Correlation between switching and fatigue in $PbZr_{0.3}Ti_{0.7}O_3$ thin films

M. Grossmann,[a] D. Bolten, O. Lohse, and U. Boettger
Institut für Werkstoffe der Elektrotechnik, RWTH Aachen, D-52056 Aachen, Germany

R. Waser
Institut für Festkörperforschung, Research Center Jülich, D-52425 Jülich, Germany

S. Tiedke
aixACCT Systems, D-52056 Aachen, Germany

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Fast pulse switching experiments with variable width and amplitude of the write pulse were performed on $PbZr_{0.3}Ti_{0.7}O_3$ thin films and the results were correlated to fatigue measurements with varying frequency and amplitude of the fatigue signal. It was found that small amplitudes in combination with a small pulse width of the write pulse does not provide sufficient switching of the ferroelectric film. Furthermore, for the fatigue measurements, it is shown that the degree of switching caused by the fatigue excitation signal strongly influences the fatigue results. In the case of complete switching, the fatigue behavior is found to be independent of the fatigue frequency and only the *number* of switching cycles is decisive for the polarization decrease. © *2000 American Institute of Physics.* [S0003-6951(00)02535-3]

In recent years, ferroelectric thin films such as $PbZr_xTi_{1-x}O_3$ (PZT) and $SrBi_2Ta_2O_9$ (Refs. 1 and 2) have been widely discussed for use in ferroelectric nonvolatile random access memories (FeRAMs). In the FeRAM device, the ferroelectric thin film has to withstand up to 10^{15} switching cycles without cell failure. However, continuous switching of the ferroelectric thin film can lead to a decrease of the polarization values, which is referred to as fatigue in the literature,[3,4] and leads to a failure of the memory cell. Therefore, intensive work has been performed to understand the physical origin of fatigue and to improve the fatigue endurance of ferroelectric thin films. In the literature, different models are discussed for the origin of fatigue. Some groups assume the electromigration of oxygen vacancies and the formation of defect planes near the thin-film–electrode interface parallel to the electrodes to be responsible for fatigue in ferroelectric (FE) films. According to this model, fatigue can be explained by the pinning of domains at charged defect planes near the interface.[5–8] In another model,[9–11] the switching of the polarization is supressed because of the blocking of domain nucleation at the electrode–thin-film interface by entrapped charges which are injected from the electrodes into the film. In a very recent paper, fatigue is explained by the growth of a passive layer, i.e., a layer with damaged ferroelectric properties, at the electrode–thin-film interface.[12] In this work, fast pulse switching experiments were performed and the results were correlated to fatigue measurements with varying frequency and amplitude carried out on the same films.

The 200 nm PZT (30/70) thin films were grown on $Pt/Ti/SiO_2/Si$ substrates by chemical solution deposition. The films were deposited by a multilayer spin-coating deposition and pyrolized after each deposition step at 400 °C, and finally crystallized in O_2 at 700 °C. X-ray diffraction patterns showed the films to be mainly [111] oriented. The Pt top electrodes were sputter deposited and the capacitor structures underwent a final postanneal at 700 °C in O_2. The capacitor structures ranged from 50×50 to $200\times200\ \mu m^2$. The electrical characterization was carried out at room temperature using the FE (hysteresis and fatigue measurements) and pulse switching modules of the aixACCT TF Analyzer 2000. The fatigue measurements were carried out by applying a bipolar rectangular pulse train of varying frequency (10 Hz–1 MHz, 100% duty cycle), and after certain numbers of switching cycles the ferroelectric properties were evaluated with a hysteresis measurement (triangular wave form, 500 Hz).

The different remanent states of polarization [$+P_r$, $-P_r$, see Fig. 1(a)] can be assigned to different logic states ''0'' and ''1.'' The stored information can then be obtained by applying a positive read pulse which drives the ferroelectric into the positive saturation ($+P_{max}$). The sense amplifier can distinguish between the two logic states by integrating the current response of the read pulse. In the switching case (from $-P_r$ to $+P_{max}$), the polarization difference is significantly larger compared to the nonswitching case ($+P_r$ to $+P_{max}$). Usually, hysteresis measurements are performed to gain basic information about the suitability of a ferroelectric thin film for FeRAM application since the hysteresis measurement reveals the expected polarization difference in the switching and nonswitching case. In Fig. 1(a), a hysteresis measurement is shown measured at 500 Hz with triangular voltage excitation. The expected polarization difference in the switching case is $58\ \mu C/cm^2$. The hysteresis was measured at 500 Hz, which is many orders of magnitude below the operation frequency of a FeRAM device.[3] Therefore, it is of great interest whether the polarization difference obtained by excitation signals which approach the real device conditions with respect to the pulse width and the amplitude also reveal a sufficient amount of polarization difference to ensure a proper FeRAM operation, i.e., a sufficient difference

[a]Electronic mail: grossmann@iwe.rwth-aachen.de

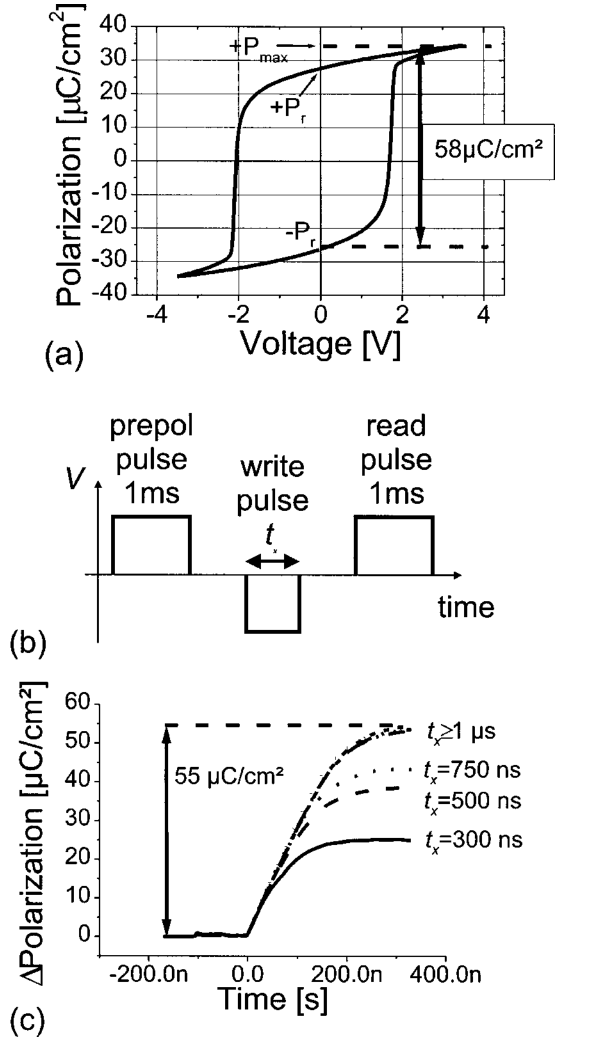

FIG. 1. (a) Hysteresis loop of a PZT (30/70) film with the indication of the expected polarization difference in the switching case (from $-P_r$ to $+P_{\max}$). (b) Sketch of the pulse measurement procedure: pulse sequence with variable pulse width (t_x) of negative write pulse. (c) Pulse measurement: change of polarization (ΔP) as a function of the width (t_x) of the negative write pulse ($V=3.5$ V $\approx 2V_c$).

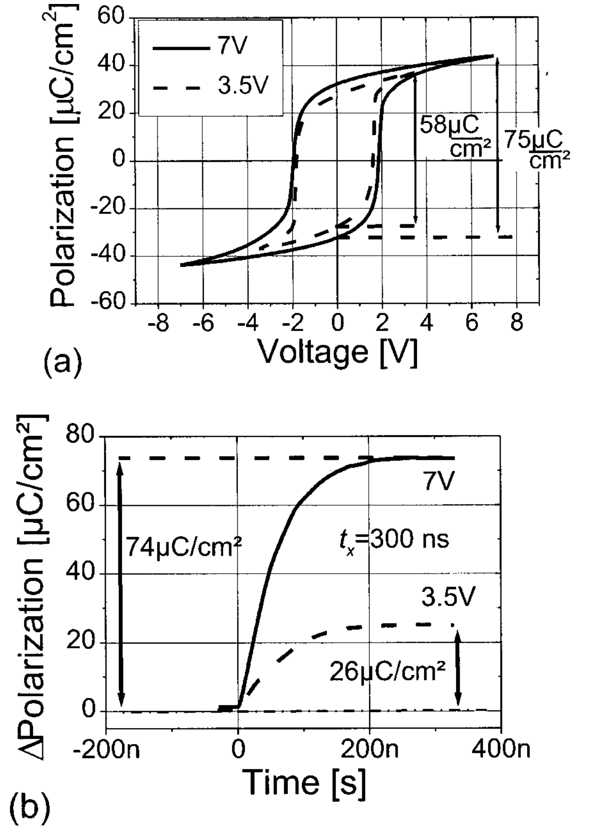

FIG. 2. (a) Hysteresis measurement for different amplitudes with the indication of the expected polarization difference in the switching case (from $-P_r$ to $+P_{\max}$). (b) Pulse measurement: change of polarization (ΔP) for different amplitudes for both write and read pulse (read pulse width: $t_x=300$ ns.

between the switching and the nonswitching case. Therefore, a fast pulse switching experiment was performed to investigate the influence of the width of the write pulse on the amount of switched polarization, i.e., obtained in the switching case. The experimental procedure is sketched in Fig. 1(b). The prepolarization pulse (width 1 ms) established the positive remanent state of polarization ($+P_r$) as the initial state. Subsequently, a write pulse with a variable pulse width ($t_x=300$ ns–1 ms) was applied. Finally, a positive read pulse (width 1 ms) was applied which, again, provided a sufficient switching to the positive polarization ($+P_{\max}$). In Fig. 1(c) the time evolution of the polarization difference, derived from the integration of the current response of the read pulse, is shown for different pulse widths t_x of the write pulse. The amplitude of the pulses was $V=3.5$ V, which corresponds to approximately twice the coercive voltage (V_c) of the film. It can be seen for this PZT film only in the case of pulses with a width of 1 μs or wider that the amount of the polarization difference is approximately obtained (55 μC/cm^2), which is expected from the hysteresis measurement (58 μC/cm^2). For smaller pulse widths the polarization difference is significantly smaller. It can be excluded that the RC time constant of the output amplifier with the ferroelectric capacitance is the reason for this behavior since this RC time constant is determined to be less than 100 ns. This assumption is confirmed by pulse measurements with higher amplitudes ($V=7$ V$\approx 4V_c$). From the hysteresis measurement, a polarization difference of approximately 75μC/cm^2 is expected [Fig. 2(a)], which in good agreement with the difference obtained by a pulse measurement at 7 V even at a pulse width of 300 ns [74 μC/cm^2 Fig. 2 (b)], showing that the RC time constant does not play a role in the switching case with 300 ns pulses. This means that for a given small pulse width only high amplitudes provide a sufficient switching of the ferroelectric, whereas smaller amplitudes in combination with small pulse widths do not switch the ferroelectric sufficiently. The deceleration of the switching with decreasing pulse amplitude in ferroelectric thin films is well known and is usually ascribed to either a domain-wall motion effect[13] or a ferroelectric relaxation phenomenon.[14]

In the following, the influence of the fatigue signal, i.e., the frequency and the amplitude of the rectangular excitation signal, on the decrease of the polarization is discussed and a correlation to the switching experiments presented in Figs. 1(c) and 2(b) is pointed out.

In Fig. 3(a), the decrease of the polarization is shown for different fatigue amplitudes. The frequency of the fatigue signal was 1 MHz. It can clearly be seen that the fatigue behavior is significantly enhanced with increasing amplitude.

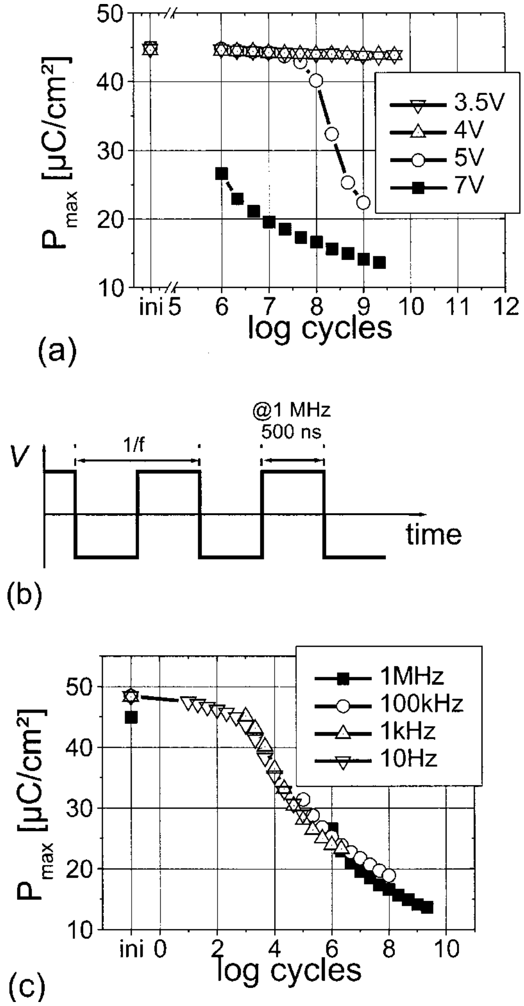

FIG. 3. (a) Decrease of the polarization during fatigue treatment with varying amplitudes (1 MHz). (b) Sketch of the fatigue excitation signal, pulse width for 1 MHz signal is indicated. (c) Decrease of the polarization during fatigue treatment with varying frequencies (7 V).

Similar results on PZT films were reported in the literature.[15] For amplitudes equal to or less than 4 V the PZT film is virtually fatigue free up to 10^{10} cycles [Fig. 3(a)]. The excitation signal was a bipolar, symmetrical signal, as shown in Fig. 3(b). Hence, the pulse width of the 1 MHz signal amounts to 500 ns, as indicated in Fig. 3(b). However, with the switching experiment performed on the same film shown in Fig. 1(c), it was demonstrated that the ferroelectric cannot be switched sufficiently for similar pulses (width $<1\ \mu$s, amplitude=3.5 V), indicating that the applied fatigue signal, at 1 MHz and small amplitudes, does not provide sufficient switching of the ferroelectric films. Thus, the insufficient switching in the case of small amplitudes in combination with high frequencies, i.e., small pulse width, seems to be the reason for the improved fatigue behavior. This assumption is confirmed by the results shown in Fig. 3(c). In that case, the excitation frequency was varied over five orders of magnitude (10 Hz–1 MHz). The amplitude of the excitation signal was 7 V. As can be seen, the decrease of the polarization is independent of the frequency, only the *number* of switching cycles is decisive. In the switching experiment shown in Fig. 2(b), it was demonstrated that the ferroelectric film can be sufficiently switched with 7 V even for a pulse width of 300 ns. Hence, in the case of the frequency variation [Fig. 3(c)], the ferroelectric was switched sufficiently for all frequencies since even at 1 MHz the pulse width amounted to 500 ns, showing that for the material under investigation only the number of switching cycles, i.e., sufficient switching, is relevant for the fatigue behavior.

In summary, a correlation between pulse switching experiments and fatigue has been pointed out. The results indicate that only sufficient switching, i.e., that the amount of polarization is switched which is expected from low-frequency hysteresis measurements (from $-P_r$ to $+P_{max}$), leads to reliable and frequency-independent fatigue data. Fatigue signals which do not provide complete switching of the ferroelectric reveal seemingly better fatigue behavior, whereas in the case of sufficient switching the fatigue behavior of the PZT films under investigation is significantly more pronounced. Thus, by evaluating the dependence of fatigue on the frequency and amplitude of the excitation signal, a careful verification is necessary, whether the fatigue signal can switch the ferroelectric completely. In this work, fatigue measurements with a variation of the frequency over five orders of magnitude were carried out and the results imply that for fatigue behavior of the PZT films under investigation only the *number* of switching cycles is relevant independent of the frequency.

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