35) with La con-
tent within the interval of 8–10 mol% shows singular characteristics of high transparency and relaxor behavior, the main objective of this work is to obtain and characterize the crystalline phase of composition (9/65/35) in the form of thin films, by using dip-coating from an organic citrate solution [16].

2. Experimental procedure

The composition of PLZT used in this study was 9/65/35 with formula Pb$_{0.9}$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 to ethylene glycol and citric acid with heating and stirring. Appropriate quantities of solutions of Zr, Ti, Pb and La were mixed and homogenized by stirring at 90°C. The solution viscosity was adjusted in the range of 20 to 51 cP by addition of water and measured by Brookfield viscosimeter. The films were deposited by a dip-coating process. The withdrawal speed of substrate from the solution was adjusted at 5 mm/min. The heating rate was also adjusted at 5°C/min. These conditions were used to obtain homogeneous and crack-free films.

PLZT films obtained from polymeric solution were deposited on silicon (100) substrates and pre-annealed at 90°C in a hot plate for polyesterification, elimination of water and the excess of ethylene glycol. Films with 1, 2 and 3 layers were prepared. For each single layer thermal treatment was performed from 450 to 700°C. A metal-oxygen bond was detected at room temperature using an infrared Impact 400-IR FT spectrometer. Phase analysis of the films was performed at room temperature using an X-ray diffractometer Siemens D-5000. The morphology and thickness of the annealed films were studied using scanning electron microscopy (Topcon SM-300) while the roughness and grain size were measured by atomic force microscopy (Nanoscope IIIa).

3. Results and discussion

PLZT powders treated in the 450–650°C range were analyzed by infrared (IR) spectroscopy. Fig. 1 shows the characteristics bands of metal-oxygen bonds, in the region of 500–620 cm$^{-1}$, for all samples. A vibration band observed in the region of 1400 cm$^{-1}$ indicates the presence of carbonate formed during decomposition of the polymeric precursors. This band is more pronounced for the lowest temperature and shorter annealing time. The amount of carbonates is reduced by increasing the annealing time from 500 to 650°C because at that temperature all carbonates are decomposed. The presence and amount of O-H stretching and vibration bands at 3400 cm$^{-1}$ and 1700 cm$^{-1}$ are not influenced by annealing and depend only on the time spent preparing the sample for IR analysis. These bands are due to water vapor from the atmosphere.

The PLZT powders annealed in the range from 450–650°C were analyzed by X-ray diffraction (XRD), Fig. 2. The characteristic peaks of a crystalline phase can be identified from 450°C as lead lanthanum zirconate titanate (PLZT). It was observed that increasing the temperature from 450 to 650°C the cristallinity of the material increases. The presence of a PbO phase was identified only for the samples heat treated at 650°C for 3 h This indicates that for longer annealing times lead-oxide volatilization takes place, with subsequent condensation on the surface of PLZT particles. The presence of PbO after annealing for 1 h at the same temperature was not observed probably because the time interval was too short to form enough PbO to be detectable by X-ray diffraction.
The X-ray diffraction data for the films deposited on silicon (100) substrates and annealed from 450 to 650°C is shown in Fig. 3. For both powder and films, the main peaks of PLZT crystalline phase were observed after annealing at 650°C for 3 h. The peak of second order for silicon (100) substrate at 2θ = 33° is identified in Fig. 3b and 3c. The presence of PLZT phase for film annealed at 650°C for 1 h was not observed; this indicates that 1 h at 650°C is not enough to obtain a significant amount of the PLZT crystalline phase by the Pechini method. Literature results for PLZT films obtained by sol-gel method at the same temperature show the presence of PLZT crystalline phase. But, in this case, the ionic concentration for the preparation of the films and the crystallite size are different [17]. The highest PLZT peak (110), identified in the powder, was not observed in the film. Actually, the films show preferential orientation on plane (111) after annealing at 450°C and 500°C for 6 h and at 650°C for 3 h.

Fig. 3e shows that after annealing at 350°C for 6 h both PLZT films and powders are amorphous. However, the presence of perovskite PLZT peaks at 450°C for 6 h was observed in calcinated powders (at 2θ = 31.3°, Fig. 2d) as well as in films (at 2θ = 38°, Fig. 3d). Although the intensities of these peaks at 450°C for 6 h are small, peaks corresponding to pyrochlore phase were not observed [18]. These results indicate that the perovskite phase of PLZT obtained from Pechini’s method is formed directly from the amorphous phase and not from decomposition of the pyrochlore phase. This behavior could be probably due to a strong ex-

![Fig. 3. XRD for PLZT thin films with two layers and annealed at: (a) 650°C for 3 h, (b) 650°C for 1 h, (c) 500°C for 6 h, (d) 450°C for 6 h and (e) 350°C for 6 h.](image)

![Fig. 4. SEM micrographs of PLZT surface films with two layers (η = 51cP and 30000x) obtained on silicon (100) substrate and annealed at: (a) 450°C for 6 h, (b) 500°C for 6 h, (c) 650°C for 1 h and (d) 650°C for 3 h.](image)
othermic process that occurs in the temperature range 400°–500°C, as related by others authors [19]. In this range, the fast decomposition of organometallic complexes avoids the formation of pyrochlore phase due to the short time for crystallization.

The surface morphology of the films was analyzed by scanning electron microscopy (SEM). Fig. 4 shows a typical film microstructure, free of cracks and having a fairly homogeneous morphology. The films heat treated at 500°C for 6 h and 650°C for 3 h were less porous, more uniform and homogeneous than films treated under other conditions. However, the films heat treated at 650°C for 3 h were the ones with the highest crystallinity and lowest roughness. Those characteristics are very important for the application of PLZT as electrooptic material.

The pyrochlore phase was not identified by scanning electron microscopy (Fig. 4d) due to the grains of pyrochlore phase being smaller than the grains of PLZT (~ 60 nm). This phase starts to grow at grain boundaries during the annealing where the PbO loss is higher. This phenomenon was also observed for sintered PZN ceramics and has implications in the rela-

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**Table 1**

Variation of grain size and roughness in function of temperature and time of annealing

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>Roughness (nm)</th>
<th>Average Grain Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>6</td>
<td>12.7</td>
<td>96 ± 4%</td>
</tr>
<tr>
<td>500</td>
<td>6</td>
<td>13.0</td>
<td>93 ± 2%</td>
</tr>
<tr>
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<td>6</td>
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</tr>
<tr>
<td>650</td>
<td>1</td>
<td>10.6</td>
<td>98 ± 3%</td>
</tr>
<tr>
<td>650</td>
<td>3</td>
<td>9.5</td>
<td>108 ± 4%</td>
</tr>
<tr>
<td>650</td>
<td>6</td>
<td>11.8</td>
<td>121 ± 2%</td>
</tr>
<tr>
<td>700</td>
<td>6</td>
<td>8.9</td>
<td>103 ± 4%</td>
</tr>
</tbody>
</table>

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Fig. 5. AFM results of PLZT (γ = 51 cP) films annealed under different conditions on silicon (100) substrate at: (a) 450°C for 6 h, (b) 550°C for 6 h, (c) 650°C for 3 h, (d) 650°C for 6 h.
Fig. 6. Roughness vs. temperature for PLZT film obtained on Si (100) substrate and annealed for 6 h.

Fig. 7. Roughness vs. solution viscosity for PLZT film obtained on Si (100) substrate and annealed at 650°C for 3 h.

relatively small pyrochlore grains compared with the PLZT [20].

The average grain size and roughness determined from surface analyses by AFM are shown in Table 1 and in Fig. 5 which illustrate the influence of annealing treatment on grain size and roughness. Due to the higher ionic mobility during the sintering process, grain growth and densification of the material were observed when the sintering temperature was increased from 450 to 650°C. Due to grain growth occurring preferentially on the z direction, perpendicular to the substrate surface, the roughness increased when the annealing temperature was increased from 450 to 600°C. This can also be explained by the absence of island coalescence up to 600°C. Therefore, the distance from the island base to the top increases with the grain growth, promoting an increase in roughness (Figs. 5 and 6). The surface roughness decreases with decreasing annealing time (from 6 to 3 h) at 650°C, since the grain size was smaller (Fig. 5c, d). The surface roughness decreases when the annealing temperature is increased from 600 to 700°C due to the island coalescence which leads to a smaller distance between the base and top of the islands.

Fig. 7 shows that by keeping a constant temperature at 650°C for 3 h and increasing the viscosity, the roughness increases, because the larger mass deposited on the substrate promotes grain growth preferentially on the z direction, perpendicular to the substrate surface, resulting in elongated grains.

4. Conclusions

PLZT thin films with preferential orientation (111) and (200) were obtained on Si (100) substrates annealed at 450°C for 3 h. The best morphological characteristics were obtained for PLZT thin films annealed at 650°C for 3 h. The crystalline PLZT phase seems to be formed from amorphous material. The roughness increases with the annealing temperature from 450 to 600°C for 6 h due to the absence of island coalescence up to 600°C. It was also observed that the roughness increases when the viscosity increases due to the preferential grain growth on z direction resulting in elongated grains. On the other hand, the decrease of surface roughness in the range of 600 to 700°C may be explained by the phenomenon of island coalescence.

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