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In situ synchrotron x-ray diffraction study of electrical field induced fatigue in Pt/PbZr$_{0.45}$Ti$_{0.55}$O$_3$/Pt ferroelectric capacitors

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Abstract

Highly brilliant synchrotron x-ray radiation was used to measure *in situ* the microstructural response of a ferroelectric capacitor subjected to bipolar rectangular pulses. High-resolution x-ray diffraction experiments were performed on a (111)-oriented PbZr$_{0.45}$Ti$_{0.55}$O$_3$ thin film with a composition in the morphotropic region and sandwiched between two platinum electrodes. From original real time measurements, the microstructural changes with electrical cycling have been evidenced and correlated with the observed polarization fatigue measured during the x-ray diffraction experiment. From concomitant variations of the diffracted intensity and the switching current maximum, several mechanisms have been discussed as a possible origin of the polarization fatigue: field induced phase transformation, oxygen vacancy self-ordering and widening of the internal bulk screening field distribution function during cyclic switching.

1. Introduction

Ferroelectric capacitors (FeCAP) attract a lot of attention, especially due to their promising integration into silicon architecture in ferroelectric random access memories (so-called FeRAM) [1]. The concept of this binary state device is based on the ability of the polarization to switch (under electrical field) from one remnant state to the other. In terms of reliability,

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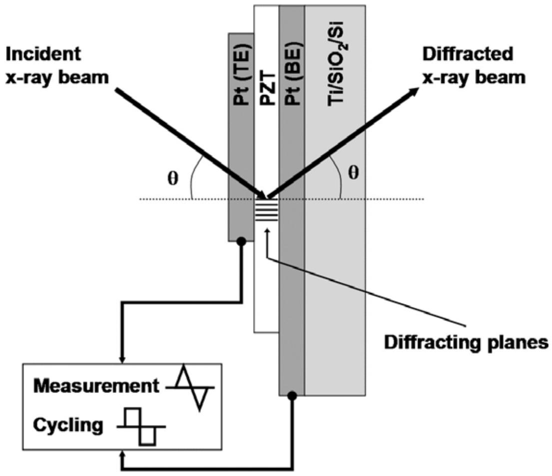

Figure 1. Experimental set-up used for *in situ* measurements: the x-ray beam was focused to illuminate the whole surface of a single capacitor (capacitor surface 0.44 mm^2) and partial diffraction patterns were recorded in transmission mode from θ–2θ scans. Tips were connected to Pt top (TE) and bottom (BE) electrodes to apply bipolar rectangular pulses during diffraction data gathering. Three times per decade, the cycling was stopped to measure switching currents and hysteresis loops (using a triangular waveform).

the decrease of remnant polarization under electrical cycling (i.e. fatigue) emphasizes the necessity to further understand the switching process of the domains within the ferroelectric film. X-ray diffraction was previously shown to be a powerful tool to characterize the domain structure modification in $Pb(Zr, Ti)O_3$ (PZT) thin films [2–8]. In most cases, experiments were performed *ex situ*, the diffraction data being collected after electrical stress [3, 8]. Sometimes, authors present *in situ* diffraction experiments but diffraction data are generally compared with *ex situ* ferroelectric characteristics [5, 7]. From original *in situ* experiments, this paper evidences a direct correlation between electrical and microstructural behaviours measured on a $Pt/PbZr_{0.45}Ti_{0.55}O_3/Pt$ capacitor submitted to bipolar rectangular cycling. A sample environment was specially designed to simultaneously measure the high-resolution synchrotron x-ray diffraction patterns and the ferroelectric characteristics such as dynamic hysteresis loops and switching currents (figure 1). Several mechanisms are discussed as a possible origin of the polarization fatigue observed in the PZT-based capacitor.

2. Experimental details

$PbZr_{0.45}Ti_{0.55}O_3$ thin film (150 nm thick) with a composition in the morphotropic region was deposited by chemical solution deposition (CSD) onto $Pt/Ti/SiO_2/Si$ substrate. The substrate was coated with the ferroelectric film using a multi-layer spin-coating technique. The film was pyrolysed after each deposition step at 400 °C and finally crystallized in O_2 at 700 °C. Finally, the Pt top electrode was sputtered through a shadow mask and the capacitors underwent an annealing at 700 °C in O_2 [9]. X-ray diffraction patterns showed the film to be mainly 111 oriented [8]. The grain size was typically 100 nm and, as reported in an earlier paper, the film presents a fibre texture with a random orientation in the plane perpendicular to the [111] direction. The full width at half maximum of the rocking curve indicated a misalignment of about 2.2° of the [111]-oriented crystallites with respect to the substrate's normal [8]. The studied ferroelectric film with composition in the morphotropic region presents a coexistence of tetragonal (T) and rhombohedral (R) phases. Out of concern for clarity, in this paper the indexations of the Bragg reflections are referred to the pseudo-cubic unit cell.

These capacitors were analysed by high-resolution x-ray diffraction on beamline BM2, station D2AM, at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The measurements were conducted with an incident wavelength of 0.772 Å selected by a double Si 111 monochromator with sagittal focusing. To obtain a high instrumental resolution, a Si 111 crystal analyser was placed on the detector arm. The x-ray beam was focused to illuminate the whole surface of a single FeCAP (capacitor surface: 0.44 mm^2). The diffraction patterns were collected in transmission mode from θ–2θ scans over the angular domain 14.9°–15.8° in 2θ (101-type Bragg reflections) by steps of 0.02°. Due to the relative sizes of the PZT grains and the x-ray spot, the diffracted intensity was averaged over a very large number of 101-oriented crystallites. The experimental set-up is sketched in figure 1.

Ferroelectric characterizations were performed using the AixACCT TF-Analyzer 2000 system. For the cyclic switching operation, 10^n ($n = 1$–8) rectangular pulses of ±5 V amplitude at 5 kHz were applied to the capacitor. At different stages of the fatigue testing (three times per decade), the switching currents and the dynamic hysteresis loops were recorded using bipolar triangular waves (±5 V and 100 Hz). To perform *in situ* measurements, tips were connected to Pt top and bottom electrodes to apply a triangular measuring signal or rectangular cycling during diffraction data gathering (figure 1).

3. *In situ* microstructural study of electrical field induced fatigue

3.1. Correlation between electrical and microstructural behaviours

Figure 2(a) compares the hysteresis loops measured at different stages during bipolar cycling. As seen in figure 2(b), the fatigue stage appears after 1×10^5 cycles and corresponds to a sharp decrease of the remnant polarization (more than 75% after 1×10^8 cycles). The polarization decrease is also accompanied by an increase of the hysteresis loop tilt and an increase of the internal bias voltage (shift of the loop towards positive voltage) (figure 2(c)). This internal bias voltage is indicative of a modification of ferroelectric domain configuration with bipolar cycling. The electrical field-induced degradation is even more pronounced on the switching current since the current shape drastically changes with increasing number of cycles (figure 3(a)): decrease of the current maximum, smearing of the current peak and shift of the peak towards higher positive voltages. All these observations are in agreement with a normal fatigue behaviour generally reported for PZT thin films with metal electrodes [9, 10].

Due to the high-frequency bipolar cycling as compared with x-ray counting time necessary to obtain reasonable statistics (10 s per angular step), only the diffracted maximum intensity of the 101-type Bragg reflections was measured up to 1×10^6 cycles. As the number of cycles increased, the diffraction lines were recorded over the whole angular range 14.9°–15.8° in 2θ. Due to the large counting time of the diffraction data, 5×10^5 cycles were applied to the capacitor during the acquisition of the first diffraction pattern. Figure 3(b) depicts the evolution of the diffraction profiles with N: a drastic diminution of the Bragg peak maximum is observed when the number of cycles increases.

First, in order to compare microstructural and electrical behaviours during bipolar cycling, the relative variations of the switching current maxima and the diffracted intensity of 101-type Bragg reflections were normalized between 5×10^5 and 1×10^8 cycles. The raw diffracted intensities were first divided by the value measured after 5×10^5 cycles and the resulting variation of the intensity ratio $R_N = \frac{I_N}{I_{5\times10^5}}$ was subsequently normalized between unity and

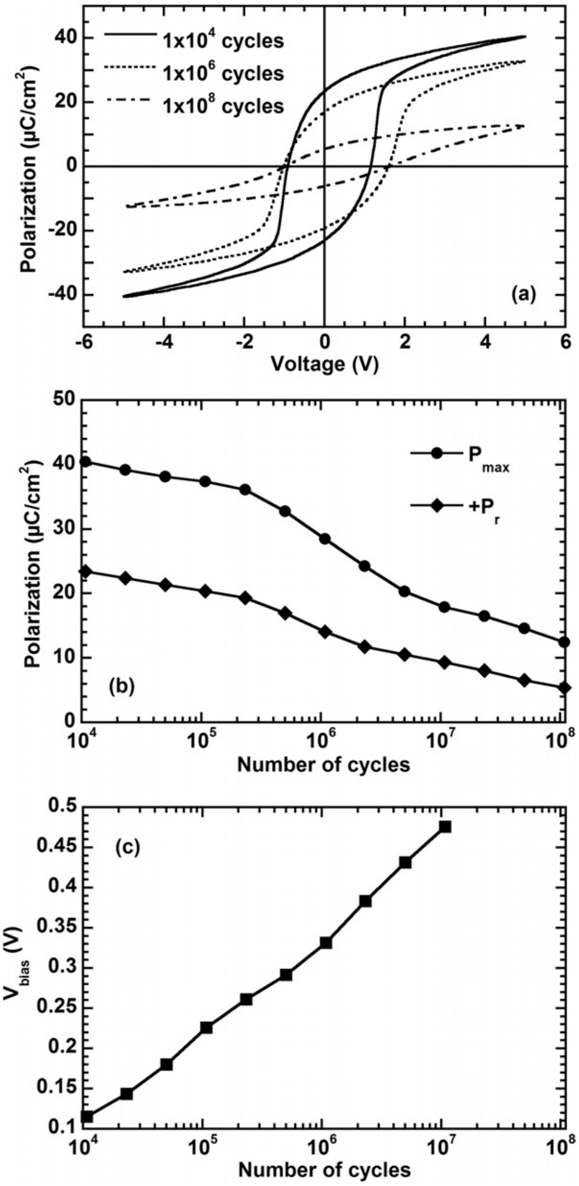

Figure 2. (a) Comparison of the dynamic hysteresis loops measured after 1×10^4, 1×10^6 and 1×10^8 switching cycles. Evolution of the remnant and maximum polarizations (b) and the internal bias voltage V_{bias} (c) measured as a function of the number of switching cycles during *in situ* x-ray diffraction experiments.

zero as follows:

$$\text{Normalized variation} = \frac{R_N - R_{1\times10^8}}{R_{5\times10^5} - R_{1\times10^8}} \qquad (1)$$

where R_N represents the intensity ratio after N switching cycles. The same procedure was used to normalize the variation of the switching currents.

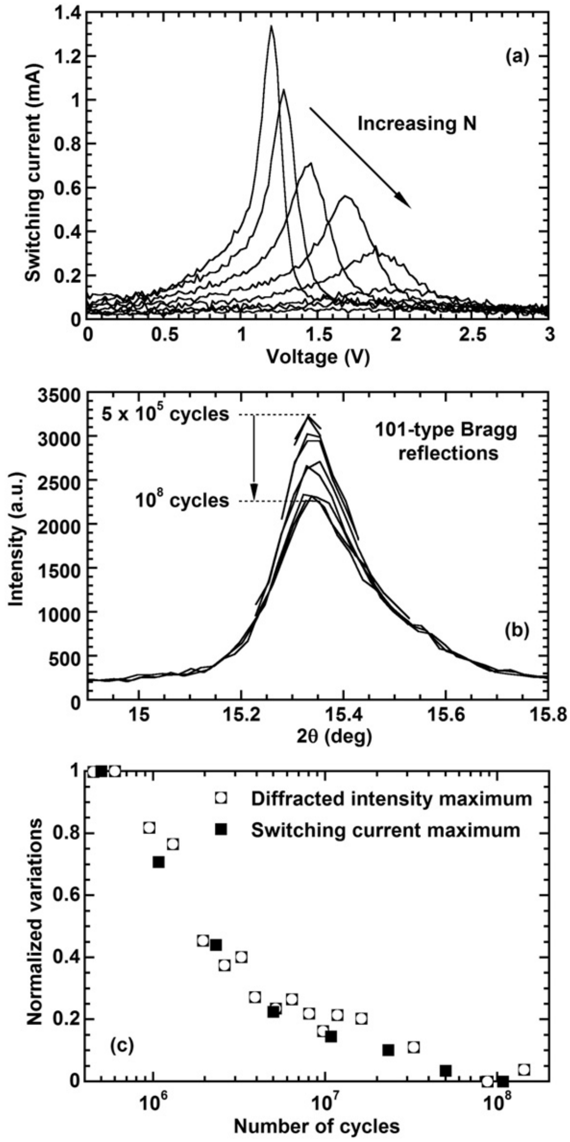

Figure 3. *In situ* fatigue measurements: (a) switching current evolution with the number of bipolar rectangular pulses N; (b) concomitant evolution of the 101-type Bragg reflection intensity; (c) normalized relative variations deduced from the maxima of switching currents and the diffracted intensity (101-type Bragg reflections). Diffraction data and switching current maxima were normalized between 5×10^5 and 1×10^8 cycles.

A good correlation is demonstrated in figure 3(c) since very similar decreases with increasing number of switching cycles are observed. This fact unambiguously evidences a direct relationship between the observed microstructural changes and the electrical fatigue.

3.2. Fatigue mechanisms

Based on the present experimental data, several alternative mechanisms are envisaged to explain the observed cycling-induced structural changes and especially the maximum variation of the

101-type Bragg reflections: (i) field-induced phase transformation between tetragonal and rhombohedral structures; (ii) self-arrangement of the oxygen vacancies; (iii) formation of a inhomogeneous internal bias field leading to a diffraction peak broadening with a subsequent decrease of its maximum.

In PZN-PT [11, 12] and PMN-PT [13, 14] ceramics and in PZT thin films [8] crystallizing in the morphotropic region, field-induced phase transformations between tetragonal and rhombohedral structures have been reported from *ex situ* x-ray diffraction. From *ex situ* experiments, Menou *et al* have shown that the same $PbZr_{0.45}Ti_{0.55}O_3$ thin film undergoes a tetragonal to rhombohedral field-induced phase transition [8]. This mechanism is certainly linked to a re-parceling of the PZT grains due to the mechanical strains appearing during cyclic stressing. In the present study, this mechanism is difficult to verify since the maximum of the 101-type Bragg reflections includes the contributions of both tetragonal (i.e. 101_T reflection) and rhombohedral (i.e. 101_R reflection) phases.

The second possible mechanism is related to the model of Dawber and Scott proposed for the fatigue prediction in PZT thin films [15]. This model, inspired from the works of Arlt *et al* [16] and Brennan [17], is based on the electromigration of oxygen vacancies along favourable crystallographic directions. Indeed, the oxygen vacancies known to be most mobile point defects in PZT thin films can provoke a domain wall pinning [18–20]. Based on the work of Beccero *et al* [21], Scott and Dawber have proposed a domain wall pinning scenario due to ordering of oxygen vacancies into two-dimensional planar arrays [15]. It has been proposed that electrical field induced self-organization of oxygen vacancies preferentially occurs in linear chains along [101] directions in the cubic perovskite structure [15, 21]. Qualitatively, this model may explain the decrease of the Bragg reflection intensity (figure 3(b)) in terms of self-ordering of oxygen vacancies in 101-type crystallographic planes. Indeed, if the oxygen vacancies are concentrated in specific crystallographic planes, their contribution decreases in the corresponding crystallographic structure factors and leads to decrease of diffracted intensity.

The third mechanism is based on the recent kinetic imprint approach proposed to explain the fatigue behaviour and leading to a widening of the internal bulk screening field distribution function during cyclic switching [22]. The increase of the dispersion leads to a decrease of the switching charge (extension of the 'frozen' domains), due to a loss of the switching in the regions with coercive field E_c exceeding the applied field E_m. It is seen that the switching charge decrease (i.e. fatigue) for a number of switching cycles larger than 1×10^5 (figure 2(b)) is followed by an essential increase of the halfwidth σ of the switching current peak *versus* applied voltage [23] measured during cycling (the decrease of $1/\sigma$ is shown in figure 4). The widening of the switching current peak reveals the growth of frozen domains in the ferroelectric film. A dependence of the dispersion on the number of cycles N for the fatigue stage has been recently proposed [23]:

$$\sigma(N) = B \times N^{1/2} + \sigma_0 \tag{2}$$

where σ_0 is the dispersion of the distribution function before fatigue and B is a constant.

Without marked change of the switching current shape, a similar behaviour can be obtained for the dependence of the current maxima on the number of cycles.

As shown from *ex situ* x-ray diffraction experiments [8], the application of a cyclic electrical field can induce structural changes such as c_T/a_T ratio leading to a slight shift of the tetragonal Bragg reflections. Thus the formation of an inhomogeneous internal bias field during cyclic switching may lead to a broadening which explains the decrease of the maxima of the 101-type Bragg reflections. Indeed, the broadening of the switching current peak is indicative of the domain structure modification with repetitive bipolar cycling. On the other hand, from *ex situ* x-ray diffraction experiments performed on fatigued PZT thin

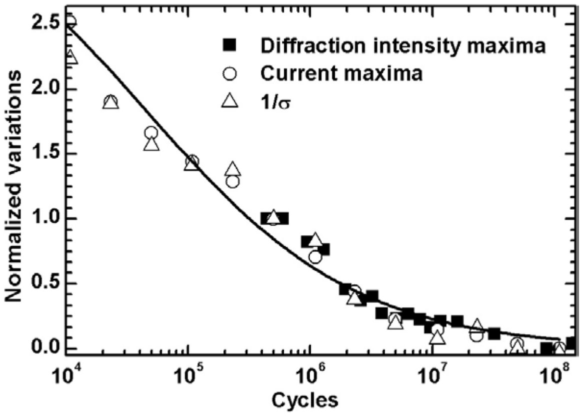

Figure 4. Relative variations of the switching current maximum, the reciprocal of the halfwidth of the switching current peak ($1/\sigma$) and the diffracted intensity of the 101-type Bragg reflections. The fitting of the experimental points derives from equation (2) (see text for details).

films, Kimura *et al* [3] and Liu *et al* [5] have interpreted the variation of diffracted intensity in terms of 90°-domain switching mechanism in favour of the *c*-domain orientation in the tetragonal phase. Consequently, the x-ray diffraction and the halfwidth of switching current peak are both sensitive to domain structure modification during bipolar cycling. In such a case, the evolutions of the diffracted intensity during cycling and the switching current have to be correlated. Figure 4 confirms such a behaviour since the dependences on N of the normalized variations of (i) the switching current maximum, (ii) the reciprocal dispersion of the distribution function ($1/\sigma$) and (iii) the maximum intensity of the Bragg reflection are very similar. The fitting of $1/\sigma(N)$ performed with an equation deriving from equation (2) well matches all the normalized data (figure 4). Unfortunately, the drastic experimental conditions (e.g. large counting times) did not allow following a possible 101-type diffraction peak broadening with increasing N. However, considering the evident relationship between electrical and microstructural behaviours, further investigations have to be performed.

Finally, in previous works Menou *et al* have reported a strong degradation of the switchable polarization when PZT-based capacitors are submitted to x-ray radiation [8, 24]. In the present conditions in which the cycling was inevitably combined with irradiation, the observed fatigue is very similar to the one previously reported [24]. It is commonly admitted that in ferroelectric materials, x-ray irradiation produces electron–hole pairs which undergo the influence of the internal field in the different domains. Menou *et al* have proposed that x rays accelerate the screening of the local depolarization field [24]. The correlated electrical and microstructural behaviours attest that the additional effects of cycling and irradiation are taken into account in the overall fatigue mechanism. Thus, this correlation is rather in favour of the kinetic imprint approach since the mobility of oxygen vacancies is not expected to be influenced by irradiation [25].

4. Conclusion

Highly brilliant synchrotron x-ray diffraction associated with *in situ* electrical measurements was proven to be a useful diagnostic tool for investigating the domain switching kinetic in PZT-based capacitors. From concomitant variations of the diffracted intensity and the switching current, several mechanisms were discussed as a possible origin of the fatigue in studied PZT-based capacitors: field induced phase transformations between tetragonal and rhombohedral structures; oxygen vacancy self-ordering and widening of the internal bulk screening field distribution function during cyclic switching. Nevertheless, considering the additional effect of x-ray irradiation, the kinetic imprint approach is privileged to explain the observed fatigue.

Acknowledgments

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