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Investigation of fatigue mechanism in ferroelectric ceramic via piezoresponse force microscopy

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Abstract

The influence of polarization fatigue on domain patterns of commercial lead zirconate titanate ceramics (PZT) was studied by piezoresponse force microscopy (PFM). It was found that the fatigue is accompanied by the appearance of ferroelastic domains formed to relieve arising mechanical stresses. The strongest effect was observed in the regions adjacent to the electrode. Annealing to the temperatures above the phase transition promotes partial recovering of the initial domain structure.

Keywords: Fatigue; Piezoelectric properties; PZT

1. Introduction

Ferroelectrics are promising materials for the fabrication of various devices including piezoelectric actuators, multilayer capacitors, pyroelectric sensors, and electrooptic modulators.[1] However, the long-standing problem of reliability and degradation in ferroelectric materials (such as fatigue, retention, imprint, and aging) limits their applicability in the above-mentioned areas. The most important type of the degradation is ferroelectric fatigue defined as the loss of switchable polarization during continuous domain switching. Several mechanisms were called to explain the nature of fatigue: domain wall pinning by trapped space charges,[2] inhibition of seeding of new domains,[3] defect agglomeration,[4] accumulation of oxygen vacancies,[5] etc. It is believed that, while in thin films the role of electrode-film interface is important, the fatigue in ceramics is mainly related to the bulk processes and crack propagation.

Recently, piezoresponse force microscopy (PFM) has received significant attention due to its ability both to resolve fine domain features and to investigate electrical properties locally (i.e., inside individual grain or domain).[6] It is extremely important that the domain structure and local probing can be directly related to the microstructure and various defects already present or appeared after the fatigue tests. This provides a unique possibility to get insight into the microscopic origin of fatigue and involved defects. The local investigation into the fatigue mechanisms has been recently initiated by several research groups[7–9] but has been focused mostly on thin films.[7,8]

The aim of our studies was the investigation of fatigue influence on domain structure of PZT ceramics via PFM.

2. Experimental

Commercial ceramic sample of the $Pb(Zr,Ti)O_3$ ceramic of composition in the tetragonal vicinity of the morphotropic phase boundary of PZT were used (PIC 151, PI Ceramic, Lederhose, Germany). The samples were cycled at 20 kV/cm (peak-to-peak value, about twice the coercive field, E_c) sinusoidal electric field at 50 Hz. To avoid the influence of arbitrary polarization state of ceramics on domain structure, the cycling filed was gradually increased from zero to the maximum within 5 s, held constant for 5×10^7 cycles and then reduced back to zero within 5 s. For thermal annealing, the fatigued samples were kept at the tem-

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perature 700 °C during 10 h in ambient air. For the PFM studies, the samples were cut perpendicular to the fatigue direction. Before the measurements, the surface was polished by diamond paste (0.25 μm) and cleaned to remove organics. Piezoresponse force microscopy measurements were performed using a commercial setup (Multimode, NanoScope IIIA, DI) equipped by standard tip-cantilever system (NCHR, Nanosensors, $k = 35$ N/m). Piezoresponse was measured under an ac voltage (amplitude 5 V, frequency 50 kHz).

3. Results and discussion

During the course of fatigue the remnant polarization value estimated from the ferroelectric hysteresis loops was decreased to ≈30% of the initial value. Annealing leads to partial rejuvenation of switching polarization, i.e., the remnant polarization was recovered to ≈80% of the value in virgin samples.

Fig. 1 shows topography and piezoresponse (domain) images of polished cross-sections of PZT ceramics before and after fatigue. In virgin samples, piezoresponse image consists mainly of so-called “watermark” structures that correspond to 180° domains with arbitrary orientation of domain walls. In addition, regular domain stripes were observed, which are commonly associated with ferroelastic domains appearing to relieve strong mechanical stress concentrated near the macroscopic defects (e.g., pulled-off grains) (Fig. 1a and b). In fatigued samples, ferroelastic domains occupy essentially larger area, in accordance with the possible increase of the concentration of macroscopic defects. Besides, in many cases the regular shape of these domains is distorted – they present “wavy” boundaries rather than plane domain walls. Since in an ideal case, the ferroelastic domain walls have to be oriented in the certain crystallographic directions, the observed tortuosity of domain walls indicates non-uniform distribution of mechanical stresses. It is widely accepted that bipolar fatigue generates microscopic defect agglomerates in bulk ceramics. Such agglomerates severely hinder the mobility of the domain walls and can even clamp it entirely (total pinning) leading to polarization reduction. The limited switching apparently gives rise to local stresses between non-switched domains (grains) and their neighborhood. These stresses can be very high and can even lead to macrocracks.[10] To relieve these stresses, ferroelastic domain patterns have to be formed (splitting of macroscopic domains into fine ferroelastic twins). Moreover, the defect agglomerates can themselves produce additional inhomogeneous stresses provoking distortion of regular ferroelastic domains. Since these domains are strongly pinned this further hardens polarization switching.

After the thermal treatment, the defects are thermally annealed leading to partial deagglomeration of defects and thus to the partial rejuvenation of switching polarization. In accordance with this idea, we observed recovering of the initial “watermark” domains in annealed samples (Fig. 1b–d).

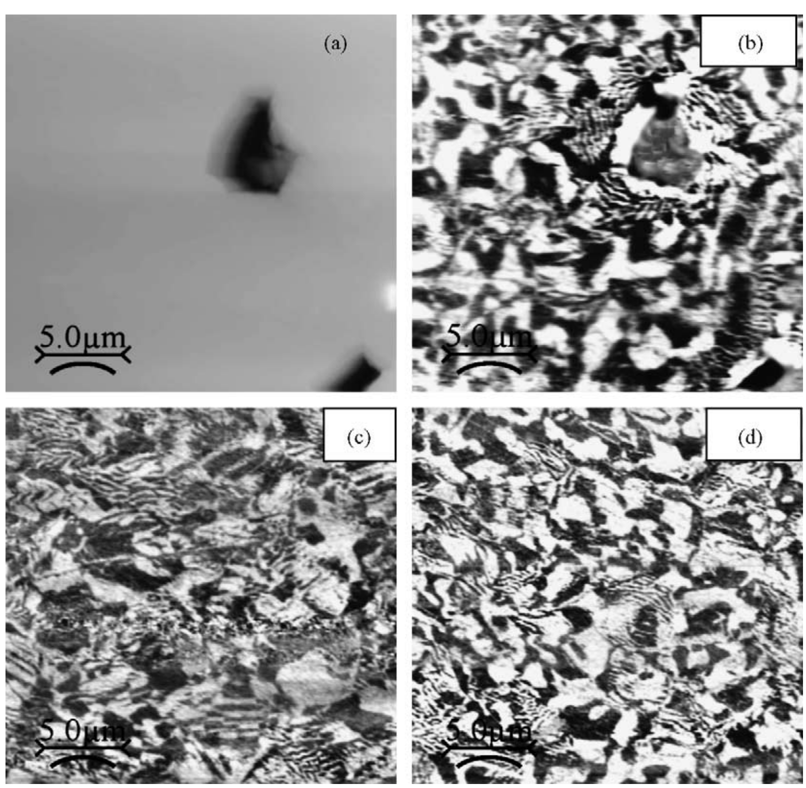

Fig. 1. Topography and piezoresponse images of PZT ceramic: (a and b) “virgin” sample; (c) fatigue (5×10^7 cycles) sample; (e) fatigued and annealed sample. The size of scans is $25 \times 25\ \mu m^2$.

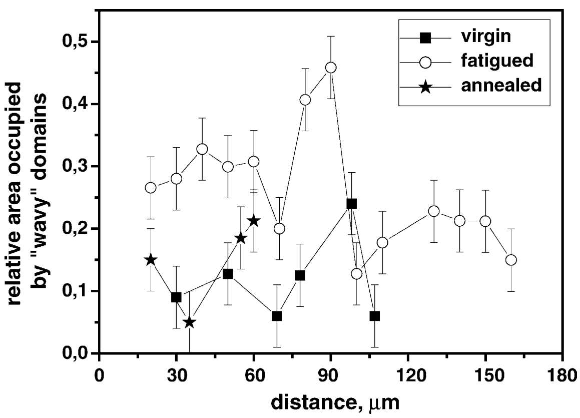

Fig. 2. Relative area occupied by distorted ferroelastic ("wavy") domains vs. distance from the electrode.

It was found that, in fatigued samples, the domain structure varies with the distance from the electrode into the sample's bulk. Namely, the concentration of distorted ferroelastic domains ("wavy" patterns) was higher near the electrode-sample interface and was significantly reduced at the distance of ∼80–100 μm from the electrode (Fig. 2). Thus, we can suggest that the inhomogeneous mechanical stresses are much stronger in the nearby electrode regions. It has been previously reported that big defect agglomerates could occur preferentially in the center of the sample rather than near electrodes.[10] Brennan has shown that ordering of point defects in two-dimensional arrays (planes) can be energetically favorable.[11] However in terms of mechanical stress, such big agglomerates would produce more uniform mechanical distortion as compared to small random agglomerates. High concentration of these small agglomerates with arbitrary shape and orientation could be a reason of strong inhomogeneity of mechanical stresses and hence of observed distortion of ferroelastic domains.

In conclusion, we observed that the bipolar electrical cycling leads to the formation of ferroelastic domains in PZT ceramics. These domains are likely to appear to relieve highly inhomogeneous mechanical stresses appeared between fully switchable and clamped grains. Another origin of this effect could be high concentration of microscopic defect agglomerates arising due to continuous polarization switching. Thermal treatment leads to partial recovery of initial domain structure.

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