

# Texture Development in Modified Lead Titanate Thin Films Obtained by Chemical Solution Deposition on Silicon-Based Substrates

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**An advanced method of X-ray diffractometry analysis, the quantitative texture analysis, is used in this work to study the preferential orientations of ferroelectric lanthanum-modified lead titanate thin films, to establish the factors affecting their development. The new, more reliable, texture data obtained allows us to discuss previous models of texture development in chemical-solution-deposited films. The results show that a fiber type, mixed  $\langle 100 \rangle$ ,  $\langle 001 \rangle$  preferential orientation, is obtained when high heating rates are used during crystallization. The degree of texture of these films decreases when successive layers are deposited before a simultaneous crystallization of the ensemble is conducted. This undesirable effect is avoided through layer-by-layer crystallization, because of the preferential nucleation of  $\langle 100 \rangle$ ,  $\langle 001 \rangle$  crystals at the interface between layers. The use of a titanium layer on the platinized silicon-based substrate leads to the development of an additional fiber  $\langle 111 \rangle$  texture component. In this case, the layer-by-layer crystallization process cannot avoid the loss of the degree of orientation (texture index) with the increase of film thickness. This is mainly caused by the appearance of interlayer porosity, which disrupts the growth of  $\langle 111 \rangle$ -oriented grains into upper layers.**

## I. Introduction

**F**ERROELECTRIC thin films are presently the focus of intense study because of their potential technological applications in microelectronics and micromechanics.<sup>1,2</sup> Among the compositions most frequently used, modified lead titanate compositions, and more specifically those modified with lanthanum, have been found suitable for the fabrication of infrared sensors,<sup>3</sup> and they are under study for microelectromechanical applications.<sup>4,5</sup>

Several methods have been used for the preparation of thin films with these compositions, but among them, chemical solution deposition methods (CSD) are preferred because of their low cost and good control of stoichiometry and thickness of the films.<sup>6</sup> Among the microstructural characteristics of the polycrystalline thin films obtained,<sup>7</sup> an important feature is the texture. In the case of ferroelectrics, polar materials, a crystallographic preferential orientation with the polar axis perpendicular to the film surface, improve greatly the final response. In lead titanate-derived compositions, an orientation along  $\langle 001 \rangle$ , the polar axis, is sought for pyroelectric applications, whereas  $\langle 111 \rangle$ -oriented films are more

desirable for memory applications because of the absence of ferroelastic effects that result in a high remnant polarization and abrupt switching behavior.<sup>8</sup> Although efforts have been devoted to find the optimal preparation conditions to fabricate highly oriented films using CSD,<sup>9–11</sup> the mechanisms that lead to the development of a specific texture are not completely understood. It is accepted that the occurrence of preferential orientations is mainly the consequence of heterogeneous nucleation of the perovskite phase on the film–substrate interface. The presence of other nucleation sites in the bulk of the film, such as pores or residual organics, results in randomly oriented films.<sup>12</sup> Besides, crystallization always takes place at temperatures above the Curie temperature, which means that initial nucleation occurs in the paraelectric cubic phase. The cubic-to-tetragonal transformation adds strain, which is relaxed in lead titanate-based compositions by the partial transformation of the  $\langle 001 \rangle$ - (*c*-axis-) oriented crystals into  $\langle 100 \rangle$ ,  $\langle 010 \rangle$  domains, which do not contribute to the total polarization of the film.<sup>13</sup> It has been reported that the stress developed on cooling to room temperature, mainly because of the thermal expansion mismatch between the film and the substrate,<sup>14</sup> is a determinant factor of the final film texture.<sup>15,16</sup>

The importance of silicon-based substrates for their integration with complementary metal oxide semiconductor (CMOS) technologies makes them the focus of intensive research. Platinum is the most commonly used bottom electrode in this type of substrate because of its resistance to oxidation at the temperatures necessary for the film processing. The deposited film crystallizes and grows on this bottom electrode. Thus, the film texture is greatly determined by the characteristics of this electrode. In the case of platinum and because of the close lattice match between platinum and lead titanate-based materials, it is expected that the preferential orientation along  $\langle 111 \rangle$ , characteristic of deposited platinum, leads to the same texture in the films grown on top. This has been found not to be always the case,<sup>12,17</sup> and several mechanisms have been suggested to explain the texture development of ferroelectric thin films on platinized substrates, in some cases using thermodynamic arguments to explain the texture selection mechanisms.<sup>18</sup> Preferential orientations along  $\langle 111 \rangle$  are attributed by some authors to the nucleation on platinum hillocks formed during the annealing of the film<sup>19</sup> or to transient intermetallic layers, either Pt<sub>x</sub>Pb,<sup>20,21</sup> Pt<sub>3</sub>Ti,<sup>22</sup> or TiO<sub>2</sub>.<sup>23</sup> Usually, titanium results from the adhesive layer between platinum and silicon, which is able to diffuse through the platinum to the film surface. Titanium's role in the nucleation of  $\langle 111 \rangle$ -oriented lead titanate-based materials has been recently analyzed.<sup>23,24</sup>

However, the conclusions obtained in the studies of oriented ferroelectric thin films mentioned above are based on the observation of incomplete texture data, mostly based on the analysis of conventional X-ray diffractometry (XRD) diagrams. Comparison of the intensities of the reflections is useful as an indication of the appearance of preferred orientations along the normal of the material surface, but not to study the global

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characteristics of the texture quantitatively. The information derived from the conventional methods allows the establishment of general trends of texture development and methods to obtain good quality textured films, but it lacks of reliable quantitative information to fully analyze the mechanisms involved. For example, to the authors' knowledge, there are few reports on the thickness effect on texture, because most of the work on preferential orientations of ferroelectric thin films gives no quantitative information on the degree of texture, which is necessary to study the problem. Besides, the presence of mixed orientations, which are present in most polycrystalline thin films, has been largely ignored. In general terms, we find that some of the models of texture development reported to date are based on incomplete experimental data. Therefore, in this work, we pose the problem of confirming or correcting, where necessary, previous ideas on texture development, based on a quantitative study of preferential orientations of modified lead titanate, CSD-derived thin films.

Because of the problem already presented, the first step to take is the complete determination of the preferential orientation characteristics of the film. Regardless of the importance of this characterization, it has not been until recently that advance methods, such as the quantitative texture analysis, commonly used in other scientific fields, have been used to study ferroelectric thin films.<sup>25–27</sup> In the present work, we use the analysis of X-ray pole figures to obtain the orientation distribution function (OD) corresponding to the films studied, which provides quantitative information of the texture components and the degree of orientation. The results obtained allow us to discuss the phenomena that lead to the development of preferential orientations in CSD ferroelectric thin films obtained with various annealing processes, which include the use of different heating rates and layer-by-layer crystallization. We also report on the role of the titanium layer in the development of  $\langle 111 \rangle$  orientations, using modified substrates with an extra titanium layer on top of the platinum bottom electrode. Another important issue addressed in this paper is the thickness effect on the induced  $\langle 111 \rangle$  texture component and on the  $\langle 001 \rangle$ ,  $\langle 100 \rangle$  orientation. The problem is that, even when the nucleation is controlled, the production of highly oriented films may have a thickness limitation. An important result concerns the elimination of this effect on the latter texture through layer-by-layer crystallization.

## II. Materials and Experimental Procedure

Thin films of lanthanum-modified lead titanate (PTL) were obtained by deposition of 0.5M, sol-gel processed solutions of  $\text{Pb}_{0.88}\text{La}_{0.08}\text{TiO}_3$ .<sup>28</sup> Solutions were spin-coated at 2000 rpm for 45 s in a class 100 clean room. The wet films were partially pyrolyzed on a hot plate at 350°C for 60 s. Crystallization was conducted at 650°C in air for all films, but different thermal processes were tested: (i) conventional process for 12 min (heating rate of 10°C/min); (ii) direct insertion in a preheated furnace (>500°C/min) for 12 min; and (iii) rapid thermal processing (RTPing) in a furnace (Model JetStar 100T, JIPELEC) at a heating rate of 30°C/s for 50 s. In processes (i) and (ii), several layers (typically of ~100 nm) were deposited and dried successively and then the whole stack was crystallized. In the RTP films, a layer-by-layer crystallization was tested: each layer was dried and crystallized before the next layer was deposited.

One to six layers were deposited. Thickness ranged from 100 to 600 nm, as determined by either profilometry or scanning electron microscopy (SEM) of cross sections of the films. Two different substrates were used: (i) Pt (100 nm)/TiO<sub>2</sub> (50 nm)/SiO<sub>2</sub>/(100)Si; and (ii) Ti (<10 nm)/Pt (100 nm)/Ti (50 nm)/SiO<sub>2</sub>/(100)Si, annealed at 650°C. Hereafter, we refer to these substrates as Pt/TiO<sub>2</sub> and Ti/Pt/Ti, respectively. Platinum and titanium electrodes were deposited by sputtering.

Measurement of experimental pole figures was conducted using a four-circle goniometer (Huber) mounted on an X-ray generator using CuK $\alpha$  radiation and 5° × 5° steps to cover the whole pole figure. A curved, position-sensitive detector (Model CPS-120,

Inel, Inc.) was used to acquire a complete diffraction pattern at each position of the specimen, which considerably decreased data acquisition times. The integrated intensities were treated and corrected for absorption, volume variations, and delocalization effects using software programs (Inel, Inc.). Pole figures were normalized into distribution densities, which were expressed as multiples of a random distribution (mrd). A specimen with no preferred orientation had pole figures with constant values of 1 mrd. From several of these pole figures, we refined the orientation distribution function,  $f(g)$ , following the Williams-Imhof-Matthies-Vinel iterative method (WIMV).<sup>29</sup> This function described the amount of crystallites with an orientation between  $g$  and  $g + dg$  ( $g = \alpha, \beta$ , and  $\gamma$  Euler angles). The quality of the refinement was assessed by the reliability factors (RP0 and RP1, for global and values >1 mrd, respectively). In the present work, we used the 001, 101, and 102 experimental pole figures, excluding the 221 reflection because of the artifacts observed that were introduced in the calculations. This corrected previously reported results<sup>5,25</sup> and improved the reliability factors of the calculations. From the OD, we calculated relevant pole figures that were not available experimentally, analyzed the different orientation components present, and calculated parameters indicative of the degree of orientation, such as the texture index,  $F^2 = (1/8\pi^2)\sum(f(g_i))^2\Delta g_i$ . The calculations to obtain and manipulate the OD were conducted using the Berkeley Texture Package (BEARTEX).<sup>30</sup>

From the OD, we recalculated the complete pole figures, which sometimes were not possible to obtain experimentally, usually because several peaks were overlapped at the same  $2\theta$  position, such as for the (111) reflection of the perovskite and the (111) reflection of the platinum layer. For a fixed position of the specimen, we calculated a figure that showed the associated crystal directions, called inverse pole figure. The inverse pole figures described the densities for crystal directions falling into a specimen direction and allowed the identification of the texture components.

Cross-section specimens of the films were observed using transmission electron microscopy (TEM; Model 2000FXII, JEOL, Tokyo, Japan) operated at 200 kV. To produce the cross-section TEM specimens, two pieces of the film were stacked with the films facing and glued. Lateral thickness was decreased in a controlled manner, using a tripod polisher until a fine wedge was produced. Large electron-transparent areas were obtained by argon-ion milling (acceleration voltage of 5 kV, beam intensity of 2.5 mA, incidence angle of 10°, and times of 1–3 h).

## III. Texture Results

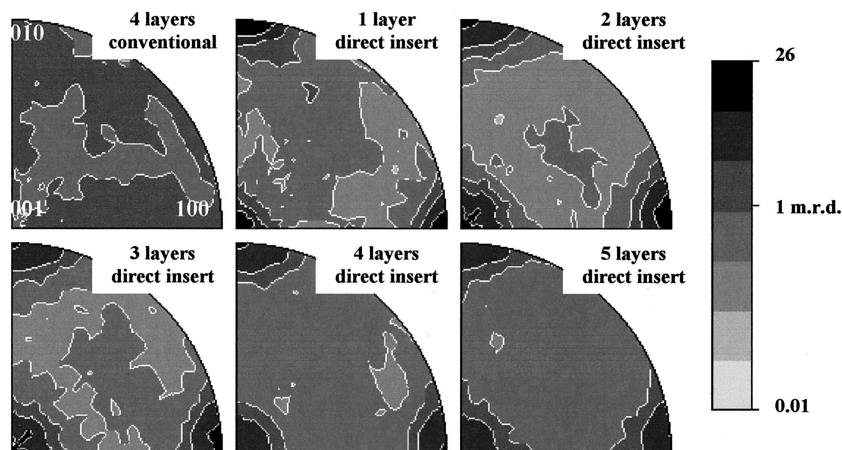
### (I) Thin Films Crystallized in a Conventional Furnace

The results of the quantitative texture analysis of PTL films crystallized in a conventional furnace, using a heating rate of 10°C/min and by direct insertion in the preheated furnace, are compared in Table I. The low values of the reliability factors RP0 and RP1 show the good quality of the refinement of the OD. All the textures observed are symmetric around the normal to the film surface, i.e., axisymmetric or fiber textures. The first result observed is that only those films prepared by direct insertion in the

**Table I. Results of the Quantitative Texture Analysis on PTL Thin Films Crystallized in a Conventional Furnace on Pt/TiO<sub>2</sub>**

Heating rate (°C/min)	Layers	Components of texture	Texture index, $F^2$ (mrd <sup>2</sup> )	RP0 (%)	RP1 (%)
10	4		1.3	14	10
>500 <sup>†</sup>	1	$\langle 001 \rangle, \langle 100 \rangle$	10.2	30	11
	2	$\langle 001 \rangle, \langle 100 \rangle$	6.6	17	13
	3	$\langle 001 \rangle, \langle 100 \rangle$	5.0	14	9
	4	$\langle 001 \rangle, \langle 100 \rangle$	3.8	12	9
	5	$\langle 001 \rangle, \langle 100 \rangle$	3.0	12	7

<sup>†</sup>Direct insertion.



**Fig. 1.** Inverse pole figures for the normal direction to the film surface of PTL films crystallized in a conventional furnace. Equal area projection and linear density scale.

preheated furnace (higher heating rate) show a significant degree of texture. The thin film crystallized using the slowest heating rate presents a random orientation (texture index,  $F^2 = 1.3 \text{ mrd}^2$ ). An equivalent film with the same number of layers prepared by direct insertion has a mixed  $\langle 001 \rangle$ ,  $\langle 100 \rangle$  orientation with a texture index of  $3.8 \text{ mrd}^2$ .

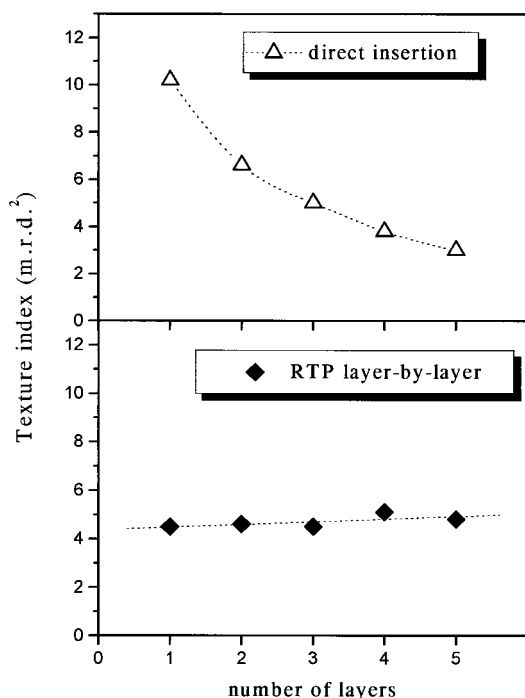
Components of the film preferential orientation are identified in the inverse pole figures of a direction perpendicular to the film surface (Fig. 1). Their contributions to the global texture can be estimated from their associated distribution density value. For the films annealed by direct insertion, we observe that the two components of the global texture,  $\langle 001 \rangle$  and  $\langle 100 \rangle$ , have similar distribution density values (mrd), and, therefore, we can estimate that their contribution to the total degree of texture is almost the same.

We also observe in Fig. 1 that the overall distribution density values decrease with the increase of the number of deposited

layers, with no change in the relative contribution of the two components of the texture identified. This is also reflected in the global texture index shown in Table I. If we plot this parameter against the number of deposited layers, we observe clearly the effect of an increasing number of deposited layers on the texture (see Fig. 2). This is, in part, because X-ray information mainly comes from the top layers of the material, because of absorption throughout the film thickness. In any case, the type of texture developed in the PTL films prepared by direct insertion is gradually lost with the increase of the amount of material that is crystallized away from the film-substrate interface.

## (2) Thin Films RTP Crystallized Layer-by-Layer

Tables II and III summarize the texture results for films deposited on the Pt/TiO<sub>2</sub> and Ti/Pt/Ti substrates. We also obtain low values of the reliability factors RP0 and RP1, which shows the good quality of the OD refinement. Again, all the textures



**Fig. 2.** Variation of texture index with increasing number of deposited layers in PTL films on Pt/TiO<sub>2</sub> crystallized by direct insertion and RTP layer-by-layer.

**Table II.** Results of the Quantitative Texture Analysis on PTL Thin Films Crystallized by RTP on Pt/TiO<sub>2</sub>

Layers	Components of texture	Texture index, $F^2$ (mrd <sup>2</sup> )	RP0 (%)	RP1 (%)
1	$\langle 001 \rangle, \langle 100 \rangle$	4.5	16	10
2	$\langle 001 \rangle, \langle 100 \rangle$	4.6	20	13
3	$\langle 001 \rangle, \langle 100 \rangle$	4.5	14	10
4	$\langle 001 \rangle, \langle 100 \rangle$	5.1	15	8
5	$\langle 001 \rangle, \langle 100 \rangle$	4.8	10	5

**Table III.** Results of the Quantitative Texture Analysis on PTL Thin Films Crystallized by RTP on Ti/Pt/Ti

Layers	Components of texture	Texture index, $F^2$ (mrd <sup>2</sup> )	RP0 (%)	RP1 (%)	$\langle 111 \rangle$ estimated contribution (%)
1	$\langle 111 \rangle$ $\langle 001 \rangle, \langle 100 \rangle$	3.2	15	11	72
2	$\langle 111 \rangle$ $\langle 001 \rangle, \langle 100 \rangle$	2.4	14	9	61
3	$\langle 111 \rangle$ $\langle 001 \rangle, \langle 100 \rangle$	2.0	14	11	47
4	$\langle 111 \rangle$ $\langle 001 \rangle, \langle 100 \rangle$	2.0	10	7	16
5	$\langle 111 \rangle$ $\langle 001 \rangle, \langle 100 \rangle$	2.1	9	5	18
6	$\langle 111 \rangle$ $\langle 001 \rangle, \langle 100 \rangle$	2.1	8	6	20

observed are axisymmetric, i.e., fiber textures. The first observation from the data in Tables II and III is that the texture indexes are lower for the films deposited on Ti/Pt/Ti. This is mainly due to the existence of more components of the global texture in these films: a strong  $\langle 111 \rangle$  orientation besides the  $\langle 001 \rangle$  and  $\langle 100 \rangle$  also are present in the films deposited on Pt/TiO<sub>2</sub>. Because  $F^2$  represents the global degree of orientation, the more directions along which the crystals orient, the more random the specimen is considered, and the lower the texture index. This fact must be considered when comparing texture indexes of materials whose texture components are different, as in this case. Therefore, conclusions regarding variations of the degree of orientation can be drawn only from  $F^2$  values of specimens with the same texture components.

As we have explained before, texture components and their contributions are obtained from the inverse pole figures (Figs. 3 and 4). Films deposited on the Pt/TiO<sub>2</sub> substrate present a mixed  $\langle 001 \rangle$ ,  $\langle 100 \rangle$  orientation (Fig. 4). Both directions have similar distribution density values (mrd), and we estimate that their contribution to the global texture is almost the same. The same type of orientation is observed for the films annealed by direct insertion (Fig. 1), as explained above.

Deposition on the Ti/Pt/Ti substrate leads to the appearance of an extra orientation component along  $\langle 111 \rangle$  (Fig. 4). The density values show that this component's contribution to the global texture decreases with the increase of the number of deposited layers (Table III). Because distribution density values of the other two components  $\langle 001 \rangle$ ,  $\langle 100 \rangle$  remain constant when the number of layers increases, the overall decrease of the texture index

(Table III) can be attributed to a gradual loss of the  $\langle 111 \rangle$  component. The texture index values stabilize around 2.0 mrd<sup>2</sup> when the number of layers is greater than four.

#### IV. Discussion on Texture Development

##### (1) Influence of the Heating Rate on the Occurrence of Texture

In this discussion, we analyze several factors that influence the development of preferential orientation in CSD thin films. One factor is the annealing parameters used during the crystallization process. The results presented in the previous section clearly indicate that, to obtain any preferential orientation in a CSD film, the use of heating rates higher than the several °C/min obtained in conventional furnaces is essential. It has been argued before that the use of slow heating rates leads to the formation of films in which more than one nucleation event is involved. Because of the slow rate, the crystallization starts during the heating process, and, as the temperature increases, more energy is available to surmount the barriers for nucleation events in addition to the energetically most favorable nucleation event.<sup>6</sup> Therefore, under these conditions, the film shows a random orientation.

The simplest approach to obtain higher heating rates is the direct insertion of the amorphous film into a preheated furnace, which results in a textured film, giving an experimental confirmation of the ideas presented above. The heating rates can be further increased using a RTP. In this case, radiation is focused on the film, producing a directional heat flow that does not exist in

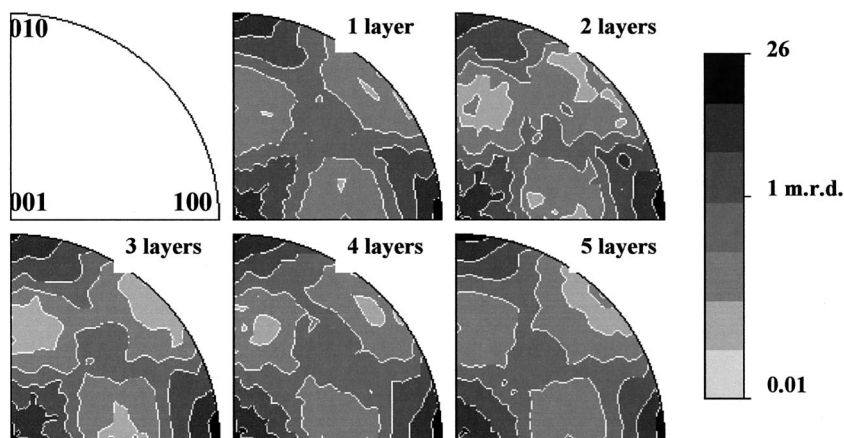


Fig. 3. Inverse pole figures for the normal direction to the film surface of PTL films on Pt/TiO<sub>2</sub> crystallized by RTP layer-by-layer. Equal area projection and linear density scale.

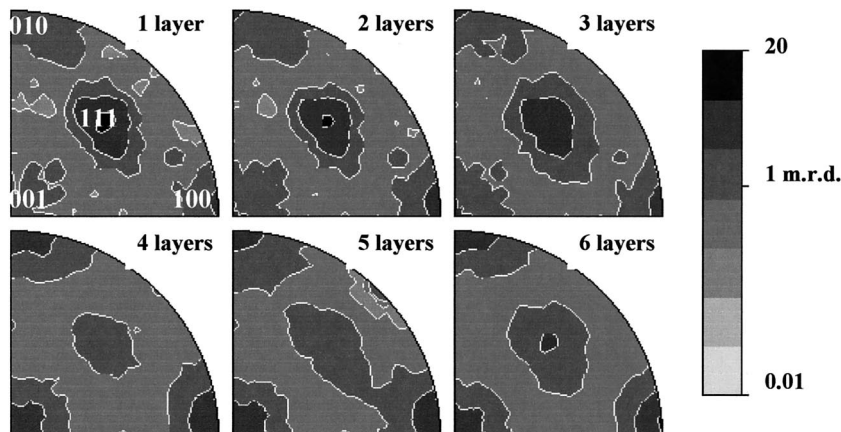


Fig. 4. Inverse pole figures for the normal direction to the film surface of PTL films on Ti/Pt/Ti crystallized by RTP layer-by-layer. Equal area projection and linear density scale.

conventional heating. This heat flow can produce a temperature gradient across the film–substrate interface and promote nucleation at this interface. However, the direct insertion experiment in a conventional furnace indicates that it is the high heating rates attainable that are mainly responsible for the high preferential orientation achieved in the RTP films, in agreement with the nucleation kinetic arguments presented above.

Moreover, all textured films reported in this work show a fiber texture. Although this characteristic of nonepitaxial-oriented films has been mentioned in previous works, full experimental evidence of this phenomenon for a set of films has been reported only by the current authors. The absence of in-plane orientation can be explained by the differences between the bottom electrode grain size and the radius of the critical nucleus,  $r^*$ .<sup>31</sup> If the platinum grain size is significantly smaller than  $r^*$ , the interfacial energy between the crystalline nucleus and the electrode has many contributions of randomly oriented grains and becomes independent of the in-plane orientation. We have observed, using atomic force microscopy, that the platinum layer is nanocrystalline.<sup>32</sup> The result is the observed fiber textures.

## (2) Influence of the Substrate on the Type of Texture

In this work we present two types of preferential orientation that are developed on different silicon-based substrates. The texture selection can be analyzed using the classical Volmer–Weber nucleation theory, from which we deduce the expressions of the energy barrier for heterogeneous nucleation:<sup>6,18</sup>

$$\Delta G_{\text{hetero}}^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2} f(\theta) \quad (1)$$

where  $\gamma$  is the interfacial energy between the crystalline nucleus and the amorphous matrix,  $\Delta G_v$  the driving force for crystallization (free energy difference corresponding to the amorphous–crystalline transformation), and  $f(\theta)$  a function related to the contact angle  $\theta$ . The value of  $f(\theta)$  is expected to decrease when there is a high level of lattice matching between the substrate and one of the crystallographic planes of the film. It is this term that is mainly affected by the modifications of the nature of the substrate.

The use of a platinized, silicon-based substrate with a titania adhesive layer produces a low titanium diffusion rate through the platinum to the surface.<sup>33</sup> Films grown on this substrate develop mixed  $\langle 100 \rangle$ ,  $\langle 001 \rangle$  orientation. The crystallization takes place in the cubic phase for these compositions (stable phase at high temperatures), and, therefore, crystals must nucleate preferentially with the (100) surfaces parallel to the substrate to obtain the observed final texture. On cooling, these cubic,  $\langle 100 \rangle$ -oriented crystals transform into tetragonal  $\langle 100 \rangle$  or  $\langle 001 \rangle$  crystals, which are no longer equivalent directions, and the observed mixed orientation is obtained. The distribution of crystals along these two directions seems to be directly related to the stress state present during the film processing.<sup>15</sup> There is no obvious lattice match between the (111) planes of the underlying platinum and the (100) planes of the cubic phase of PTL. Therefore, we should not expect a decrease of the value of  $f(\theta)$ , which decreases the energy barrier for this specific direction and explains a preferential orientation along  $\langle 001 \rangle$ ,  $\langle 100 \rangle$  directions. It seems that the reason resides more in a lower interfacial energy  $\gamma$  for (100) planes of the cubic phase of PTL. Also, as during growth, crystals compete for the available space; those with their faster growth direction (100) perpendicular to the substrate contribute to a large volume fraction of the film. A process to obtain textured films grown on substrates with unrelated structures has been developed based on those principles.<sup>34</sup> Therefore, we can conclude that this type of orientation corresponds to the most energetically favorable nucleation, which can be called “natural” nucleation of the lead titanate-based materials, meaning that any other orientation needs to be induced by changing the  $f(\theta)$  factor. This type of nucleation does not need, in principle, any special surface, and, therefore, it can take place at the film–substrate interface and at the interfaces between deposited layers. This fact is the principle to eliminate the thickness effect for

this type of textures through the layer-by-layer crystallization process.

The need to promote another type of orientation is initiated by the search for an orientation that leads to a large value of net polarization in the direction perpendicular to the film surface. In our case, there is an associated percentage of crystals with the polar axis in the plane of the film, those oriented along  $\langle 100 \rangle$  directions. Obviously, these crystals do not contribute to the net polarization perpendicular to the film surface. To avoid this noncontributing fraction of the material, other orientations have been searched in the literature, mainly along  $\langle 111 \rangle$ . In this work, we change the substrate to obtain that type of preferential orientation. Expressing this in terms of Eq. (1), we attempt to make the value of  $f(\theta)$  lower, which favors other types of nucleation. The idea is based in previous works that have studied the role of a very thin titanium or titania layer in the nucleation of the perovskite.<sup>23,24</sup> The usual source of titanium is the diffusion through platinum from the adhesive layer, but, in this case, we deposit an extra titanium layer on top of the platinum. Previous Rutherford backscattering spectrometry (RBS) analysis shows that this layer is fully incorporated in the perovskite structure during crystallization of the phase.<sup>24</sup> The result is a film that presents, besides the natural  $\langle 100 \rangle$ ,  $\langle 001 \rangle$  mixed orientation, an important contribution of  $\langle 111 \rangle$ -oriented crystals. The appearance of texture contributions other than the induced  $\langle 111 \rangle$  orientation has not been reported before because of the limitations of the traditional texture analysis used, which do not allow easily the study of several texture components simultaneously. This observation helps explain the role of the different factors of Eq. (1) for texture selection.

The mechanisms that lead to  $\langle 111 \rangle$  nucleation remain unclear, and several proposals are found in the literature.<sup>22,23</sup> However, we observe that, even lowering the energy barrier for nucleation along other directions by a modification of  $f(\theta)$ , and probably converting the substrate-induced nucleation into the most energetically favorable, the so-called natural nucleation is present. This reflects the importance of the existence of a minimum in the interfacial energy between the crystalline nucleus and the amorphous matrix, which is material specific and difficult to avoid when other orientations are searched. The natural preferential heterogeneous nucleation appears, in principle, on any surface. This can be a serious obstacle when a single orientation, close to the epitaxial case, is the objective to improve the physical properties of the film.

In our specific case, what we want to establish is that, contrary to the case of  $\langle 100 \rangle$  crystals,  $\langle 111 \rangle$ -oriented crystals nucleate only on the film–substrate interface. Therefore, the contribution of these crystals to the global texture of the film is lower the higher the number of deposited layers, unless a significant number of  $\langle 111 \rangle$ -oriented crystals serves as seeds for the crystal nucleation of the subsequently deposited layers (again, by lowering  $f(\theta)$ ).

## (3) Thickness Effect on Texture and Layer-by-Layer Crystallization Process

After discussing the texture selection mechanisms, we proceed with another important issue in thin-film fabrication: how to produce films of the required thickness without altering the degree of orientation. To the authors' knowledge, this problem has not been extensively studied in the literature, probably because of the lack of reliable quantitative texture data clearly indicating which texture components are affected by film thickness. In this study, the results obtained by the quantitative texture analysis show that those films obtained by a simultaneous crystallization of all the deposited layers present a decrease of the degree of texture as the number of deposited layers increases (Table I). This can be seen clearly in the plot of Fig. 2 for the series of films with different number of layers prepared by direct insertion. These results indicate that the higher amount of oriented material must be concentrated in the deepest layers, close to the film–substrate interface. The increase of the number of layers, with less oriented crystallites, results in a decrease of the volume fraction of textured material. All this suggests that homogeneous nucleation in the bulk of the films cannot be avoided. RTP crystallization of each layer

before the next one is deposited, i.e., layer-by-layer, in principle solves the problem. Each as-deposited layer can serve as a seeding layer for the next. The results confirm that the method eliminates the thickness effect on the texture of the films deposited on the Pt/TiO<sub>2</sub> substrate, as the evolution of the texture index of RTP layer-by-layer films plotted in Fig. 2 clearly shows.

To investigate the nature of the nucleation process, TEM cross section of the RTP layer-by-layer films are prepared and analyzed. Figure 5 shows a representative micrograph of a three-layer film. Between deposited layers there are pores that allow us to distinguish the different layers. This porosity may be due to a nonuniform covering of the surface by the solution. However, the same solution shows excellent wetting characteristics on the platinum electrode, producing a good film–substrate interface. Previous studies by the authors have shown that, whereas roughness of the platinum layer (measured by atomic force microscopy) is in the range 0.7–3.0 nm, the CSD film deposited on top is 8–11 nm.<sup>25</sup> We can attribute the bad wetting of the solutions on the PTL film surfaces to this roughness difference between the two surfaces. Although some grains may transmit their orientation to grains in upper layers, the presence of interlayer pores disrupts this type of nucleation.

Under these circumstances, the layer-by-layer crystallization process cannot keep effectively the orientation components induced only by the substrate. This is the case for <111>-oriented crystals, which nucleate directly on the titanium-rich substrate. The only mechanism available to transmit their orientation to upper deposited layers is that there is an important nucleation of the new crystals on the <111>-oriented grains. The appearance of a high amount of porosity between layers stops this type of nucleation and results in the tendency observed in the texture results: as the volumetric fraction of the film that represents the first layer decreases, the <111> contribution to the total texture decreases (Table III). Therefore, to conserve preferential orientations nucleated only on the film–substrate interface, the elimination of the porosity between layers is necessary. It seems that this requires a decrease of the PTL surface roughness, as explained above. This is, at present, the subject of further work.

The situation is different for the <100>,<001> mixed orientations. As explained before, the mixed orientations are related to the nucleation of <100> crystals on unrelated structures. This means that, if there is no other nucleation mechanism active, the formation of perovskite on any nucleation site is preferentially <100>. If this nucleation site is the film–substrate interface, a

preferential <100> orientation perpendicular to the substrate surface is created. Layer-by-layer crystallization results in similar defective surfaces between layers, where <100> preferential nucleation also takes place. These extra nucleation sites compensate the loss of <100>,<001> orientation because of the thickness increase, and the degree of texture is not lost with the increase of deposited layers (Fig. 2). Therefore, the layer-by-layer crystallization process of CSD films has proved to be effective in eliminating the thickness effect on textures not induced specifically at the film–substrate interface.

## V. Conclusions

The development of preferential orientations in ferroelectric CSD thin films on silicon-based substrates is analyzed by quantitative texture analysis, which provides a thorough analysis of the type and the degree of the orientation of the films. All films present fiber textures. It has been shown that a high heating rate is necessary during the crystallization process of the CSD films to obtain oriented films. If no other driving force is present, the natural preferential orientation obtained in modified lead titanate films is a mixed <100>,<001> orientation, whose origin is the preferential nucleation and growth of <100> crystals in the high-temperature cubic phase. This is due to its low interface energy, which results in a preferential nucleation at the film–substrate interface and layer-to-layer interfaces. The use of a titanium-covered substrate has been successful in obtaining an additional <111> texture. The nucleation sites of these crystals are only at the film–substrate interface.

The increase of the number of deposited layers produces a decrease in the texture index. For films with the natural <100>,<001> orientation, this effect can be suppressed by a layer-by-layer crystallization process. The interface created between layers serves as a nucleation site of <100> crystals. In the case of <111> orientation, nucleated only at the film–substrate interface, this processing method cannot avoid the decrease of the contribution of this component to the total texture of the film because of the porosity accumulated at the interface between layers. The effectiveness of the layer-by-layer crystallization process is related in this case to the elimination of that porosity.

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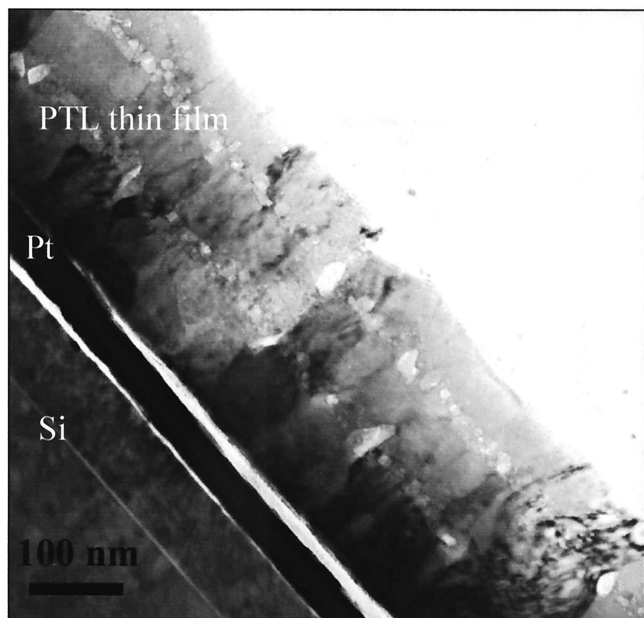


Fig. 5. TEM cross-section micrograph of a PTL film with three layers deposited on Pt/TiO<sub>2</sub> and crystallized by RTP layer-by-layer.

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