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Nonlinear dielectric response in ferroelectric thin films

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Electrical permittivity dependence on electric external bias field was investigated in PZT thin films. The results revealed the existence of two mechanisms contributing to the electrical permittivity. The first one was related to the domain reorientation, which was responsible for a strong no linear dielectric behavior, acting only during the poling process. The second mechanism was associated with the domain wall vibrations, which presented a reasonable linear electrical behavior with the applied bias field, contributing always to the permittivity independently of the poling state of the sample. The results also indicated that the gradual reduction of the permittivity with the increase of the bias field strength may be related to the gradual bending of the domain walls. It is believed that the domain wall bending induces a hardening and/or a thinning of the walls, thus reducing the electrical permittivity. A reinterpretation of the model proposed in the literature to explain the dielectric characteristics of ferroelectric materials at high electric field regime is proposed.

Key words: Thin films, PZT, polarization switching, domain wall, electrical permittivity.

Respuesta dieléctrica no lineal en películas delgadas ferroeléctricas

Se ha estudiado la dependencia de la permitividad eléctrica con un campo bias externo en láminas delgadas de PZT. Los resultados revelaron la existencia de dos mecanismos que contribuyen a la permitividad eléctrica. El primero está relacionado con la reorientación de dominios, actúa sólo durante el proceso de polarización y es responsable de un comportamiento dieléctrico fuertemente no lineal. El segundo mecanismo se asocia a las vibraciones de las paredes de dominio, presentando un comportamiento eléctrico razonablemente lineal con el campo bias aplicado, contribuyendo siempre a la permitividad independientemente del estado de polarización de la muestra. Los resultados indicaron también que la reducción gradual de la permitividad con el aumento de la fuerza del campo bias podría estar relacionada con el "bending" gradual de las paredes de dominio. Se cree que el "bending" de las paredes de dominio induce a un endurecimiento y/o adelgazamiento de las paredes, reduciéndose así la permitividad eléctrica. Se propone una reinterpretación del modelo propuesto en la literatura para explicar las características dieléctricas de los materiales ferroeléctricos en un régimen de alto campo.

Palabras clave: Lámina delgada, PZT, cambio de polarización, paredes de dominio, permitividad eléctrica.

1. INTRODUCTION

Over the last decades intensive studies have been conducted in order to understand the electrical properties of ferroelectric materials. These efforts are justified due to several practical applications of these materials in the electronic industry (1). Among the technological potentialities, there is a special interest in to employ ferroelectric thin films as high dielectric constant capacitors (2). Indeed, ferroelectric systems emerge from the dielectric class as the highest dielectric constant materials, even when compared to other polar systems (2, 3).

When the dielectric properties of the ferroelectric materials are investigated, special care must be taken in order to consider the high complexity of the ferroelectric domains and domain walls structures as well as the intricate domain dynamics involved under different electric field regimes. At low bipolar electric field regime, which means a field much lower than the coercive field (E_C), it is not expected any domain switching. Thus, the dielectric response can be related to a true linear electrical permittivity, which contribution is from the domain wall vibrations (4). On the other hand, under high electric field regime domains and domain walls are forced to be reoriented by the polar axes along those permissible crystallographic directions (5). Then, it is reasonable to expect that the strong transient present in the domain reorientation as well as the significant changes in the domain configuration induced due to the poling process affect in some extent the dielectric properties. Although the knowledge of dielectric properties of ferroelectric materials is very important from practical and theoretical point of view, few studies have been developed in order to determine a correlation between linear and nonlinear dielectric response with the domain switching process.

The aim of this work is to investigate the electrical permittivity dependence on low and high electrical field regimes in PZT thin films. From the results, it will be discriminated the domain and domain wall contributions to the electrical permittivity during and after the polarization switching process. The experimental results are compared with those expected from the theoretical models proposed in the literature.

2. BRIEF DESCRIPTION OF THEORETICAL MODELS

2.1. Electrical permittivity at low electric field regime

It has been widely attributed that at low electric field regime the 90° domain wall vibrations is the main polarization mechanism responsible for the high dielectric permittivity values observed in ferroelectric materials (6, 7, 8). In this regime field, the displacements of 90° domain walls (DW) are assumed to be small and reversible. Then, the vibration of DW mathematically has been expressed by the equation of the forced harmonic oscillator (8, 9). In this model, proposed by Arlt and co-workers (4, 7), the DW displacement is always an elastic deformation being proportional to the force constant, *k*, supposing a linear regime to the DW vibrations. It is also proposed that the force constant *k* is directly proportional do the elastic constant and inversely proportional to domain width (4). However, no studies have been reported relating possible influences of high electric bias fields on the domain structures and, consequently, on the force constant.

2.2. Electrical permittivity at high electric field regime

One of the most widespread methods employed to investigate the dielectric properties of ferroelectric materials at high electric field regimes is the investigation of the electric bias field dependence of the electrical permittivity (ε vs. E) (10, 11, 12). The nonlinear behavior of ε vs. E curve has been attributed to the domain reorientation process (13). Thus, Bar-Chaim and co-workers (13) have proposed a model in order to explain the dielectric response of ferroelectric materials during the polarization switching process. It is predicted that with the increase of the electric field the gradual increase of the dielectric constant corresponds to a continuous increase of the amount of domains in the reversal process, until the permittivity reaches a maximum. The theoretical results predicting the domain contribution to the electrical permittivity is shown schematically in figure 1. However, after the maximum, still increasing the bias field the permittivity decreases continuously until reaches the stabilization (point B). It is attributed that the dielectric constant decreases with the increase of the electric bias field due to a continued reduction of the amount of domains that are in the reversal process. Finally, when the bias field is gradually removed the increase in the dielectric constant (from point C to O in figure 1) is related to the backswitching. Nevertheless, as it will be shown later, some expected theoretical results are not verified experimentally. Thus, some reconsideration in the proposed model will be made to clarify the dielectric behavior of ferroelectric materials during and after the poling process.

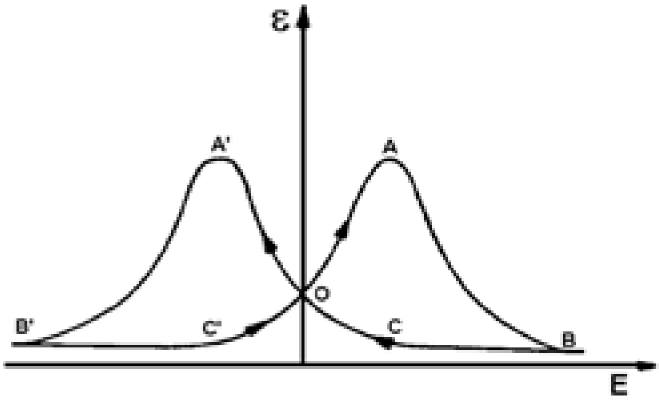

Figure 1: Theoretical results predicting the domain reorientation contribution to the electrical permittivity dependence on the electric bias field (13).

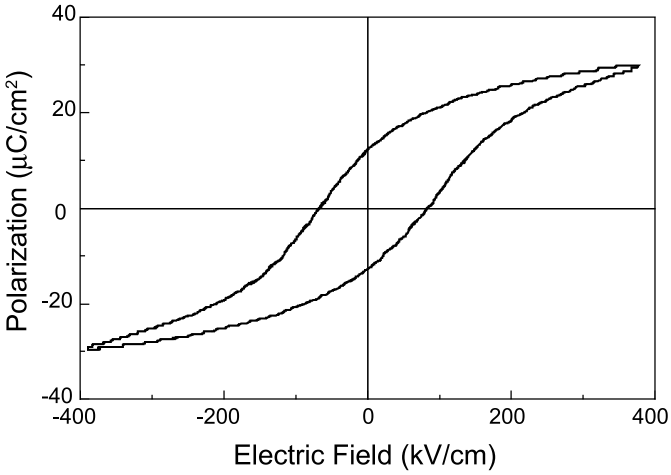

Figure 2: Hysteresis loops for the PZT thin film measured at 1 kHz.

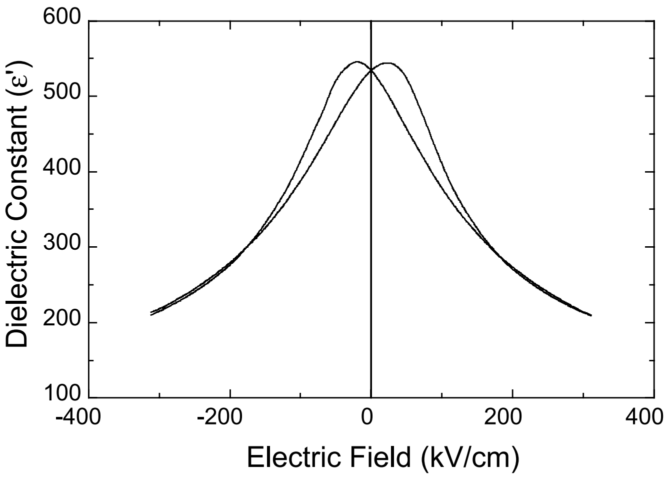

Figure 3: Electric bias field dependence of the relative electrical permittivity for the PZT thin film measured at 10 kHz.

3. EXPERIMENTAL PROCEDURE

$Pb(Zr_{0.53}, Ti_{0.47})O_3$ thin films were prepared using the oxide precursor method, as detailed described in previous works (14). The films were deposited on platinized substrates (Pt/Si) by spin coating. After that, they were annealed at 360 °C for 2 h to remove residual solvents being crystallized at 700 °C for 10 min by RTA process. The films showed a good quality with high homogeneity and high stoichiometry control (14). Scanning electron microscopy showed that the average grain size lies around 100 nm and the films are 500 nm thick. The measurements were performed in a metal-ferroelectric-metal (MFM) configuration. To measure dielectric and ferroelectric properties, several gold electrodes (0.5 mm diameter) were deposited over an area of 1×1 cm^2 on the films through a mask to form MFM capacitors. A Sawyer-Tower circuit was used for the hysteresis loops measurements at 1 kHz. The electrical permittivity was measured in thin films with a LCR Meter Agilent 4284A with a small ac signal of 50 mV_{rms} of amplitude at 10 kHz as function of a bias electric field strength (ε vs. E). All measurements were made at room temperature.

4. RESULTS AND DISCUSSION

Figure 2 shows the hysteresis loops obtained for the PZT film at 1 kHz. The values found for the remanent polarization (P_R) as well as for the coercive field (E_C) were 13 μC/cm² and 76 kV/cm, respectively. The data also reveal that the hysteresis loop has a strong backswitching, which is characterized by the difference between the saturation and remanent polarizations. The electric bias field dependence of the electrical permittivity is shown in figure 3. The bias field was switched from negative to positive polarity and to the negative polarity again and its intensity was similar to that used in the ferroelectric measurements. It is observed one peak for each field polarity. The field where each peak appears has almost the same value that E_C, obtained from the hysteresis loops curves (figure 2). In this measurement it is reasonable to expect some contribution of the domain switching process to the electrical permittivity.

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In order to investigate the electrical permittivity of the film without the domain reorientation influence, the film was firstly poled from –300 kV/cm to +300 kV/cm at a linear rate of 25 kV/cm per second to align the domains in the positive field direction. After this poling procedure, the field was removed and new five consecutive dielectric measurements were done, but now, always applying the bias field from 0 to +300 kV/cm (in the sample previously poled with the same electric field rate). Figure 4 (a) shows the results (for the sake of simplicity only the first and the last measurements are shown). The results reveal that although a peak is always present, its intensity gradually decreases occurring at lower field intensities with the increase of the number of times in which the bias field is applied. Another point that must be stressed is that after the peak the electrical permittivity is almost independent of the number of times in which the field is applied. In the other words, the dielectric curves are almost superposed. Figure 4 (b) shows the electrical permittivity dependence on the bias field when the bias field is applied in the film and the measurement is now made during its gradual removal, which means from +300 kV/cm to 0. In this procedure the maximum bias field (+300 kV/cm) was applied abruptly and removed gradually (25 kV/cm per second). This procedure reduces the backswitching effect. It is noticed in figure 4 (b) that the peak practically disappears, being slightly noticed near zero bias field. In addition, the curves are again reasonably linear with the field and almost independent of the number of times in which the electric field is applied.

Comparing the experimental results with the theoretical ones (figures 1 and 4) it is verified that the model reproduces qualitatively well the peak and the continuous decrease of the dielectric constant with the increase of the bias field. However, it must be emphasized that the theoretical curve from point B to point C is parallel to bias field axis (independent of the bias field), which is not observed experimentally. Indeed, figure 4 shows that the permittivity increases immediately with the gradual removal of the bias field. This same experimental behavior is also observed by other researches (10, 13, 15). In this work, it is believed that the non-accordance between theoretical and experimental results for ε vs. E lies in the assumption imposed in the theoretical model that all dielectric behavior is due exclusively to the domain reorientation process (13). Thus, based on the experimental results, some reconsideration must be made in order to clarify these discrepancies. First, the assumption that the dielectric behavior is dictated uniquely by the domain reorientation during all electric field cycle should be reconsidered. This hypothesis is partially consistent when the spontaneous polarization really follows the electric bias field (e.g. from the point O (unpoled) to point B (poled) in figure 1). However, when the field is removed the ferroelectric sample is already poled, thus the gradual decrease of the field (B→O) is accompanied only by some backswitching. In fact, according to the proposed theoretically, if the backswitching of the domains had the same magnitude that obtained during the polarization process, the dielectric curves increasing and decreasing the bias field (O→B and B→O) would be exactly the same. In the other words, they would be superposed. This hypothesis is inconsistent because ferroelectric materials always present a remanent polarization after the poling process (figure 2).

An analysis of figures 4 allows us to make other consideration. The fact that figure 4 (a) always shows a peak during the continuous re-poling processes may be related directly to the backswitching effect. Indeed, due to abrupt removal of the field a considerable amount of domains return to their equilibrium position (see figure 2). Thus, when the field is successively re-applied the reorientation of these domains takes place and, consequently, the peak in the dielectric curve is still noticed, however, with less intensity. The reason for the gradual

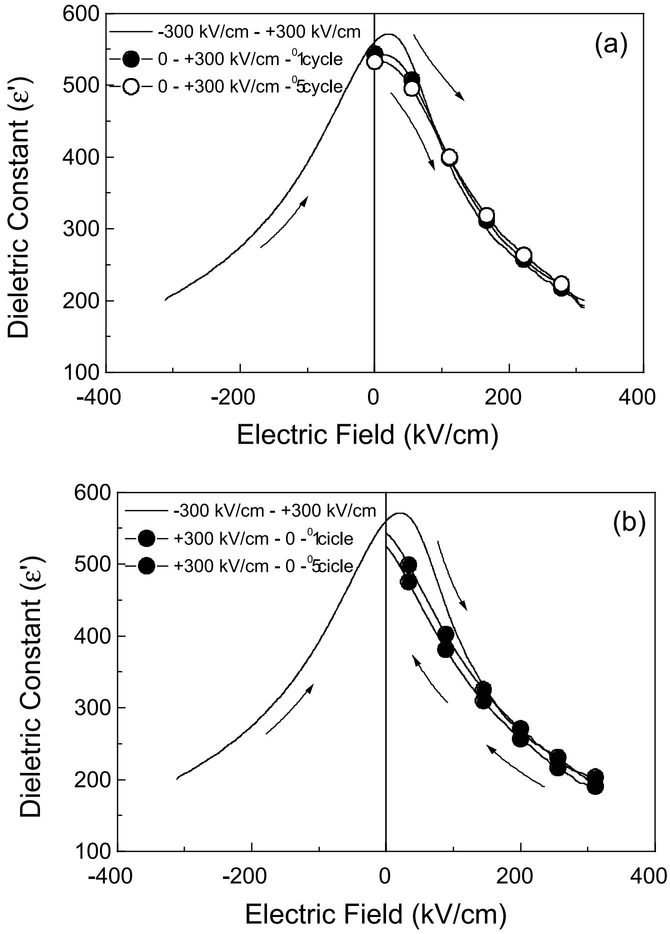

Figure 4: Electrical permittivity dependence on the electric bias field for the PZT thin film previously polarized: (a) measured during the gradual increase of the bias field and removing completely the bias field at the end of each re-poling process; (b) measured during the gradual removal of the bias field.

reduction of the intensity of the peak as well as it to be observed at lower field intensities can be explained assuming that successive re-poling processes stabilize the polarization (16). Nevertheless, when the electric field is applied and maintained for a long time and after that gradually removed (figure 4 (b)) the backswitching effect is significantly minimized. Therefore, the peak practically disappears, being slightly noticed near to zero bias field, as observed in figure 4 (b). From these results, it is possible conclude that the non-linearity in the ε-E curves (the peak) have their origin from the influence of the domain reorientation, as supposed theoretically. However, our measurements clearly reveal that excluding the domain reorientation (for a sample previously poled) the electrical permittivity always decreases with the increase of the electric bias field. Therefore, the hypothesis that the decrease of the dielectric constant is due to a gradual decrease in the amount of domains that are in reversing process is unsuitable. A possible reason to explain the dielectric behavior after the domain reorientation process takes place will be explained below.

How these measurements are performed at high bias field regimes it is reasonable to postulate that the rearrangement of domain walls is large enough to modify the dielectric characteristics. It has been shown that an applied electric field can produce a pressure that acts on the walls bending them in the same way as a membrane supported at several points (17, 18, 19). Therefore, it is proposed in this work that the gradual decrease in the dielectric constant may be related to a continuous hardening and/or thinning of the 90° domain walls due to their gradual bending between pinning sites forced by the driving field. Indeed, the domain wall bending increases significantly the surface tension that is proportional to the curvature of the walls (19, 20). The hardening in the walls can be associated with an increase in the elastic constant of the material, thus leading to a decrease of electrical permittivity (4). A schematic description of the dielectric constant dependence on the bias field is shown in figure 5. In this figure it is presented our hypothesis about how the domain reorientation and the bending of the domain walls contribute to the electrical permittivity under a high electric bias field.

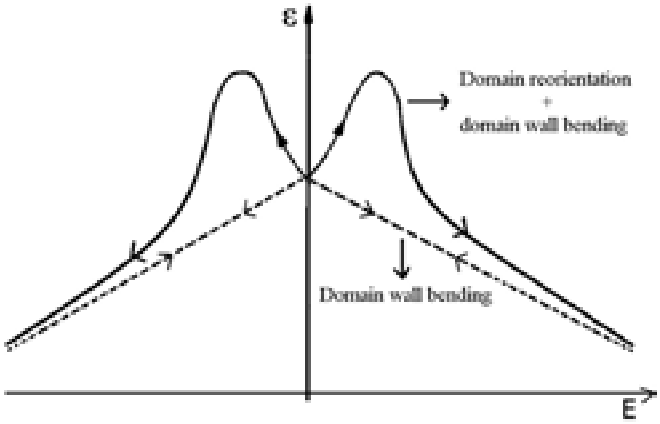

Figure 5: Schematic description of the contribution of domain reorientation and domain wall bending to the dielectric constant dependence on the electric bias field.

5. CONCLUSIONS

In this work, the electrical permittivity dependence with external bias field was investigated in PZT thin films. The peak observed in the dielectric constant was attributed to the domain reorientation that is able to contribute to the permittivity only during the poling process. On the other hand, the decrease in the electrical permittivity was related to hardening and/or thinning of 90° domain walls. It was supposed that this hardening/thinning is caused by the gradual bending of the 90° domain walls, consequently, reducing their vibrations. A reinterpretation of the Bhar-Chaim´s model was proposed.

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