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Electric field inhomogeneity as a cause for fatigue in lead zirconate titanate ferroelectrics

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Abstract

The profile of ferroelectric fatigue in lead zirconate titanate ceramic in the thickness direction was investigated by thinning the fatigued samples continuously from both sides symmetrically. The electrical properties of fatigued samples exhibited a gradual recovery with the samples being thinned and then remained nearly unchanged, however, well below the values at fresh state. The results revealed that fatigue was not limited to the near-electrode regions, but throughout the ceramic samples in the thickness direction. The electric field inhomogeneity in ferroelectric ceramics during bipolar switching was proposed to be responsible for ferroelectric fatigue and the fatigue profile through phase decomposition.

Keywords: C. Ferroelectric properties; C. Fatigue; D. PZT

1. Introduction

Perovskite (ABO_3) oxide ferroelectric materials offer many potential applications in next generation nano-electronic technology as well as multilayered ceramic components, such as ferroelectric random access memories, ferroelectric field effect transistors, magnetoelectric devices, and multilayered piezoelectric transformers [1]. However, some promising ferroelectric materials suffer from fatigue when used in conjunction with metal electrodes such as Pt, Au and Ag, for example lead zirconate titanate (PZT), bismuth ferrite ($BiFeO_3$) and barium titanate ($BaTiO_3$) [2–11]. Therefore, a full understanding of ferroelectric fatigue is clearly of both scientific and technological interest.

The polarization fatigue was frequently suggested to be attributed to the formation and accumulation of defects at the ferroelectric/metal electrode interface caused by for example, charge injection-induced local phase decomposition, accumulation of oxygen vacancies, diffusion of electrode materials into the ferroelectric oxides or stress-induced microcracks [2–5,12–16]. By contrast, the domain wall pinning mechanism suggested that fatigue may occur in the central parts of ferroelectrics [17]. Previously, Lou et al. proposed that the local phase decomposition caused by charge injection from the electrodes into the ferroelectrics under repeated polarization switching should be responsible for fatigue [2,3]. In one of our latest work, evidences for the phase decomposition at the metal electrode/ceramic interfaces in PZT thin films were presented [18]. Jiang et al. proposed that fatigue is closely related to the electrode/ceramic interface [15,19]. The fatigue endurance can be enhanced to above 10^8 switching cycles for hot-pressed pore-free La-doped PZT ceramic prepared using an improved pre-cleaning procedure, much higher than that for specimens cleaned by conventional procedures. Zhang et al. studied the fatigue behavior of PZT ceramic with different silver paste electrodes [16]. They observed that the polarization of a fatigued PZT sample with air-dried silver paste electrodes can be restored by removing a 10 μm thick near-electrode volume underneath both electrodes. By contrast, the PZT ceramic with silver paste electrodes sintered at 800 °C was not recovered

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after removal of a 130 μm thick sample layer underneath each electrode. They proposed that the mechanisms for fatigue in the bulk are likely to be different from the near-electrode volume.

Up to now, the location of polarization fatigue in ferroelectrics as well as the corresponding mechanisms remains unclear. The role of fatigue in the central parts of ferroelectrics has not been clarified experimentally. Nevertheless, these studies are of great importance for a better understanding of the fatigue mechanism and relevant controlling techniques. Therefore, the fatigue profile in PZT ceramic was investigated in the present study by gradually thinning fatigued PZT ceramic samples from both sides symmetrically. Based on the experimental results and analyses, the electric field inhomogeneity in ferroelectric ceramics during bipolar switching as a fatigue mechanism was proposed.

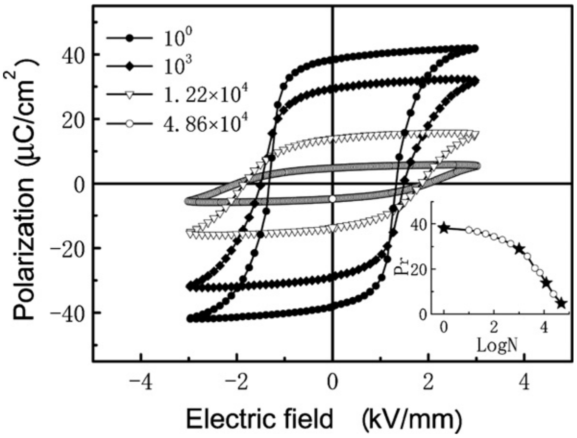

Fig. 1. Hysteresis loops of a PZT ceramic sample after different cycles of polarization switching. The inset plots the remanent polarization as a function of the switching cycle with the four fatigue states in this figure being marked in asterisk.

2. Experimental details

The PZT ceramic pellet samples synthesized by solid state reaction were provided by Institute of Acoustics of Chinese Academy of Sciences. The reference composition was $Pb(Zr_{0.52}Ti_{0.48})O_3$ with Sr^{2+} and Ni^{2+} as additives. The average grain size was about 4 μm. First, the upper and lower surfaces of a PZT pellet with a diameter of 10 mm were polished using 2000 grid water sand paper to a thickness of 0.97 mm. Silver pastes were brushed onto the surfaces of the pellet, followed by firing at 600 °C for 10 min. Second, the sample was electrically poled in silicone oil at 120 °C for 20 min with an electric field of 3 kV/mm, and then was fatigued under a triangular electric field of 10 Hz and 3 kV/mm using an aixACCT TF analyzer 2000. Third, the pellet sample was thinned symmetrically from both sides using 2000 grid water sand paper. The thinning was conducted in flowing water in order to avoid any abrasion-induced heat. For electrical measurements, room-temperature silver pastes were brushed onto the thinned ceramic pellet as electrodes because no firing was needed for this type of silver pastes. Then after the electrical measurements, the fatigued sample was thinned to another thickness and so on and so forth. Parallel experiments with unfatigued samples were also conducted while no effects of the thinning process and silver paste species on electrical properties of the samples were observed.

The relative dielectric constant (ε) of the ceramic sample was measured at 1 kHz using a Fluke 8846A multimeter. The piezoelectric coefficient (d_{33}) was measured using a ZJ-6A piezoelectric analyzer (Institute of Acoustics of Chinese Academy of Sciences). The hysteresis measurements were conducted using the aixACCT TF analyzer 2000. The ceramic samples obtained in parallel experiments were used for structural observations by scanning electron microscopy (SEM, Zeiss SUPRA-55).

3. Results and discussion

Fig. 1 illustrates the evolution of polarization fatigue of a PZT ceramic sample. It can be seen that the hysteresis loop becomes squashed while the coercive field increases monotonically with increasing switching cycle. The decrease of the remanent polarization (P_r) during fatigue is plotted in the inset of Fig. 1. Fig. 2 shows the cross-sectional SEM images of the electrode/ceramic interfaces and the central parts of a fatigued sample obtained in parallel experiments. No indications for microcracks in PZT grains or along the grain boundaries can be observed.

Fig. 3a–c shows the changes in ε, d_{33} and remanent polarization (P_r) of the fatigued sample when it was thinned, respectively. The black dots stand for the experimental data. The initial values of ε, d_{33} and P_r of the sample at fresh state are given in dash line. For the fatigued sample before thinning, ε, d_{33} and P_r have very small values. With decreasing thickness, ε, d_{33} and P_r all increase and then remain at nearly unchanged

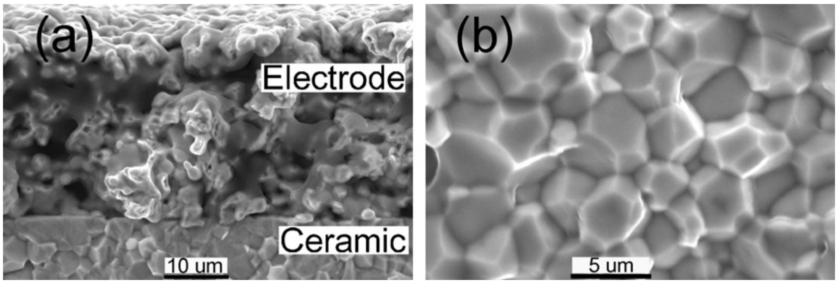

Fig. 2. Cross-sectional SEM images of (a) the Ag electrode/ceramic interface and (b) central parts of a seriously fatigued PZT ceramic sample.

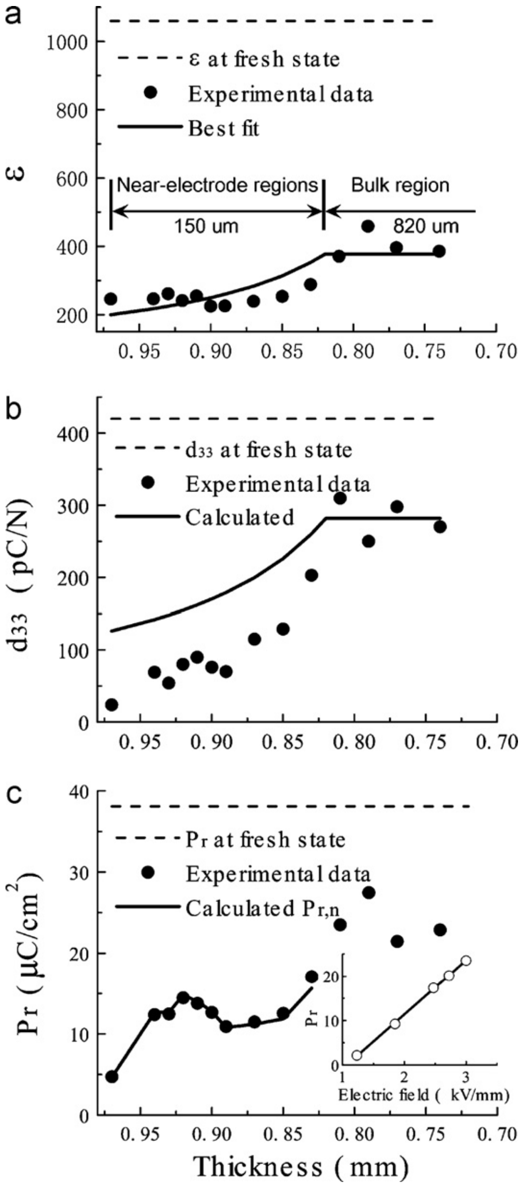

Fig. 3. Changes in electrical properties of the fatigued PZT sample when it was gradually thinned: (a) dielectric constant ε, (b) piezoelectric coefficient d_{33}, and (c) remanent polarization P_r. The hysteresis measurements were conducted with a triangular wave electric field of amplitude 3 kV/mm. The open circles and the solid line in the inset of Fig. 3c stand for the measured P_r of the bulk region and a linear fit to the measured P_r, respectively.

higher values, forming a plateau in the curves. However, these plateau values are distinctly smaller than those of the sample at fresh state. Therefore, the results in Fig. 3a–c strongly suggest that fatigue occurs throughout the PZT ceramic samples in the thickness direction.

In some earlier studies, microcracks were sometimes observed near the electrode/ceramic interfaces in fatigued ferroelectric ceramics. This experimental fact is understandable because ferroelectric materials are piezoelectric due to the loss of crystal symmetry above all. During the polarization switching, strains will be generated in these materials. Therefore, polarization fatigue is sometimes accompanied with the formation of microcracks. However, these microcracks were not always observable in fatigued ferroelectric materials as in this study and many other studies [13,14]. Moreover, evidences for microcracks in ferroelectric films have hardly been reported in literature. In our parallel experiments, the fatigued PZT pellet samples could be restored almost completely upon 700 °C annealing in air for 30 min. Therefore, the possibility of microcracks as a main cause of fatigue is excluded because the microcrack damage generated during fatigue is permanent and cannot be healed by this thermal annealing. For the present case, the fatigue should be nearly purely electrical.

In the following, a structure model consisting of two near-electrode regions and a bulk region physically in series is used for analysis of the experimental data of ε, d_{33} and P_r. For simplicity, these regions are assumed to be homogeneous in the thickness direction. First, the measured ε data in Fig. 3a can be described as a step function of the sample thickness L. Then we have

$$\frac{L}{\varepsilon} = \frac{l}{\varepsilon_b} + \frac{L-l}{\varepsilon_n} \quad \text{for } L > l, \tag{1}$$

and

$$\varepsilon = \varepsilon_b \quad \text{for } L \le l, \tag{2}$$

where l is the thickness of the bulk region, ε_b is the relative dielectric constant of the bulk region, and ε_n is the relative dielectric constant of the near-electrode regions.

The dielectric constant of the near-electrode regions and the bulk region of 56 and 377 for the fatigued sample, respectively, are obtained through best fit using a least-squares method. The near-electrode regions have a total thickness of 150 μm, which agrees with results in literature [13,14].

Then this structure model is used for analysis of the d_{33} curve in Fig. 3b. Because of the extremely low d_{33} for the fatigued sample before thinning, the near-electrode regions are assumed to be nonpiezoelectric. Considering the technique used for measuring the piezoelectric coefficient, we have $Q = d_{33,b}F$, where Q is the charges induced by the bulk region of the fatigued sample under an external mechanical force F, and $d_{33,b}$ is the piezoelectric coefficient of the bulk region. The average value of 282 pC/N of the measured piezoelectric coefficients of the bulk region is used for the calculation. Q will cause a potential U. As the bulk region is in series with the two near-electrode regions, the potential will charge the whole sample. According to the structure model, the whole sample will see the charges $q = C \cdot U$. Here, C denotes the capacitance of the fatigued sample at different thicknesses, which can be calculated using Eqs. (1) and (2). If we neglect the dependence of dielectric constant of the different fatigue regions on constraint and electric field for approximation, the apparent piezoelectric coefficient $d_{33} = q/F$ of the sample can be calculated out. The calculation result is shown in solid line in Fig. 3b, which reflects the same tendency of changes in d_{33}.

With the sample being thinned, P_r of the fatigued sample exhibits an evident recovery, as shown in Fig. 3c. After the near-electrode regions are removed completely, P_r remains nearly unchanged. Therefore, the near-electrode regions must have fatigued more than the bulk region. A $P_{r,b}$ of 23.8 μC/cm^2 for the bulk region is calculated using the measured P_r with the near-electrode regions being removed completely. This value corresponds to only 62.5% of the initial P_r of the sample at fresh state. On the other hand, the remanent polarization of the bulk region $P_{r,b}$ is equal to P_r for the fatigued sample during thinning. Then the continuity equation gives

$$\varepsilon_0\varepsilon_b E_b + P_{r,b} = \varepsilon_0\varepsilon_n E_n + P_{r,n} \tag{3}$$

where E_b is the electric field in the bulk region, E_n is the electric field in the near-electrode regions, and $P_{r,n}$ is the remanent polarization of the near-electrode regions. The inset of Fig. 3c shows the measured P_r (open circles) of the bulk region as a function of the electric field. Normally, P_r should tend to be saturated with increasing the electric field for ferroelectrics. In contrast, the measured P_r and the electric field have a good linear relationship within the electric field range used for the measurement. The solid line stands for the linear fit to the measured P_r. Tentatively, it is assumed that no saturation of P_r is reached for the bulk region within the electric field range. Accordingly, E_b and E_n of the fatigued sample at different thicknesses can be calculated out (not shown here). Then $P_{r,n}$ can be obtained using Eq. (3). The contribution of the linear dielectric polarization to the whole electric displacement is rather small as compared to that of the non-linear ferroelectric polarization. Therefore, $P_{r,n}$ is nearly equal to $P_{r,b}$, as shown in Fig. 3c. However, E_n is about one order of magnitude higher than E_b.

Previously, a new fatigue mechanism of local phase decomposition caused by charge injection from the electrodes was put forward by Lou et al. [2,3]. Evidences for the phase decomposition at the electrode/ceramic interfaces in PZT thin films were reported in one of our latest work [18]. The present study reveals that fatigue can occur throughout the PZT ceramic samples in the thickness direction, but not limited to the interface regions only. Therefore, fatigue must be both interface and bulk-related. In another word, defects that lead to fatigue exist in the near-electrode regions as well as in the bulk region.

In this clue, it is not appropriate to assume that the phase decomposition is caused merely by charge injection from the electrodes because of the vast difference between the thickness of the sample used in the present study and the mean free path of injected energetic electrons. Rather, it is proposed here that phase decomposition in ferroelectric materials may occur near the interfaces or in the bulk around defect regions with low dielectric constant ε_d and low remanent polarization P_d due to the extremely high voltage during polarization switching. The electric field in these defect regions beyond the coercive field is given as $E_d \approx (P_f - P_d)/\varepsilon_0\varepsilon_d$ according to the continuity equation $\varepsilon_0\varepsilon_f E_f + P_f = \varepsilon_0\varepsilon_d E_d + P_d$ where P_f, ε_f and E_f are the remanent polarization, dielectric constant and electric field of the normal ferroelectric regions, respectively. These defects can be pores, inclusions or raw materials for synthesis of PZT. With increasing number of switching cycles, the volume of these defect regions increases due to the phase decomposition at the interfaces between the defect phases and normal ferroelectric phases. The E_d can be quite large under external alternating current (AC) field beyond the coercive field due to the non-linear ferroelectric polarization, whereas it is much smaller for the current material system if bipolar electric field below the coercive field or unipolar electric field is applied. This can answer for the wave-form and voltage amplitude dependences of fatigue as reviewed previously [2,4]. As there are often more structural defects or nonstoichiometry at the metal electrode/ceramic interfaces (hence more defect regions or with higher defect density) than in the central bulk, which can be generated during the sample preparation process, the interface regions normally suffer from fatigue more severely. This answers for the fatigue profile observed in the present study. Note that $E_d \approx (P_f - P_d)/\varepsilon_0\varepsilon_d$ does not necessarily conflict with the electric field of $E_d \approx P_f/3\varepsilon_0\varepsilon_d$ proposed previously because that equation was derived from a microscopic angle which depended on how the shape of ferroelectric domains was chosen [2,3]. Rather, we give the derivation of the general electric field inhomogeneity as a cause for fatigue from an electrostatics angle and extended the applicability of the phase decomposition mechanism to the central parts of ferroelectric ceramics. This fatigue mechanism is also consistent with the very recent experimental results of Zhukov et al. who observed that the distribution of local electric field in fatigued PZT ceramic exhibited a decrease in height and a broadening as compared with the virgin samples [20].

Furthermore, it is proposed that fatigue endurance of ferroelectric ceramics could be improved by minimizing the electric field inhomogeneity in both bulk ferroelectrics and thin films during polarization switching, which is helpful for fatigue control in ferroelectric materials. By using this scenario, the extremely high fatigue endurance of hot-pressed PZT ceramic as well as the increase in fatigue endurance of PZT ceramics with increasing density observed by Jiang et al. can be reasonably explained [15,19]. It is also consistent with the results of Angadi et al., who found that PZT bulk ceramic even with oxide electrodes suffer from fatigue [21].

4. Conclusions

The fatigue profile in PZT ceramic samples was investigated by gradually thinning the fatigue ceramic samples. The entire PZT ceramic samples fatigued upon repeated polarization switching, but not only the near-electrode regions. The electric field inhomogeneity-induced phase decomposition across the ferroelectrics in the thickness direction as a reasonable fatigue mechanism was proposed.

Acknowledgements

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