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Intrinsic effective elastic tensor of ferroelectric polycrystalline lead titanate based thin films with fiber-type texture

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Abstract

The intrinsic effective elastic tensor of polycrystalline lead titanate based thin films with mixed <001>,<100> fiber-type texture has been calculated by a volume average of the elastic coefficients of the individual crystallites, taking into account their actual crystallographic orientation relative to the film reference system. This is introduced in the calculations through an orientation distribution function, which is obtained by the quantitative analysis of experimental X-ray pole figures using a recently developed method: the combined approach. $PbTiO_3$ single crystal data have been used in the calculations. The elastic anisotropy of the single crystal tensor is strongly reduced for the textured thin films and depends on the relative contributions of the <001> and <100> texture components, being only negligible when both contributions are similar. The results presented in this work, and that can be applied to any other textured films with different compositions, contribute to the knowledge of the effective elastic tensor of these ferroelectric films, an important class of materials used in micro-electro-mechanical-systems, which is essential for the design of the devices.

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1. Introduction

Piezoelectric thin films, and, among them, ferroelectric lead titanate based perovskites, play an important role as promising materials for the core part of micro-electro-mechanical-systems (MEMS): the transducer element [1,2]. Several material properties define the performance of the device, like the stress state, the piezoelectric and the elastic coefficients of the film. The latter determine important operational parameters of the device, such as, for example, the spring constant and the resonance frequency in the case of a cantilever. Following with this example, in the design of a piezoelectric force sensor for scanning force microscopy based on a piezoelectric thin film deposited on a cantilever [3], we need to reach a compromise between the values of the spring constant of the system, which should be as low as possible to yield high sensitivity in a narrow detectable range, and the first resonance frequency, which, in turn, should be high to avoid excitation by external noise and to allow a fast scan rate. This is achieved by the right selection of the lengths and widths of the different elements of the system based on an estimation of the values of these two parameters, whose full equations can be found in the work of Itoh and Suga [3], and that depend directly on the Young's modulus of each layer that forms the cantilever, including the piezoelectric film. As we can see, the design of the right force sensor for the microscope, and of any other MEMS including piezoelectric films, requires a previous knowledge of the elastic properties of the film to be used.

However, very little is known of the effective elastic tensor of piezoelectric thin films. This is mainly due to the difficulties in measuring mechanical properties in films, as the measurements are strongly influenced by the much thicker substrate. Besides, most of the studies assume that films are elastically isotropic, which reduces the number of

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independent elastic coefficients to two. This assumption does not have to be true in all cases, especially for textured films of compositions that present large intrinsic elastic anisotropy, as it is the case for most ferroelectrics. The problem is that, to obtain a full set of elastic parameters, one would need to use several of the available methods of measurements, namely, Brillouin light scattering [4], resonance ultrasound spectroscopy [5], beam bending tests, beam resonance tests and nanoindentation [6]. As a consequence, there is scarce reliable information in the literature on the characteristics of the elastic tensor of piezoelectric thin films, and it is common to find that coefficients measured in bulk ceramics are used instead for the design of piezo-MEMS [7,8]. To the authors' knowledge, there have been few attempts to measure the elastic coefficients of ferroelectric thin films [9–11]. Nanoindentation with spherical tipped indenters was used to characterize ferroelectric thin films [11], obtaining the spherical indentation stiffness coefficient, which for isotropic homogeneous materials can be related to the Poisson's ratio (v) and the Young's modulus (E) by a simple formula: $(1-v^2)/E$. However, a similar expression cannot be written for anisotropic materials. These and other limitations of all the available techniques to measure the elastic tensor make necessary the search of an alternative method that allows, if not the exact determination of the elastic coefficients of the film, the study of their characteristics, in order, for example, to determine whether the assumption of elastic isotropy can be made in all cases, which is an important premise to analyze the results of some measurement methods, as explained above.

In this paper we report the calculation of the effective elastic tensor of textured ferroelectric thin films by a volume average of the elastic coefficients of the individual crystallites, taking into account their actual orientation relative to the film reference system. This crystallographic orientation or texture has previously been determined experimentally. We prove the feasibility of this procedure for modified lead titanate thin films prepared by deposition of sol–gel derived solutions, which have been shown to have excellent piezoelectric properties and are being considered for a wide range of sensor and actuators applications [12–14].

Besides, the high anisotropy of properties shown by their parent composition, the lead titanate, is expected to result in a significant elastic anisotropy for films textured along<001>. Previous results on modified lead titanate thin films [15,16], also obtained by chemical solution deposition methods on substrates with unrelated structures, show that a fiber type, mixed <100>,<001> preferential orientation is developed during crystallization. Considering that the polar axis is along the <001> direction in tetragonal lead titanate based compositions, a strong texture component along that direction will result in an improvement of the ferroelectric behavior of the film. Therefore, the distribution of crystals along <100> and <001> in thin films with this type of texture has attracted much attention. The studies concluded that this distribution is related to the stress state present during the ferroelectric to paraelectric phase transition during cooling [17], and can be tailored by the modification of the substrate. We use this result to produce oriented films with varying distributions of the crystals oriented along <100> and <001> directions, and then analyze their influence on the characteristics of the elastic tensor.

2. Preparation of the oriented films and determination of the texture

Tetragonal Ca modified lead titanate thin films ($Pb_{0.76}Ca_{0.24}TiO_3$) (hereinafter PCT) were obtained by the spin coating deposition of sol–gel derived solutions [18] at 2000 r.p.m. for 45 s. A class 100 clean room is used for deposition on the substrates. The wet deposited films were partially pyrolized on a hot plate at 623 K for 60 s. Crystallization was carried out typically by rapid thermal processing (heating rate of 30 K s^{-1}) at 923 K for 50 s. Deposition is carried out on two types of Pt buffered substrates: Pt/TiO_2/(100)Si or Pt/(100)MgO. As the stress state is mainly due to the different expansion coefficients of film and substrate, we have increased the contribution of the <001> component by changing from the Si-based substrate (PCT-Si), which produces a tensile stress, to the MgO-based one (PCT-Mg), whose stress is compressive and favors the orientation of crystals with their long axis (<001>) perpendicular to the film surface.

The crystallographic orientations obtained were analyzed by quantitative texture analysis (QTA) [19,20] of the X-ray diffraction pole figures. Measurements were carried out using a four-circle goniometer (Huber) mounted on an X-ray generator (CuKα radiation) and equipped with a curved, position-sensitive detector (Model CPS-120, Inel, Inc.) covering an angle of 120° (spatial resolution 0.03°). A $5° \times 5°$ grid measurement was carried out to cover the whole pole figure. The use of a linear detector accelerates considerably the data acquisition compared with punctual detectors, but results in asymmetrical positions that requires the localization of the peaks into the pole figure coordinates as they do not correspond exactly to the goniometer rotation angles [21]. 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 [22]. Pole figure data are normalized into distribution densities and expressed as multiple of a random distribution (m.r.d.), which is equivalent to volume percentage per 1% area. A specimen with no preferred orientation has pole figures with constant values of 1 m.r.d. An example of several pole figures obtained for one of the films analyzed in this paper is shown in Fig. 1.

From several of the experimental pole figures we obtain by an iterative process the orientation distribution (OD)

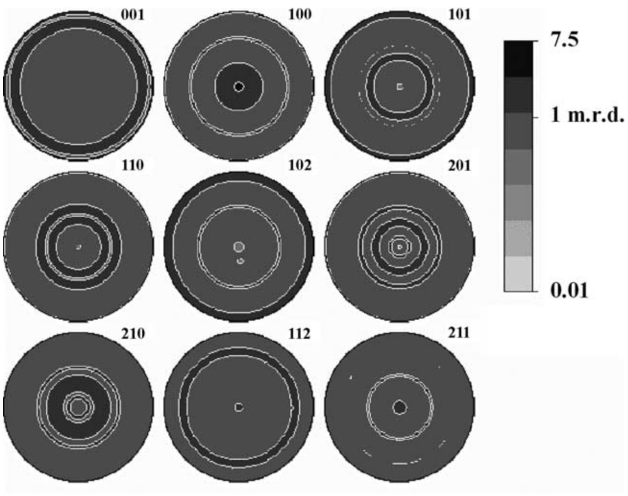

Fig. 1. Pole figures (recalculated from the OD) of a PCT thin film deposited on a Pt buffered Si-based substrate. Equal area projection and logarithmic density scale. (m.r.d.—multiple of a random distribution).

function of the sample: $f(\mathbf{g})$. This function describes the amount of crystallites with an orientation between $\mathbf{g}$ and $\mathbf{g}+d\mathbf{g}$ ($\mathbf{g}=\alpha$, β and γ Euler angles). Among the several methods of resolution of the OD we chose the WIMV (Williams, Imhof, Matthies and Vinel) iterative method [23] with a later modification by Liu et al. [24]. If we keep the sample direction constant (i.e. the normal to the film surface) and represent the associated crystal directions, we obtain an inverse pole figure (Fig. 2). The analysis of these inverse pole figures allows the identification of the texture components present in the film (as shown in the figure), and also the estimation of their individual contributions to the global texture. However, the reliable separation of the contributions of some texture components in the tetragonal lead titanate based compositions, like <001> and <100>, has only been possible by the use of the more recently developed combined approach, as previously reported by the authors [15]. In this approach we combine the quantitative texture analysis and the Rietveld refinement methods in order to obtain a simultaneous and more precise determination of the structure and the texture of the films [25,26]. In a first step a Rietveld refinement is carried out on the set of diffraction diagrams measured at different sample orientations, and the results are taken as input data for the QTA analysis, which corrects the diagrams to be used in the next Rietveld analysis, completing a first cycle. In this cyclic procedure, the 001 and 100 peaks are deconvoluted first, improving greatly the determination of the peak intensities, which are the basis for a correct evaluation of the contribution of these two important texture components. Calculations were carried out with the "Materials Analysis Using Diffraction" package (MAUD) [27,28]. In the calculations of the elastic tensor of the films we will introduce the OD obtained experimentally for each of the films to account for the effects of the texture.

3. Calculation of the elastic tensor

The elastic tensor of a polycrystalline material can be determined by a volume average of the elastic properties of the constituent crystals, weighted by the orientation distribution function. In general terms, the volume average of a tensorial quantity $\mathbf{t}$ is denoted by [29]:

$$<\mathbf{t}> = \int \mathbf{t}(\mathbf{g}) f(\mathbf{g}) d\mathbf{g} \qquad (1)$$

$f(\mathbf{g})$ is the orientation distribution function as defined above. The integral is defined over the domain of the orientation angles $\mathbf{g}$, which locates one single crystallite orientation relative to the film reference system. By convention, the 3-axis of this reference system corresponds to the direction normal to the film plane, and 1- and 2-directions are arbitrarily chosen, as it does not have any effect on the calculations due to the fiber character (symmetric around one axis) of the texture of the films analyzed. Among the various averaging procedures, we choose the geometric mean, first developed by Aleksandrov and Aisenberg and later improved by Matthies and Humbert [30]. The main advantage of this method is that it obeys the condition that

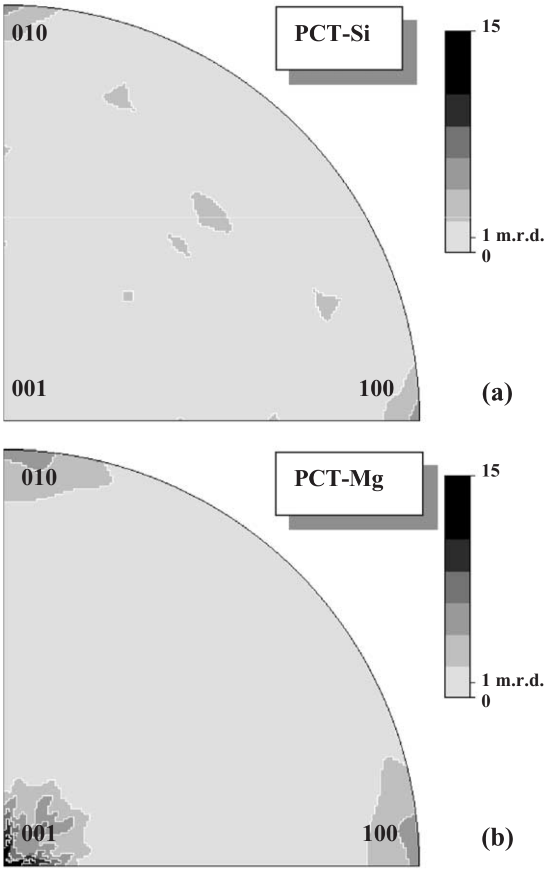

Fig. 2. Inverse pole figures for the normal direction to the film surface of PCT thin films deposited on different Pt buffered substrates: (a) PCT-Si and (b) PCT-Mg. Equal area projection and linear density scale. (m.r.d.—multiple of a random distribution).

the averaging of the inverse is equal to the inverse of the average property, not fulfilled by the simpler arithmetic mean, and which, as a consequence, has produced a series of different approaches: the Voigt (mean of the stiffness tensor **C**) and Reuss (mean of the compliance tensor **S**) averages which do not lead to equivalent results, and an intermediate value given by the Hill average. With the geometric mean we obtain the same polycrystalline elastic properties independently of whether the single crystal compliance or stiffness is used to calculate the average. Besides, the geometric mean produces values that reproduce quite well the experimental data [30]. In this work we present the results of these calculations applied to obtain the effective elastic tensor of polycrystalline oriented films from the single crystal properties. Due to the fact that complete studies of the elastic properties of single crystals for specific compositions, like the Ca modified lead titanate studied here, are not available in the literature, we will use the results obtained by Kalinichev et al. on pure lead titanate [31]. The calculations for the determination of the compliance tensors have been carried out with the help of the Berkeley Texture Package (BEARTEX) [32].

4. Results and discussion

The deposition of PCT films on Si or MgO-based substrates results in a different contribution of the <100> and <001> components to the global texture. This is clearly seen in the inverse pole figures for a direction perpendicular to the film surface (Fig. 2(a) and (b)). We estimate from these figures that the <001> contribution goes from 17% (PCT-Si) to 68% (PCT-Mg) (see Table 1). The use of conventional QTA leads to an artificial similar estimated contributions for both directions, showing the difficulties found in the texture analysis of these films, as explained before, and that requires the use of advanced procedures like the combined analysis. As we have not found experimentally any thin films showing a real similar contribution of <001> and <100> texture components, and for the sake of comparison, we will use the results obtained by conventional QTA of a La modified lead titanate film (PLT) [16], with a similar degree of orientation to the PCT films studied here.

Table 1 collects the results of the calculations of the elastic compliance tensors. We use the experimental OD of a randomly oriented thin film [16], to perform a first check on the results of the averaging procedure. They show a virtually isotropic tensor for this film with only two independent coefficients (s_{11} and s_{12}, with $s_{44}=s_{11}-s_{12}$). We also observe that the values of these two coefficients are consistent with an averaging of the single crystal tensor ($\mathbf{S}^{\mathrm{C}}$): s_{11} shows an intermediate value between s_{11}^{C} and s_{33}^{C}, and s_{12} is between s_{12}^{C} and s_{13}^{C}. These are expected results for the compliance tensor of a randomly oriented film and make a first validation of the averaging procedure followed.

The introduction of a preferred orientation produces a certain degree of anisotropy to the effective compliance tensor, as results of Table 1 shows. The anisotropy observed seems only to be related to the sample axis along which the preferred orientations appear: the 3-axis, perpendicular to the film surface. This is consistent with the fiber character of the texture, which makes contributions to the elastic coefficients along *the* 1- and 2-axis equivalent. This is characteristic of an hexagonal symmetry, class 6mm, whose elastic tensor [33] has the same characteristics as the ones shown in Table 1. Therefore, we can study the anisotropy of the elastic tensor by comparing the values of the s_{33}/s_{11} and s_{13}/s_{12} ratios. These values are higher when the contribution of crystals oriented along <001> increases. The ratios are higher than 1.0 when this contribution is high enough (≈68% for PCT-Mg), showing that a large presence of <001> oriented crystals contribute to produce a tensor where $s_{33}>s_{11}$ and $s_{13}>s_{12}$. An opposite tendency is observed when the proportion of crystals oriented along <100> is larger than along <001> (PCT-Si). Furthermore, when both contributions are similar the tensor becomes almost isotropic (PLT in Table 1). This

Table 1
Calculated compliance coefficients (s_{ij}) of modified lead titanate thin films with random and mixed <001>, <100> orientations

Compliance coefficients [10^{-3} GPa^{-1}]	$PbTiO_3$ single crystal (data set A [31])	Film random orientation	PCT-Si <001> contrib. ≈ 17%	PLT <001> contrib. ≈ 49%	PCT-Mg <001> contrib. ≈ 68%
s_{11}	6.5	10.1	10.5	10.0	9.7
s_{22}	6.5	10.0	10.5	10.0	9.7
s_{33}	33.3	9.8	9.0	10.3	11.3
s_{44}	14.5	13.2	12.8	12.9	13.1
s_{55}	14.5	13.2	12.8	13.0	13.1
s_{66}	9.6	13.4	14.0	13.5	12.7
s_{12}	−0.35	−3.3	−3.5	−3.2	−3.0
s_{21}	−0.35	−3.3	−3.5	−3.2	−3.0
s_{13}	−7.1	−3.2	−3.1	−3.4	−3.6
s_{31}	−7.1	−3.2	−3.1	−3.4	−3.6
s_{23}	−7.1	−3.2	−3.1	−3.4	−3.6
s_{32}	−7.1	−3.2	−3.1	−3.4	−3.6
s_{33}/s_{11}	5.1	0.97	0.86	1.03	1.16
s_{13}/s_{12}	20.3	0.97	0.89	1.06	1.20

The estimated contribution of the <001> texture component contribution is indicated. $PbTiO_3$ single crystal data are also shown for the sake of comparison.

corroborates the strong influence of these texture components on the anisotropy of the effective compliance tensor.

Another feature worth commenting on is that the elastic anisotropy of the film, though still present, is strongly reduced compared to the single crystal. This somehow partially validates the assumptions made in most of the studies of mechanical properties of films, to simplify the solution of the complex equations derived. For example, in the nanoindentation studies mentioned above, the fact that ferroelectric films are not far from the isotropic case makes possible a direct interpretation of the results.

It should be pointed out here that the method explained in this work only considers the intrinsic crystal contributions to the elastic properties of the films. However, this does not limit its validity as it has been shown that extrinsic contributions related to the ferroelectric/ferroelastic domain wall motion does not contribute significantly to the linear coefficients [34]. Other factor that can affect the elastic coefficient is the microstructure, basically, porosity and grain size. The porosity can be introduced in the calculations through a mechanical model in which we consider a two-phase system composed of the bulk material and pores. The grain size fundamentally affects the arrangement of the ferroelectric/ferroelastic domains, which is effectively introduced in the calculations through the orientation distribution function. All these makes us conclude that the average process proposed in this work is a valid approximation to obtain the effective elastic tensor of piezoelectric thin films.

5. Conclusion

An alternative method to obtain the intrinsic effective elastic tensor of polycrystalline oriented thin films by a volume average process that takes into account the texture has been presented. This allows to analyze the anisotropy character of the elastic tensor, which is most of the times assumed to be isotropic. The method has been applied to the case of lead titanate based thin films obtained by deposition of sol–gel derived solutions and with a mixed <100>,<001> orientation. The results show that the relative contribution of the texture components plays an important role, never before considered by other authors, in the control of the elastic properties of the films, which is determinant for the performance of MEMS applications. A non-negligible elastic anisotropy is obtained when the contributions of the texture components along <001> and <100> are different, which is the case for the oriented films deposited on Si- and MgO-based substrates, although it is small compared with the one corresponding to the single crystal tensor.

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