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Local Piezoelectric Properties of Oriented PZT Based Ferroelectric Thin Films

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A series of PZT based ferroelectric thin films obtained by multitarget sputtering with different preferential orientations are studied by piezoresponse force microscopy (PFM). The modification of the substrate by the deposition of an extra TiO_x layer, and the use of MgO-based substrates instead of the usual Si-based ones, change the preferential orientation of the films. The results of the analysis of the local piezoelectric properties allow us to discuss the origin of some special features observed, like the appearance of protruding grains in films with specific orientations, and the homogeneity of the piezoelectric performance at the nanoscale.

Keywords Oriented films; piezoresponse force microscopy; PZT; PLZT

Introduction

The preparation of highly oriented ferroelectric thin films is the subject of intense work due to the large improvement of the properties that is achieved when the film is preferentially oriented along certain crystallographic directions. The reduction of the device dimensions driven by the miniaturization trends followed by the microelectronics industry has shifted the attention to the study of the local properties of these films at the nanometer scale, more relevant for their potential application in the new nanodevices [1]. In the case of ferroelectric thin films and their application in random access memories, the uniformity of the films minimizes the undesired variation of properties among memory nanocells fabricated from them. The implication is that it is important to control parameters such as grain size and crystallographic orientation of ferroelectric films in the nanometer range. The development of the piezoresponse force microscopy (PFM), currently widely used for the characterization of the local ferroelectric properties at the nanoscale [2, 3], is essential to fulfill this objective. However, the influence of the global texture on the local properties of highly oriented ferroelectric films has only occasionally been studied [4, 5].

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$Pb(Zr_xTi_{1-x})O_3$ (PZT) based thin films have attracted a large amount of attention due to their applications in non-volatile memories [6] and microelectromechanical systems [7]. In the Ti-rich compositions, a preferential orientation of the films along the polar axis (⟨001⟩ for the tetragonal phase) is usually sought, although an orientation along the ⟨111⟩ direction may be more desirable for memory applications because the absence of ferroelastic effects results in a high remnant polarization and abrupt switching behavior [8]. If no other driving force is present, the reported natural preferential orientation obtained in lead titanate derived films is a mixed ⟨100⟩, ⟨001⟩ orientation [9]. To induce other preferential orientations the use of seeding layers or the change of the substrate choice is necessary. Among these methods, the introduction of an additional layer of TiO_x, on which we grow the PZT films, results in a ⟨111⟩ preferential orientation [10, 11]. The same TiO_x layer plays a major role in the epitaxial growth of (001) PZT films on Pt(100)/MgO(100) [12]. These studies have shown the feasibility of achieving orientation control of sputtered PZT thin films through the controlled oxidation of a Ti layer covering the Pt buffered substrates.

In this work, highly oriented PZT and PLZT films have been grown by RF magnetron sputtering on Pt buffered Si and MgO substrates covered by an ultrathin TiO_x layer, which results in a series of films with different preferential orientations. Based on the analysis of their local ferroelectric behavior by PFM, we discuss the influence of texture on the properties of ferroelectric thin films at the nanoscale.

Experimental Procedure

We have prepared films of two compositions: $Pb(Zr_{0.28}Ti_{0.72})O_3$(PZT) and $Pb_{0.85}La_{0.10}Zr_{0.40}Ti_{0.60}O_3$(PLZT). All films were deposited at 550°C by multi-target RF magnetron sputtering of three metallic targets (Pb, Zr, Ti) for PZT and an additional ceramic target ($La_2Ti_2O_6$) for PLZT compositions. A gas with an $O_2/(Ar + O_2)$ ratio of 0.25 at a pressure of 0.8 Pa was used. The distance between the target and the substrate was kept at 40 mm. Under these conditions the deposition rate was 1–2 nm/min. The films are deposited on Pt buffered substrates with the following heterostructures: Pt(111)/TiO_x/SiO_2/Si(100) (TiO_x is an adhesive layer) and Pt(100)/MgO(100). Note that while the Pt layer in the Si-based substrate is polycrystalline ⟨111⟩ oriented, the growth on the MgO single crystal is epitaxial. Prior to the PZT or PLZT deposition a 3 nm TiO_x layer is sputtered on the substrates, under the same conditions used for the ferroelectric film. Crystallographic properties were examined with a Seifert X-ray diffractometer using Cu Kα radiation. The degree of orientation was estimated by calculating the Lotgering factor [13] from the X-ray integrated intensities obtained for the films and using the powder diffraction files of tetragonal PZT (JCPDS 50-0346) and PLZT (JCPDS 46-0504).

A commercial scanning force microscope (SFM) (Nanotec® Electrónica with WSxM® software) was used to study the surface topography and local piezoelectric activity of the films by piezoresponse force microscopy (PFM) [2, 3]. The tip senses the surface oscillations induced in the sample by an ac electric field applied between the tip and the sample, due to the converse piezoelectric effect. In this work we use conductive commercial Pt/Ir coated (Nanosensors) or n-doped Si (Olympus) tips on cantilevers with nominal force constants of 42 N/m. An ac voltage of 1 V at 50 kHz is used in the measurements. The amplitude of the sample vibration provides information on the magnitude of the piezoelectric coefficient, while the phase signal allows determining if the polarization is parallel or antiparallel to the electric field applied in every position of the sample. In this work we only measure the out-of-plane piezoresponse signal of the films. Macroscopic polarization loops were

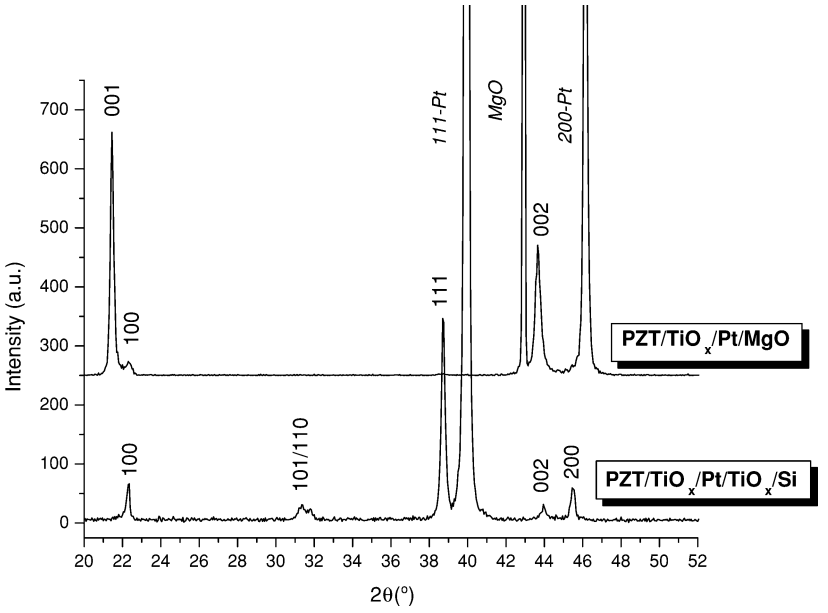

Figure 1. X-ray diffraction diagrams of PZT films deposited on different substrates.

obtained with a conventional Sawyer-Tower circuit with a 500 Hz sine wave, for which Pt top electrodes were deposited by RF magnetron sputtering without heating the substrate and patterned (250 × 250 μm) by a lift-off U.V. photolithographic process.

Experimental Results and Discussion

The deposition of tetragonal perovskite PZT and PLZT films on different substrates results in different crystallographic textures, as evidenced by the X-ray diffraction results (Fig. 1 and 2). We have also calculated the Lotgering factors, f, for the main texture components (Table 1) in order to estimate the degree of orientation achieved in each film [13]. If values range from 0 (non-oriented) to 1 (fully oriented). We induce a preferential orientation along $\langle 111 \rangle$ by the use of a TiO_x layer on top of a typical Si-based substrate [11]. This produces similar Lotgering factors in both PZT and PLZT films, indicating that the texturing mechanisms in doped and non-doped PZT in the tetragonal phase must be similar. Preferential

Table 1
Main texture components and corresponding Lotgering factors, f, of PZT and PLZT ferroelectric films deposited on different substrates

Film	Substrate	Main texture component	Lotgering factor
PZT	$TiO_x/Pt(111)_{poly}/TiO_x/Si(100)$	$\langle 111 \rangle$	$f_{111} = 0.70$
PLZT	$TiO_x/Pt(111)_{poly}/TiO_x/Si(100)$	$\langle 111 \rangle$	$f_{111} = 0.68$
PZT	$TiO_x/Pt(100)/MgO(100)$	$\langle 001 \rangle$	$f_{001} = 0.93$
PLZT	$TiO_x/Pt(100)/MgO(100)$	$\langle 001 \rangle$	$f_{001} = 0.84$

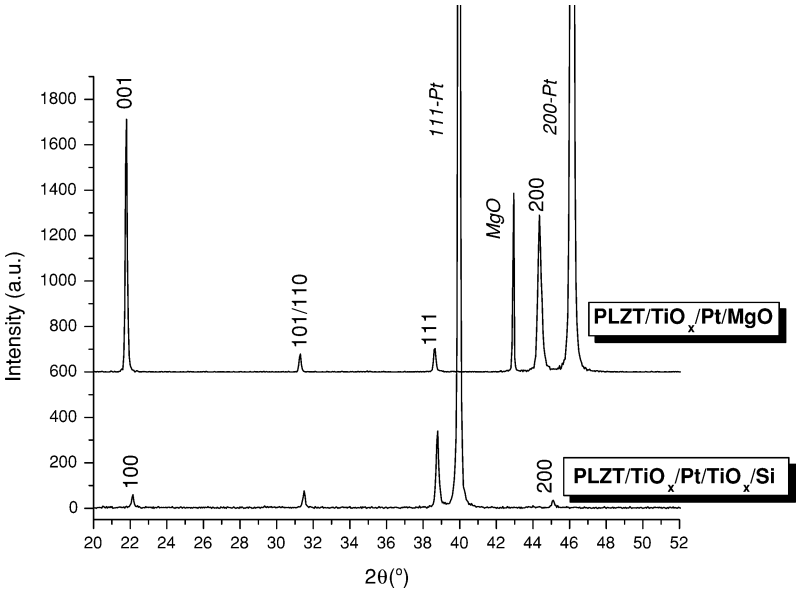

Figure 2. X-ray diffraction diagrams of PLZT films deposited on different substrates.

orientation along the polar axis direction (⟨001⟩) is achieved on the MgO-based substrates for both PZT and PLZT films as expected [12], with Lotgering values close to 1, which suggests their epitaxial growth. However, the lower Lotgering factor obtained for the PLZT film indicates that a certain volume of the film is randomly oriented. The reasons behind this loss of orientation are not clear. We should consider that the orientation control of the films, and more critically the epitaxial growth, is achieved by the oxidation of the Ti layer. Although the mechanisms are not fully understood yet, the degree of oxidation depends on

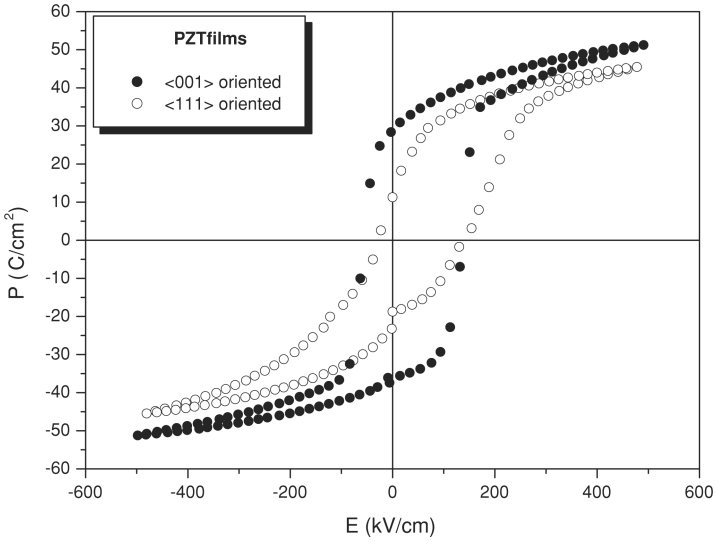

Figure 3. P-E hysteresis loops of PZT films with different textures.

the deposition parameters both of the TiO_x layer and the ferroelectric film, in particular on oxygen partial pressure [12]. The use of a $LaTiO_3$ ceramic target for PLZT preparation may change this, resulting in the observed variation in the degree of orientation. This will be the subject of further work.

At a macroscopic level, the influence of the crystallographic orientations on the macroscopic properties of the films is evidenced by the ferroelectric hysteresis loops of Fig. 2. An orientation along the polar axis ($\langle 001 \rangle$ in this case) results in a significant increase of the remnant polarization, which is a clear advantage for its potential use in microdevices. However, for applications in nanodevices it is necessary to study that the relevant properties are homogeneously distributed at the nanoscale.

To study the local distribution of the piezoelectric properties on these films we use Piezoresponse Force Microscopy (PFM) and the results are shown in Figs. 4 and 5. It must be noted that the piezoelectric coefficient detected is a function of the several coefficients of the piezoelectric tensor [14]. If we take by convention the z-axis perpendicular to the film surface, the longitudinal piezoelectric coefficient d_{zz}, which is what is actually measured by the tip, for tetragonal crystals (point group 4 mm) can be expressed as [3,1 4]:

$$d_{zz}(\theta) = (d_{31} + d_{15}) \sin^2 \theta \cos \theta + d_{33} \cos^3 \theta,$$

where θ is the angle between the measurement direction and the direction of spontaneous polarization, [001]. It is important to take into account this relationship for the interpretation of the PFM results. In the case of PZT and PLZT, because of the values of the three piezoelectric coefficients, the second term dominates, which means that the out-of-plane measured piezoelectric coefficient, d_{zz}, decreases continuously as the spontaneous polarization, P, move away from the normal of the film. There is an almost linear correlation between $d_{zz}(\theta)$ and $P(\theta)$ in this case [14], and we can say that the amplitude of the piezoresponse signal is directly related to the polarization.

The analysis of the surface topography for the PZT film deposited on TiO_x/Pt/MgO (Fig. 4(a)) reveals a flat surface, which corresponds to an epitaxial film with a typical c/a/c/a polydomain structure [15]. The a domains are tilted with respect to the film normal and results in a small step between c domains, which is what we observed. When we study this domain structure by PFM, the out-of-plane piezoresponse amplitude (Fig. 4(b)) shows a network or straight dark lines in the background that correspond to those steps observed in the topography image. This confirms that they are a domains, with no out-of-plane polarization component. But superimposed we have a network of wavy black lines, not constricted within the limits of the c/a/c/a domains. These lines separate regions with the polarization (P_z) in opposite directions as it can be deducted from the phase piezoresponse image (Fig. 4(c)), i.e., they are 180° ferroelectric domain walls. This type of walls does not necessarily have to follow any definite crystallographic direction, unlike 90° domains, which explains their wavy appearance. The epitaxial nature of this film makes the distribution of the piezoresponse amplitude values rather uniform, mainly disrupted by the 180° domain walls, which can be easily eliminated by switching the polarization vector with the application of a sufficiently large electric field. This, together with the fact that the maximum of the transverse piezoelectric coefficient is in the $\langle 001 \rangle$ direction, confirms that (001) epitaxial films are preferred for their use in applications at the nanoscale.

The topography of the $\langle 111 \rangle$ oriented PZT film shows the aspect of a polycrystal with rounded grains (Fig. 4(d)). Grain boundaries appear as black line in the piezoresponse

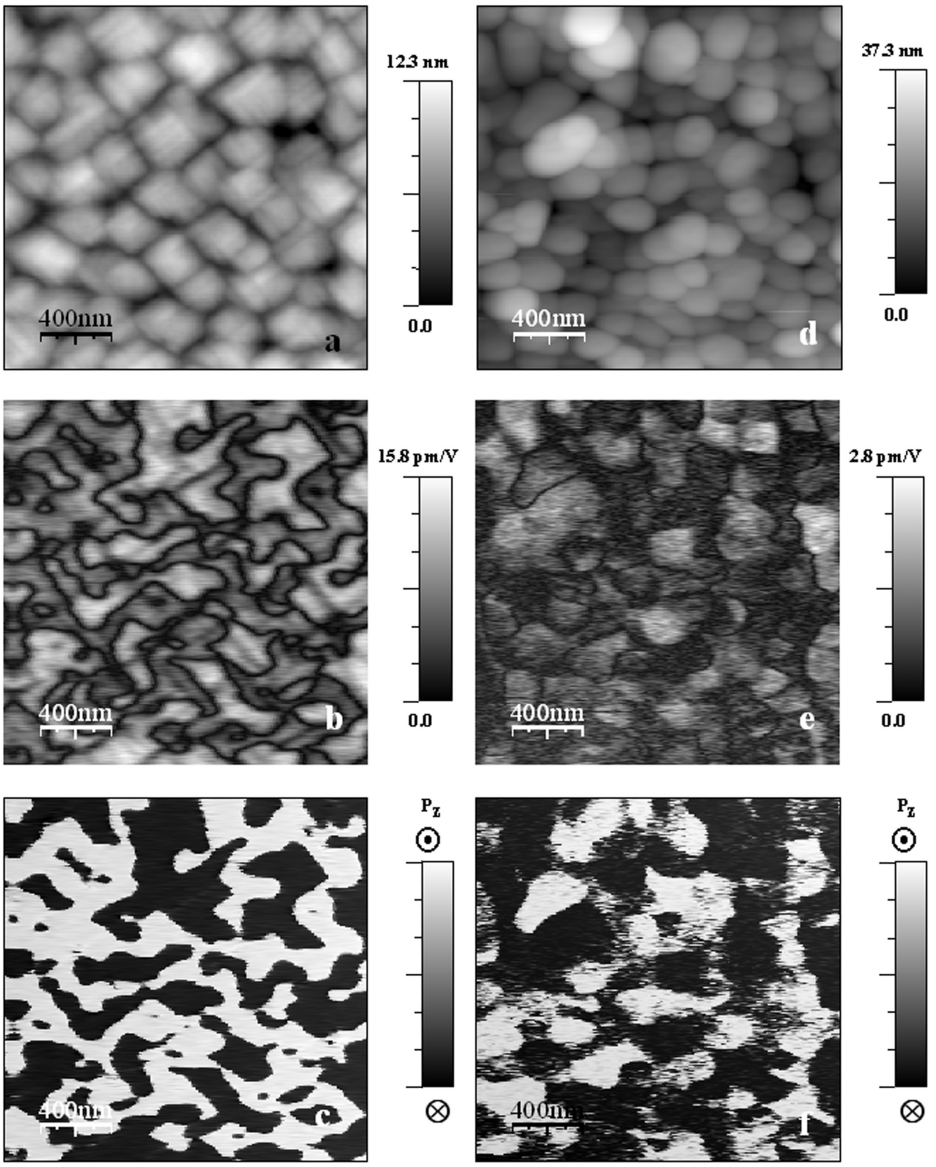

Figure 4. SFM images of PZT films deposited on an MgO (a–c) and on a Si-based substrate (d–e). Top to bottom: topography, piezoresponse amplitude and piezoresponse phase.

amplitude image as expected (Fig. 4(e)). However, in some regions groups of grains seem to behave as if they were just one. The electric field applied to probe the material may excite, overall in the case of the smaller grains, not only the grain below the tip, but all the neighboring grains, resulting in some cases in a collective response, which is reflected in the piezoresponse images. The grains observed are single domain, probably due to their small size. The phase piezoresponse image (Fig. 4(f)) shows an almost equal distribution of crystals with the polarization vector pointing towards the film surface and pointing towards the substrate. This is what we should expect in a polycrystalline film

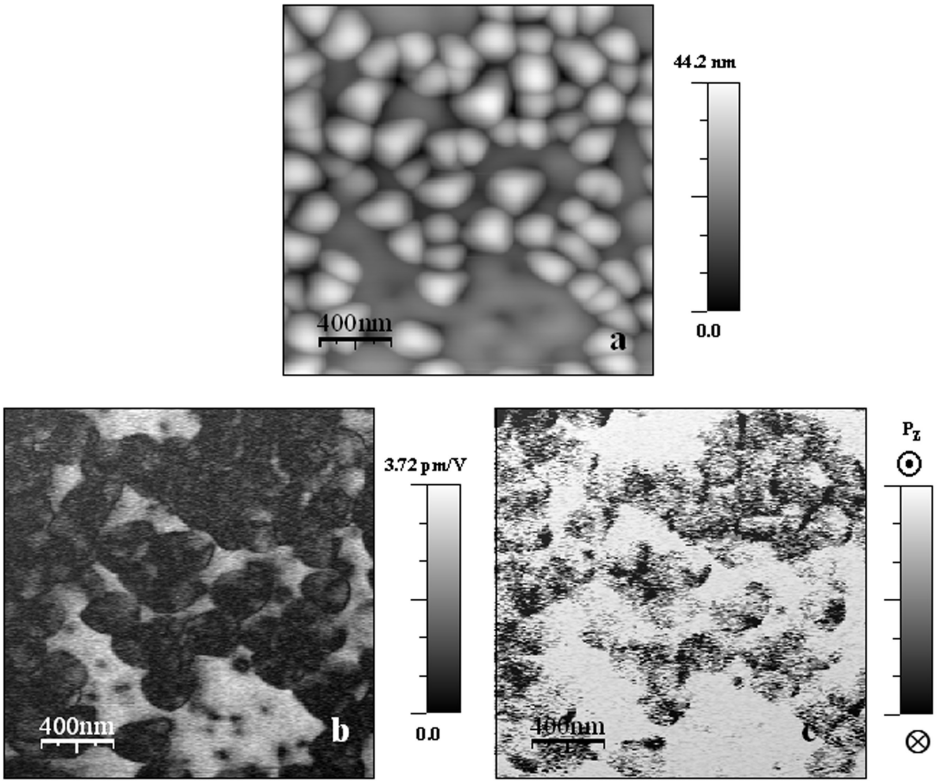

Figure 5. SFM images of PLZT films deposited on Ti/Pt/MgO: (a) topography; (b) amplitude and (c) phase of the piezoresponse signal.

without the application of an electric field. The grain-to-grain variations of the piezoelectric response observed may be an important drawback for the reliability of nanodevices based on these films, as there will be few grains per capacitor, making the properties of each of them too different. To avoid this, a higher degree of orientation is therefore desirable.

This effect of inhomogeneous distribution of the piezoelectric response can be studied more clearly with the PLZT film deposited on the MgO-based substrate, which shows a reduction of the degree of ⟨001⟩ orientation in comparison with the corresponding PZT film (Table 1). The study of the topography of the film surface (Fig. 5(a)) reveals the appearance of protruding grains distributed on a flat surface similar to the (100) epitaxial PZT film (Fig. 4(a)). Before the analysis with PFM, the origin and nature of these protruding grains was difficult to establish. The flat regions have the highest values of piezoresponse (Fig. 5(b) and (c)), so they can be ascribed to regions oriented along the polar axis (⟨001⟩), most probably epitaxially grown on the substrate. According to the PFM results, the protruding grains are not oriented in that direction and are, therefore, correlated to the reduction of the degree of orientation in this film, corresponding with the volume of the film with random orientation. The consequence is that the differences in the local piezoelectric response between the flat regions and the grains are significantly larger than in the previous ⟨111⟩ oriented film, which is bound to produce larger capacitor-to-capacitor variations in a prospective application in a nanodevice.

Conclusions

The analysis of the piezoelectric behavior at the nanoscale of several polycrystalline PZT based thin films with different orientations reveals inhomogeneities that, except for the (001) epitaxial film, may not to be tolerable for their application in nanodevices. We have studied here the two main preferential orientations that can be induced in these tetragonal perovskite films by modifications of the substrate: ⟨001⟩ and ⟨111⟩. The orientation along the polar axis should be preferred, but any reduction of the degree of orientation will produce larger property variations among the oriented and non-oriented regions than the ones observed in ⟨111⟩ oriented films. These aspects must be taken into account when thinking of taking advantage of the nanoscale properties of these films.

It is also important to note that the nanocharacterization by PFM can shed light onto some local features of the films, like the observed protruding grains, whose origin and nature cannot be studied by other means. This makes PFM an essential tool in the analysis of oriented ferroelectric films.

Acknowledgments

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