

Tailoring of the elastic properties by texture control in ferroelectric thin films for MEMS

J. Ricote¹, M. Algueró¹ and D. Chateigner²

¹ Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, E-28049 Madrid, Spain

² Laboratoire de Cristallographie et Sciences des Matériaux-ISMRA, F-14050 Caen, France

Keywords: Texture, Elastic properties, Orientation Distribution Function, Ferroelectric Thin Films, Modified Lead Titanate

Abstract. The use of piezoelectric thin films in advanced devices such as microelectromechanical systems (MEMS), not only rests on high piezoelectric coefficients, as the ones achieved in some ferroelectric lead titanate derived compositions, but also on their mechanical properties. This makes the study of the correlation between texture and elastic properties of high interest for the processing of piezoelectric thin films with tailored properties, regardless of which, not much related work has been reported up to now. In this paper we present the analysis of the variations observed in the elastic tensor of a series of modified lead titanate thin films with different orientations. The different textures were induced either by deposition on modified substrates or by changes of the annealing scheme. Orientation distribution functions (ODF) for all films were obtained by an advanced texture quantitative analysis of x-ray diffraction data of several pole figures. From the ODF and the single crystal tensor, we are able to calculate the effective elastic properties of the films by a geometric averaging procedure. This is a promising result in the tailoring of the mechanical properties of these piezoelectric thin films for applications.

Introduction

Microelectromechanical systems (MEMS) have been studied for decades [1], growing in the last decade as an important area of technology. The demand for more sophisticated sensors and actuators is leading nowadays to a great effort devoted to the improvement of the MEMS performance, which involves directly the materials used [2]. Piezoelectric and, among them, ferroelectric thin films play an important role as materials used in the core part of MEMS: the transducer element [3]. Among the material properties to take into account in the design of the device, we have the piezoelectric coefficients, the stress state and the elastic compliance tensor. For example, in the design of a microcantilever for a scanning probe microscope [4], we have to consider the spring constant and the resonance frequency. Although these parameters are usually expressed in terms of a technical modulus like the Young's modulus, the constituent equations show that they are related to the coefficient s_{11} of the film [5]. This is similar for other devices based on vibrating membranes [6], where for example s_{12} is also relevant. Therefore, the control of the values of the elastic coefficients of the material is of the utmost importance for the final MEMS performance.

In the case of polycrystalline thin films, elastic properties are known to depend on the distribution of crystallographic orientations or texture. However, the correlation between these parameters has not been clearly established yet. Although much work is devoted to the control of the preferential orientations of polycrystalline films by modifications of the processing route or the substrate [7-9], only phenomenological studies of the relation between texture and physical properties are found. This is probably due to the lack of quantitative information on the texture of films, which has been presented only recently for ferroelectric thin films by the authors [10,11]. The calculation of the properties of the polycrystal, averaging the single crystal properties, must take into

account the texture, which needs to be introduced in the calculations in the form of a function. The orientation distribution function (ODF) is obtained by the so-called quantitative texture analysis of experimental data.

In this work we use the ODF obtained for several ferroelectric thin films to calculate the corresponding compliance tensors and analyze the modifications introduced by the texture. This will shed light on the correlation between the elastic properties and texture. The possibility to produce tailored elastic properties by texture control for MEMS applications will be then discussed.

Procedure for the calculation of the elastic tensor of textured films

Tensor properties of a polycrystal can be determined by an adequate volume average of the properties of the constituent crystals. To carry out this process, we must write the tensors in a common coordinate system. For each crystal, the components of the tensor must be obtained in sample coordinates from the crystallographic components by tensor transformation. Therefore, we define first the film reference system, where the 3-axis corresponds to the direction normal to the larger surface of the film, and 1- and 2- axis are mutually perpendicular to the 3-direction (Fig. 1). Note that 1- and 2- directions are arbitrarily chosen, which does not have any effect on the calculations due to the fiber character (axisymmetric) of the texture of the films analyzed.

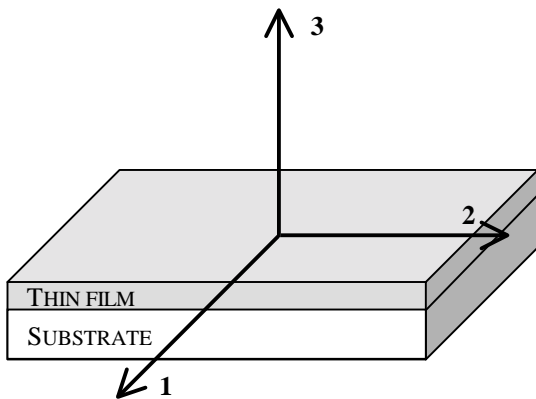


Figure 1. Thin film coordinate system

In our case, elastic properties are anisotropic, and therefore the texture is a determinant factor that must be introduced in the calculations [12]. In general terms, the volume average of a tensorial quantity \mathbf{t} is denoted by:

$$\langle \mathbf{t} \rangle = \int \mathbf{t}(\mathbf{g}) f(\mathbf{g}) d(\mathbf{g}). \quad (1)$$

being $f(\mathbf{g})$ the orientation distribution function (ODF) and $\mathbf{g} = \alpha\beta\gamma$, $\alpha\beta\gamma$, three Euler angles that locate one single crystallite orientation relative to the macroscopic sample frame. The integral is defined over the domain of the orientation angles \mathbf{g} . Among the various averaging procedures, we choose the geometric mean, first developed by Aleksandrov and Aisenberg and later improved by Matthies and Humbert [13]. The main advantage of this method is that the average of the reciprocal is automatically consistent with the reciprocal of the average property, which is not true for other procedures, like the Voigt, Reuss or Hill average. With the geometric mean procedure we then obtain intrinsically the same polycrystal elastic properties, independently of whether the single crystal compliance or stiffness is used to calculate the average. Furthermore, the geometric mean method produces results intermediate between the ones obtained by the Reuss and Voigt approaches, which represent the extreme values of the elastic coefficients. They are also reported to

be in agreement with the results obtained by the best approaches known today, such as the self-consistent scheme [12].

Complete studies of the elastic properties of single crystals for specific compositions are difficult to find in the literature. This is the case for modified lead titanates, the composition analyzed in this paper. Due to the difficulty of obtaining PbTiO_3 single crystals suitable for measurements, scarce information on single crystal properties of these compositions are found in the literature. A complete set of elastic properties have been obtained by Li et al. [14] and Kalinichev et al. [15] by Brillouin scattering. As we will analyze the variations of the elastic coefficients with texture, and not the actual values, we will use these values for the calculations of the modified lead titanate tensors. We can consider them as a good approximation to the real values, and the trends obtained in the calculations should be unaffected.

Determination of the orientation distribution function $f(\mathbf{g})$ was carried out by the analysis of experimental X-ray pole figures as reported elsewhere [11,16]. The used refinement method is the WIMV (Williams-Imhof-Matthies-Vinel) iterative method [17]. From $f(\mathbf{g})$ we obtain the texture components and the texture index F^2 , a parameter indicative of the overall degree of orientation of the film:

$$F^2 = 1/8\pi^2 \int [f(\mathbf{g})]^2 d(\mathbf{g}). \quad (2)$$

The calculations to obtain and manipulate the ODF, and the determination of the compliance tensors have been carried out with the Berkeley Texture Package (BEARTEX) [18].

Results and discussion

The ODF of a series of La modified lead titanate (PTL) and Ca modified lead titanate (PTCa) thin films with different textures were determined. Preparation details are described elsewhere [19]. Lead titanate based films are obtained by the deposition of sol-gel derived solutions on platinized substrates, usually Si based, but MgO or SrTiO_3 single crystal substrates are also used. In order to induce texture in these films different annealing routes and substrates are used. The use of a rapid thermal processing during crystallization for these compositions favors the appearance of preferential orientations, which are along $\langle 100 \rangle, \langle 001 \rangle$ perpendicular to the film surface (3-axis), if there is no interaction with the substrate that disrupts this type of nucleation. The introduction of a texture component along $\langle 111 \rangle$ directions parallel to the 3-axis requires a modification of the substrate, by the introduction of a thin layer of Ti that allows the nucleation of this kind of orientation.

Table 1 summarizes the compliance coefficients of several of these PTL thin films, calculated from the measured values of a PbTiO_3 single crystal. For this study we select one film with random orientation, another with the mixed $\langle 100 \rangle, \langle 001 \rangle$ orientation, and a third one with a strong contribution of a $\langle 111 \rangle$ component.

The first thing that we can observe is that the strong anisotropy of the elastic tensor corresponding to the single crystal is much reduced in the polycrystalline material. PbTiO_3 has a tetragonal structure, which is reflected in its compliance tensor¹: $s_{11}^C = s_{22}^C \neq s_{33}^C$; $s_{44}^C = s_{55}^C \neq s_{66}^C$; $s_{12}^C = s_{21}^C$; and $s_{13}^C = s_{31}^C = s_{23}^C = s_{32}^C$. The reduction of the anisotropy is such that we obtain compliance tensors very close to the ones corresponding to an isotropic material, where $s_{11} = s_{22} = s_{33}$; $s_{12} = s_{21} = s_{13} = s_{31} = s_{23} = s_{32}$; and $s_{44} = s_{55} = s_{66} = s_{11} - s_{12}$. This reduces the independent compliance coefficients to s_{11} and s_{12} . We observe that the values of these two coefficients are consistent with an averaging of their corresponding single crystal coefficients: s_{11} shows an intermediate value between s_{11}^C and s_{33}^C , and s_{12} value is between s_{12}^C and s_{13}^C .

¹ For tensor components referring to the single crystal we use a superscript C.

Table 1. Calculated compliance coefficients (s_{ij}) of textured PTL thin films

Compliance coefficients [10^{-3} GPa^{-1}]	PbTiO ₃ single crystal data (Data set A from [15])	PTL film random orientation	PTL film <100>,<001> mixed orientation ($F^2 = 6.6 \text{ mrd}^2$)	PTL film <111> orientation ($F^2 = 2.4 \text{ mrd}^2$)
s_{11}	6.5	10.1	10.1	9.9
s_{22}	6.5	10.0	10.1	9.9
s_{33}	33.3	9.8	10.3	9.9
s_{44}	14.5	13.2	12.9	13.3
s_{55}	14.5	13.2	12.9	13.2
s_{66}	9.6	13.4	13.3	13.2
s_{12}	-0.35	-3.3	-3.2	-3.2
s_{21}	-0.35	-3.3	-3.2	-3.2
s_{13}	-7.1	-3.2	-3.4	-3.2
s_{31}	-7.1	-3.2	-3.4	-3.2
s_{23}	-7.1	-3.2	-3.4	-3.2
s_{32}	-7.1	-3.2	-3.4	-3.2

However, the averaging process of the elastic coefficients does not produce exactly the same results for the different textures. If we look closer, we can see that for the randomly oriented film there is still small differences of the compliance coefficients along one direction, e.g., $s_{33} \neq s_{11}$ or $s_{13} \neq s_{12}$. Although the differences are small, they reflect the large elastic anisotropy of the crystals, which is difficult to average out. We increase these differences if there is a certain amount of crystals oriented along <100> and <001> directions parallel to the 3-axis as they contribute with extreme values of the compliance coefficients, very different in 1- or 2- and 3-directions. Unfortunately, there is a similar contribution (~50% each) in both <100> and <001> directions, and the difference between s_{11} and s_{33} coefficients is not large.

The introduction of a preferential orientation along other crystallographic orientations different from the <100> or <001>, will produce a higher amount of crystals contributing with more isotropic elastic coefficients. This is because the anisotropic direction of the oriented crystals, <001>, does not coincide with any of the reference axis of the polycrystalline film, and the contributions to the polycrystal compliance coefficient along that direction are reduced. This also results in a decrease of the s_{11} and s_{33} values of the film. This is what is observed for the films in which a strong <111> texture component is introduced, as it can be seen in Table 1. Comparing the compliance tensors of the random and the <111>-oriented film, we observe that the later is more isotropic than the former, stressing the role of crystals oriented along more isotropic directions in suppressing any anisotropy.

We have just mentioned that for this crystalline system the anisotropic direction is the crystallographic direction <001>. The fact that these compositions crystallize in the cubic phase implies that orientations along <001> directions are always associated with a similar texture component along <100>. If both components are present in a similar proportion, their effects can be cancelled out. In polycrystalline, non-epitaxial films, it is difficult to separate both components to study them separately. However, the use of substrates that introduce compressive stress during the cooling process to the room-temperature tetragonal phase, favor the orientation along <001> [20]. We have calculated the elastic tensors for a series of films with different texture contributions along <001> to study the effect of the preferential orientation of crystals with the anisotropic axis perpendicular to the film surface, i.e., parallel to axis 3. Results of the calculations are summarized in Table 2.

Table 2. Calculated compliance coefficients (s_{ij}) of textured PTCa thin films

Compliance coefficients [10^{-3} GPa $^{-1}$]	PTCa film <001> contrib. \approx 55% ($F^2 = 5.1$ mrd 2)	PTCa film <001> contrib. \approx 62% ($F^2 = 2.1$ mrd 2)	PTCa film <001> contrib. \approx 79% ($F^2 = 7.9$ mrd 2)
s_{11}	9.7	10.0	9.3
s_{22}	9.8	9.4	10.0
s_{33}	10.8	10.6	11.5
s_{44}	13.2	13.2	13.4
s_{55}	13.2	13.7	13.1
s_{66}	12.8	12.8	12.6
s_{12}	-3.1	-3.1	-3.0
s_{21}	-3.1	-3.1	-3.0
s_{13}	-3.4	-3.4	-3.5
s_{31}	-3.4	-3.4	-3.5
s_{23}	-3.4	-3.3	-3.7
s_{32}	-3.4	-3.3	-3.7

We can deduce from the comparison of the films with a <001> contribution of 55% (first column) and with a contribution of 79% (last column) that the increase of the percentage of crystals oriented along the <001> direction results in an increase of the s_{33} values. This is accompanied by an increase of the anisotropy of the tensor, associated to the lower contribution of these crystals to the compliance along the other two main axes, together with the increase of the values along the 3 direction. Note that the increase of the s_{33} value is less important for the PTCa film with a 62% contribution of <001> texture component due to its lower overall degree of orientation (F^2), which means that there is lower number of oriented crystals in this film.

It can be concluded from the previous results that the values of the elastic tensor of a polycrystal can be modified by the inducement of a preferential orientation along different directions. It is important to separate the effects of orientations along the elastically anisotropic directions and those far from them. This is an important result that can be used to produce modified lead titanate films with tailored mechanical properties for MEMS devices. In the introduction we remarked the influence of the s_{11} coefficient in several parameters that determine the performance of the device, as the resonance frequency or the spring constant of a cantilever. We have reported the variations introduced in the value of s_{11} by the induction of different textures. If we compare the values of s_{11} or the equivalent s_{22} (note that these axis are arbitrarily chosen) for all films we conclude that we can modify their values by two different approaches. The induction of a <111> orientation normal to the film surface does not only result in lower values of s_{11} and s_{22} than for the randomly oriented films, but also reduces the tensor anisotropy. The latter is an important factor in the advancement of the production of films with tailored properties, as it facilitates the solution of the fundamental equations that relate the functional parameters of a device and the elastic coefficients of the material.

The other approach that can be used to modify the values of the coefficient s_{11} and s_{22} , is the control of the orientations along the <001> direction perpendicular to the film surface. Variations of the substrate nature lead to an increase of this orientation contribution which in turn results in a reduction of these elastic parameters. Contrary to the case of <111> orientations, the tensor anisotropy increases, but the advantage is that then the reduction of the values is higher. It must be mentioned at this point that due to the fact that in these compositions the polar axis is along the <001> direction, the ferro-piezoelectric behavior of the film improves with this type of orientation, which also results in an improvement of the MEMS performance.

Conclusions

We have shown that advanced X-ray characterization of ferroelectric thin films is used to calculate the anisotropic effective elastic coefficients provided the corresponding single crystal elastic tensors are known. A correlation between the inducement of texture along elastically anisotropic directions and elastic tensors has been established. The results obtained will be used as a guide for further research aiming to tailoring of the mechanical properties for MEMS applications by texture control.

Acknowledgements

This work has been funded by European Union project GROWTH program (G6RD-CT99-00169) ESQUI ("X-Ray Expert System for Electronic Films Quality Improvement").

References

- [1] W.E. Newell: Science vol. 161, 1320 (1968), p. 1320
- [2] S.M. Spearing: Acta mater. vol. 48 (2000), p. 179
- [3] D.L. Polla and L.F. Francis: MRS Bull. vol. 21, no. 7 (1996), p. 59
- [4] T. Itoh and T. Suga: Nanotechnology vol. 4 (1993), p. 218
- [5] J.G. Smits and W.S. Choi: IEEE Trans. Ultrasonics, Ferroelectrics, Freq. Control vol. 38, no. 3 (1991), p. 256
- [6] P. Muralt, M. Kohli, T. Maeder, A. Kholkin, K. Brooks, N. Setter and R. Luthier: Sensors and Actuators A Vol. 48 (1995), p. 157
- [7] K.G. Brooks, I.M. Reaney, R. Klissurska, Y. Huang, L. Bursill and N. Setter: J. Mater. Res. vol. 9, no. 10 (1994), p. 2540
- [8] C.M. Foster, Z. Li, M. Buckett, D. Miller, P.M. Baldo, L. E. Rhen, G.R. Bai, D. Guo, H. You and K.L. Merkle: J. Appl. Phys. vol. 78, no. 4 (1995) p. 2607
- [9] S.Y. Chen and I.W. Chen: J. Am. Ceram. Soc. vol. 81, no. 1 (1998) p. 97
- [10] D. Chateigner, H.R. Wenk, A. Patel, M. Todd and D.J. Barber: Integrated Ferroelectr. vol. 19 (1998) p. 121
- [11] J. Ricote, D. Chateigner, L. Pardo, M. Algueró, J. Mendiola and M.L. Calzada: Ferroelectrics vol. 241 (2000), p. 167
- [12] U.F. Kocks, C.N. Tomé and H.R. Wenk: *"Texture and anisotropy"* (Cambridge University Press, United Kingdom, 1998).
- [13] S. Matthies and M. Humbert: Phys. Stat. Sol. B vol. 177 (1993), p. K47
- [14] Z. Li, M. Grimsditch, X. Xu and S.K. Chan: Ferroelectrics vol. 141 (1993), p. 313
- [15] A.G. Kalinichev, J.D. Bass, B.N. Sun and D.A. Payne: J. Mater. Res. vol. 12, no. 10 (1997), p. 2623
- [16] J. Ricote and D. Chateigner: Bol. Soc. Esp. Cerám. Vidrio vol. 38, no. 6 (1999), p. 587
- [17] S. Matthies and G.W. Vinel: Phys. Stat. Sol. B vol. 112 (1982), p. K111
- [18] H.R. Wenk, S. Matthies, J. Donovan and D. Chateigner: J. Appl. Cryst. vol. 31 (1998), p. 262
- [19] M.L. Calzada, M. Algueró and L. Pardo: J. Sol-Gel Sci. and Technol. vol. 13 (1998), p. 837
- [20] J. Ricote, D. Chateigner, M.L. Calzada and J. Mendiola: Bol. Soc. Esp. Cerám. Vidrio vol. 41, no. 1 (2002), p. 80