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Pulse polarization inversion and phase transition in ferroelectric and antiferroelectric thick films

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Abstract

Fast switching in thin ferroelectrics has been investigated from the respective switching current and voltage wave form signals. The polarization inversion process, established for PZT (45/55) thin films in a nanosecond time scale, takes place at the ''dynamic coercive electric field'' and is mainly limited by the electric circuit components. Due to the low impedance of the ferroelectric during switching, the voltage across the ferroelectric rises only when polarization inversion is getting accomplished. Hence a voltage dependence of the switching has not be found. Pulse phase transition experiments in antiferroelectric PZT (95/5) have been performed, which show that the dynamic behavior of the transition between the ferroelectric and the antiferroelectric state follows the same principle. Thus, fast phase transitions can be realized, too. Derived from the voltage and current wave form data, ''pulse hysteresis loops'' have been established.

Keywords: Ferroelectric properties; Films; Pulse switching; PZT; Sol–gel processes

1. Introduction

Fast polarization inversion normally is achieved by using pulsed voltage, a method which is based on the early experiments of Fatuzzo and Merz,[1] who applied it in order to (partially) switch ferroelectric bulk material. With the rising interest in thin films, the experimental technique has been adapted to these materials and was refined by different groups. The state-of-the-art of nanosecond switching of ferroelectric thin films, also especially addressing circuit aspects and its influence on the switching speed, has been reviewed by Larsen et al.[2] The main limitation for polarization switching results from the high capacity of the thin films and the related low coercive voltage, which causes serious problems to pulse generation and seems to be today's major obstacle for sub-nanosecond polarization inversion. In a recent publication, we reported on fast switching at the coercive electric field, confirming the decisive influence of the pulse circuit components.[3]

Phase transitions in antiferroelectric material are much less investigated. Pioneer work has been performed by Cross et al., who studied the phase transition speed in antiferroelectric (AFE) bulk ceramics,[4] as well as the field forced switching[5] and the charge release on backward switching[6] in AFE thin films. In the present work, we analyze the switching dynamics of ferroelectric thin films and the phase transition behavior in antiferroelectric thin films from the respective current and voltage waveform signals.

2. Experimental technique and thin films used

The material used for the present study is ferroelectric PZT (45/55) and antiferroelectric PZT (95/5), elaborated by chemical solution deposition (CSD) and multiple spin-coating. The films had an overall thickness of approximately 1.25 and 2.4 μm, respectively and were deposited onto RuO_2 coated steel substrates. The substrate serves as the bottom electrode, a second electrode was established by evaporating gold electrodes of 500×500 μm^2 surface on top of the films. Typical 50 Hz hysteresis characteristics of the films used in the present study are shown in Fig. 1.

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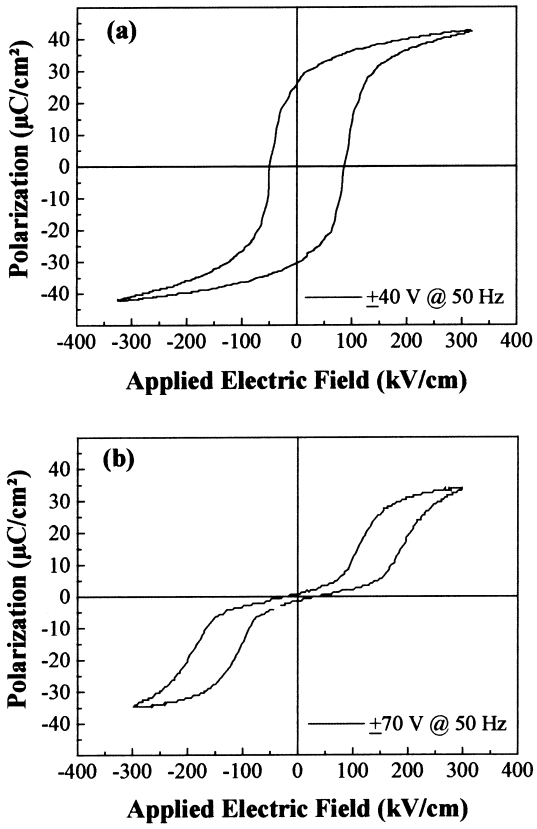

Fig. 1. 50 Hz hysteresis loop of (a) ferroelectric PZT (45/55) and (b) antiferroelectric PZT (95/5) thin films elaborated by CSD and deposited on RuO_2 coated steel substrates.

Spin-coating of the PZT (45/55) onto an RuO_2 interface layer has been chosen for its benefit of an essentially smaller coercive field and thus a more "square" hysteresis loop. Modification of the interface PZT/substrate by introducing the RuO_2 layer improves crystallization and thus yields the better electric characteristic.[7]

In a recent study of the electric properties of PZT depending on the Zr/Ti-ratio the co-existence of ferroelectric and antiferroelectric phases especially for $PbZrO_3$ had been shown, resulting in a non-zero remanent polarization P_0 at zero applied electric field. The contribution of the ferroelectric phase, however, decreases with the addition of only a few percent of Ti and is almost not anymore visible at PZT (95/5); hence a clear antiferroelectric double hysteresis has been obtained.[8]

The method of pulse switching and pulse phase transition is based on the application of fast rising rectangular voltage pulses. Using a low impedance, high current pulse generator, the films are connected to the pulse and measuring circuit via micro-manipulated contact needles while trying to reduce the mismatch of impedance to a maximum degree. The voltage is applied to the top electrode and the electric field across the film is determined differentially by using two voltage probes. The current is deduced from the voltage at a measuring resistor R_m in series with the PZT thin film. Details of the pulse generator and the measuring circuit have been reported elsewhere.[3]

3. Results and discussion

Fast polarization inversion in ferroelectric PZT (45/55) has been studied by applying the classic sequence of one pre-orientation pulse followed by two consecutive pulses of the opposite polarity and sufficient duration in order to successively inducing switching and non-switching. The wave forms for the case of positive switching and non-switching pulses are shown in Fig. 2 for the applied voltage signal (Fig. 2a) and the corresponding switching current (Fig. 2b), for different measuring resistors R_m, respectively. The nominal pulse generator voltage U_g was constant and corresponds to an electric field of approximately 320 kV/cm.

In the rising part of the first positive pulse, three slopes can be distinguished in Fig. 2a: First, an initial fast rise of the signal up to a voltage between 15 and 20 V, little depending on the measuring resistor, second, a rather flat part of different width depending on R_m, and third, the final rise to the nominal voltage of 40 V. The first part of the voltage wave form corresponds to capacitive charging of the ferroelectric up to the dynamic coercive field where switching sets on. Switching takes place at the flat middle part of the signal. Since the coercive electric field of the thin film has a certain distribution (see hysteresis characteristics of Fig. 1a which is not vertical at the coercive field value), the voltage level where polarization inversion is established is not really constant. However, the end of the switching process is again visible as a change in the slope of the voltage signal, and the much faster rise to the nominal pulse generator voltage can be well distinguished.

As the ferroelectric has almost zero resistance during polarization inversion, switching is governed by the measuring resistor R_m in series with the ferroelectric, which in fact limits the maximum switching current to $I_{max} = (U_g - U)/R_m$. U_g and U are the nominal generator voltage and the actual measured voltage of Fig. 2a, respectively. Hence switching (and the final voltage rise up to the nominal voltage) becomes slower as R_m is increased. The limiting role of R_m is also well visible from the switching current wave forms of Fig. 2b, where the amplitude of the current decreases with increasing R_m. Integration of the different current wave forms yields the same value, proving that the same amount of polarization has been switched independently from the measuring resistor. The small negative current signals corresponding to the end of the positive voltage pulse indicate dielectric discharging of the ferroelectric.

The second positive pulse applied to the ferroelectric shows the case of non-switching. Since the charge to be

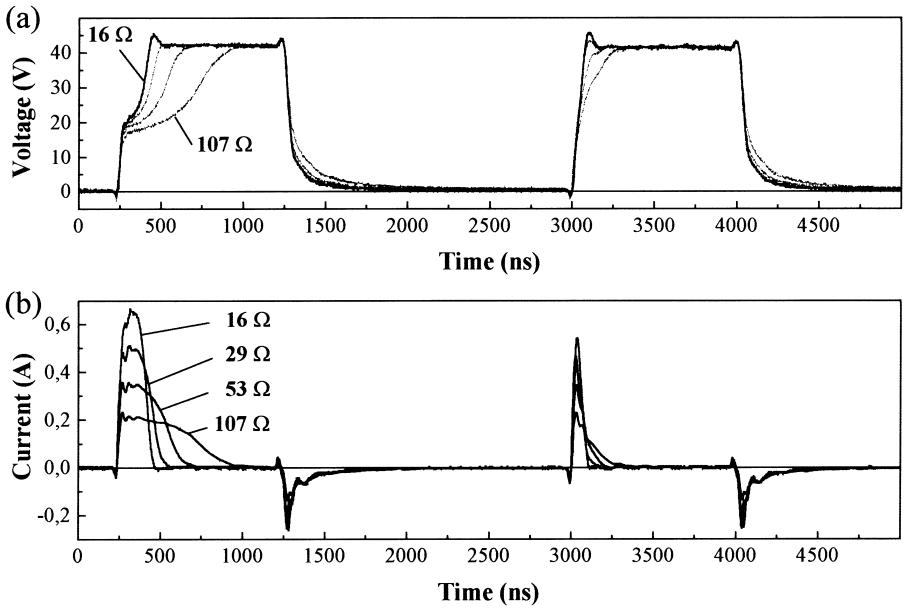

Fig. 2. Pulse switching of ferroelectric PZT (45/55) thin films, showing (a) the voltage wave form and (b) the corresponding switching current signal for different measuring resistors R_m and for the switching (first) and the non-switching (second) pulse, respectively.

transferred is considerably smaller, also the influence of the measuring resistors is less significant. Nevertheless, a slower rise of the voltage correlated to smaller current signals is still visible as the resistor value increases.

Fast phase transitions has been studied in antiferroelectric PZT (95/5) thin films. As can be anticipated from the double hysteresis loop recorded at 50 Hz (Fig. 1b), only unipolar voltage pulses are necessary in order to describe a minor cycle (i.e. a positive pulse for the cycle in the first quadrant). Hence the field forced antiferroelectric–ferroelectric transition and ferroelectric–antiferroelectric relaxation can be investigated with one single pulse. This is shown for the voltage signal wave form in Fig. 3a and for the phase transition current wave form in Fig. 3b, for different measuring resistors R_m, respectively.

At the rising part of the voltage signal one can distinguish at least two different slopes (Fig. 3a). The initial fast rise indicates dielectric charging of the thin film and corresponds to a motion along the flat bottom part of the antiferroelectric hysteresis loop. This is also marked by

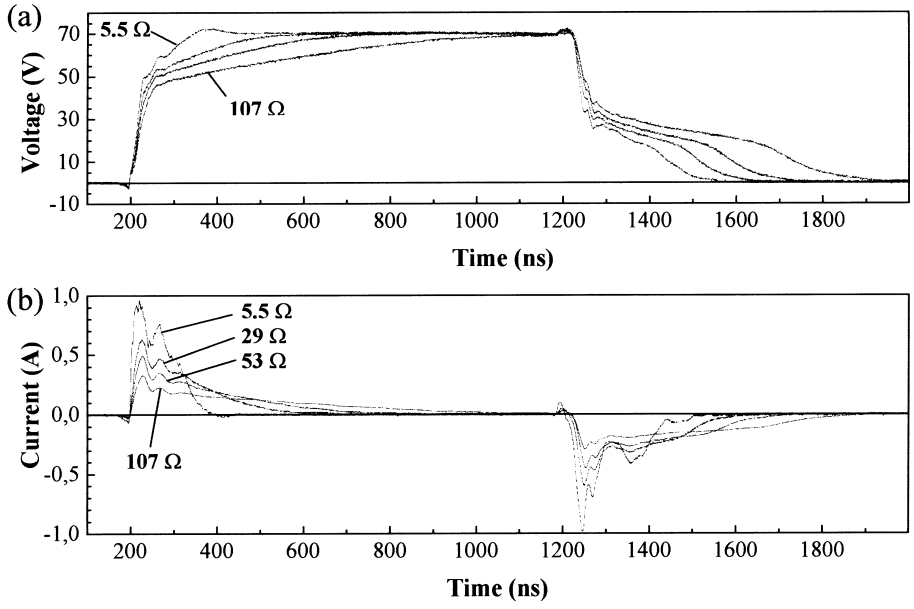

Fig. 3. Pulse phase transition between the antiferroelectric and the ferroelectric state in PZT (95/5), showing (a) the voltage wave form and (b) the corresponding phase transition current signal of the thin film.

the first distinct peak of the current wave forms. Around a voltage of approximately 45 V the antiferroelectric–ferroelectric (AFE–FE) transition sets on, which can be recognized by the change of the slope in the voltage signal. Similar to the case of the ferroelectric switching, the phase transition process is limited by the maximum current I_{max}, and as the resistor R_m is smaller, a higher current into the antiferroelectric thin film is possible (Fig. 3b). The end of the phase transition is established at approximately 65 V just below the nominal pulse generator voltage of 70 V, and is visible as a slight change in the slope of the signal. The duration of the phase transition can also be deduced from the current signal, and corresponds to the second peak of the wave form. The further charging to the saturation state (flat part at the top of the double hysteresis loop) cannot be distinguished, since, in the case of the pulse measurements, the applied voltage was not high enough.

The ferroelectric–antiferroelectric relaxation can be observed at the end of the positive voltage pulse. There is a fast decay of the voltage, corresponding to a first peak of the current wave form, to approximately 30 V where the transition sets on. The duration of the relaxation is marked by the smaller slope in the voltage wave form and can be well distinguished as the second peak of the current signal. Not depending on R_m, relaxation to the antiferroelectric phase seems to be complete at a voltage of approximately 18 V, where the slope of the voltage signal again becomes more negative, indicating dielectric discharging of the film.

Establishing of a "pulse hysteresis loop" from the voltage and current data is possible by integrating the pulse current signal and tracing point by point the obtained charge wave form versus the electric field deduced from the voltage wave form. In Fig. 4a and b are shown the pulse hysteresis loops of the ferroelectric PZT (45/55) and the antiferroelectric PZT (95/5) films, respectively. When comparing this loops to those of the classic 50 Hz switching, one can see that there is only a small difference in polarization with larger values for the 50 Hz case. The coercive field of the ferroelectric films is considerably larger for the pulse switching method. Also the dynamic antiferroelectric- ferroelectric transition field seems to be significantly increased, whereas spontaneous ferroelectric-antiferroelectric backwards transition is not influenced by the different methods. When establishing the pulse loops for different measuring resistors (i.e. different switching currents and times), the pulse hysteresis loops approach the case of the 50 Hz loop as switching becomes slower (not shown in the figure).

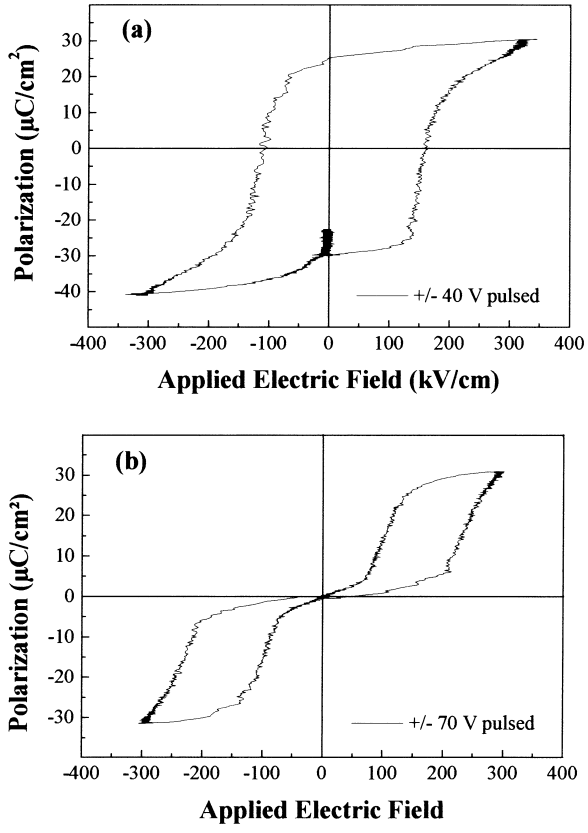

Fig. 4. "Pulse hysteresis loops" deduced from the current and voltage signals of (a) fast polarization switching in PZT (45/55) and (b) fast phase transition in antiferroelectric PZT (95/5) thin films.

4. Conclusions

The dynamic behavior of pulse switching in ferroelectric thin films and of pulse phase transition in antiferroelectric thin films has been studied. From the voltage wave forms, the dynamic coercive field and the electric fields where the forwards and backwards phase transition sets on can be deduced, and the current wave forms indicate the duration of the different processes. In general, when comparing the data from the pulse switching study to the results obtained from 50 Hz switching, the fast inversion and field induced AFE–FE transition processes exceed higher electric fields. Once the respective process has been initiated at its dynamic coercive field, however, the velocity of the switching or phase transition is governed by the maximum possible current through the measuring resistor. Thus, the intrinsic switching time has not been achieved and a voltage dependence cannot be found. In order to have access to both, the current limited regime of switching and the material's intrinsic switching process, scaling with different electrode areas and investigations on TGS are under preparation, which is known to switch less fast, and thus should allow to verify the observations made for the PZT thin films. Establishing of pulse hysteresis loops from the fast switching and phase transition data may serve to characterize the dynamic properties at high frequency, and is a means to compare the behavior of different materials.

References

1. Fatuzzo, E. and Merz, W. J., Switching mechanism in triglycine sulfate and other ferroelectrics. *Phys. Rev*., 1959, **116**, 61–68.
2. Larsen, P. K., Cuppens, R. and Dormans G. J. M., Pulse switching characterization of ferroelectric thin films. In *Proceeding of NATO ARW on Science and Technology of Electroceramic Thin Films. In NATO ASI Series E: Applied Science*, Vol. 284 ed. O. Auciello and R. Waser. Kluwer Academic Publishers, Dordrecht, 1995, pp. 201–221.
3. Averty, D., Limousin, P. and Gundel, H. W., Dynamic properties of polarization switching in ferroelectric thin films. In *Proceedings of the 12th International Symposium on Integrated Ferroelectrics (ISIF 2000)*, Aachen, Germany, 12–15 March 2000, to be published in *Integrated Ferroelectrics*.
4. Pan, W. Y, Gu, W. Y. and Cross, L. E., Transition speed on switching from a field-induced ferroelectric to an antiferroelectric phase upon the release of the applied electric field in $(Pb,La)(Zr,Ti,Sn)O_3$ antiferroelectric ceramics. *Ferroelectrics*, 1989, **99**, 185–194.
5. Brooks, K. G., Chen, J., Udayakumar, K. R. and Cross, L. E., Electric field forced phase switching in La-modified lead zirconate titanate stannate thin films. *J. Appl. Phys*., 1994, **75**, 1699–1704.
6. Xu, B., Moses, P., Pai, N. G. and Cross, L. E., Charge release of lanthanum-doped lead zirconate titanate stannate antiferroelectric thin films. *Appl. Phys. Lett*., 1998, **72**, 595–595.
7. Yi, J., Seveno, R. and Gundel, H. W., Sol–gel derived PZT/RuO_2 multilayer films on stainless steel substrates. *Integrated Ferroelectrics*, 1999, **23**, 199–214.
8. Seveno, R. and Gundel, H. W., Preparation of antiferroelectric PZT thin films on bare and RuO_2 coated steel substrates. In *Proceedings of the 12th International Symposium on Integrated Ferroelectrics* (ISIF 2000), Aachen, Germany, 12–15 March 2000, to be published in *Integrated Ferroelectrics*.