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Quantitative texture analysis applied to the study of preferential orientations in ferroelectric thin films

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The occurrence of preferred crystallographic orientations, or texture, is a determinant factor of the behaviour of polar materials, like ferroelectric thin films. This is the reason why numerous works have been focused in the preparation of highly oriented films for pyroelectric sensors and electromechanical applications. Traditionally, preferred orientations were determined by the analysis of the main reflections obtained by X-ray diffraction, which only in some cases are characteristic of the texture of the material. Regardless of the interest of this subject, the quantitative texture analysis of ferroelectric thin films has not been systematically applied. This consists in the measurement of pole figures with a goniometer, and the determination of the orientation distribution function. In this work we summarise briefly the principles of the quantitative texture analysis and we demonstrate its application to the study of different ferroelectric thin films: La and Ca modified lead titanate (PTL and PTC) and lead zirconate titanate (PZT). This method allows the study of the characteristics of the type of texture and the identification of the different components that contribute to the final texture of the material. An indicative value of the texture strength is also obtained for both the ferroelectric film and the substrate layers. This information allows us the study of the process that leads to the orientation in thin films, and to obtain correlation~~s~~ between texture and physical properties.

Keywords: Quantitative texture, preferential orientation, thin films, ferroelectrics

Aplicación del análisis cuantitativo de la textura al estudio de orientaciones preferentes en láminas delgadas ferroeléctricas

La aparición de orientaciones cristalográficas preferentes, o textura, es un factor determinante del comportamiento de materiales policristalinos polares, como las láminas delgadas ferroeléctricas. Por este motivo se han realizado numerosos estudios conducentes a la producción de láminas orientadas para la fabricación de sensores piroeléctricos y dispositivos electromecánicos. Tradicionalmente, la orientación preferente se estudia por medio del análisis de las reflexiones principales obtenidas por difracción de rayos X, que sólo en ciertos casos son características de una determinada textura. A pesar del gran interés de este tema, no se ha aplicado de una forma sistemática el análisis cuantitativo de la textura de láminas ferroeléctricas, que comprende la obtención de figuras de polo por medio de difracción de rayos X usando un goniómetro, y el cálculo a partir de estas de las funciones de distribución de orientaciones. En este trabajo se resumen brevemente los principios del análisis cuantitativo de la textura y se muestra su aplicación al estudio de diversas láminas delgadas ferroeléctricas de titanato de plomo modificado con La y Ca (PTL y PTC) y zirconato titanato de plomo (PZT). Este método permite la caracterización del tipo de textura, la identificación de las distintas componentes que contribuyen a la orientación final del material y la obtención de un valor indicativo del grado de textura de la lámina y, en su caso, de las capas sobre las que esta se crece. Esta información nos permite estudiar los procesos que conducen a la orientación en las láminas y obtener correlaciones de ésta con el comportamiento macróscopico.

Palabras clave: Textura cuantitativa, orientación preferente, láminas delgadas, ferroeléctricos

1. INTRODUCTION

Ferroelectrics are polar materials, characterised by a spontaneous electric polarisation, which can be inverted by the application of an electric field. In order to obtain polarisation in polycrystalline materials, like ceramics or thin films, a poling process, i.e., the application of a strong electric field, is required to orient the polar vectors of the individual crystallites in such a way that the average over the volume is not zero. Therefore, thin films showing a preferred orientation with the polar axis perpendicular to the film surface will not require poling and, at the same time, will show improved ferropiezoelectric properties with respect to the films with random orientations. This is the reason why highly oriented films are usually required for technological applications. As a result, studies of the preferred orientations, or texture, are required for the control and optimisation of the preparation process of highly oriented ferroelectric thin films for the production of pyroelectric sensors and electromechanical devices [1,2]. A thorough characterisation of the texture is especially interesting for the study of the mechanisms responsible for the development of preferred orientations, which at present are not well understood.

The traditional method to study preferred orientations of ferroelectric thin films is the analysis of the integrated intensities of the main X-ray reflections, producing a texture coefficient for each crystallographic plane [3,4]. For example, the Harris method [3] is based in the comparison between the intensity of the peaks obtained for a random specimen and those for the oriented film. In some cases, a particular solution is used, calculating for example an orientation ratio from the comparison of the peak intensities of two reflections directly related to the main polar axes of the material [5], forgetting any other contributions to the texture. These comparisons are useful as an indication of the appearance of preferred orientations along the normal to the material surface, but not to study the global characteristics of the texture quantitatively.

Recently, some works present rocking curves [6], where the specimen is tilted with respect to the X-ray beam, and the variations of the intensity values of a specific reflection are studied. Although available in most of the modern X-ray diffractometers, which makes it appropriate as a technique for routine analysis, the information on the texture of the film remains partial. Firstly, the range of tilt angles is restricted, allowing the study of the preferred orientations only in a narrow spatial region around the normal of the film surface. Secondly, for certain types of texture, the rotation of the sample in the holder will not produce necessarily the same evolution of the diffracted intensities for a specific reflection, making necessary the measurement of several rocking curves in order to obtain reliable information. And thirdly, no information on potential in plane orientation is provided only tilting the sample.

The solution to all these problems is the use of a goniometer, with two perpendicular axes of rotation, which allows the measurement of the peak intensities for any orientation of the sample. Pole figures are obtained, which contain all the required texture information. From several experimental pole figures it is possible to obtain an orientation distribution function [7], which contains information about all the components contributing to the crystal orientation and allows us to quantify how textured the material is. In certain favourable cases (crystal symmetry, texture shape) it is also possible to derive the polarisation and the dielectric and piezoelectric properties from that distribution function and the microscopic tensors [8].

In spite of the interest of this subject, complete quantitative studies of the pole figures are rarely found in the literature of ferroelectric thin films [9,10]. In this work we show the principles and application of quantitative texture analysis to ferroelectric thin films.

2. METHOD OF QUANTITATIVE TEXTURE ANALYSIS

In the analysis of the preferred orientation or texture of thin films we use pole figures. A pole figure is the angular distribution of a chosen crystal direction **h** with respect to the sample co-ordinates, i.e., the fraction of crystals with crystal direction **h** parallel to the sample direction **y**, $P_{\mathbf{h}}(\mathbf{y})$. As the diffracted intensities at a given Bragg angle (ω) are proportional to the number of planes in reflection position for that orientation, we can obtain pole figures by the combination of X-ray diffraction and an Eulerian cradle to rotate the sample into any orientation.

Experimental pole figures were obtained using an INEL X-ray generator (Cu K$\overline{\alpha}$ wavelength) equipped with a Huber four-circle goniometer. Sample rotations (χ,φ) are shown in Figure 1. A 5°x5° grid measurement was carried out to cover the whole pole figure. A position sensitive detector (INEL CPS-120), covering an angle of 120°, acquired a complete diffraction pattern at each position of the sample (spatial resolution 0.03°). The use of this kind of detector accelerates considerably the data acquisition compared to punctual detectors, but results in non Bragg-Brentano, or asymmetrical positions, which requires the correction of the localisation of the peaks into the pole

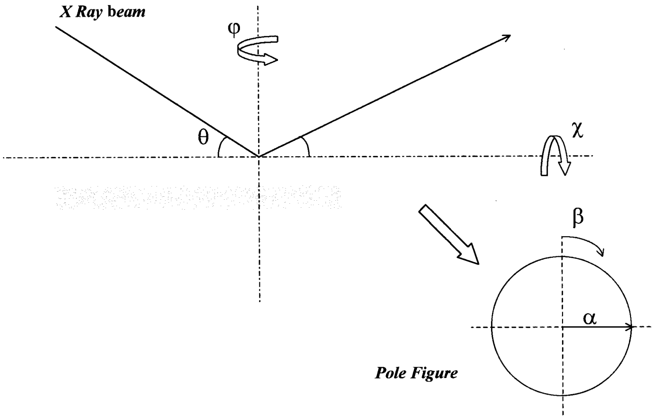

Figure 1. Scheme of the experimental set up with the sample rotation angles (χ,φ) and the co-ordinates (α,β) of the resulting pole figure.

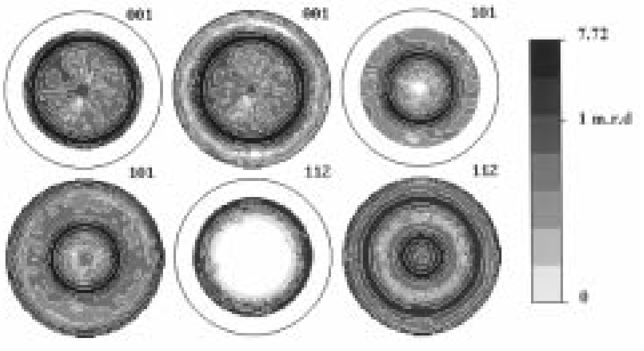

Figure 2. Example of experimental and recalculated pole figures successively used for the refinement of the OD. (Equal area projection and logarithmic density scale)

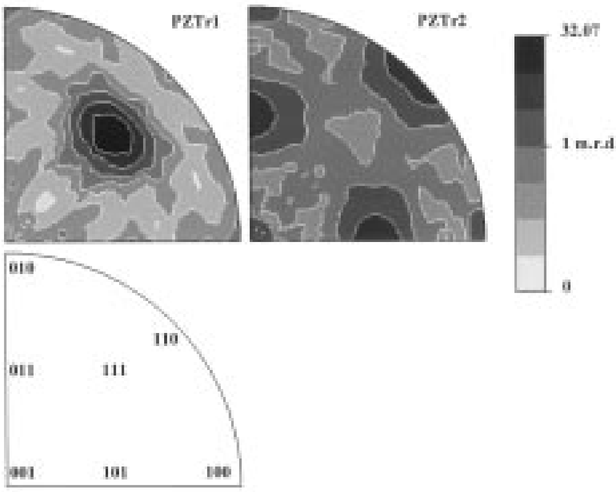

Figure 3. Examples of inverse pole figures for the normal direction to the film obtained from two rhombohedral PZT thin films. (Equal area projection and logarithmic density scale)

figure co-ordinates (α,β) (Figure 1). In this case, the positions do not correspond exactly to the goniometer rotations (χ,φ) and must be corrected [11]. Other effects like the variations produced by changes in the probe volume and absorption in thin films, due to the fact that their thickness is less than the penetration depth, are also taken into account [12]. These corrections were performed using INEL software packages.

We can only measure incomplete pole figures. The elongation of the irradiated area at high tilt χ angles leads to defocusing, which produces line broadening and a decrease of the peak maximum values. As this does not affect integrated intensities, with a linear detector, the defocusing effect is out of concern for an infinite sample size. In practice, the sample is limited in size, and the high χ values (70°-90°) are not reliable because of geometrical effects. Besides, for a specific incidence angle (θ) we cannot measure planes for a specific reflection (ω) which are oriented below a certain angle (δ_ω) with respect to the normal of the sample surface ($\delta_\omega = \omega - \theta$). This is called the blind area of the pole figure. The incidence angle used was 11°, in order to obtain as much information as possible from the important 100/001 pole figure. Examples of incomplete experimental pole figures can be found in Figure 2. They are normalised into distribution densities. To normalise, all data points over the whole pole figure are summed and weighted with respect to their area contribution. Densities are expressed as multiple of a random distribution (m.r.d.), which is equivalent to volume percentage per 1% area. A sample without any preferred orientation has pole figures with constant density values of 1 m.r.d., while a textured sample shows regions with values above and below 1 m.r.d.

From the experimental pole figures we can obtain the orientation distribution (OD), f(**g**). This function describes the amount of crystallites with an orientation between **g** and **g**+d**g** (**g** = αβγ, Euler angles). Only those pole figures that contain reliable information are used (without artificial intensity peaks from the substrate, influence of other phases, geometrical problems…), after having checked that the data are sufficient to refine the full orientation distribution space. From the several methods of resolution of the OD we chose the WIMV (Williams-Imhof-Matthies-Vinel) iterative method [13]. The quality of the refinement is assessed by the reliability factors (RP0 and RP1, for global values and values above 1 m.r.d., respectively) and by comparing the experimental and recalculated pole figures (Figure 2). The calculations to obtain and manipulate the OD have been carried out with the Berkeley Texture Package (BEARTEX) [14].

From the OD, we can determine bulk parameters indicative of texture like the texture index, F^2:

$$F^2 = \frac{1}{8\pi^2} \sum_i \left[f(g_i) \right]^2 \Delta g_i \qquad [1]$$

The texture index shows the strength of the texture and it is 1 for random materials, increasing for oriented samples. The OD allows too the calculation of interesting pole figures that cannot be measured, i.e., the corresponding to the (111), reflection very close in these compositions to the (111) of the Pt layer, and which is the preferred orientation in some cases.

If we keep the sample direction constant and represent the associated crystal directions, we obtain an inverse pole figure, like the ones shown in Figure 3 for a direction normal to the film. It describes the densities for crystal directions falling into that sample direction. The analysis of the inverse pole figures allows the identification of the texture fibre components. They are distribution functions f(g), centered in orientations g_i, in such a way that the sum of all of them generates the OD. In the case of fibre textures the inverse pole figure of the symmetry axis represents the OD. From the levels obtained in the inverse pole figure we can estimate the contribution of each component to the texture of the material.

TABLE I. VARIATIONS OF THE TEXTURE INDEX WITH THE NUMBER OF LAYERS OF LANTHANUM MODIFIED LEAD TITANATE (PTL) THIN FILMS. RELIABILITY FACTORS OF THE OD REFINEMENT (RP0 AND RP1) ARE ALSO INDICATED.

Number of layers	Texture Components	Texture index	RP0 (%)	RP1 (%)
1	<001>,<100> <221>	10.5	36	16
2	<001>,<100> <221>	7.5	24	19
3	<001>,<100> <221>	6.2	22	16
4	<001>,<100> <221>	4.6	18	12
5	<001>,<100> <221>	3.9	19	15

3. TEXTURE OF FERROELECTRIC THIN FILMS

The textures of several ferroelectric thin films have been studied, all of them within the technologically important group of perovskite lead titanate based materials: lanthanum and calcium modified lead titanates (PTL and PTC) and lead zirconate titanate (PZT). They are ideal candidates for texture studies due to the need of highly textured films for piezo and pyroelectric applications. Not only the ferroelectric films have been studied, but the texture of the Pt layer on top of which they are grown. However, the results can be affected of larger errors due to the effects of absorption occurred in the layer above it.

The first observation is the appearance, for all the films studied, of an axial symmetry of the texture, i.e., fibre textures, with the fibre axis perpendicular to the film surface (Figure 2). This is a common feature for both the Pt layer (<111> fibre textured perpendicular to the film surface for all the films analysed, irrespective of the substrate used) and the perovskite films, which reflects the strong influence of the texture of the substrate on the final texture of the films.

The quantitative analysis of those pole figures allows, through the normalised orientation distribution function, the comparison between different films. The first available information is the identification of the preferred orientations, or components of the texture, present in the material. In Figure 3 we show the inverse pole figures corresponding to the perpendicular to the film surface of two rhombohedral PZT films deposited on the same kind of substrate. In PZTr1 we observe a clear <111> fibre texture, while the PZTr2 figure corresponds to a <110> fibre texture, with a small component in <100>. The strength of the texture of the film can be compared through the texture index. In this case PZTr1 is clearly more oriented, with a texture index of 13 m.r.d.^{2} compared to the 2.5 m.r.d.^{2} of PZTr2. However, we should take into account that the appearance of multiple components lowers the value of the texture index, so these comparisons must be done with care.

The comparative analysis of the texture index is more meaningful among films with the same texture components. Table I summarises the texture results obtained for several tetragonal PTL thin films, which were prepared with different number of layers deposited on the same substrate as reported elsewhere [15]. All of them present a mixed <100>, <001> orientation perpendicular to the film surface, with a very small component in <221>. It can be observed that the texture index decreases with increasing the number of deposited layers. This is a very interesting result regarding the evolution of the texture development in the film. It seems to indicate a progressive loss of the texture strength with the distance to the substrate. This may correspond to a situation of heterogeneous nucleation, i.e., crystals nucleating throughout the thickness of the film, which becomes increasingly important for the thicker films and reduces the degree of orientation.

We have mentioned before the influence of the substrate on the final properties of the film. In order to analyse this relationship PTC films were grown on different substrates [16] under the same conditions and the textures were compared (Figure 4). While films deposited on the traditional Pt/TiO_2/Si(100) (PTC) do not present any significant crystal orientation, a mixed <001>, <100> fibre texture perpendicular to the film surface is developed for the other two films. Stress effects on the film were considered to explain the preferred orientation observed [17]. Comparing the texture strength, the most textured film (F^2=32.1 m.r.d.^{2}) is the one deposited on Pt/$SrTiO_3$(100) (PTCS). However, the best pyroelectric properties [17] are found for the film deposited on Pt/MgO(100) (PTCM) with F^2=5.2 m.r.d.^{2}. If we analyse the contributions to the final texture of the different components, we observe that in PTCM the component <001> corresponding to the polar axis is the most important of the two (higher density levels in the inverse pole figure). As this component is the one influencing the ferroelectric behaviour of the film, PTCM presents higher pyroelectric coefficients than PTCS. This shows how not only the values of the texture strength should be considered, but the contributions of the different components.

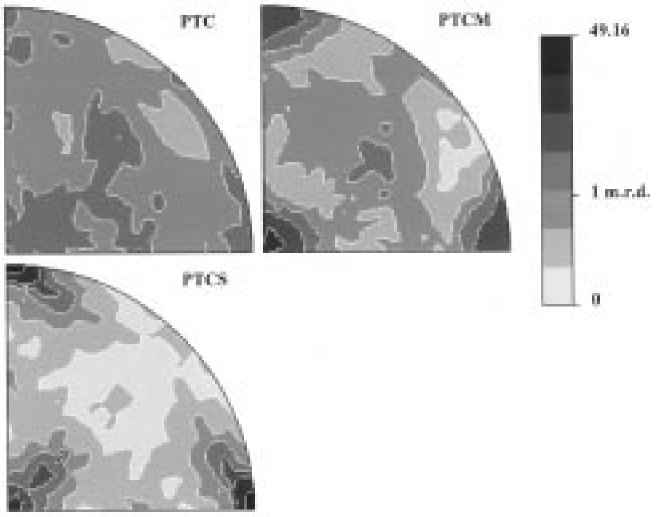

Figure 4. Inverse pole figures for the normal direction, obtained from calcium modified lead titanate thin films deposited on different substrates: (a) PTC on Pt/TiO_2/Si(100), (b) PTCM on Pt/MgO(100), (c) PTCS on Pt/$SrTiO_3$(100). (Equal are projection and logarithmic density scale)

TABLE II. TEXTURE INDEX OF TWO TETRAGONAL LEAD TITANATE ZIRCONATE (PZTT) DEPOSITED ON DIFFERENT SUBSTRATES. RELIABILITY FACTORS OF THE OD REFINEMENT (RP0 AND RP1) ARE ALSO INDICATED

Sample	Substrate	Texture Component	Texture index	RP0 (%)	RP1 (%)
PZTt1	Pt/Ti/Si(100)	<111>	32	20	11
PZTt2	Au/Pt/Ti/Si(100)	<111>	19	20	11

The problem of the development of texture in thin films is complex and many factors have to be taken into account. It has been reported that the appearance of <111> preferred orientation in PZT films is caused by the nucleation of the perovskite on the Pt layer through a transient PbPt intermetallic phase [18]. The texture analysis of two films with the same thickness, same processing conditions and deposited on a Pt/Ti/Si with and without a Au layer on top, has been carried out in order to see the influence of the intermetallic on the texture (Table II). The Au layer should inhibit the appearance of any PbPt intermetallic. A decrease of the texture strength and the crystalliny are observed, but the <111> preferred orientation normal to the film surface is retained. Probably the Au layer does not favour the crystallisation of the perovskite, but do not stop the development of the <111> texture. This shows that although the intermetallic plays an important role in the development of this preferred orientation, it is not the only factor to consider.

With these examples we have shown how the new information available with the quantitative texture analysis gives a new insight of the mechanisms that lead to the development of certain textures in ferroelectric thin films. We have seen as well the comparison of the texture parameters with the final ferroelectric behaviour of some films. We believe that these preliminary results justify further and wider use of this method in ferroelectric materials, both in ceramic and thin film form.

4. SUMMARY

A quantitative texture analysis has been applied to ferroelectric thin films. This analysis involves the measurement of pole figures with a goniometer and the refinement of an orientation distribution function. We can obtain complete information on the preferred orientations of the thin films and of the Pt layers of the substrate. The geometry of the texture is identified and all contributions to the texture are revealed. The calculation of a texture index allows easy comparison among different samples.

Examples of this analysis on lead titanate based thin films show the importance of this kind of analysis to understand different aspects of the development of textures in thin films. Also the results are correlated to the interesting properties of these ferroelectric materials, like the pyroelectric coefficients.

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