Preferential orientation of ferroelectric calcium modified lead titanate thin films grown on various substrates

J. RICOTE, D. CHATEIGNER*, M.L. CALZADA, J. MENDIOLA

Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, 28049 Madrid, Spain
*Laboratoire de Physique de l'État Condensé, Université du Maine, 72085 Le Mans, France

Among all the factors that determine the development of preferential orientation or texture in polycrystalline thin films, the most important is the nature of the substrate. A preferential orientation of the crystallites with the polar axis perpendicular to the film surface results in an important improvement of the ferroelectric behaviour. In the search for the substrate that produces highly oriented ferroelectric thin films, this work analyses by quantitative texture analysis calcium modified lead titanate thin films deposited on platinised Si, MgO and $SrTiO_3$ substrates. A mixed preferential orientation along <100> and <001> is obtained. From the results of this study we discuss the factors that contribute to the different final textures. First, we analyse the different texture strength of the Pt layer observed in the three substrates, and the growth of the ferroelectric film on them, whose orientation seems to develop independently of the Pt in this case. And secondly, we study the effect of the stress developed during the crystallisation process, caused by the difference in thermal expansion coefficient between each of the substrates and the film, especially on the domain structure formation at the paraelectric cubic- ferroelectric tetragonal phase transition.

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

Orientación preferente de láminas delgadas ferroeléctricas de titanato de plomo modificado depositadas sobre distintos substratos

La aparición de orientaciones preferentes o textura en láminas delgadas policristalinas se puede potenciar de muchas maneras, pero probablemente el factor más importante a tener en cuenta es la naturaleza del substrato. Si se logra una orientación preferente de los cristales de la lámina con el eje polar perpendicular al plano de la lámina el comportamiento ferroeléctrico del material mejora. Englobado en la búsqueda del substrato más adecuado para obtener láminas delgadas ferroeléctricas orientadas, este trabajo estudia por medio de análisis cuantitativo de texturas láminas delgadas de titanato de plomo modificado con calcio depositadas sobre substratos de Si, MgO y $SrTiO_3$ con electrodos de Pt. Se obtiene una orientación preferente mixta a lo largo de <100> y <001>. A partir de los datos obtenidos se analizan los factores que contribuyen a las diferentes texturas obtenidas. Por un lado se discute el diferente grado de texturación del Pt sobre los tres substratos, y la formación de la lámina ferroeléctrica sobre ellos, cuya orientación parece desarrollarse independientemente del Pt en este caso. Y por otro, se estudia el efecto de las tensiones presentes durante el proceso de cristalización provocadas por las diferencias entre los coeficientes de expansión de cada uno de los substratos y la lámina, especialmente en el paso de la fase paraeléctrica cúbica a ferroeléctrica tetragonal,

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

1. INTRODUCTION

The search for highly oriented thin films is especially important for ferroelectric materials, and a considerable effort has been dedicated to this topic. The presence of any kind of preferential orientation, or texture is a determinant factor of the physical properties of ferroelectric materials, and, therefore, of their applications. Among the wide range of technological applications of ferroelectric thin films, we emphasise those related to the fabrication of infrared sensors and microelectromechanical systems (MEMS), for which calcium modified lead titanate compositions have proved to be very promising (1,2). The question of how to induce a preferential orientation in ferroelectric thin films to improve their properties for applications is not fully solved, although different approaches have been considered.

There are several factors that may affect the development of preferential orientations in thin films. These can be related to the

steps previous to the film deposition like for example the nature of chemical precursors and solution preparation conditions in sol-gel derived films (3). But usually the final texture is mainly related to the crystallisation temperature, soaking time or heating rate (4,5). Thickness is another factor to be taken into account, and affects mainly the degree of orientation of the film, not the type of orientation (6). Most of these studies use Si based substrates with Pt on top, which serves as bottom electrode. Pt seems to be one of the very few elemental conductors that remains sufficiently stable during processing of the ferroelectric film, and that is why is widely used. The mechanisms that lead to the development of preferential orientations of the ferroelectric film on the Pt layer are still under discussion. Some authors postulate the formation of hillocks in the Pt layer after annealing, which are nucleation sites for the oriented crystallites (7). Therefore, an annealing of the substrate prior to the

deposition of the film is recommended. The formation of a transient intermetallic layer with a closer lattice match to Pt than the lead titanate based ferroelectric has also been suggested, either Pt_xPb (8,9) or Pt_3Ti (10). Therefore modifications of the substrate are induced to promote the appearance of such layers, like the use of a Ti layer on top of the Pt to promote most probably the intermetallic Pt_3Ti, and which successfully induces the desired orientation on modified lead titanate films (11). Alternatively we can try to modify the traditionally obtained <111> texture of Pt by the use of other substrates different to the Si based, like MgO (12) or $SrTiO_3$ (13). A Pt orientation along <100> will enhance in principle orientation along the polar axis <001> in the lead titanate based thin films, thus improving their ferroelectric properties.

On cooling, the paraelectric phase transforms into the ferroelectric and ferroelectric domains appear. All this process may take place under stress, whose origin can be the lattice mismatch, the different thermal expansion of film and substrate or the volume changes due to the phase transformation on cooling (14). Some authors point other causes of stress, like the size of colloidal particles (15) and the wetting of the substrate by the solution (16).

In this work we will focus on the texture differences achieved by the use of different substrates. In order to do that, we analyse ferroelectric Ca modified lead titanate thin films deposited on several platinised substrates. We use a quantitative texture analysis method, which, although used regularly in other scientific areas, has not been until recently applied to ferroelectric materials (17). From the texture results obtained both for the film and the Pt layer, we discuss the mechanisms that lead to the development of texture in these films.

2. EXPERIMENTAL PROCEDURE

Thin films of Ca-modified lead titanate (PTC) were obtained by spin-coating deposition of sol-gel processed solutions of $Pb_{0.76}Ca_{0.24}TiO_3$ with 10% excess PbO on two different substrates: Pt/MgO (100) (PTC-Mg); and $Pt/SrTiO_3$ (100) (PTC-Sr) (18). They were crystallised at 700°C for 50 s by rapid thermal processing.

Quantitative texture analysis (17) was used to characterise the preferential orientations of both PTC and Pt layers. Measurement of experimental pole figures was carried out with a Huber four-circle goniometer mounted on an INEL X-ray generator (Cu K_α wavelength) using 5°x5° steps to cover the whole pole figure. A curved position sensitive detector (INEL CPS-120) was used to acquire a complete diffraction pattern at each position of the sample, decreasing considerably data acquisition times. The integrated intensities were treated and corrected for absorption, volume variations and delocalisation effects, using INEL software programs. Pole figures are normalised into distribution densities, which are expressed as multiples of a random distribution (m.r.d.). A sample without any preferred orientation has pole figures with constant values of 1 m.r.d. From several of these pole figures we refined the orientation distribution (OD), f(**g**), following the Williams-Imhof-Matthies-Vinel iterative method (WIMV) (19). This function describes the amount of crystallites with an orientation between **g** and **g**+d**g** (**g** = αβγ, Euler angles). The quality of the refinement is assessed by the reliability factors (RP0 and RP1, for global values and those above 1 m.r.d., respectively). From the OD we can calculate pole figures which are not available experimentally, analyse the different orientation components present, and calculate parameters

indicative of the texture strength, like the texture index:

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

The different texture components are identified through the representation of inverse pole figures. In this case we keep the sample direction constant and represent the associated crystal directions. Those directions showing higher distribution density values are considered components of the global texture, and their relative contribution can be assessed. The calculations to obtain and manipulate the OD mentioned above have been carried out with the Berkeley Texture Package (BEARTEX) (20).

3. TEXTURE RESULTS AND DISCUSSION ON TEXTURE DEVELOPMENT

3.1. Pt layer

The quantitative analysis of the texture of the Pt layer on the traditional substrate TiO_2/Si and on the alternative substrates MgO and $SrTiO_3$ produces the results shown in Table 1. The low values of the reliability factors RP0 and RP1 show the good quality of the OD refinement. The Pt layer presents preferential orientation only along <111> for the three substrates. This is concluded from the inverse pole figures shown in Figure 1. The small contribution along <001> observed for $Pt/SrTiO_3$ is ascribed to an artefact of the calculation produced by the difficulty in separating reflections of $SrTiO_3$ and Pt. According to the values of Table 1, texture strength is lower for the Pt layer deposited on MgO

TABLE I. COMPARISON OF THE TEXTURE OBTAINED FOR A Pt LAYER DEPOSITED ON THREE DIFFERENT SUBSTRATES.

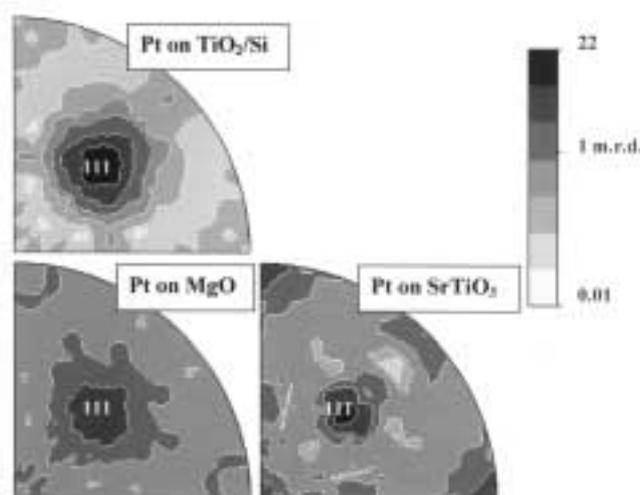| Substrate	Texture Components	Texture Index (mrd^2)	RP0 (%)	RP1 (%)
Pt on TiO_2/Si	<111>	10.3	27	16
Pt on MgO	<111>	3.4	22	14
Pt on $SrTiO_3$	<111>	7.1	34	19

Figure 1. Inverse pole figures for the normal direction to the film surface of Pt layer deposited on different substrates. (Equal area projection and logarithmic density scale)

Boletín de la Sociedad Española de Cerámica y Vidrio. Vol. 41 Núm. 1 Enero-Febrero 2002

81

and SrTiO$_3$, which means that they have a smaller fraction of crystals oriented along <111>. The 111 recalculated pole figures (Figure 2), apart from the maximum in the centre, present rings of high distribution values, indicating texture rotational symmetry around an axis, which is called fibre texture. {111} planes of oriented crystals diffract when the sample is at 0°(centre of the pole figure) and at ~70°, where the other {111} planes of the same crystal are at the Bragg position. In the case of epitaxial growth, the film grows like a single crystal on the substrate, and diffraction is produced at specific sample positions, producing isolated maxima in the pole figure. In other polycrystalline films, crystals grow with less restrictions, and rotation of the sample about the fibre axis produces the same probability of finding diffracting planes, and rings appear in the pole figures. In summary, the Pt layer presents <111> fibre texture when deposited on any of the substrates used in this work.

Pt is cubic with a = 3.923 Å. When it is deposited on traditional Si based substrates, it grows on the adhesive layer of TiO$_2$ (orthorhombic a = 5.456 Å, b = 9.182 Å, c = 5.143 Å) or Ti (hexagonal a = 2.951 Å, c = 4.683 Å). Despite of these unrelated structures we obtain Pt with preferential orientation, probably due to special orientational relations of low interfacial energy. As the <111> orientation is kept for the other two substrates, such relations seem to remain valid for them also. MgO (100) and SrTiO$_3$ (100) were chosen because of their better match with Pt: MgO is cubic a = 4.211 Å and SrTiO$_3$ is also cubic a = 3.904 Å. Therefore, it was expected to obtain a certain degree of <100> Pt orientation, like the results reported on Pt deposited on MgO in (12) and (21), although the <111> orientation was not completely lost. Apparently we were not able to find the combination of sputtering conditions necessary to trigger the massive nucleation of <100> oriented crystals. It seems that the energy requirements are lower for the nucleation of crystals with low interfacial energy, (111) oriented for Pt, which at the same time have the ability to grow preferentially over other crystals during heat treatment. A process to obtain highly textured films on substrates with unrelated structures has been developed based on those principles (22). The lack of epitaxial relationships results in the fibre texture observed in the pole figures.

The degree of <111> orientation decreases when the Pt is deposited on MgO or SrTiO$_3$. Although we were not able to create the conditions for the development of any significant <100> orientation, it is plausible that a certain amount of oriented crystals along that direction nucleate. And, due to the structural similarity some other crystals with other orientations too. Their fraction will be kept too low to be detected. Under those circumstances the fraction of <111> oriented crystals will diminish in MgO and SrTiO$_3$ substrates, and therefore the overall texture index, the same way our results show.

3.2. PTC film.

PTC films are grown on top of the Pt layers analysed, and the texture results are shown in Table 2. Contributions from reflections coming from the substrate, overall from SrTiO$_3$ (100), have been eliminated, correcting previously reported results (6). Texture index values are similar to the ones obtained for other modified lead titanates deposited on Si based substrates (17). The preferential orientation is mainly along two directions: <001> and <100> for both films, as deduced from the inverse pole figures of Figure 3. The PTC film grown on
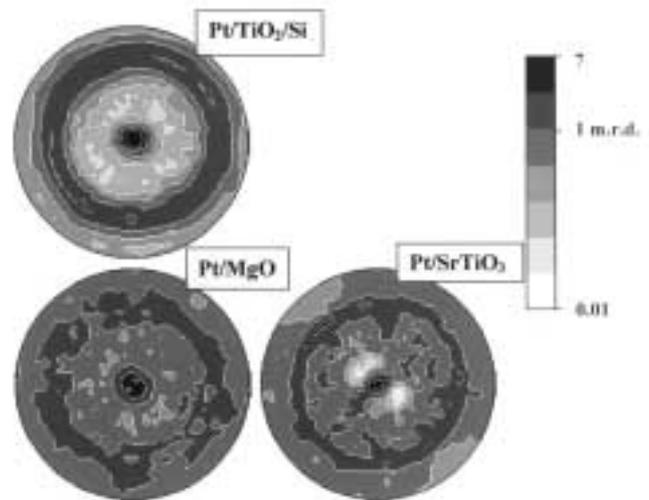

Figure 2. 111 recalculated pole figures of Pt layer deposited on different substrates showing the axysymmetry of the <111> texture. Note that scale maximum has been reduced to better represent the lowest textured sample (Equal area projection and logarithmic density scale)

TABLE II. TEXTURE RESULTS OF PTC FILMS GROWN ON PLATINISED MgO AND SrTiO$_3$ SUBSTRATES.

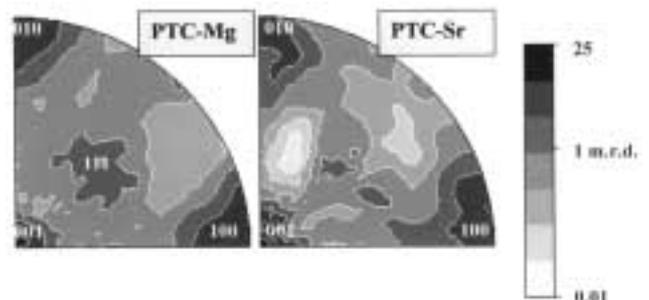| Film	Substrate	Texture Components	Texture Index (mrd^2)	RP0 (%)	RP1 (%)
PTC-Mg	Pt/MgO	<001>,<100>	5.1	21	10
PTC-Sr	Pt/SrTiO$_3$	<001>,<100>	7.9	27	14

Figure 3. Inverse pole figures for the normal direction to the film surface of PTC films grown on two different substrates: Pt/MgO and Pt/SrTiO$_3$. (Equal area projection and logarithmic density scale)

82

Boletín de la Sociedad Española de Cerámica y Vidrio. Vol. 41 Núm. 1 Enero-Febrero 2002

Pt/MgO presents a very weak contribution from crystals oriented along <111> as the corresponding pole figure shows, but it is too small to be considered significant.

Recalculated pole figures are shown in Figure 4. It can be observed that the highest distribution density values are in the centre of the 001 and 100 pole figures, as corresponds to a mixed preferential orientation along these two directions perpendicular to the film surface. The fraction of crystals with this orientation gives rise to high distribution density values around 55° of inclination respect to the normal in the 111 pole figures (also shown). (Remember that 55° is approximately the angle between <111> and <001> or <100> directions.) The fact that these values in the 111 pole figure form a uniform ring tells us that the orientation has rotational symmetrical around an axis, and therefore it is a fibre texture. Note also the density values in the centre of the 111 pole figure of PTC-Mg film, caused by the weak <111> texture
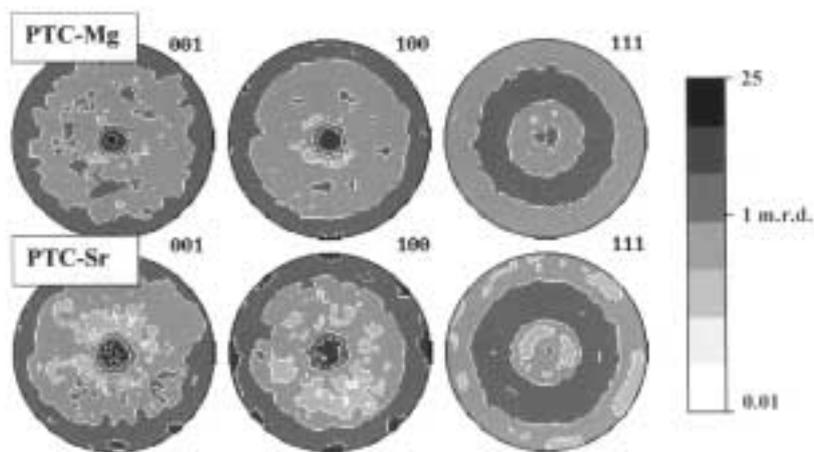

Figure 4. 001, 100 and 111 recalculated pole figures of PTC thin films grown on two different substrates: Pt/MgO and Pt/SrTiO$_3$. (Equal area projection and logarithmic density scale)

contribution already mentioned. In order to estimate the contributions of the two orientation components, we compare the values from the centre of the 001 and 100 pole figures. We observe that these values are higher for the 001 pole figures, which means that the texture component <001> is more important than the <100> for both films.

The lack of lattice matching between (111) planes of Pt and (100) of the cubic phase of PTC is evident. Nevertheless, the nucleation of PTC takes place preferentially with (100) crystals, which after the cubic to tetragonal transition on cooling, results in a mixture of {100} and {001} crystals, and the mixed orientation measured. It is important to note that the nucleation takes place in the film-substrate interface, i.e., it is an heterogeneous nucleation that results in a textured film. If other nucleation sites like pores were present, there would not be any preferential orientation in the film. This is controlled by the processing conditions. Anyway, as for the Pt layer, we find again a case of preferential growth of a film on a substrate with unrelated structures. It seems that in this case the low interfacial energy planes are the (100) of the cubic PTC. The final fibre character of the texture, observed in the pole figures (Figure 4), is a consequence of the lack of epitaxial relationships as explained above. We can conclude from these results that the search for a better lattice match of the film with the Pt layer, e.g., by promoting <100> orientations, is not a determinant factor for the development of the film texture.

Although it would seem that the situation described is the most advantageous, due to the fact that we obtained an orientation with the polar axis perpendicular to the film surface, we should take into account the <100> associated component that appears on cooling when the cubic phase transforms into tetragonal. Crystals oriented along <100> directions have the polar axis in the plane of the film, and therefore, do not contribute to the net polarisation of the film. This may affect negatively the ferroelectric behaviour of the film, and that is why it is searched in the literature the mechanisms that promote the nucleation of other more favourable orientations, like <111>. However, good pyroelectric properties were obtained from the PTC films studied here (13), due most probably to the higher fraction of crystallites oriented <001> than <100>, as our results show.

This can be attributed to the presence of compressive stress during the paraelectric-ferroelectric phase transition on cooling (14). Tensile stress makes the polar axis <001> be preferentially aligned in the plane of the film. Instead, compressive stress induces the polar axis to be perpendicular to the film substrate. Among the origin of stress, the different thermal expansion coefficients of the film and the substrates can be considered in this case the most important. If we calculate the thermal stress involved in this transformation, we find that both PTC-Mg and PTC-Sr films develop compressive stress (13), favouring the <001> orientation over the <100>, as our results show. Therefore, the choice of these two substrates have shown to be advantageous to the production of oriented films with a large fraction of crystals oriented along the polar axis perpendicular to the film substrate.

4. CONCLUSIONS

Quantitative texture analysis of ferroelectric Ca modified lead titanate films deposited on several platinised substrates provides us with specific information to discuss the development of textures when substrate and film have unrelated structures. The analysis first of the <111> fibre texture of the Pt substrate shows how, on each of the substrates tested, crystals of low interfacial energy (111) nucleate and grow without epitaxial relation with the underlying substrate. Only under certain sputtering conditions on substrates with close structures, it has been reported in the literature that different orientations can be achieved.

We have shown also that the ferroelectric films deposited on those platinised substrates develop a mixed preferential orientation along <100> and <001>, although there is not any clear structural relation with the underlying Pt layer. Therefore changes in the orientation of this layer do not affect in principle the texture of the film, whose orientation seems to develop independently in this case. Due to the compressive stress present during the paraelectric-ferroelectric transition on cooling, the component with the polar axis perpendicular to the film surface is favoured. This results in an improvement of the ferroelectric behaviour of the films.

ACKNOWLEDGEMENTS

REFERENCES

1. A. Seifert, P. Muralt, N. Setter, "High figure-of-merit porous $Pb_{1-x}Ca_xTiO_3$ thin films for pyroelctric applications", Appl. Phys. Lett. **72**[19], 2409-2411 (1998).

2. A.L. Kholkin, M.L. Calzada, P. Ramos, J. Mendiola, N. Setter, "Piezoelectric properties of Ca-modified $PbTiO_3$ thin films", Appl. Phys. Lett. **69**[23], 3602-3604 (1996).

3. C. Chen, D.F. Ryder Jr, W.A. Spurgeon, "Synthesis and microstructure of highly oriented lead titanate thin films prepared by a sol-gel method", J. Am. Ceram. Soc. **72**[8], 1495-1498 (1989).

4. K.G. Brooks, I.M. Reaney, R. Klissurska, Y. Huang, L. Bursill, N. Setter, "Orientation of rapid thermally annealed lead zirconate titanate thin films on (111) Pt substrates", J. Mater. Res. **9**[10], 2540-2553 (1994).

5. V.Y. Shur, E.B. Blankova, A.L. Subbotin, E.A. Borisova, D.V. Pelegov, S. Hoffmann, D. Bolten, R. Gerhardt, R. Waser, "Influence of crystallisation kinetics on texture of sol-gel PZT and BST thin films", J. Eur. Ceram. Soc. **19,** 1391-1395 (1999).

6. J. Ricote, D. Chateigner, L. Pardo, M. Algueró, J. Mendiola, M.L. Calzada, "Quantitative analysis of preferential orientation components of ferroelectric thin films", Ferroelectrics **241,** 167-174 (2000).

7. G.A.C. Spierings, J.B.A. Van Zon, P.K. Larsen, "Influence of platinum-based electrodes on the microstructure of sol-gel and MOD prepared lead zirconate titanate films", Integrated Ferroelectrics **3,** 283-292 (1993).

8. S.Y. Chen, I.W. Chen, "Temperature-Time texture transition of $Pb(Zr_{1-x}Ti_x)O_3$ thin films: role of Pb-rich intermediate phases", J. Am. Ceram. Soc. **77** [9], 2332-2336 (1994).

9. Z. Huang, Q. Zhang, R.W. Whatmore, "Structural development in the early stages of annealing of sol-gel prepared lead zirconate titanate thin films", J. Appl. Phys. **86**[3], 1662-1669 (1999).

10. T. Tani, Z. Xu, D.A. Payne, "Preferred orientations for sol-gel derived PLZT thin layers", Ferroelectric Thin Films III, Materials Research Society Symposium Proceedings Vol 310, pp. 269-274, Materials Research Society. Pittsburgh, USA (1993).

11. M.L. Calzada, R. Poyato, J. García-López, M.A. Respaldiza, J. Ricote, L. Pardo, "Effect of the substrate heterostructure on the texture of lanthanum modified lead titanate thin films" J. Eur. Ceram. Soc. (in press).

12. J.S. Lee, H.H. Kim, H.J. Kwon, Y.W. Jeong, "Texture control and interfacial structures of $SrBi_2Ta_2O_9$ thin films on Pt", Appl. Phys. Lett. **73**[2], 166-168 (1998).

13. R. Jiménez, M.L. Calzada, J. Mendiola, "Preferred orientation of solution derived (Pb, Ca)TiO_3 thin films on $SrTiO_3$ and MgO", Proceedings of the Eleventh IEEE International Symposium on Applications of Ferroelectrics, pp. 155-158, Ed. E. Colla, D. Damjanovic and N. Setter. IEEE Catalog number 98CH36245. Montreux. Switzerland (1998).

14. B.A. Tuttle, T.J. Garino, J.A. Voigt, T.J. Headley, D. Dimos, M.O. Eatough,"Relationships between ferroelectric 90º domain formation and electrical properties of chemically prepared $Pb(Zr,Ti)O_3$ thin films",Science and Tecnology of Electroceramic Films, Ed. O Auciello and R. Waser, NATO ASI Series. Serie E: Applied Sciences **284,** 167-175 (1995).

15. H.X. Qin, J.S. Zhu, Z.Q. Jin, Y. Wang, "PZT thin films with preferred orientation induced by external stress", Thin Solid Films **379,** 72-75 (2000).

16. J. Mendiola, M.L. Calzada, P. Ramos, M.J. Martín, F. Agulló-Rueda, "On the effects of stresses in ferroelectric (Pb, Ca)TiO_3 thin films", Thin Solid Films **315,** 195-201 (1998).

17. J. Ricote, D. Chateigner, "Quantitative texture analysis applied to the study of preferential orientations in ferroelectric thin films", Bol. Soc. Esp. Cerám. Vidrio **38**[6], 587-591 (1999).

18. R. Sirera, M.L. Calzada, "Multicomponent solutions for the deposition of modified lead titanate films", Mat. Res. Bull. **30**[1], 11-18 (1995).

19. S. Matthies, G.W. Vinel, "On the reproduction of the orientation distribution function of texturised samples from reduced pole figures using the conception of a conditional ghost correction", Phys. Stat. Sol. B **112,** K111-K120 (1982).

20. H.R. Wenk, S. Matthies, J. Donovan, D. Chateigner, "BEARTEX: a windows-based program for quantitative texture analysis", J. Appl. Cryst. **31,** 262-269 (1998).

21. K. Iijima, R. Takayama, Y. Tomita, I. Ueda, "Epitaxial growth and the crystallographic, dielectric and pyroelectric properties of lanthanum-modified lead titanate thin films", J. Appl. Phys. **60**[8], 2914-2619 (1986).

22. K.T. Miller, F.F. Lange, "Highly oriented thin films of cubic zirconia on sapphire through grain growth seeding", J. Mater. Res. **6**[11], 2387-2392 (1991).

◆ ◆ ◆

84

Boletín de la Sociedad Española de Cerámica y Vidrio. Vol. 41 Núm. 1 Enero-Febrero 2002