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Properties of morphotropic phase boundary $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ films with submicron range thickness on Si based substrates

M. Algueró[1], M. Stewart[2], M.G. Cain[2], P. Ramos,[3] J. Ricote[1] and M.L. Calzada[1]

[1]Instituto de Ciencia de Materiales de Madrid, CSIC. Cantoblanco, 28049 Madrid, Spain

[2]National Physical Laboratory. Hampton Road, Teddington TW11 0LW, United Kingdom

[3]Departamento de Electrónica, Universidad de Alcalá. 28871 Alcalá de Henares, Spain

Abstract

The electrical properties of $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$-$xPbTiO_3$ films with composition in the morphotropic phase boundary region around $x=0.35$, submicron thickness and columnar microstructure, prepared on Si based substrates by chemical solution deposition are presented and discussed in relation to the properties of coarse and fine grained ceramics. The films show relaxor characteristics that are proposed to result from a grain size effect on the kinetics of the relaxor to ferroelectric transition. The transition is slowed down for grain sizes in the submicron range, and as a consequence intermediate polar domain configurations with typical length scales in the submicron- and nanoscales are stabilised. A high saturation polarisation can be attained under field, but fast polarisation relaxation occurs after its removal, and negligible remnant values are obtained. At the same time, they also show spontaneous piezoelectricity and pyroelectricity. Self polarisation is thus present, which indicates the existence of an internal electric field that is most probably a substrate effect. Films would be then in a phase instability, at an intermediate state between the relaxor and ferroelectric ones, and under a bias electric field, which would explain the very high spontaneous pyroelectric response found.

1. Introduction

Piezoelectric, ferroelectric films are being integrated in Si-based microelectromechanical systems to implement sensing and actuation [1], and are also considered for nanoelectromechanical systems [2]. The material most often used is perovskite P(Zr,Ti)O_3 (PZT) around the morphotropic phase boundary (MPB), which has been the key to commercial high sensitivity piezoelectric ceramics; a mature and ubiquitous technology [3]. The MPB is a region in the phase diagram that separates ferroelectric rhombohedral and tetragonal polymorphs, and in which the single crystal piezoelectric coefficients are very high thanks to a mechanism of polarisation rotation [4]. Also, ferroelectric/ferroelastic domain wall motion significantly contributes to the piezoelectric response [5]. The highest d_{33} coefficients are provided by soft PZT, for which values of ~600 pC N^{-1} are achieved by enhancing wall mobility through compositional modification [6]. However, domain wall motion is limited in films, and negligible in thin layers with submicron range thickness because of substrate clamping [7]. This has shifted interest to alternative MPB materials with higher crystal piezoelectric coefficients than PZT, among which relaxor based $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMN-PT) stands out.

PMN-PT single crystals with composition at the rhombohedral side of the MPB region; (1-x)PMN-xPT with $0.3 \leq x < 0.35$, present effective d_{33} piezoelectric coefficients above 2000 pC N^{-1} along the <001> direction [8], and textured 0.675PMN-0.325PT ceramics have already been processed with coefficients above 1500 pC N^{-1} [9]. In the case of conventional ceramics, 0.65PMN-0.35PT shows piezoelectric coefficients comparable with those of soft PZT with significantly less domain wall contribution [10,11]. However, films do not show such good electromechanical properties. The best results have been reported for epitaxial 0.67PMN-0.33PT films on (001) $SrRuO_3$/$SrTiO_3$ substrates with a thickness of 3.3 μm, which show only a d_{33} of 250 pC N^{-1} [12]. On Si substrates, a coefficient of ~180 pC N^{-1} has been reported for <100> oriented columnar 0.7PMN-0.3PT films with a thickness of 1.5 μm [13], which was even lower when thickness decreased to the submicron range [14]. Although low, the coefficients obtained were higher for <100> oriented films than for similarly prepared <111> oriented layers, which indicates that the mechanism of polarisation rotation is still active to some extent in the films. Therefore, it is worth carrying out further work to understand the mechanisms that reduce the piezoelectric activity of this promising material in thin film form.

We present here a study of the properties of columnar MPB PMN-PT thin films with submicron thickness, and discuss them by taking into account grain size effects; recently reported down to the nanoscale in ceramics [15,16], and the role of the film/substrate interface. It is intended to shed light onto the mechanisms responsible of the distinctive features shown by this type of film.

2. Experimental

Thin films were prepared by chemical solution deposition (CSD). A diol-based sol-gel procedure was used to synthesise the precursor solutions [17]. Around 0.3M diluted solutions were deposited on $Pt/TiO_2/Si$ substrates by spin coating. Crystallisation was carried out by rapid thermal annealing in O_2. A temperature of 650ºC, a time of 6 s and a heating rate of 200ºC s^{-1} were chosen; conditions that allow perovskite single phase layers of (1-x)PMN-xPT with $0.3 \leq x \leq 0.4$ to be obtained according to X-ray diffraction data. Deposition and crystallisation were repeated 4 times to obtain films with a thickness of ~0.25 μm. A columnar microstructure results with typical diameters of 0.2-0.4 μm. More details of the preparation and microstructure of the films can be found elsewhere [18].

The electrical properties were studied on an array of Pt top electrodes with a diameter of 350 μm that was deposited on the films by sputtering.

The temperature dependence of the dielectric permittivity and losses was measured with a HP 4284A Precision LCR meter at 9 frequencies between 100 Hz and 1 MHz. Measurements were dynamically carried out during heating at 1 K min^{-1} from room temperature (RT) to 573 K.

Room temperature ferroelectric hysteresis loops were measured with a modified Sawyer-Tower circuit and a Tektronix TDS520 oscilloscope. A HP 8116A pulse generator was used to apply voltage sinusoidal waves with an amplitude between 0.5 and 12 V and a frequency of 200 Hz.

The longitudinal piezoelectric coefficient was measured by optical interferometry. The system developed at National Physical Laboratory makes use of common path optics to isolate environmental noise [19]. Displacements in the subpicometer range are measured through the use of lock-in techniques under applied voltage sine waves with amplitudes between 0.05 and 0.20 V at frequencies between 5 and 20 kHz.

Local piezoelectric measurements were carried out with a commercial scanning force microscope (Nanotec® with WSxM® software; Nanotec Electrónica) in which piezoresponse force microscopy (PFM) has been implemented. 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.

Finally, pyroelectricity was also characterised. Thermal triangular waves were applied and the pyroelectric currents were dynamically measured with a Keithley 6514 Electrometer.

3. Results and discussion

The temperature dependences of the relative permittivity and dielectric losses for a 0.65PMN-0.35PT thin film are shown in Figure 1 at several frequencies. Relaxor type behaviour is observed; permittivity is highly dispersive and decreases as frequency increases at temperatures below a broad maximum, whose position shifts towards higher temperatures with frequency [20]. The relaxor character of the maximum in permittivity is further confirmed by the observation of its shift with composition across the solid solution, as expected and previously reported [18]. High temperature electrical conduction is responsible for the significant increase in dielectric losses above 400 K, and the presence of dispersion in the permittivity at temperatures above the maximum. This phenomenon has also been observed in PMN-PT films grown on $LaNiO_3$/Si substrates by pulsed laser deposition, and associated with hopping of oxygen vacancies [21].

This behaviour is very different to that of coarse grained ceramics with the same composition, which is also shown in Figure 1 for a material with a grain size of 4 μm. A well defined dielectric anomaly, typical of a first order ferroelectric phase transition, is observed, with a transition temperature of 442 K. This transition is between a ferroelectric phase and a high temperature relaxor state, which have been reported to exist up to 0.5PMN-0.5PT [22]. However, the behaviour of the PMN-PT films studied here is similar to that of a fine grained ceramic with a grain size of 0.15 μm, also shown in the figure. In this case, relaxor type behaviour is observed. Results of bulk ceramics correspond to materials with high chemical homogeneity, processed from nanocrystalline powder synthesised by mechanochemical activation, and therefore, these differences cannot be attributed to compositional variations. Details of the processing can be found elsewhere [23]. A thorough study of these ceramics concluded that a grain size effect is associated with the mechanisms of development of ferroelectric long range order in relaxor based systems. When grains go down to the submicron range in size, approaching the nanoscale, the transition from the relaxor to the ferroelectric state is slowed down. As a consequence, intermediate submicron/nanometer sized crosshatched polar domains persist down to room temperature, and a relaxor-type electrical behaviour is observed [15]. This slowing down with the decrease in grain size has experimentally been observed for 0.8PMN-0.2PT between 0.36 and 0.21 μm [16]. The lateral size of the columnar grains of the film with 0.25 μm thickness is 0.2-0.4

μm, so it is reasonable to assume that the relaxor-type behaviour observed is similarly a consequence of the reduced grain size of films. Note that permittivity values for the thin film are smaller than those of the fine grained ceramic, in spite of the column size not being smaller in the former than the grain size in the latter. This is most probably an effect of the substrate/film interface that acts as a low dielectric permittivity layer in series with the film, and causes the depletion of permittivity; a phenomenon widely observed and discussed in the ferroelectric thin film literature [1], and specifically in PMN-PT films [24-26].

The ferroelectric hysteresis loop for a 0.65PMN-0.35PT film is shown in Figure 2, along with those for the coarse and fine grained ceramics. Note that electric fields necessary for polarisation switching were an order of magnitude higher in the case of films than in ceramics. The increase of coercive field with the decrease in thickness is also a widely observed phenomenon in films [27]. In the case of the MPB PMN-PT films, it is remarkable that a saturation polarisation, P_S, as high as 25 μC cm^{-2} is attained, which is basically the value for the coarse grained material. However, retention is very poor, and a remnant polarisation, P_R, of only 6 μC cm^{-2} is obtained, compared with 23 μC cm^{-2} for the ceramic. Similar results have previously been reported on PMN-PT films prepared by CSD on Si substrates, in which a P_R of 8.5 μC cm^{-2} was found for the thinnest films investigated (0.35 μm) [14]. Again, the behaviour is similar to that of the fine grained ceramic, for which significant saturation polarisation can be achieved with poor retention. This was also attributed to the same grain size effect in the domain configuration, and thus, it seems to confirm that the thin film effect is basically a grain size effect. The high values of the saturation polarisation indicate that the submicron/nanometer sized crosshatched ferroelectric domains present in the small grains are able to rearrange under an electric field, most probably by coarsening of favourably aligned domains. This results in polarisation values similar to those of coarse grain materials with micron-sized lamellar domains [15]. However, the coarsened domains are not stable, and the domains return to their original configuration after removal of the field, resulting in very low values of remnant polarisation.

These characteristics are also found for other properties of the MPB PMN-PT films. The longitudinal piezoelectric coefficient was measured under applied electric field along a ferroelectric hysteresis loop, and it is shown in the inset of Figure 3. Saturation coefficients approaching 60 pC N^{-1} were obtained, but retention was very poor, in good agreement with the ferroelectric properties. Also, note that the piezoelectric loop is shifted along the field-axis. This indicates the presence of an internal electric field across the film that results in a self polarisation, and thus in spontaneous piezoelectricity. This spontaneous response is illustrated in Figure 3, and a d_{33} piezoelectric coefficient of 25 pC N^{-1} is obtained.

To further understand the intrinsic nature of the phenomena observed, piezoresponse force microscopy studies were carried out, as they provide information closer to the behaviour of the individual crystals. The first observation is that there are not significant variations of the spontaneous piezoelectric response within and among the grains, according to the out-of-plane piezoresponse amplitude image, and the corresponding phase image shown in Figure 4. This is again evidence of self polarisation that seems to be remarkably homogenous across the layer. An internal electric field is thus present, which induces this polarisation that is directed towards the substrate, and the piezoelectric response observed. The measurement of piezoelectric hysteresis loops in individual grains produced the same results as the macroscopic ones shown in Figure 3. Again, poor retention characteristics are evident. This is very well illustrated by the comparison of the in-field piezoelectric loops with the remnant ones, which is shown in Figure 5. Note that the in-field loops are similar to the macroscopic ones of the inset of Figure 4. The fast decay of the piezoelectric response after the application of the poling pulse in the remnant loops results in the measurement of similar values of the effective piezoelectric coefficient, regardless of the value of the electric field applied during the pulse (Fig. 5b). Measurements shown are taken only a few tenths of s after removing the field. Besides, it must be noted that the coefficients obtained tend to the value of the spontaneous coefficient observed in the in-field loops. The presence of self polarization in the films is also corroborated by these measurements.

In order to understand the peculiarities of the polarisation relaxation in PMN-PT thin films, the time dependence of the piezoresponse after applying a poling voltage was studied. Polarisation decay in normal ferroelectrics is associated with the movement of domain walls after removal of the external field characterized by a slow kinetics. However, in relaxors the polarisation induced by an electric field disappears much faster. As we have already shown, this is also the case in the MPB PMN-PT films, and so, due to the short times involved, we chose to use the measurement of the evolution of the piezoelectric response just at one position below the tip, rather than the analysis of images of a poled area at different time intervals. Figure 6a shows an example of the decay of the out-of-plane piezoelectric coefficient after the application of an electric pulse of 10 V during 0.2 s. After a study of several curves, using different electric pulses, we conclude that the relaxation times are between 0.05 and 0.10 s, with no correlation with the duration of the poling pulse. The results show that the curves seem to be affected by other factors that make it difficult to draw more conclusions about the relaxation process. The analysis of the evolution of the piezoelectric response with longer times (Fig. 6b) shows that there are temporal fluctuations of the effective d_{33} coefficient measured, not observed when these experiments are performed in similar, normal ferroelectric $PbTiO_3$ films. This may indicate that the self polarisation observed in these films is very sensitive to the interaction between tip and sample, like variations of surface charges, of stress, stray electric fields… Nevertheless, both the fast polarisation relaxation and the temporal fluctuations of the spontaneous response are consistent with the film being in an intermediate state between the relaxor and ferroelectric ones.

Therefore, the macroscopic and local piezoelectric measurements clearly indicate the presence of a self polarisation in the films that must be associated with the existence of an internal electric field across the layer. This phenomenon has previously been observed in ferroelectric thin films, and associated with a Schottky-type electric contact between the film and bottom electrode [28], or with strain gradients and the flexoelectric effect [29]. This field is most probably, already present during the cooling of the film through the relaxor to ferroelectric transition after crystallisation. In ceramics with a grain size of 0.15 μm, the presence of a high electric field during the initial stages of the development of the ferroelectric long range order from the relaxor state; this is at ~440 K, has been shown to speed up the kinetics of the transition and to promote the coarsening of the submicron/nanometer sized crosshatched domains towards micron sized lamellar domains, which results in an increase of the piezoelectric activity [15]. This is most probably the mechanism by which a self polarisation appears in the films, which would be associated with the coarsening of favourably aligned domains under the internal electric field in a layer next to the substrate. A schematic drawing of the polar domain configuration is depicted in Figure 7. This is obviously an oversimplification, and a graded configuration most probably exists. Its thickness would be defined by the mechanism that originates the bias electric field; in the case of a flexoelectric origin, by the characteristic length of the strain relaxation.

Recently, giant pyroelectric response has been reported for 0.8PMN-0.2PT single crystals under bias field at the relaxor to ferroelectric transition [30]. This is a composition characterised by slow kinetics of the phase transition and by submicron/nanometer scale ferroelectric domain configurations [16]. Although with a different composition, a similar situation is observed in our MPB PMN-PT films. Submicron/nanoscale domains are stabilised as a consequence of the small grain size and an internal electric field is present, associated with the film/substrate interface. This results in large spontaneous pyroelectric response (Figure 8). Coefficients between 3-5 $\times10^{-2}$ μC cm^{-2} K^{-1} were obtained without any previous poling. These values are remarkable and comparable with best ferroelectric films on Si substrates after poling [31].

This can be considered a new material concept for pyroelectric applications. The enhancement of the pyroelectric properties at a phase instability, in this case the relaxor to ferroelectric transition in the presence of an electric field, is engineered in thin film form by the combination of grain size and substrate effects. The enhancement of properties at phase instabilities is a general concept, of which the high electromechanical response of ferroelectric perovskite solid solutions at the morphotropic phase boundary between rhombohedral and tetragonal polymorphs has been proposed to be a case example [32].

4. Conclusions

The properties of columnar MPB PMN-PT films with submicron range thickness on Si-based substrates present distinctive characteristics. On the one hand, the films show electrical properties very similar to fine grained ceramics; permittivity typical of relaxor, and ferroelectric hysteresis loops characterised by significant saturation polarisation and poor retention. On the other hand, films also present spontaneous piezoelectricity and pyroelectricity. The former effect is proposed to be a grain size effect associated with the slowing down of the kinetics of the relaxor to ferroelectric transition, and the stabilisation of intermediate submicron/nanoscale polar domain configurations. The latter effect is a film effect associated with the presence of an internal electric field across the film, most probably next to the interface that causes a localised coarsening of the domain configuration and a self polarisation. The film is thus at a phase instability, at an intermediate state between the relaxor and ferroelectric phases, and under a bias electric field, which could explain the very high spontaneous pyroelectric response.

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Figure captions

Figure 1. Temperature dependences of the relative permittivity and dielectric losses at several frequencies of a columnar 0.65PMN-0.35PT film with 0.25 μm thickness, compared with those of coarse grained (CGC; grain size of 4 μm) and fine grained (FGC; 0.15 μm) ceramics.

Figure 2. Room temperature ferroelectric hysteresis loop of a columnar 0.65PMN-0.35PT film with 0.25 μm thickness, compared with those of coarse grained (CGC; grain size of 4 μm) and fine grained (FGC; 0.15 μm) ceramics.

Figure 3. Spontaneous piezoelectric response of a MPB PMN-PT film. The inset shows the piezoelectric coefficient under bias field along the ferroelectric hysteresis loop.

Figure 4. Scanning force microscopy of a MPB PMN-PT film: (a) topographic image, (b) out-of-plane piezoresponse amplitude image of the same area, and (c) corresponding phase image.

Figure 5. Local piezoelectric loops in a MPB PMN-PT film: (a) in-field, (b) remnant after increasing times.

Figure 6. Time variation of the local piezoresponse: (a) after the application of a poling pulse, (b) in a wider time window enclosing the poling pulse.

Figure 7. Simplified schematic of the proposed thickness domain gradient in the MPB PMN-PT films, resulting in self polarisation .

Figure 8. Spontaneous (before any poling) pyroelectric response of a MPB PMN-PT film under a triangular thermal wave.

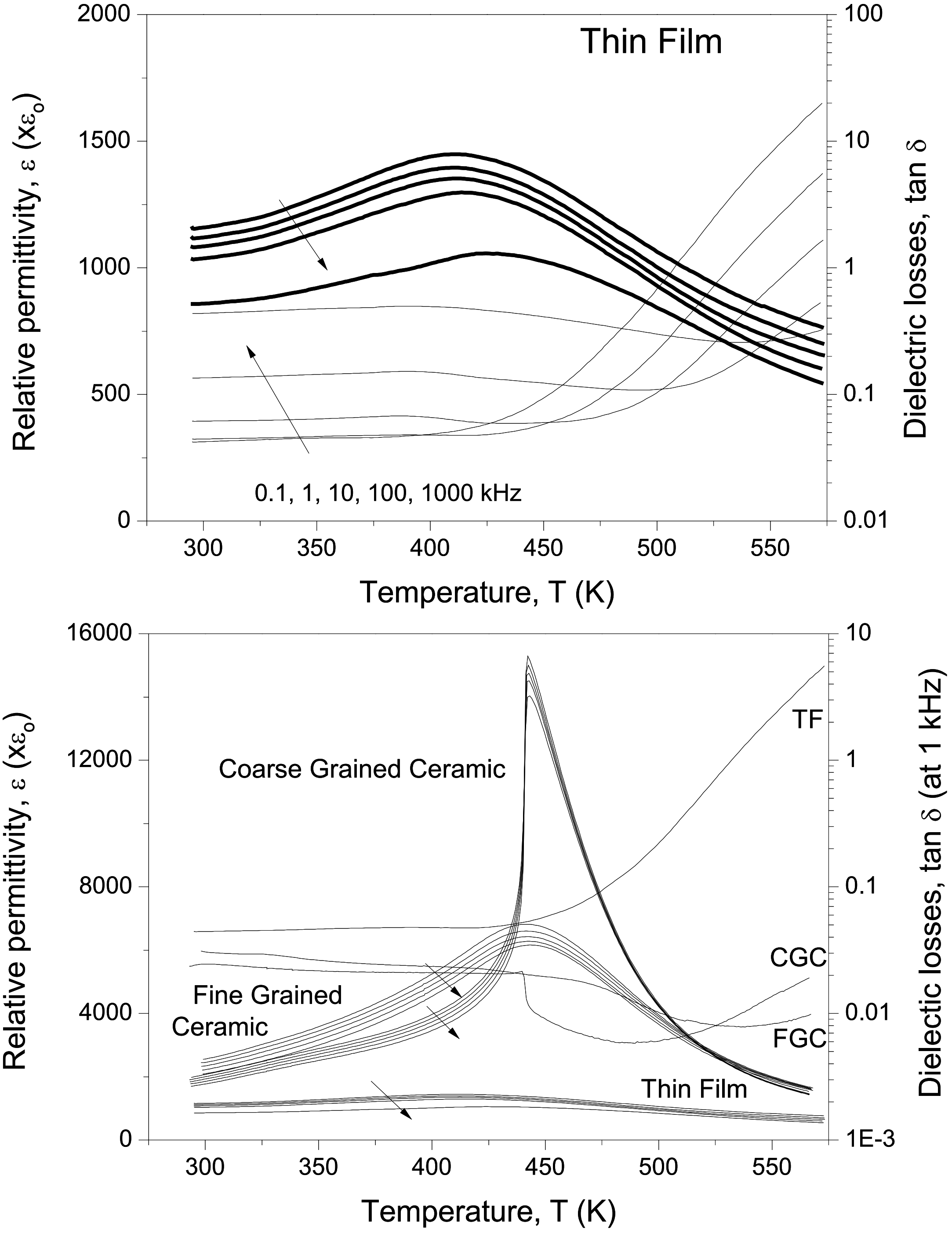
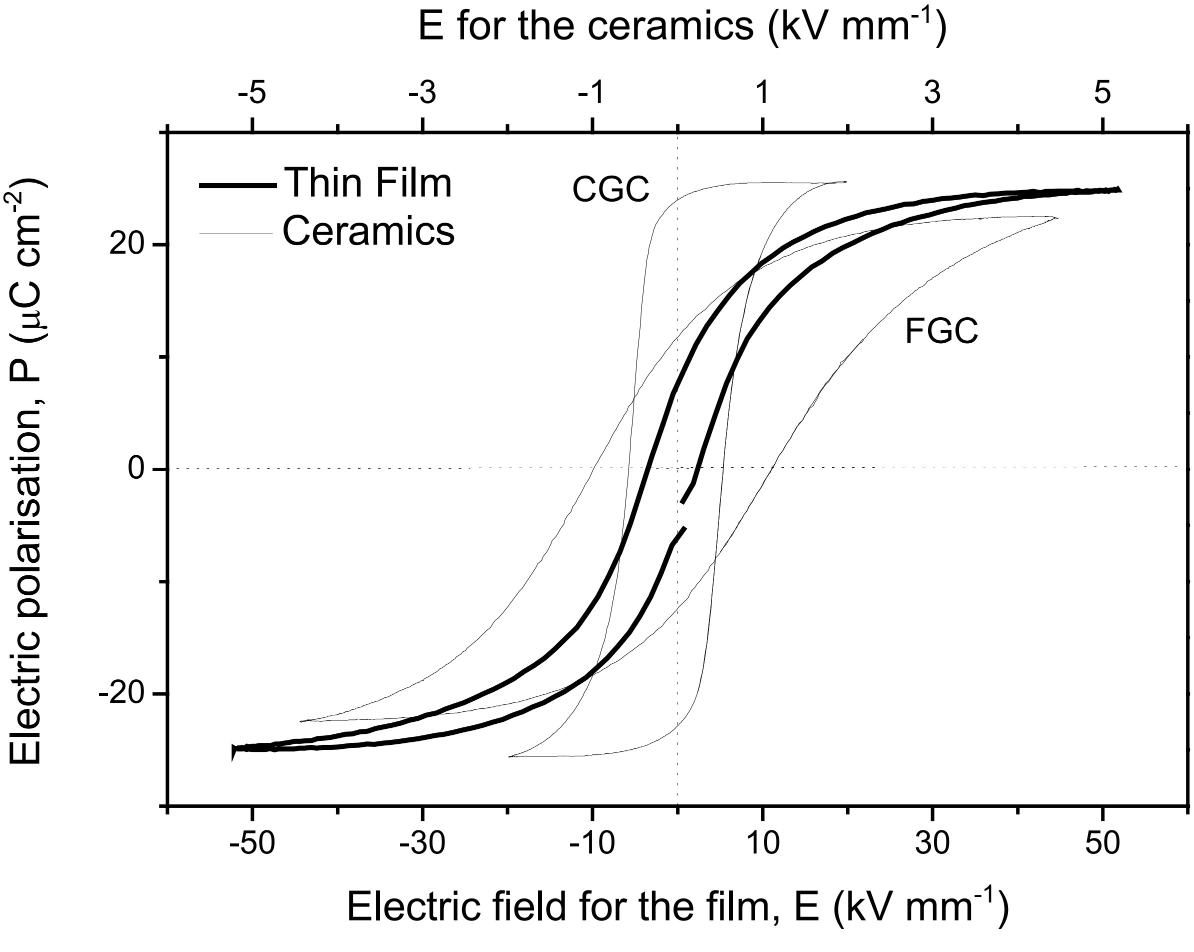


Figure 1 . Algueró et al



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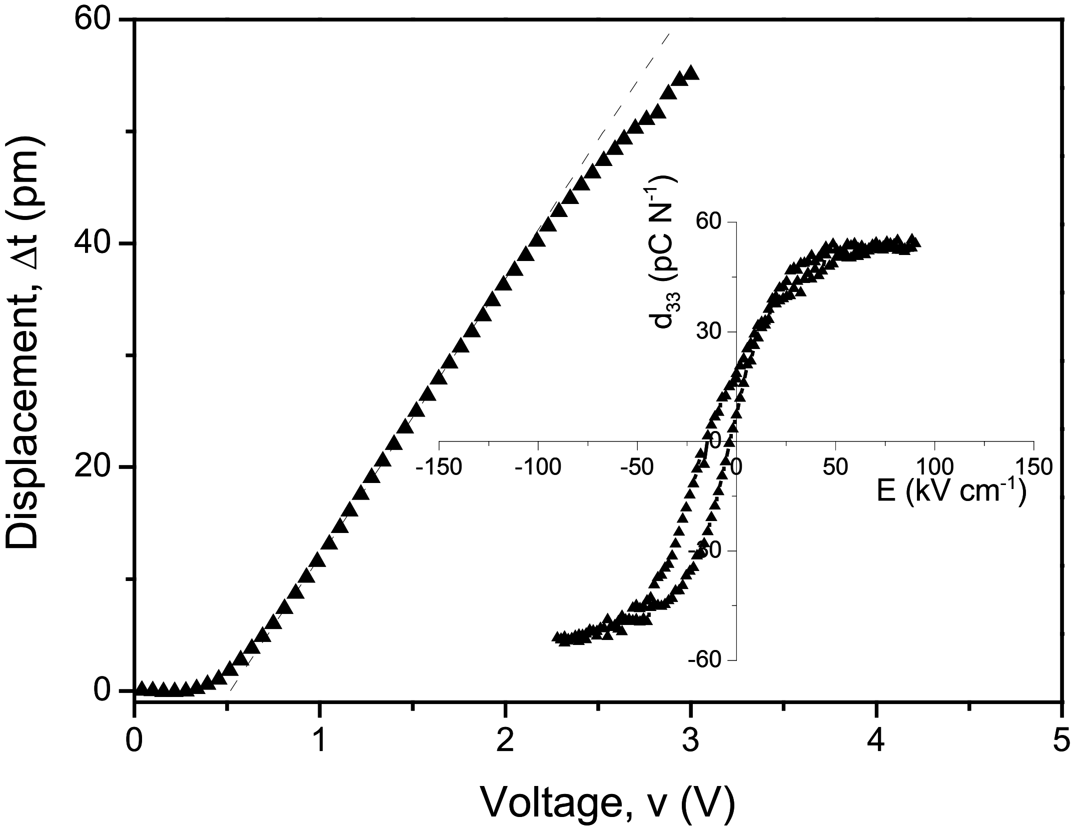

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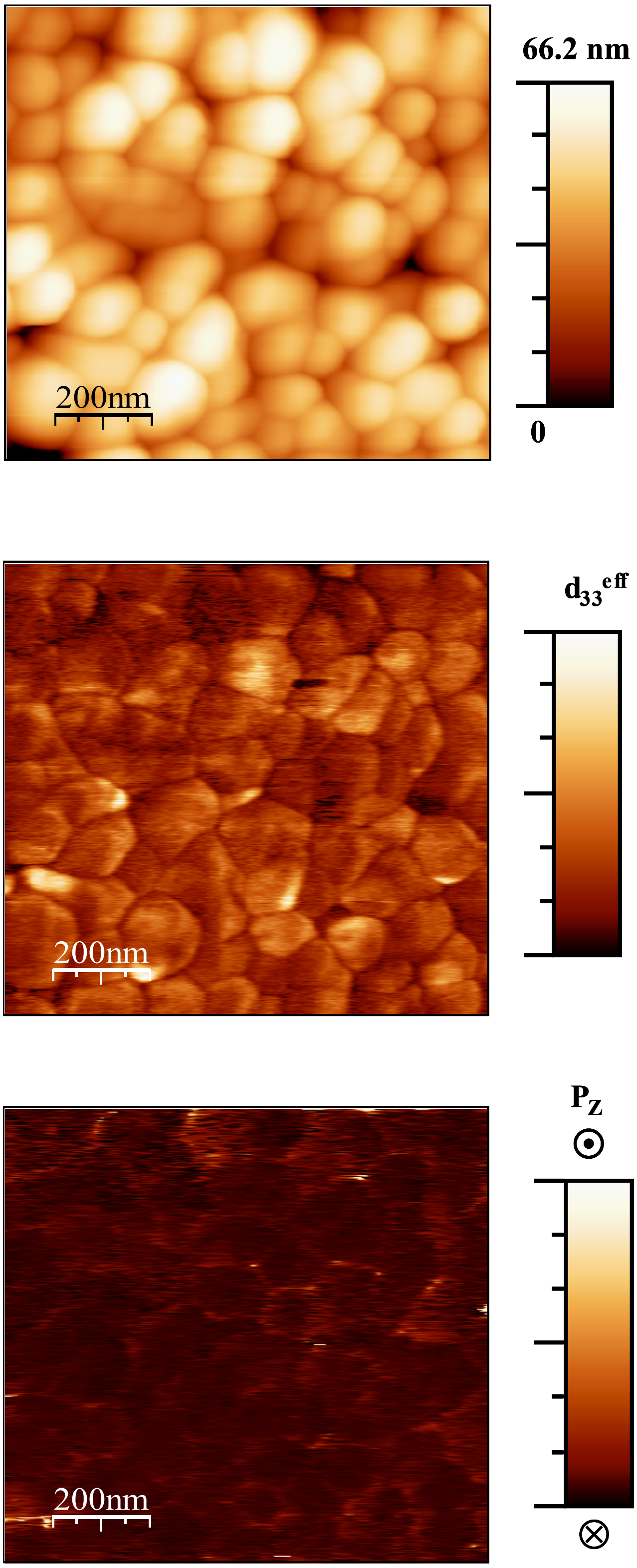

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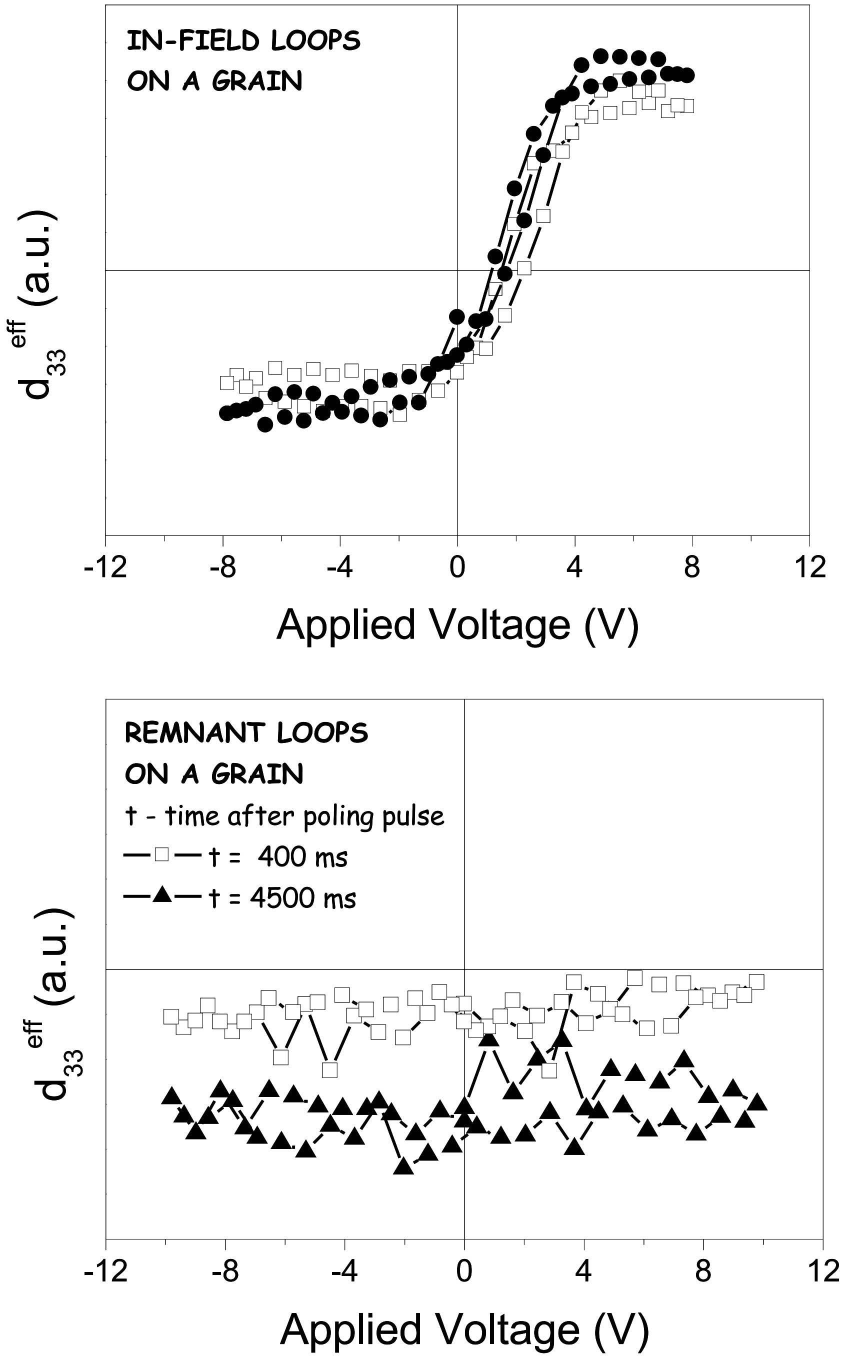

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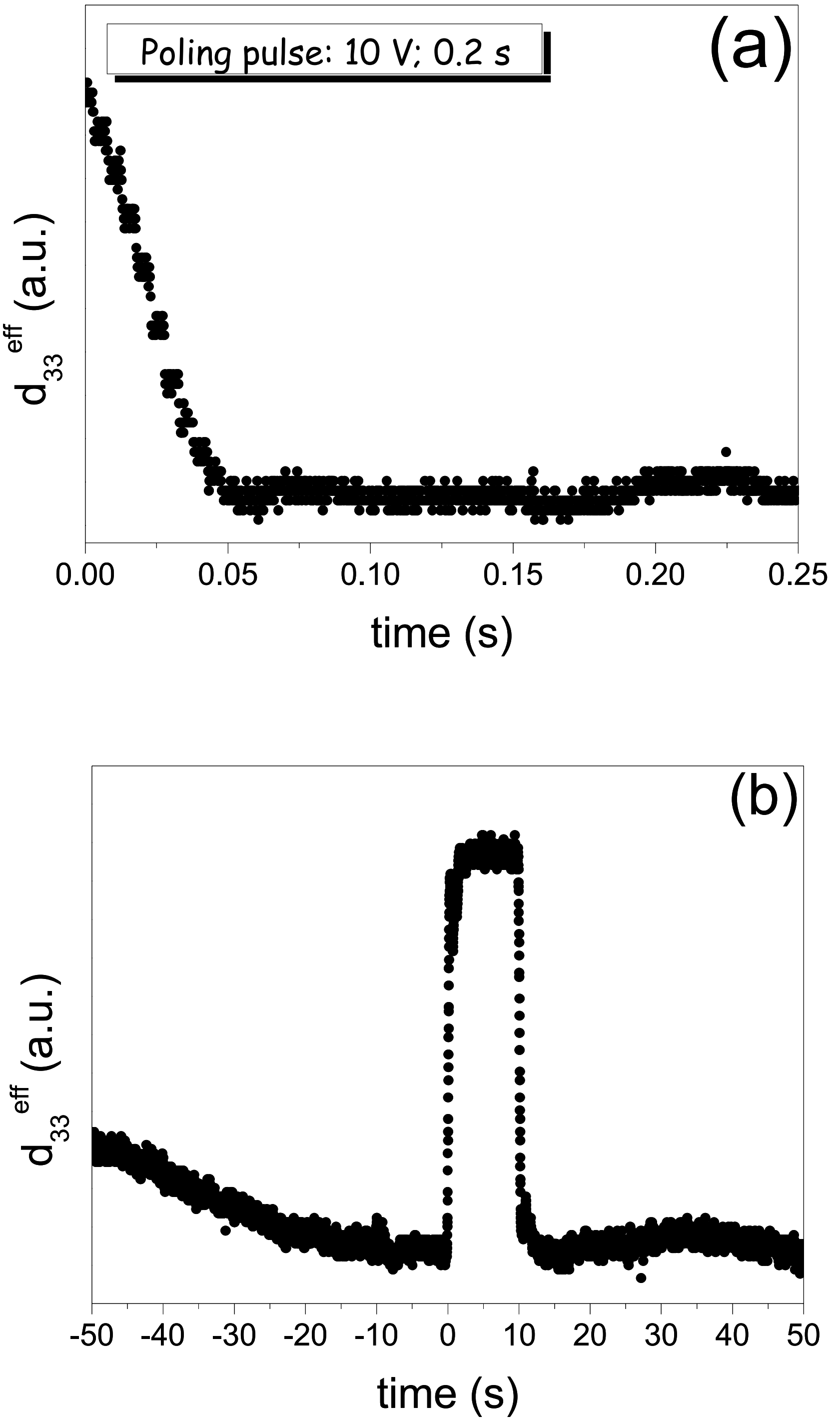

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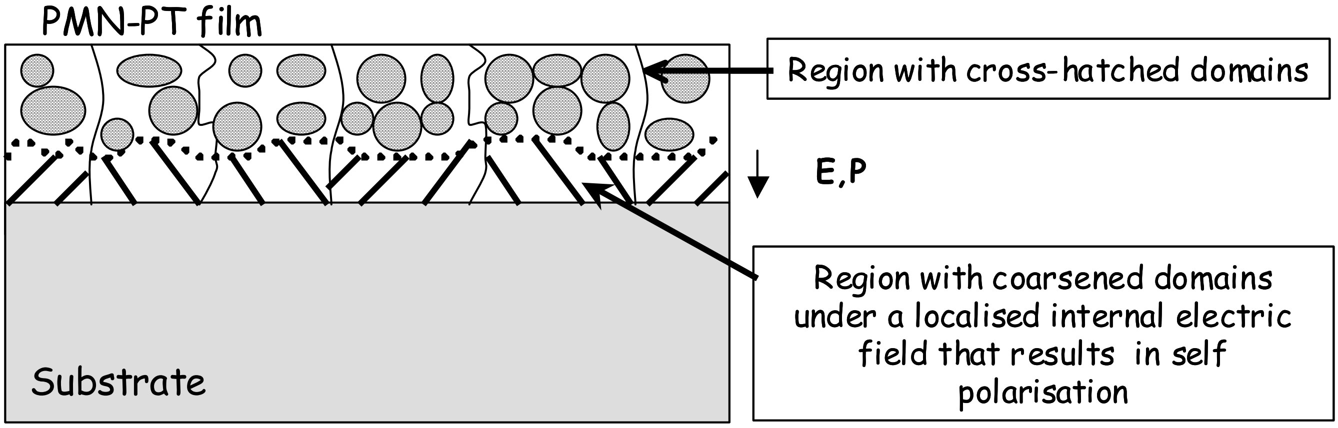

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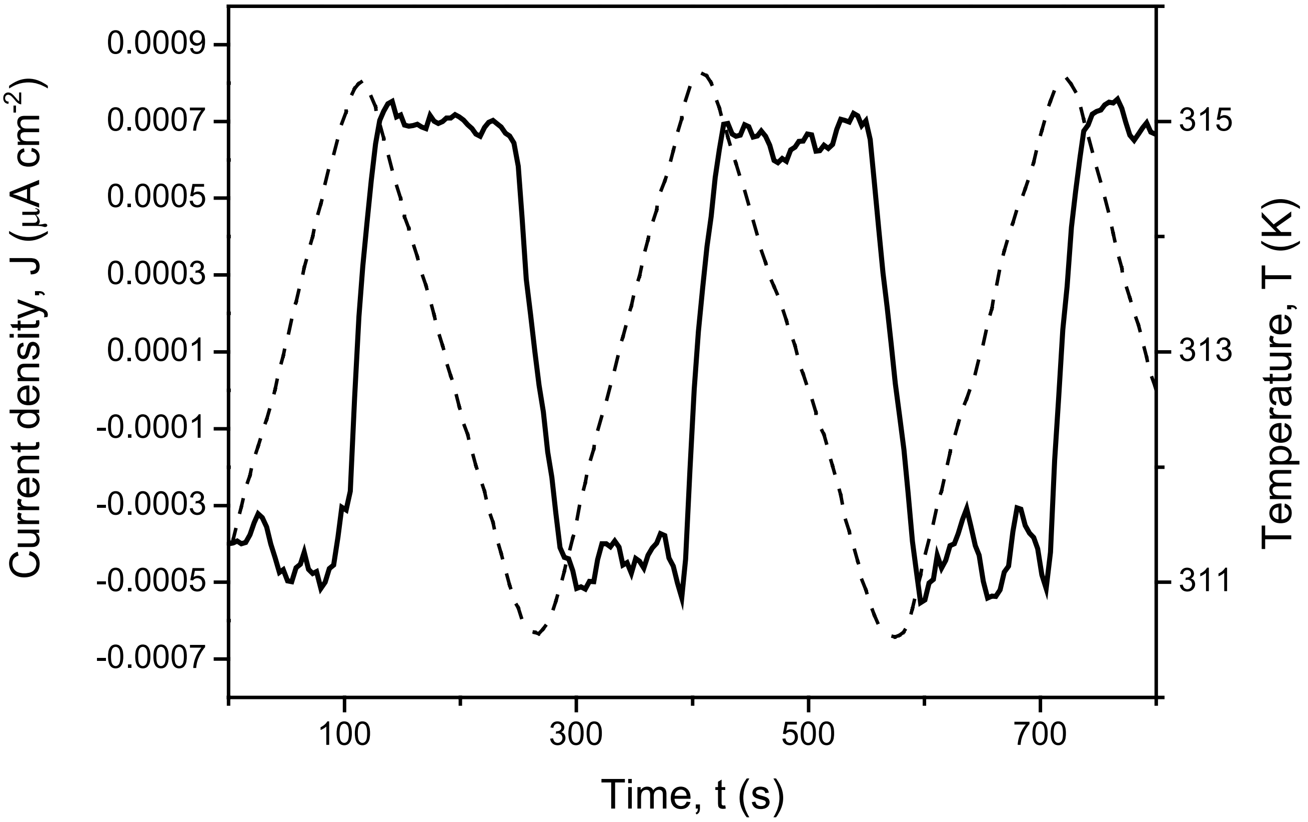

Figure 8. Algueró et al.