

Fabrication of continuous ultrathin ferroelectric films by chemical solution deposition methods

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The integration of ferroelectrics in nanodevices requires firstly the preparation of high-quality ultrathin films. Chemical solution deposition is considered a rapid and cost-effective technique for preparing high-quality oxide films, but one that has traditionally been regarded as unsuitable, or at least challenging, for fabricating films with good properties and thickness below 100 nm. In the present work we explore the deposition of highly diluted solutions of pure and Ca-modified lead titanates to prepare ultrathin ferroelectric films, the thickness of which is controlled by the concentration of the precursor solution. The results show that we are able to obtain single crystalline phase continuous films down to 18 nm thickness, one of the lowest reported using these methods. Below that thickness, the films start to be discontinuous, which is attributed to a microstructural instability that can be controlled by an adequate tailoring of the processing conditions. The effect of the reduction of thickness on the piezoelectric behavior is studied by piezoresponse force microscopy. The results indicate that films retain a significant piezoelectric activity regardless of their low thickness, which is promising for their eventual integration in nanodevices, for example, as transducer elements in nanoelectromechanical systems.

I. INTRODUCTION

Ferroelectric lead titanate based thin films have extensively been studied for their applications as active elements in nonvolatile ferroelectric memories (NV-FeRAM)^{1,2} and microelectromechanical systems (MEMS).³ However, the modern electronics industry demands an ever-larger degree of integration, shrinking the device dimensions down to the nanoscale. The reduction of the lateral memory cell size in FeRAMs means higher storage densities, which has recently reached 10 Tbit/in.^{2,4} Regarding the nanoelectromechanical systems (NEMS), one of the major challenges they face now is

related to the search of alternative transduction elements,⁵ as most of the techniques used in MEMS reach their limits in the nanoscale. Several attempts have been carried out, such as the use of piezoresistors for sensing⁶ or piezoelectric actuation of semiconductor GaAs,⁷ but the use of piezoelectric transduction with ferroelectric films has not been explored yet. Further development in the fabrication methods of ferroelectric oxide nanostructures to be integrated in the new nanodevices is therefore a key issue, not only because of their technological potential, but also because of the unique properties of ferroelectrics with reduced dimensions.^{8–11}

Among the strategies used to prepare high-quality ferroelectric films for their integration in devices, chemical solution deposition (CSD) methods present clear advantages with respect to other deposition techniques, such as the high degree of compositional control, large

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deposition areas, and low costs. These characteristics have made them the preferred choice to prepare a wide range of electronic oxide films.¹² However, CSD has traditionally been regarded as an unsuitable method for the deposition of ultrathin films (below 100 nm). This is because of the incomplete coating of the substrates observed for very thin films prepared by CSD. This lack of continuity is responsible for shorts in the capacitor structure and renders the ultrathin CSD films useless for applications. Several studies have reported that the films break up into discrete islands for thickness below a critical value and after high-temperature annealing.^{13,14} The resulting structures with nanometric lateral sizes have been used to develop a method of self-patterning of nanostructures for high-density memories,^{15,16} although they still present several practical problems. One of them is their distribution in regular patterns, which can be solved by depositing the films onto patterned structures^{17,18} or by microemulsion-aided preparation methods, which have shown the first evidences of periodic order of the ferroelectric nanostructures when deposited on single-crystal substrates.¹⁹ Although this may be a good bottom-up approach for the fabrication of regular arrays of capacitors for memory cells, the more complex structures used in NEMS may require most probably a lithography-based, top-down approach. For this, it is essential to prepare high-quality, continuous ultrathin ferroelectric films, preferably on Si-based substrates, so they can eventually be integrated as transducer elements in NEMS.

Although there are not many reports on the subject, the strategies used to prepare ultrathin ferroelectric films by CSD are varied. The use of solid solutions of Bi_2SiO_5 and ferroelectric compositions²⁰ allows the preparation of ultrathin films (13–25 nm) at lower crystallization temperatures than those of the original ferroelectrics. Another approach to obtain the thinnest continuous film possible is based on the control of grain growth by the use of rapid thermal processing (RTP) and the deposition of the Pt top electrode on the amorphous film before annealing.²¹ The authors claim that an excessive grain growth may lead to highly irregular layers, with shorts in the capacitor structure, and they achieve strontium bismuth tantalate films down to 25 nm thickness, although the paper gives no indication about the strategy followed to achieve the different thickness. By multiple depositions of very diluted solutions, ferroelectric films down to approximately 20–50 nm thickness with macroscopically addressable properties have recently been achieved,²² showing once again an apparent lowest thickness limit for CSD films. This limit seems to be broken only when no high-temperature annealing procedures are required for the preparation of the film, mostly in nonferroelectric compositions,^{23,24} although a successful result on ferroelectric lanthanum modified lead zir-

conate titanate with thickness as small as 9 nm just published²⁵ confirms the viability of CSD to produce ultrathin ferroelectrics. In the present work, we explore the challenges of CSD preparation of ferroelectric ultrathin films by the deposition of highly diluted solutions, which also allows crystallization at relatively low temperatures.^{26–28} We present the preparation of pure and Ca-modified lead titanate ferroelectric films from several highly diluted solutions reducing the film thickness down to ~18 nm. From the analysis of the results we discuss the factors that control the growth of ultrathin films with a good coverage of the substrate by CSD. The piezoelectric behavior of the films is studied by piezoresponse force microscopy.

II. EXPERIMENTAL PROCEDURE

Air-stable precursor solutions of PbTiO_3 (PT) and $(\text{Pb}_{0.76}\text{Ca}_{0.24})\text{TiO}_3$ (PCT) nominal compositions with a 10 mol% PbO excess were synthesized by a sol-gel route that uses a diol (1,3 propanediol) as solvent in the case of the PT composition,²⁹ and a mixture of diol and water for the PCT.³⁰ The stock solutions were diluted with 1,3 propanediol to obtain concentrations between 0.3 and 0.025 M. This type of solution has proved to be an appropriate precursor for the preparation of ultrathin films.²⁸ The diluted solutions were then deposited by spin coating at 2000 rpm for 45 s onto Pt/TiO₂/SiO₂/(100)Si substrates. A single layer was deposited. After drying at 350 °C for 60 s on a hot plate, crystallization was carried out in air by rapid thermal processing (RTP) at 650 °C for 50 s, with a heating rate of ~30 °C/s.

Grazing incidence x-ray diffraction (GIXRD) with a Siemens D500 diffractometer (Berlin-Munich, Germany) at an incidence angle of 1° was used to confirm that the films are single perovskite phase. Film thicknesses were determined by spectroscopic ellipsometry. Measurements were carried out in a phase-modulated ellipsometer Jobin Yvon UVISSEL (Longjumeau, France) operating between 1.5 and 4.5 eV. The sample structure was simulated as two layers (film and substrate) and voids using the Bruggeman effective medium approximation. A dense PCT ceramic and a naked substrate were used as references for the film and substrate, respectively. We observe that an increase of the void content is related to an increase of roughness or the result of the loss of continuity in the film. A fairly good agreement between measured and calculated complex dielectric coefficients is obtained.

To study the films by transmission electron microscopy (TEM), cross sections were prepared using a focused ion beam workstation (FEI FIB2000, Hillsboro, OR) following the so-called lift-out method.³¹ A protective layer was deposited onto the surface to protect the film during the cutting of the thin lamella. Due to the ion

beam exposure this layer becomes gradually amorphous in its outer part, although it is crystalline close to the ultrathin films under study. This can be observed in the TEM images. The cut and freed lamellas were transferred to Cu grids with a Narishige micromanipulator (Tokyo, Japan). The samples were studied with a Tecnai-20 FEG TEM (FEI) working at 200 kV.

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).³² In this work, we have used conductive commercial Pt/Ir coated tips (Nanosensors) on cantilevers with a force constant of 42 N/m and resonance frequency of 320 kHz to apply an ac voltage of 1 V at 50 kHz. Remanent local piezoelectric hysteresis loops have been obtained at different locations for the films studied.

III. RESULTS AND DISCUSSION

The ultrathin films prepared by CSD of diluted solutions are perovskite single phase according to the grazing incidence x-ray diffraction data shown in Fig. 1. Apart from some reflections coming from layers of the substrate, such as Pt or TiO_2 , the rest can be identified as belonging to the perovskite phase. Reflections 001 and 002 are not observed, most probably because of a strong preferential orientation of the films, although no systematic texture analysis has been carried out, and GIXRD data can be misleading. The variation of the film thickness with the dilution of the precursor solutions is shown in Fig. 2 for the single perovskite phase PT and PCT films. In both PT and PCT films, as the concentration of the precursor solution (c) decreases, the film thickness (t) decreases. This is the expected tendency according to theoretical models developed for films deposited by spinning of solutions.³³ Simple correlations such as $t = A c^n$ have been proposed for spin-coated polymer films³⁴ (where A and n are parameters that depend on the chemical system and the spinning speed). The effect of the crystallization on the final thickness is not considered in these models, and in principle it cannot be applied to our problem, although a good fit of our data can be obtained with second-order polynomial functions (lines in Fig. 2), which are not far from the predictions of the simplified models mentioned. However, it can be seen that this correlation is lost for the thinnest films, obtained from solutions with concentrations below 0.1 M. This can be explained by a study of cross sections of these films with TEM (Fig. 3). The films obtained from solutions with concentrations of 0.1 M or above [Fig. 3(a)] are continuous, i.e., with a full coverage of the substrate. The thicknesses measured in the micrographs corroborate the values obtained by ellipsometry. Direct measurements on the micrograph of Fig. 3(a) give film thickness values

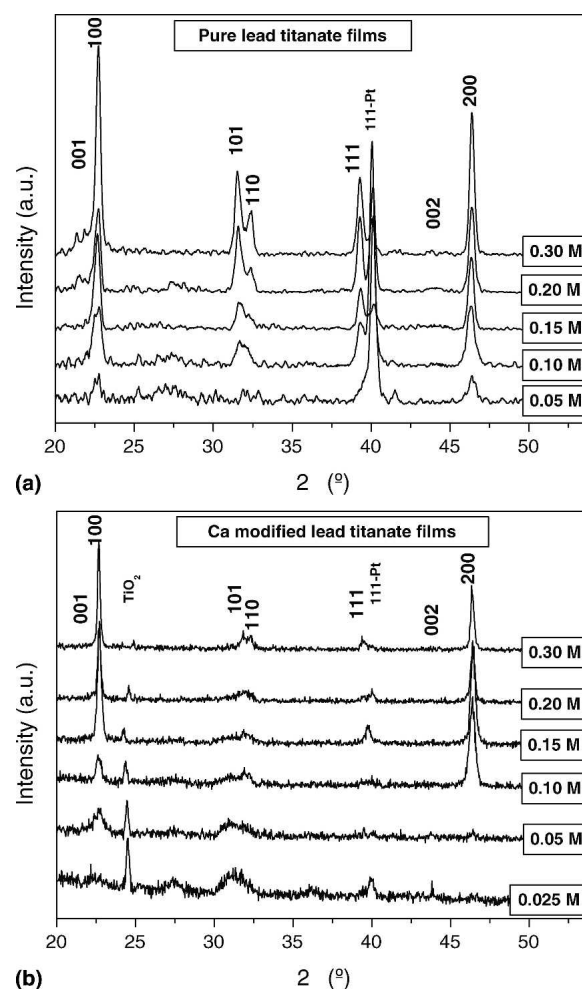


FIG. 1. Grazing incidence x-ray diffraction diagrams of ultrathin films obtained from the deposition of diluted solutions with different concentrations. (a) Pure lead titanate. (b) Ca-modified lead titanate films. The positions of 001 and 002 reflections of the perovskite are indicated for information only.

between 15 and 19 nm, which reflects the small height variations of the grains. Values from the fitting of the ellipsometry curves on the same film (agreement factor of the simulation: $R^2 = 0.91$) produce a similar value: 18 nm. This is the thinnest continuous film we have prepared. Films prepared with more diluted solutions result in discrete islands randomly distributed on the surface, as can be seen in Fig. 3(b). The height of these structures is between 17 and 21 nm, larger than the thickness value (9 nm) obtained by ellipsometry, which is in fact an average of the heights over areas with and without islands of material.

The analysis of the surface topography of the PT films was carried out by SFM (Fig. 4). A decrease of the grain size as the concentration of the precursor solution and the film thickness decrease is observed: from 100–200 nm of the film prepared from a 0.3 M solution [Fig. 4(a)] to 60–120 nm of the one from 0.1 M [Fig. 4(d)]. The grain size is rather large compared with the measured film

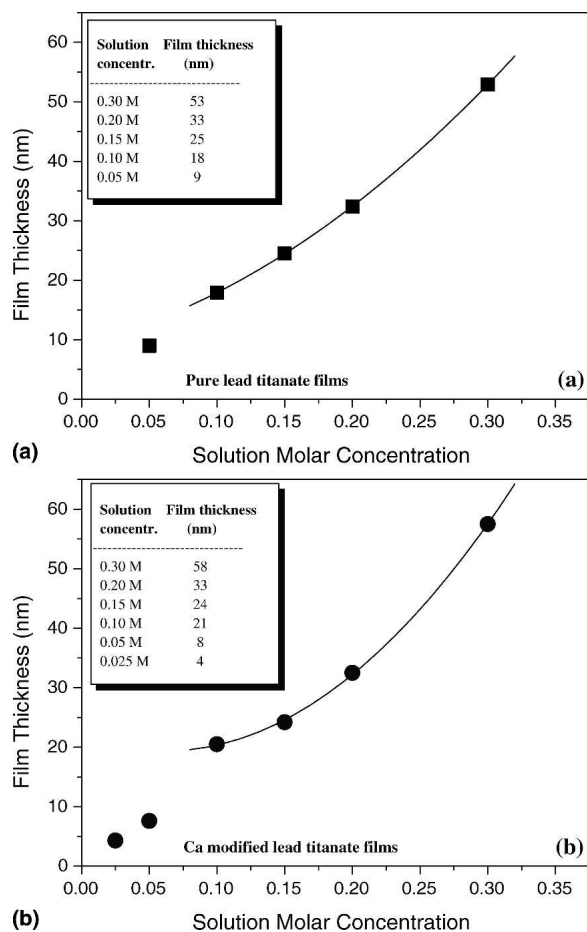


FIG. 2. Evolution of the film thickness (determined by ellipsometry) with the concentration of the precursor solution.

thickness (below 60 nm), which indicates a large lateral, in-plane growth of the crystals. This corroborates the idea that the grains grow 3D until grain size is larger than thickness. A further decrease of the thickness by reducing the concentration of the precursor solution results in the formation of isolated structures instead of a thinner continuous film. This is in agreement with the model that predicts that above a critical grain size to thickness ratio, the grain growth is no longer the dominant energy reduction mechanism, and spheroidization and the formation of isolated structures occurs.¹³ These results suggest that the key to producing thinner continuous films is the control of this ratio, i.e., the reduction of the grain size by the adequate choice of the processing parameters of the films. This can be achieved by a reduction of the preparation temperature, but this must be above the one of phase formation. This is an important limitation in ferroelectrics, which usually requires high crystallization temperatures, and may explain why thinner CSD films are only available when lower processing temperatures are required.^{23,24} Although it has been reported that the crystallization temperatures can be reduced by a ultra-

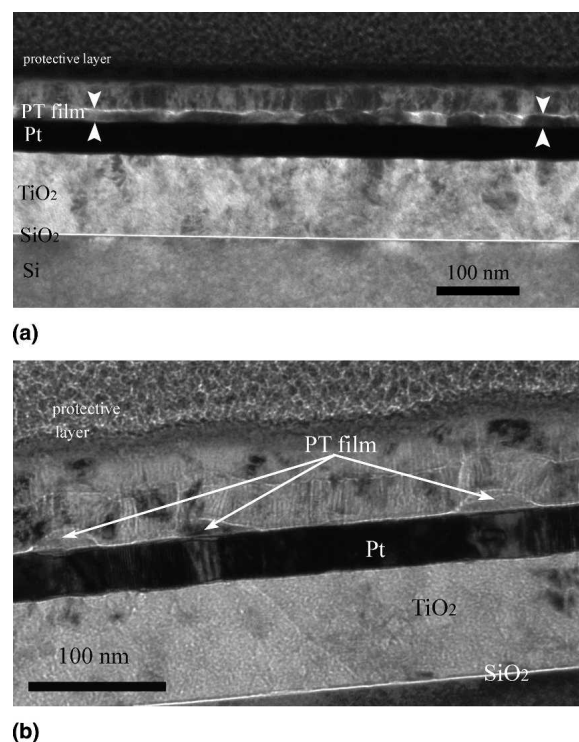


FIG. 3. Transmission electron microscopy images of cross sections of the pure lead titanate films obtained from solutions with concentrations: (a) 0.1 M and (b) 0.05 M.

violet (UV)-assisted method,²⁷ other parameters can lead to thickness reduction, such as modifications of the solvent chemistry. Further work in this direction is in progress and will be reported separately.

However, variants of the same mechanism that should be taken into account can be observed in other systems, as shown by the study of the films of Ca-modified lead titanate films (Fig. 5). The main difference is that in this case the initial grain size is smaller, which seems to correlate with the introduction of Ca^{2+} . Ca-modified lead titanate films are derived from solutions with higher heterogeneity than those of pure lead titanate. In fact, the former is a solution resulting from the mixture of a Pb-Ti-sol and an aqueous Ca-acetate solution, and the latter is a real Pb-Ti-sol.³⁵ Although this difference may be an important factor, it should also be considered that the thermal decomposition of Ca^{2+} and Pb^{2+} reagents (in both cases acetates) are not the same either. While Ca acetate decomposes through the formation of an intermediate carbonate stable at high temperatures,³⁶ Pb acetate transforms directly in CO_2 , H_2O , and PbO at relatively low temperatures. Therefore, the nucleation and crystallization process cannot be the same, leading to different microstructures, as observed when Figs. 4 and 5 are compared. This effect has been reported for other films containing alkaline-earth cations, such as BaTiO_3 and SrTiO_3 ,³⁷ and discussed for Ca-modified PbTiO_3 in a previous paper.³⁸ It seems that grain growth is somehow

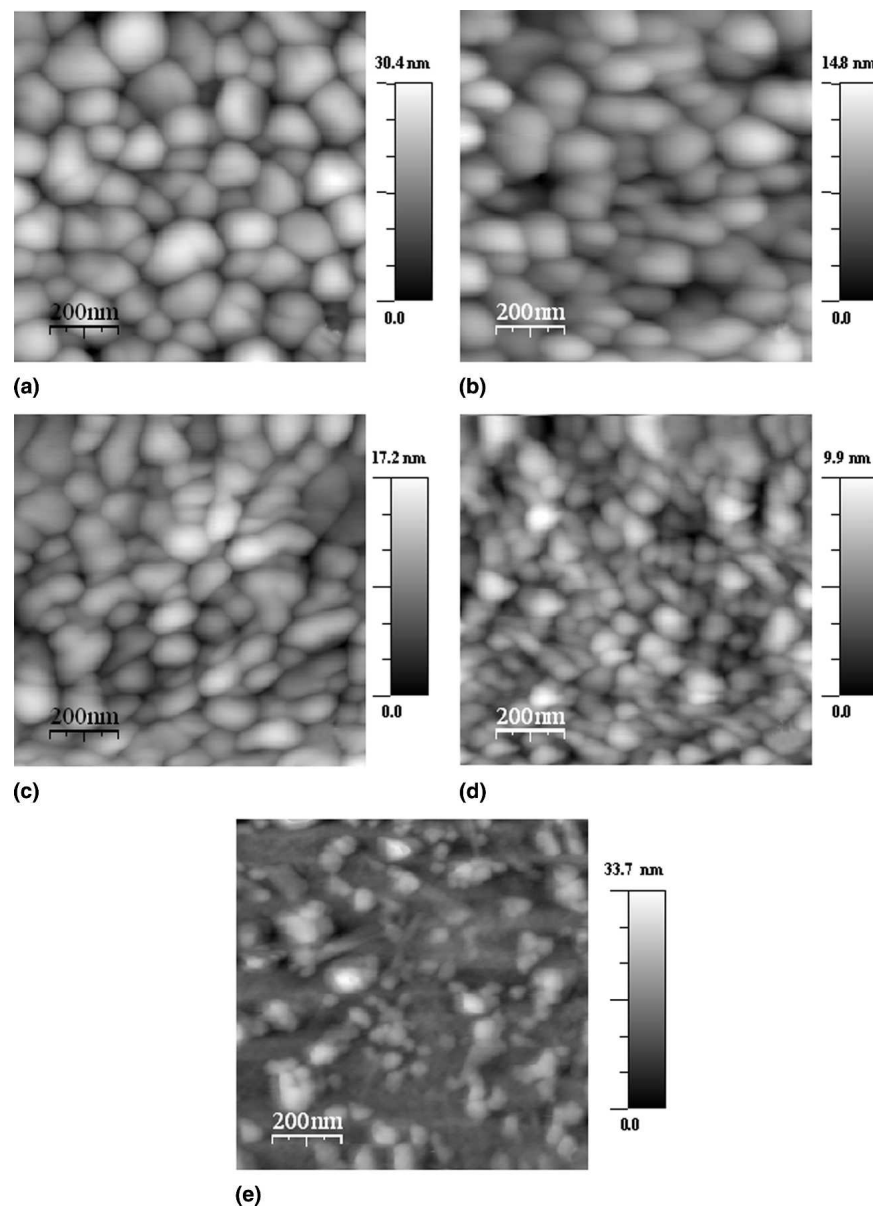


FIG. 4. Topography images of the surfaces obtained by scanning force microscopy of the lead titanate films obtained from solutions with concentrations: (a) 0.3M, (b) 0.2 M, (c) 0.15 M, (d) 0.1 M, and (e) 0.05 M.

inhibited in this system, which results instead in the formation of clusters of grains, visible in the films with larger thickness [Figs. 5(a) and 5(b)], but not clearly in the films obtained from more diluted solutions [Figs. 5(c) and 5(d)], which can be attributed to a decrease of the cluster size due to the thickness reduction. Moreover, when the concentration of the dilution is below 0.1 M the films break into separated clusters of grains [Figs. 5(e) and 5(f)], which may be explained if we consider that in this case the cluster size, instead of the grain size, is the factor that controls the formation of continuous films. The mechanisms seem to be similar, but the factor whose control will allow us to prepare continuous film below a certain thickness by this method is now the cluster size.

To assess the piezoelectric activity, we have measured local piezoelectric hysteresis loops (Figs. 6 and 7) on those grains showing the highest out-of-plane piezoresponse values. Our results show that the reduction of the film thickness from ~ 50 to ~ 20 nm in both pure and Ca-modified is accompanied by a decrease of the d_{33}^{eff} values, which is in agreement with the tendency already observed in similar thicker polycrystalline ferroelectric films, with values in the range of 0.5 to 8 μm .^{39,40} One of the possible factors causing this reduction of the piezoelectric activity may be the increase of the residual stress with the decrease of the film thickness. This will reduce the mobility of the non- 180° ferroelectric domain walls, which is responsible for one of the most important

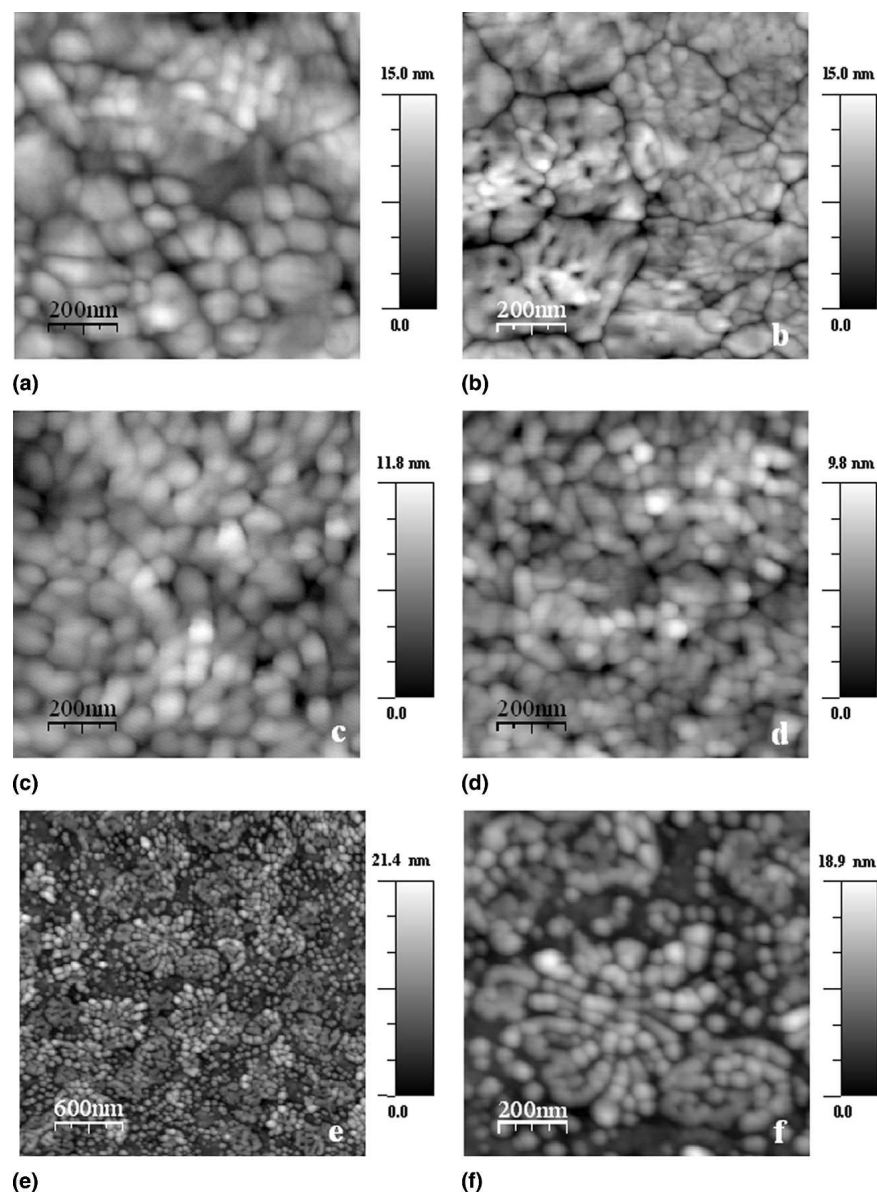
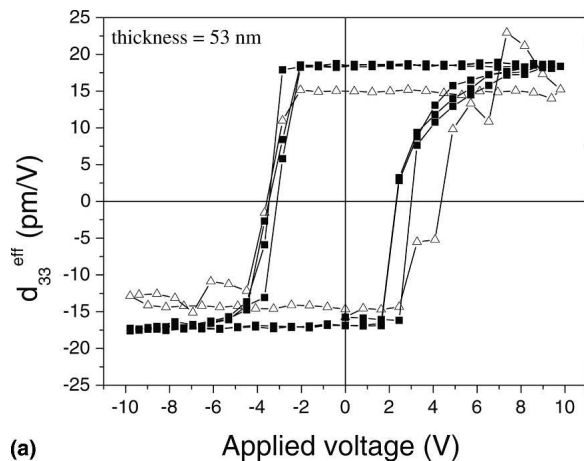


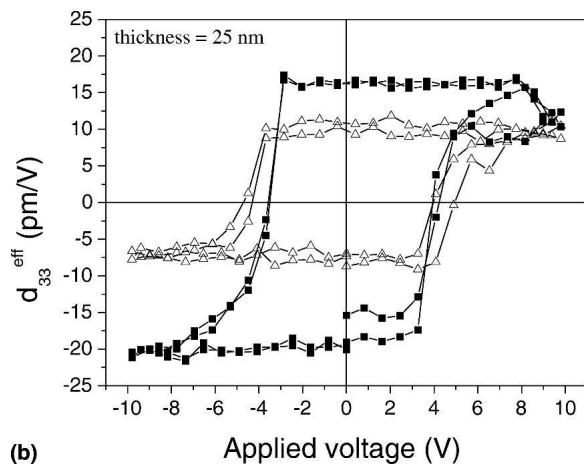
FIG. 5. Topography images of the surfaces obtained by scanning force microscopy of the Ca-modified lead titanate films obtained from solutions with concentrations: (a) 0.3M, (b) 0.2 M, (c) 0.15 M, (d) 0.1 M, (e) and (f) 0.025 M.

contributions to the piezoelectric coefficient. However, in our case PFM images confirm that grains are monodomain, and therefore this argument is not applicable. Other factors such as crystallographic orientation or grain size effects must be considered. As the nucleation sites of the oriented grains are at the interface between substrate and film, a decrease of the thickness when a single layer is deposited usually results in stronger preferential orientations in the films,⁴¹ which is accompanied by a change of their piezoelectric behavior. It is difficult to assess the texture evolution in such thin films, where the small amount of material deposited makes it hard to obtain strong diffraction peaks to undertake a reliable texture characterization. However, we can argue that we

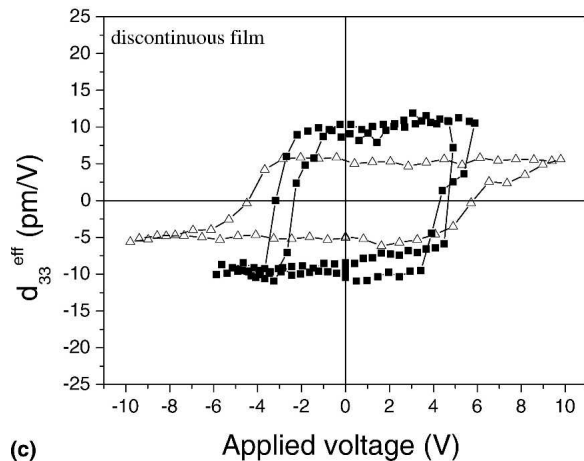
will obtain similar preferential orientation to the one obtained in thicker films prepared by the same processing approach used in this paper.⁴² On platinized Si-based substrates, preferential orientation was observed along the nonpolar axis $\langle 100 \rangle$. Therefore, even in the case that this orientation is stronger for the ultrathin films, it will not lead to strong variations of the piezoelectric behavior. By this argument texture variation may be discarded as a relevant factor for our CSD polycrystalline ultrathin films. It is well known that the effect of grain size, which decreases when the thickness is reduced (Figs. 4 and 5), is correlated with a decrease of the domain width. In our case, as the grains are monodomain as confirmed by PFM images, size reduction induces a decrease in the



(a)



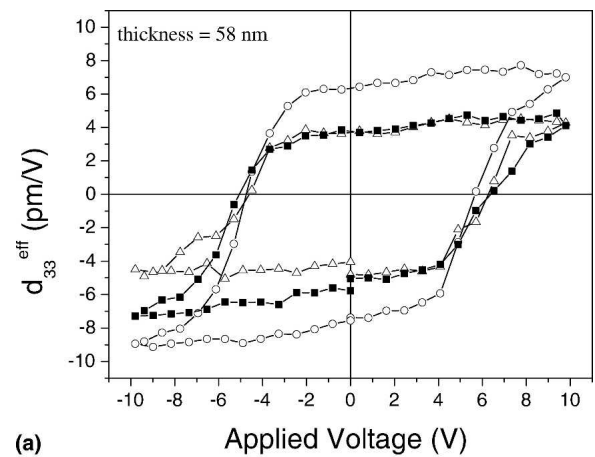
(b)



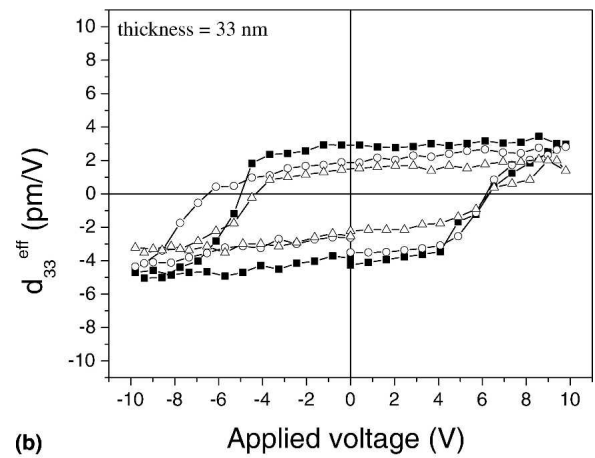
(c)

FIG. 6. Local remanent piezoelectric hysteresis loops of lead titanate continuous films with different thickness: (a) 53 nm, (b) 25 nm, and (c) discontinuous film. The loops shown for each film were measured in different grains.

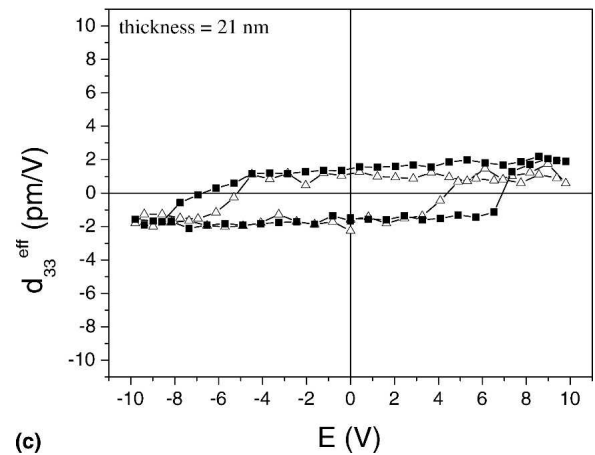
polarization of the crystal, resulting in a deterioration of the permittivity and the piezoelectric activity. The difficulties in assessing with precision the contribution of all these interrelated factors in films with such a low thickness complicate the task of establishing correlations between piezoelectric response and thickness, as it has been



(a)



(b)



(c)

FIG. 7. Local remanent piezoelectric hysteresis loops of Ca-modified lead titanate films with different thickness: (a) 58 nm, (b) 33 nm, and (c) 21 nm. The loops shown for each film were measured in different grains.

extensively studied in epitaxial ultrathin ferroelectric films.⁴³ However, we can conclude that in our case the grain size plays an important role that should be studied in more detail by the evaluation of films of similar nanometric thickness and different grain size.

Although the quantitative interpretation of the results obtained by PFM should be carried out with care because

of several factors intrinsic to the measurement method,⁴⁴ such as, among others, the non-negligible electrostatic interactions between the tip and the surface or the inhomogeneous character of the electric field applied, we observe a significant piezoelectric activity even in the thinnest films. This does not disappear even when the films break up into isolated structures, as can be seen in Fig. 6(c). If we compare the values with the piezoelectric coefficients obtained for GaAs integrated recently as piezoelectric actuator in a NEMS,⁷ they are still one order of magnitude higher. This makes the PbTiO₃ ultrathin films studied here promising materials for use as transducer elements in devices with reduced dimensions.

IV. CONCLUSIONS

The preparation of continuous ultrathin ferroelectric films by chemical solution deposition methods down to 18 nm thickness has been achieved by the deposition of highly diluted solutions. The variation of the concentration of the precursor solution allows the control of the film thickness until a critical grain size to thickness ratio is reached, when the films break into isolated structures. The results obtained suggest that the control of the grain size, or cluster size, through the choice of the optimum processing parameters can lead to the production of thinner films with a full coverage of the substrate. Thickness reduction, although producing a decrease of the local piezoelectric coefficients of the films, does not mean a complete loss of the piezoelectric response, which is still competitive for applications in nanodevices. The polycrystalline nature of these films deposited on platinized Si-based substrates makes grain size an important parameter to consider for tailoring their physical properties.

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