

Depolarization of a piezoelectric film under an alternating current field

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In this article, we demonstrate that a sol-gel-derived niobium-doped lead zirconate titanate film can be depolarized by the application of alternating current (ac) fields of diminishing amplitude and we explain the phenomenon based on the concept of the Preisach model. The amplitude of the ac fields is decreased from 20 to 2 MV/m in ten steps. The observed piezoelectric coefficient of the film decreases after each ac field step. Depending on the initial polarization and the direction of the ac fields, the piezoelectric coefficient can decrease to a very small value indicating the complete depolarization of the film. Our results reveal the existence of a distribution of the switching fields in the microdomains (Preisach dipolar units), and that because of mutual interactions the magnitudes of the switch-up and switch-down fields for each microdomain are not necessarily the same. Our results also suggest that the sputter deposition of the top electrode can induce more “down-state” microdomains, thus giving rise to an initial polarization in the film. Because of interactions with other microdomains or other effects, part of these microdomains exhibit very high switching fields.

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I. INTRODUCTION

In recent years, ferroelectric films, represented by lead zirconate titanate (PZT), have been extensively studied for various applications, such as ultrasonic micromotors, micropumps, and cantilever-actuators in the microelectromechanical systems.^{1,2} In most of the studies, the ferroelectric properties of the film are investigated by the polarization hysteresis (P - E) loop measurement, in which an alternating current (ac) field is applied to the film sample and the induced polarization charge is measured. In general, the amplitude of the ac field is increased in steps until a saturated P - E loop is obtained, from which the remanent polarization P_R and coercive field E_c of the film are determined. It is clear that, based on the observed unsaturated P - E loops under an ac field of smaller amplitude, there should exist a distribution of E_c , and the observed E_c (from the saturated P - E loop) may simply be the maximum value. However, there is not too much work giving detailed discussions on the coercive field and its distribution in a ferroelectric film. It is also generally believed that, after the P - E loop measurements, the film is polarized (or partially polarized) to have the net polarization (given by P_R) oriented along the direction of the electric field in the second-half of the ac cycle. However, this may be true only for an as-prepared film without initial polarization. The P - E loop measurement involves only the switching of polarization, it provides limited information about the net polarization of a film, in particular for a polarized film by a high direct current (dc) electric field.

In the present work, we will demonstrate that ac fields of progressively decreasing amplitude can depolarize a polarized ferroelectric film and show that a direct relation between the observed remanent polarization and the net polarization

may not exist. Sol-gel-derived niobium-doped PZT films with a large initial polarization will be used for the study. The net polarization of the film will be evaluated by the measurement of the piezoelectric coefficient d_{33} using a single-beam laser interferometer. The depolarization phenomenon will be explained based on the concept of the Preisach model.³⁻⁵ The central point of the model is the assumption that there is a distribution of the switching fields (i.e., coercive fields) in the microdomains of the materials. On the basis of the results, the origin of the initial polarization will be discussed.

II. THE PREISACH MODEL

The Preisach model was originally developed for modeling the hysteresis behavior of ferromagnetics and has been generalized for studying the hysteresis behavior of ferroelectric ceramics^{6,7} and films⁸ recently. In the generalized model, it is assumed that each microdomain (dipolar unit) of a ferroelectric material switches up as the external field increases to a value larger than the switch-up field, U , and switches down as the external field decreases to a value smaller than the switch-down field, V . The resulting squared hysteresis loop is called a hysteron [Fig. 1(a)]. An isolated hysteron has a

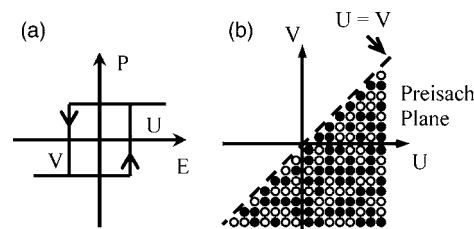


FIG. 1. (a) A hysteron—a squared polarization hysteresis loop with two normalized spontaneous polarization states. (b) Distributions of the polarization states (solid symbols: down state; open symbols: up state) for an as-prepared ferroelectric film with random dipole orientation.

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symmetrical loop about the zero-field axis, i.e., $U = -V$. As a result of the interaction between the microdomains, the magnitudes of the switch-up and switch-down fields (i.e., $|U|$ and $|V|$) become different from each other. Thus, depending on the strength of the interaction field and its distribution, U and V can have any values provided that $U > V$.^{3,4} Figure 1(b) depicts on the $U-V$ plane all the possible microdomains of an as-prepared ferroelectric film with random dipole orientation. It should be noted that each circular symbol situated at (U, V) on the plane represents a group of microdomains with the switching fields U and V . A solid symbol denotes the down-state [refer to Fig. 1(a)] while an open symbol denotes the up-state. The distribution of the microdomains (including all in the up-state and down-state) in the $U-V$ plane is described by the Preisach function $P(U, V)$, which is an intrinsic characteristic of a ferroelectric material.

III. EXPERIMENT

The niobium-doped lead zirconate titanate $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})_{0.98}\text{Nb}_{0.02}\text{O}_3$ (abbreviated as PNZT) films were prepared using a sol-gel method. A PNZT precursor solution was spin coated on a Pt/Ti/SiO₂/Si substrate and then pyrolyzed at 450 °C for 10 min. After the deposition of three layers, the film was annealed in an oxygen atmosphere at 600 °C for 3 min. in a rapid thermal processor. By repeating the process a few times, a PNZT film of thickness 1.2 μm was obtained. The film was then annealed at 680 °C for 20 min. in a furnace. A series of platinum top electrode (of diameter 1 mm and thickness 150 nm) was deposited on the film by dc or radio frequency (rf) sputtering in a pure argon atmosphere for the subsequent measurements.

A Sawyer–Tower circuit was used to apply an ac field at 1 Hz to the film sample and to measure the “remanent” polarization P_R at the same time. It should be noted that P_R is defined as the observed polarization value at the end of the application of the E field; so it may not be the same as the remanent polarization measured from a saturated $P-E$ loop. It has been shown that for polycrystalline films with polydomain structure, the longitudinal piezoelectric coefficient d_{33} is coupled to the (net) polarization P and permittivity ϵ via a general equation

$$d_{33} = 2Q_{\text{eff}}P_{\epsilon}, \quad (1)$$

where Q_{eff} is the effective electrostriction coefficient.^{9,10} For PZT thin film, Q_{eff} is only weakly dependent on the electric field and temperature. Therefore, the net polarization of a ferroelectric film can be evaluated by the measurement of d_{33} at weak fields.

The experimental details of the d_{33} measurement using a single beam laser interferometer have been reported in previous publication.¹¹ A small ac field E at 15 kHz was applied to the film sample in the thickness direction; the surface displacement (Δt) induced in the sample was measured using a heterodyne laser interferometer (SH-120, B.M. Industries). d_{33} was then calculated as

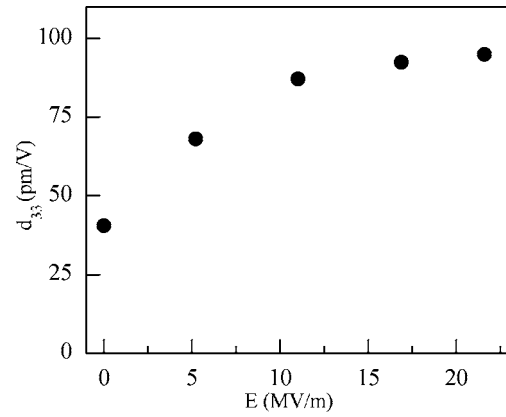


FIG. 2. Variations of the piezoelectric coefficient d_{33} of a PNZT film with dc field in the poling process.

$$d_{33} = \frac{\Delta t/t}{E}, \quad (2)$$

where t is the thickness of the PZT films. The substrate bending, which usually induces enormous error in the measurement using the single beam laser interferometry method, was effectively suppressed by gluing the substrate tightly to a large and rigid platform.¹¹ The orientation of the net polarization was also determined in the measurement by comparing the phases of the applied ac field and the voltage signal generated by the surface vibration.¹² As the signal was phase shifted during the signal processing in the interferometer, a film sample with the net polarization orienting upwards (i.e., in the up-state) was used for the calibration. For a film with the net polarization orienting downwards (i.e., in the down-state), there will be a change of π in the observed phase difference between the applied ac field and the voltage signal.

IV. RESULTS AND DISCUSSION

First, the PNZT films were fully polarized by a series of dc field steps at room temperature. At each step, a dc field was applied to the film sample for 3 min, and then d_{33} of the film was measured. Figure 2 shows the poling curve of a PNZT film (with the top electrode deposited by dc sputtering at room temperature). Since the PNZT film was partially polarized to the down-state after the dc-sputter deposition of the top electrode,^{13,14} it had an initial d_{33} value of 40 pm/V. The dc fields were applied along the same direction of the initial polarization (i.e., downwards). As shown in Fig. 2, the film was further polarized by a small dc field (e.g., 5 MV/m) and became fully polarized under a dc field of 22 MV/m, giving a large d_{33} value of 95 pm/V. This indicates that the microdomains of the film switch at different fields and a distribution of the microdomains having different “local” switching fields may exist. For a low poling field, there is only a small fraction of domains switched down, and hence, the observed d_{33} value is small. As the poling field increases, more domains are switched and consequently the observed d_{33} value increases. Our result also implies that there should be a good number of the microdomains having a local switching field in the range of 0–12 MV/m.

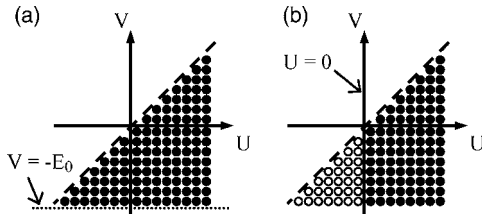


FIG. 3. Distributions of the polarization states (solid symbols: down state; open symbols: up state) for a ferroelectric film: (a) after the dc field decreased from 0 to $-E_0$ and (b) after the dc field increased from $-E_0$ to 0.

In terms of the Preisach model, the poling process can be described as follows. As a dc field of magnitude E_0 (e.g., 22 MV/m, pointing toward the bottom electrode) is applied (i.e., the field decreases from 0 to $-E_0$), all the microdomains switch down (as $-E_0 < \text{all } V$) as shown in Fig. 3(a). After the 3-min poling time, the field is removed (i.e., the field increases from $-E_0$ to 0), the microdomains with $U < 0$ switch up, resulting in the configuration of the polarization states as shown in Fig. 3(b).

Next, a series of dc or ac field steps were applied to the fully polarized PNZT films. It has been observed that if a downwards dc field of magnitude smaller than that of the maximum poling field (i.e., 22 MV/m for our films) was applied, the observed d_{33} remained almost unchanged, suggesting that there was no change in the polarization states. This result can be explained in terms of the Preisach model, by following the procedures described above with $E_0 < 22$ MV/m. This result is also consistent with the poling results that a small dc field can further polarize the film, without affecting the initial polarization, and give a larger d_{33} (Fig. 2).

Unlike dc fields, if ac fields of magnitude smaller than that of the maximum poling field were applied to a polarized film, the observed d_{33} and P_R decreased considerably. Figure 4 shows the variations of d_{33} and P_R for a fully polarized PNZT film with ac field. The ac field was applied to the bottom electrode of the film sample (with the top electrode grounded), so that the electric field was parallel to the original net polarization of the film in the second-half of the ac cycle. The amplitude of the ac field was decreased from 20 to 2 MV/m in ten steps. At each step, six cycles of the ac

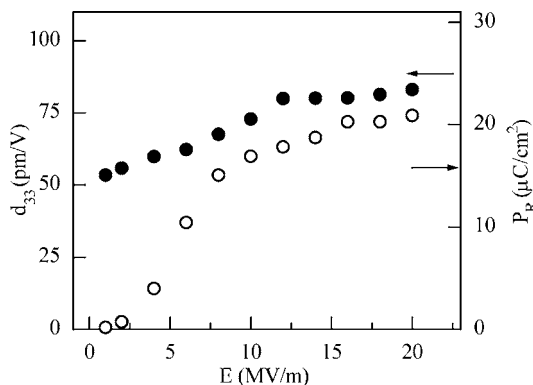


FIG. 4. Variations of the piezoelectric coefficient d_{33} and remanent polarization P_R of a PNZT film with ac field in the depoling process. The ac field steps are applied to the bottom electrode of the film sample.

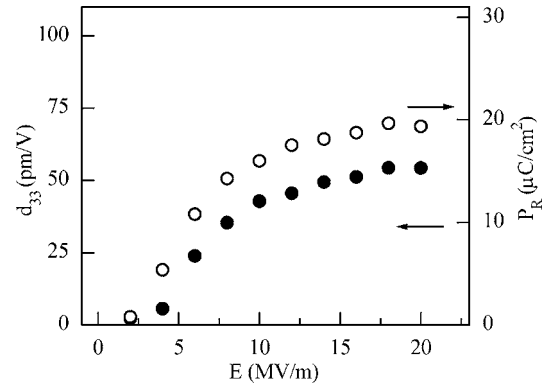


FIG. 5. Variations of the piezoelectric coefficient d_{33} and remanent polarization P_R of a PNZT film with ac field in the depoling process. The ac field steps are applied to the top electrode of the film sample.

voltage were applied and then d_{33} of the film was measured. The observed P_R and d_{33} did not change significantly if more cycles of the ac voltage were applied. As shown in Fig. 4, the observed d_{33} decreases with decreasing ac field, and has a value slightly larger than that of the as-prepared film as the field decreases to 2 MV/m (50 pm/V vs 40 pm/V). This clearly shows that the net polarization of the film is reduced after each step and the film is almost depolarized to the original polarization states after the whole process. It is noted that the net polarization remains pointing downwards in the whole depolarization process. Similar results have been reported for sol-gel-derived PZT films.¹⁵ But in that work, the film did not possess a large initial polarization and the polarized film was completely depolarized by the application of ac fields of diminish amplitude. The observed P_R also decreases with decreasing ac field (Fig. 4). However, unlike d_{33} , P_R decreases to almost zero as the field decreases to 2 MV/m, showing the inadequacy for correlating the P - E loop measurement with the piezoelectric properties of ferroelectric films.

The polarized PNZT films could also be depolarized by ac fields applied in a reverse direction, i.e., the ac field was applied to the top electrode, instead of the bottom electrode. Figure 5 shows the resulting variations of the observed d_{33} and P_R with ac field. Similar to the previous case, d_{33} decreases with decreasing ac fields, indicating the depolarization of the film. However, for this case, d_{33} decreases by a larger amount after the first ac field step and becomes almost zero after the whole depolarization process (Fig. 5). It is noted that the net polarization switches to pointing upwards after the first ac field step. This should be caused by the fact that the electric field was anti-parallel to the original net polarization (i.e., pointing upwards) in the second-half of the ac cycle. It is also noted that P_R has a similar value at each step to the case where the ac fields are applied to the bottom electrode (Fig. 4). This suggests that the overall switching charges are the same and the observed remanent polarization does not affected by the switching sequence: up and then down or down and then up.

The depolarization phenomena can be explained based on the concept of the Preisach model. As the film was first fully polarized to the down-state, it should have the configu-

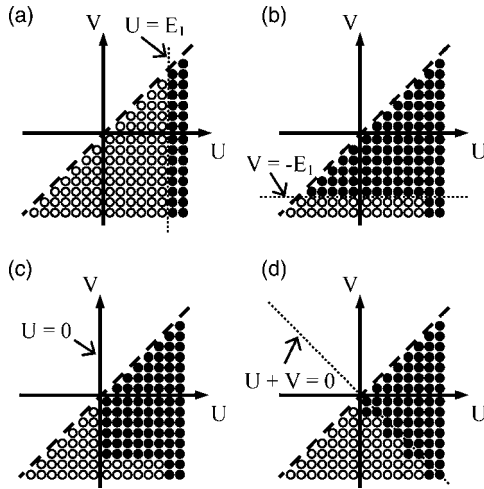


FIG. 6. Distributions of the polarization states (solid symbols: down state; open symbols: up state) for a ferroelectric film: (a) after the ac field increased from 0 to E_1 ($E_1 < E_0$); (b) after the ac field decreased from E_1 to $-E_1$; (c) after the ac field increased from $-E_1$ to 0; and (d) after the application of several cycles of ac field with successively smaller amplitude.

ration of the polarization states as shown in Fig. 3(b). Next, consider the application of an ac field of amplitude E_1 ($E_1 < E_0$) to the bottom electrode of the film. As the field increases from 0 to E_1 (upwards), the microdomains with $U < E_1$ switch up [Fig. 6(a)]. Then the microdomains with $V > -E_1$ switch down as the field decreases from E_1 to $-E_1$ [Fig. 6(b)]. Last, when the field increases from $-E_1$ to 0 during the last quarter of the cycle, the microdomains with $U < 0$ switch up [Fig. 6(c)]. It can be seen that after a complete cycle of the ac field, a fraction of the microdomains changes their state from down to up, thereby leading to a decrease in the net polarization, and hence, a decrease in d_{33} (Fig. 4). This process continues upon the application of ac fields with diminishing amplitude, ending up with the configuration of the polarization states as depicted in Fig. 6(d).

As shown in Fig. 6(d), the microdomains are divided into two groups of up and down states of similar size. The net polarization is clearly dependent on the number of the microdomains with different U 's and V 's. If the Preisach function $P(U, V)$ (defining the number of microdomains with the switching fields U and V) is symmetrical about the line $U+V=0$ in the $U-V$ plane [see Fig. 6(d)], the net polarization, and hence, the resulting piezoelectric coefficient will be very small. Otherwise, both the net polarization and piezoelectric coefficient will be large, like our results shown in Fig. 4. As the net polarization remains pointing downwards during the whole depolarization process, there are more down-state microdomains (denoted by the solid symbols) than the up-state microdomains (denoted by the open symbols). This may imply that there are more microdomains with $U > -V$, or that there are down-state microdomains which have very large U and V (i.e., >22 MV/m, not shown in the $U-V$ plane shown in Fig. 6) and hence are not affected by the depoling ac fields. These microdomains were switched to the down-state after the sputter deposition of the top electrode. Because of the interaction with other microdomains or some other effects (e.g., pinning), their switching fields U and V became very large (i.e., >22 MV/m).

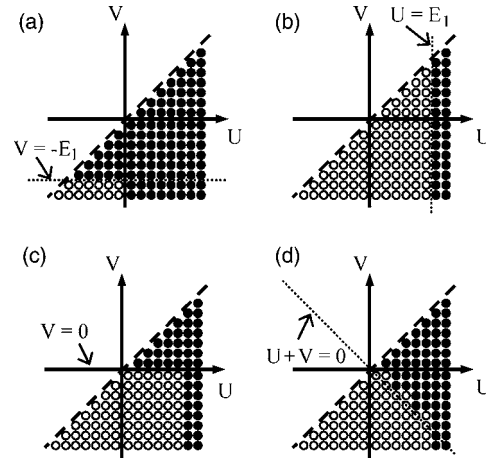


FIG. 7. Distributions of the polarization states (solid symbols: down state; open symbols: up state) for a ferroelectric film: (a) after the ac field decreased from 0 to $-E_1$ ($E_1 < E_0$); (b) after the ac field increased from $-E_1$ to E_1 ; (c) after the ac field decreased from E_1 to 0; and (d) after the application of several cycles of ac field with successively smaller amplitude.

It is easily seen that if there are only microdomains with $U=-V$ (i.e., isolated microdomains, no mutual interaction) the polarized film cannot be depolarized by the procedures described earlier. The microdomains which have switched from the down-state to the up-state in the first-half of the ac cycle will switch back to the down-state in the second-half of the ac cycle, so there is no change in the configuration of the polarization states of the microdomains. In other words, our results agree with the argument in the Preisach model that there is interaction between the microdomains, thus modifying the switching fields so $U \neq V$ in general.

Following similar procedures, the configurations of the polarization states for the film depolarized by ac fields applied in a reverse direction are obtained, giving the results shown in Fig. 7. It can be seen that most of the microdomains switch up after the first cycle of the ac field, leading to a change in the net polarization from pointing downwards to upwards [Figs. 7(a)–7(c)]. Although the exact Preisach function $P(U, V)$ is not known, the net number of the microdomains in the up-state (cancelled by the down-state microdomains) is apparently smaller than that in the down-state for the previous case [Fig. 7(c) versus Fig. 6(c)], thus giving smaller magnitudes of the net polarization and piezoelectric coefficient (Fig. 5 versus Fig. 4). The final configuration of the polarization states is also different from that for the previous case [Fig. 7(d) versus Fig. 6(d)]. There are apparently more microdomains in the up-state. However, as shown in Fig. 5, the observed d_{33} of the film sample is almost zero. This may again imply that the Preisach function is not symmetrical about the line $U+V=0$ (with more microdomains having $U > -V$), or that there are down-state microdomains resulting from the sputter deposition of the top electrode with very large U and V (i.e., >22 MV/m).

Similar to the poling results (Fig. 2), the depolarization results (Figs. 4) also imply that, other than those having very large U and V , there should be a good number of the microdomains having U and V in the range of 0 to 12 MV/m. The Preisach function $P(U, V)$ for the films is, hence, greatly nonuniform and nonsymmetrical. Such a distribution of the

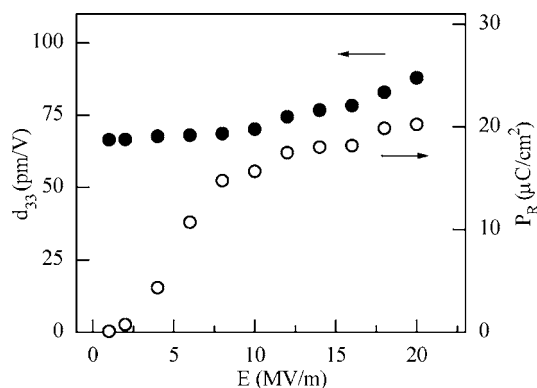


FIG. 8. Variations of the piezoelectric coefficient d_{33} and remanent polarization P_R of a PNZT film with ac field in the depoling process. The ac field steps are applied to the bottom electrode of the film sample.

microdomains will give rise to nonlinear piezoelectric responses of the films as reported by Robert *et al.*¹⁶

PNZT films with a larger initial polarization have also been depolarized by the ac field steps. The films were prepared following the same sol-gel procedures, but with the top electrode deposited by rf sputtering at 175 °C. It has been shown that the films were almost completely polarized to the down-state after the deposition of the top electrode, yielding a large initial d_{33} value of about 95 pm/V.¹⁴ Following similar procedures, the films were depolarized by ac fields applied to the bottom and top electrodes, giving the results shown in Figs. 8 and 9, respectively. For the film with the ac fields applied to the bottom electrode, the observed d_{33} decreases with decreasing ac field and remains at a large value after the whole depolarization process (Fig. 8). This is similar to the case where the film has a smaller initial polarization. Similarly, for the film with the ac fields applied to the top electrode, the observed d_{33} decreases by a large amount (Fig. 9) and the net polarization switches from pointing downwards to upwards after the first ac field step. However, unlike the film with a small initial polarization, d_{33} decreases to almost zero and the net polarization switches back to pointing downwards as the ac field decreases to around 8 MV/m. As the ac field continues to decrease, d_{33} increases and the net polarization remains pointing downwards.

In terms of the Preisach model, these two films have the

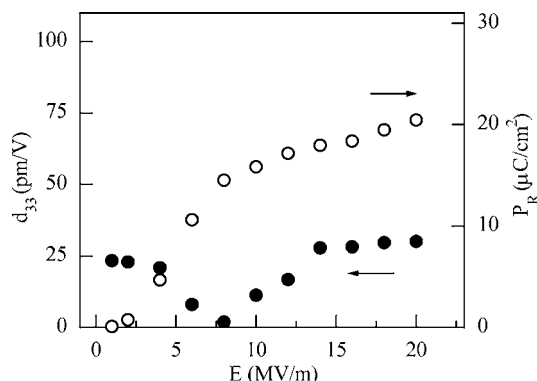


FIG. 9. Variations of the piezoelectric coefficient d_{33} and remanent polarization P_R of a PNZT film with ac field in the depoling process. The ac field steps are applied to the top electrode of the film sample.

same final configurations of the polarization states as the films with a smaller initial polarization (Figs. 6 and 7). This suggests that the rf sputtering process induces more down-state microdomains which, because of mutual interactions or other effects, exhibit very large switching fields U and V . After the ac field step of 8 MV/m, although there are more microdomain groups in the up-state, the net polarization switches back to pointing downwards as a result of the nonuniform Preisach distribution of the microdomains. Kigelman *et al.* has reported similar results of the change of the piezoelectric coefficient phase angle in lead magnesium niobate (PMN) thin films.¹⁷ Although PMN is relaxor ferroelectrics, the as-prepared PMN thin film possessed oriented polar regions and exhibited piezoelectric response in the absence of a bias dc field. The polar regions of the film may act as Preisach microdomains, and the variation of the observed d_{33} with ac field is a consequence of the distribution of the local coercive field in the polar regions.

V. CONCLUSION

We have demonstrated that a polarized PNZT film can be effectively depolarized by the application of several cycles of ac field with successively smaller amplitude. The amplitude of the ac field is decreased from 20 to 2 MV/m in ten steps. The observed d_{33} decreases after each ac field. Depending on the initial polarization and the direction of the ac fields, it can decrease to a very small value indicating the complete depolarization of the film. The phenomenon can be explained based on the concept of the Preisach model. Our results suggest that there is interaction between the microdomains (Preisach dipolar unit), thus causing the magnitudes of the switch-up and switch-down fields of each microdomain become not necessarily the same. Our results also suggest that the sputter deposition of the top electrode can induce more down-state microdomains, thus giving rise to an initial polarization in the film. Because of interactions with other microdomains or other effects, part of these microdomains exhibit very high switching fields.

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