Effects of ferroelectric fatigue on the piezoelectric properties (d_{33}) of tetragonal lead zirconate titanate thin films

P. Gerber, C. Kügeler, U. Ellerkmann, P. Schorn, U. Böttger, and R. Waser
Institute of Materials in Electrical Engineering and Information Technology 2(IWE2), Aachen University, D-52074 Aachen, Germany

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The fatigue of the electromechanical properties of tetragonal $PbZr_x$, $Ti_{1-x}O_3$ thin films is investigated. The decrease of electromechanical small-signal response is compared to the fatigue of the electric properties and examined in detail. Property fatigue is attributed mainly to switching-failure of the unit cells. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1886259]

$Pb(Zr_x,Ti_{1-x})O_3$ (PZT) ceramics exhibit superior ferroelectric, piezoelectric, and pyroelectric properties. Therefore, PZT thin films are used in a wide range of applications such as actuators, force sensors, optical infrared sensors, and ferroelectric memories. In order to use these films to their full potential, thorough research of their properties is needed.[1–3] The decrease of switchable polarization (polarization fatigue) is one of the limiting factor hindering the full commercialization of PZT in ferroelectric memories.[4] Polarization fatigue is dependent on the operation conditions of the ferroelectric device (switching vs nonswitching). Therefore, fatigue characterization mainly focuses on the investigation of the polarization losses, since this is the major electric property utilized in ferroelectric memories. On the other hand, mechanical applications of ferroelectrics often operate the material in nonswitching and/or linear mode. Hence, fatigue of the electromechanical properties is investigated with less determination. However, research considering the electromechanical properties offers a different point of view on the internal processes of ferroelectrics. Therefore, it can be utilized to elucidate the reasons for electric fatigue. In this work, we investigate fatigue of the electromechanical properties in tetragonal PZT in detail.

The PZT thin films are prepared using chemical solution deposition (CSD) on double side polished $Pt(111)/TiO_2/SiO_2/Si$ substrates (25.4×25.4 mm^2). After spin coating and pyrolysis of three coatings, the films are annealed using rapid thermal annealing at 700 °C for 5 min in oxygen. This results in a film thickness of 130 nm. Pt top electrodes are sputter deposited with electrode areas ranging from 0.01 mm^2 to 1 mm^2. The backside is finally vapor deposited with Au to achieve better reflectivity. Film orientation is determined by standard θ-2θ x-ray diffraction (XRD) and sample thickness is measured by a DEKTAK profilometer. The effective piezoelectric small-signal coefficient $d_{33,\mathrm{eff}}$ and large-signal strain S are measured using a double-beam laser interferometer with a minimum resolution of 0.2 pm. For small-signal measurements, the fast measurement method proposed in Ref. 5 is used. The relative permittivity is measured with the same setup, but using the measured electric current through the sample as input for the lock-in amplifier.[6] In order to characterize fatigue, the software was modified to incorporate fatigue cycles by repeated switching.[7]

Figure 1 depicts the fatigue of piezoelectric small-signal coefficient d_{33} measured on the PZT (30/70). For this measurement, the largest available top electrode size of 1 mm^2 is used in order to limit an impact of the electrode geometry on the measured electromechanical response, which was found for smaller electrode geometries.[8] This limits the cycling frequency to 10 kHz in order to ensure complete switching of the sample during fatigue. Hence, the maximum number of cycles is limited to 10^9 in order to keep the measurement time short (28 h). The measured response is stable up to 10^5 cycles. After switching the sample 10^6 times, d_{33} starts to decrease monotonously until the measurement is stopped after 10^9 cycles. Also, the remanent $d_{33,r}$ loss is slightly higher than the loss of the maximum $d_{33,\mathrm{max}}$, indicating increased backswitching or higher reversible contributions. Since we measured a highly (111)-oriented sample, the piezoelectric properties are dominated by intrinsic effects.[9] The effective small-signal behavior of the sample can be described by

$$d_{33\ \mathrm{eff,sample}} = d_{33\ \mathrm{eff,cell}} \cdot X, \tag{1}$$

where $d_{33\mathrm{eff,cell}}$ is the effective piezoelectric coefficient of a single unit cell and X is the percentage of unit cells switched into one direction ranging from −1 to 1. Therefore, if two domains neighboring each are switched into opposite directions (180° domain wall), the contained unit cells will strain against each other and decrease the electromechanical response of the sample.

Hence, a decrease of the small-signal response can be explained by either complete failure of the ferroelectric unit cells inside a domain or by domains pinned in opposite directions. Examples for the former could be total clamping of the center ion or surrounding cell and the unit cell losing its tetragonal shape. The latter is one of the main fatigue mechanisms reported by Tagantsev *et al.*[4] and can be seen as de-

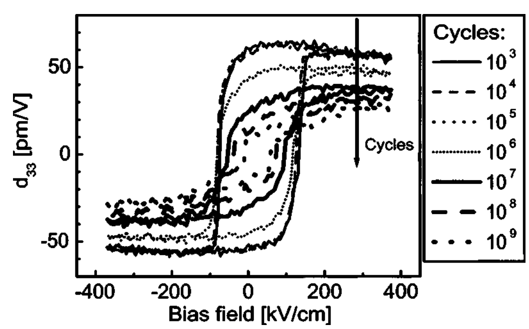

FIG. 1. Piezoelectric small-signal coefficient d_{33} of PZT (30/70) measured at different fatigue states ($f_{\mathrm{bias}}=1$ Hz, $f_{\mathrm{ac}}=8$ kHz, $V_{\mathrm{ac}}=100$ mV$_{\mathrm{rms}}$).

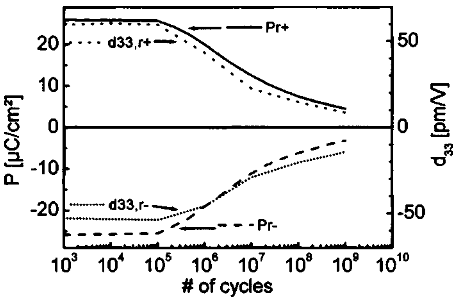

FIG. 2. Remanent piezoelectric small-signal coefficient $d_{33,r}$ of PZT (30/70) measured at different fatigue states (f_{bias}=1 Hz, f_{ac}=8 kHz, V_{ac}=100 mV_{rms}) in comparison to the remanent polarization at the same state (f_{bias}=100 Hz).

crease of the maximum *X* reached in saturation. Also, the fatigue of the properties in positive and negative saturation is nearly symmetrical. Combined with the fact, that the electromechanical small-signal measurements are, unlike hysteresis measurements, not symmetrized along the *Y*-axis, this verifies that the fatigue rate is equal for both switching directions.

Comparing the fatigue of the electromechanical properties to the fatigue of the electric polarization (Fig. 2), it can be seen, that both properties fatigue at the same time and with comparable rates. This is not the case in PZT thin films with a composition near the morphotropic phase boundary, as reported for PZT (45/55) in Ref. 7. It should be noted however, that a smaller top electrode was used for the hysteresis fatigue measurement in order to increase the cycling frequency. Hence, the measurement time can be reduced by a factor of 10. On the other hand, the fatigue rate should be independent of the cycling frequency, as long as complete switching of the sample is ensured.[4]

Measurements of the fatigue of the electric and electromechanical properties of tetragonal PZT (40/60) (Fig. 3) reflect the results found in PZT (30/70). Increased relative loss of d_{33} can be explained partially be the increased electromechanical properties in comparison to Ti-richer composition (30/70). Again, electric and electromechanical fatigue start after the same number of cycles, though both measurements were done with different switching frequencies. Hence, the fatigue mechanism seems to be independent of the measurement parameters and depends only on the number of cycles. Why this conclusion is not applicable for Zr-richer materials

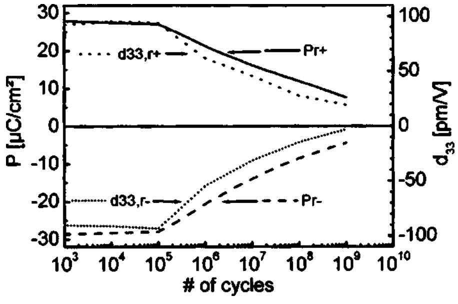

FIG. 3. Remanent piezoelectric small-signal coefficient $d_{33,r}$ of PZT (40/60) measured at different fatigue states (f_{bias}=1 Hz, f_{ac}=8 kHz, V_{ac}=100 mV_{rms}) in comparison to the remanent polarization at the same state (f_{bias}=100 Hz).

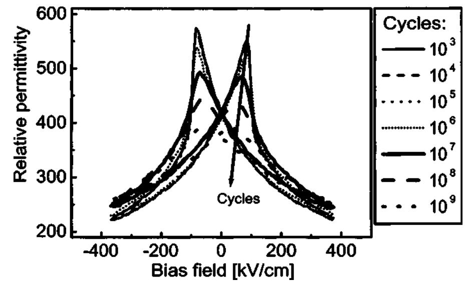

FIG. 4. Relative permittivity ε of PZT (30/70) measured at different fatigue states (f_{bias}=1 Hz, f_{ac}=8 kHz, V_{ac}=100 mV_{rms}).

near and beyond the morphotropic phase boundary, should by investigated in future works.

In order to identify the mechanism responsible for the fatigue of the sample properties, we have measured the relative permittivity of the sample at different fatigued states in Fig. 4. Considering the permittivity in saturation and in remanent state, where the response is dominated by intrinsic effects, only a small loss (approx. 10%) is found. Pinned unit cells contribute to the electric small-signal response irrespective of the direction of their pinned polarization, because the center ion is able to move out of their equilibrium state in field direction and therefore to contribute to the measured current. Hence, the value of *X* should have only a minor impact on the electric small signal response as long as it is dominated by intrinsic effects.

Therefore, the fatigue has to be caused by domain pinning and not by unit cell failure. Complete cell failure would result in a higher loss of the electric small-signal response. Also, the losses are higher near the coercive field, where the response is dominated by reversible extrinsic effects (switching). These, on the other hand, are dominated by the number of unit cells being switched.

During electromechanical measurements, unit cells pinned in opposite directions inhibit each other from contributing to the sample strain. Hence, the different amounts of loss considering the intrinsic contributions during both small-signal measurements can be explained.

In conclusion, the fatigue of the electric and electromechanical properties of tetragonal PZT was investigated. The loss of both properties was found to be of the same order of magnitude and to be caused by a unit cell or switching failure mechanism. Investigation of the electric small-signal fatigue allowed further isolation of the mechanism to a switching failure by domain pinning.

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