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Pulse characterization of antiferroelectric $PbZrTiO_3$ thin films

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Abstract

Antiferroelectric $PbZrTiO_3$ thin films were prepared by chemical solution deposition and spin-coated onto RuO_2 coated metal substrates. The field induced transition from the antiferroelectric (AFE) to the ferroelectric (FE) phase and the spontaneous AFE–FE relaxation were investigated in PZT (95/5) thin films by applying fast rising voltage pulses in unipolar or bipolar sequences. The transition between the two phases can be described from the voltage and phase transition current wave forms, respectively, and the transition fields can be deduced from these curves. The data from the pulse transition experiments were used to trace a "pulse hysteresis loop", which is compared to the classic double hysteresis loop obtained by a Sawyer-Tower circuit. The influence of the applied voltage and of the Zr/Ti ratio on the phase transitions dynamics is discussed.

Keywords: Sol–gel processes; Films; Ferroelectric properties; PZT; Functional applications

1. Introduction

Pulse switching of ferroelectric material has been investigated since many years and is subject to numerous publications. Contrary to that, the dynamics of phase transitions between the antiferroelectric (AFE) and the ferroelectric (FE) state due to fast rising electric fields is much less reported. Backward phase transition in antiferroelectric $(Pb,La)(Zr,Sn,Ti)O_3$ bulk material has been studied by Pan et al.[1] who found switching times of the order of few microseconds. The corresponding forwards phase transition has been investigated by Brooks et al.[2] who reported switching within typically 300 ns. More recently, antiferroelectric thin films were also studied by Xu et al.[3] using $PbZrTiO_3$ of about 0.4 μm thickness, equally doped with lanthanum at the A- and with tin at the B-site of the perovskite structure, and deposited by a modified sol–gel method on conventional silicon substrates. Field forced FE–AFE backwards transition times below 10 ns were reported for these films.

In the present study, we use a fast electric pulse method, originally applied for switching of ferroelectric thin films, in order to induce the AFE–FE phase transition and subsequent spontaneous FE–AFE relaxation.

2. Experimental methods

The antiferroelectric $PbZrTiO_3$ (PZT) thin films were elaborated by chemical solution deposition (CSD) and multiple spin-coating onto RuO_2 coated steel substrates, resulting in an overall layer thickness of approximately 2.4 μm. Modification of the interface PZT/substrate by introducing the RuO_2 layer was chosen for the benefit of improved crystallization, resulting in a more "square" double hysteresis loop. Different Zr/Ti-ratio at the high zirconium end of the PZT phase diagram was studied, PZT (95/5) showing the most clear antiferroelectric double hysteresis with almost no remnant polarization.[4] A more detailed discussion of the preparation route of the PZT thin films and the role of the RuO_2 interface, also reporting on different interface layers, can be found elsewhere.[5] The metal substrate serves as the bottom electrode, the second electrode is established by evaporating gold on top of the films with a thickness of approximately 300 nm. Typical 50 Hz hysteresis loops and current–voltage characteristics of a PZT (95/5) antiferroelectric thin film are

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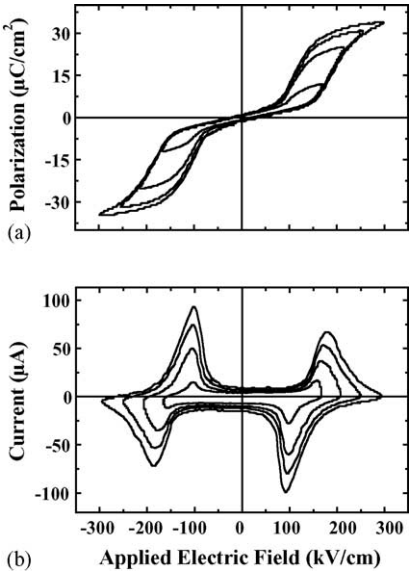

Fig. 1. 50 Hz hysteresis loops (a) and current–voltage characteristics (b) of PZT (95/5) antiferroelectric thin films.

shown for different applied voltages in Fig. 1a and b, respectively.

The fast phase transition method is derived from the partial switching experiment of Fatuzzo and Merz[6] where the ferroelectric is in series with a grounded measuring resistor R_M. In order to reduce the mismatch of impedance between a fast high current pulse generator and the ferroelectric, the films were connected via micro-manipulators to the pulse and measuring circuit. Different pulse sequences were used as shall be specified with the discussion of the experimental results. The electric field applied is determined differentially by two voltage probes, the phase transition current is deduced from the voltage at the resistor R_M (50 Ω). Establishing of a "pulse hysteresis loop" from the current and voltage data is possible by integrating the pulse current signal and tracing point by point the thus obtained charge wave form versus the electric field which is deduced from the voltage signal.[7]

3. Pulse phase transition in antiferroelectric PZT

In order to induce the forward and backwards transition between the AFE and the FE phase, unipolar fast rising voltage pulses of 1 μs duration were applied to PZT (95/5) in series with the measuring resistor R_M. The voltage and phase transition current signals are shown in Fig. 2a and b for the nominal pulse generator voltages U_{GEN} = 80, 100 and 120 V, respectively.

In the beginning of the voltage wave form (Fig. 2a), a fast rise can be seen, which corresponds to the flat portion in the central part of the 50 Hz hysteresis loop. Independently from the nominal applied voltage, the signal rises to a voltage $U_{AFE–FE}$ of approximately 50 V, which can be identified with the onset of the field induced AFE–FE phase transition. During the subsequent more slow rise of the voltage, the phase change takes place (corresponding to the steep part of the hysteresis loop) which is totally established when the voltage reaches the nominal pulse generator voltage U_{GEN} (saturation at the hysteresis loop). As the generator voltage is increased, the transition occurs faster, which is due to the fact that an increased voltage U_{GEN} results in a higher phase transition current according to the simple formula $I = (U_{GEN} - U_{AFE–FE})/R_M$ since the thin film is in series with the measuring resistor. The higher the current I, the faster the transition, indicating that the dynamics is governed by the circuit components and does not reflect the intrinsic phase transition time, which is in accordance to what has been reported earlier on the influence of the measuring resistor.[7] The current wave forms of Fig. 2b also confirm this assumption. Two positive current peaks can be distinguished, the first corresponding to capacitive charging of the thin film up to the phase transition field, the second peak delivering the charge necessary in order to establish the AFE–FE transition. As U_{GEN} increases, the current I increases as well, and the transition is being established faster. Spontaneous FE–AFE relaxation takes place at the end of the positive voltage pulse (Fig. 2a). The initial steep fall from the different nominal applied voltages to a common level of approximately 30 V corresponds to well pronounced negative peaks of the transition current (Fig. 2b) and signifies discharging from polarization saturation along the flat portion at the upper part of the hysteresis. At the rather distinct level of 30 V, the negative slope of the voltage wave form decreases considerably, which means that relaxation to the antiferroelectric phase sets on. Contrary to the field forced forward transition, the voltage and current wave forms of the spontaneous FE–AFE relaxation are identical for all pulse generator voltages. When the backwards transition is finished, discharging of the thin film occurs (around the time mark 2000 ns).

4. Establishing of the "pulse hysteresis loop"

In the classic Sawyer-Tower circuit, the charge accumulated at a linear capacitor serves to establish the hysteresis loop. By integrating the phase transition currents of Fig. 2b, the development in time of the charge, contributing to the forward and backwards phase transition, can be obtained in a similar way. Hence a "pulse hysteresis loop" can be established by tracing this charge versus the applied electric field. In Fig. 3a, the data of Fig. 2 (and those for smaller voltages), showing unipolar voltage pulses, are used, thus resulting in a pulse hysteresis loop in the first quadrant. In Fig. 3b, "pulse double hysteresis loops" are shown which were established from the pulse phase transition current and voltage data of bipolar pulse sequences of different voltage amplitude. When comparing the pulse hysteresis loops of Fig. 3b to those established by 50 Hz cycling (Fig. 1a), one can see an increased width of the loops and a slight diminution of inducible polarization in the case of the pulse phase transition.

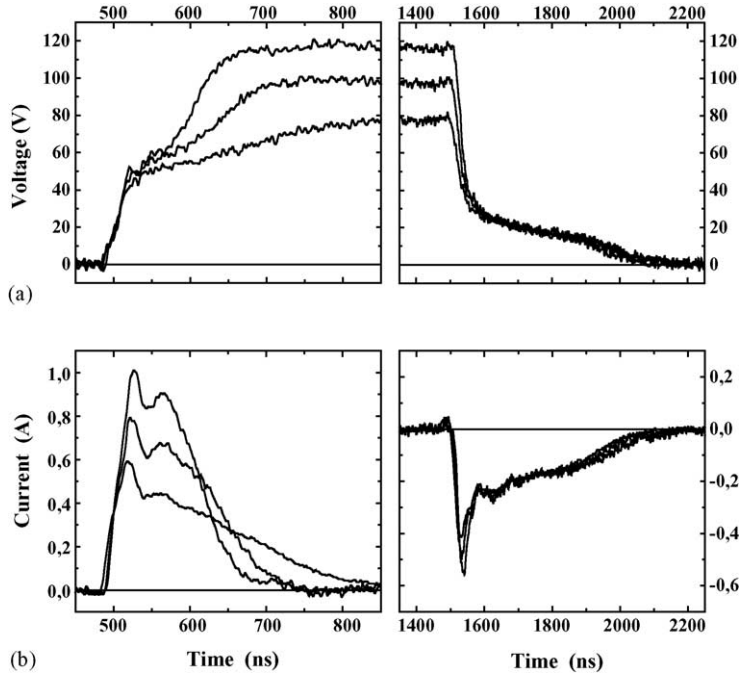

Fig. 2. Pulse phase transition in antiferroelectric PZT (95/5): voltage (a) and phase transition current signals (b) for 80, 100 and 120 V.

The results from the 50 Hz and the pulse phase transition experiments are compared for the average phase transition fields $E_{AFE–FE}$ and $E_{FE–AFE}$ and the maximum polarization P_S in Fig. 4a and b, respectively. The 50 Hz average phase transition field is determined from the current–voltage characteristic of Fig. 1b and corresponds to the position of the current peak where the change between the two phases is maximal. In the case of the pulse phase transition, $E_{AFE–FE}$ and $E_{FE–AFE}$ are defined as the positions of the maximum slopes of the pulse hysteresis loops. The values of maximum polarization were taken directly from the respective hysteresis loops.

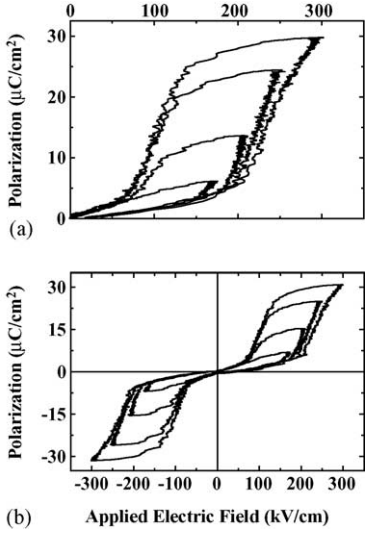

Fig. 3. Pulse hysteresis loops for unipolar (a) and bipolar (b) voltage.

From Fig. 4a it can be seen that the width of the 50 Hz hysteresis loop ($E_{AFE–FE} - E_{FE-AFE}$) remain almost constant above approximately 60 V, indicating a saturated hysteresis loop, and the value of maximum polarization P_S (Fig. 4b) augments only slowly due to capacitive loading of the sample. As the AFE–FE phase transition field of the thin film is higher for the pulse transition, saturation of the hysteresis was not attained in this case. The width of the pulse hysteresis loop still augments, and the maximum polariza-

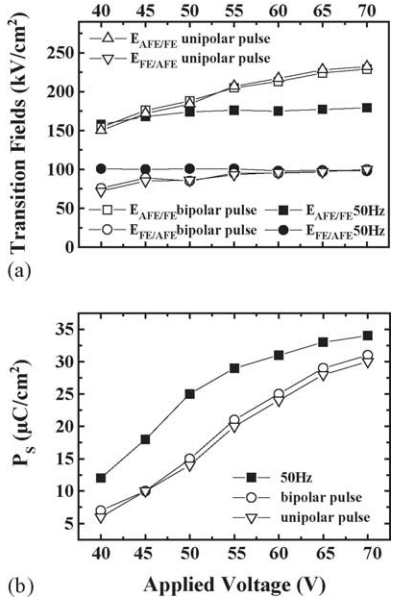

Fig. 4. Average transition fields $E_{AFE–FE} - E_{FE–AFE}$ (a) and maximum polarization (b) in the case of a 50 Hz and a pulse phase transition.

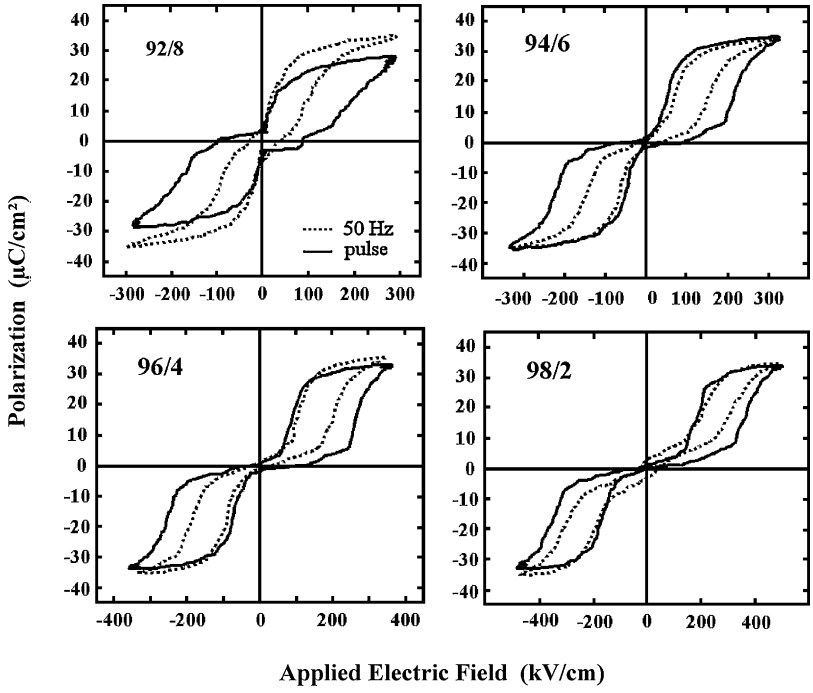

Fig. 5. 50 Hz and pulse hysteresis loops for antiferroelectric PZT thin films of different Zr/Ti ratio.

tion is more far from saturation, but approaches the 50 Hz value for the highest applied voltages. The transition fields for the unipolar and the bipolar pulse sequences are essentially identical.

In general, the FE–AFE relaxation seems to take place at fields comparable to those of the 50 Hz case, except for lower voltages where smaller fields were measured. In these cases, however, the antiferroelectric loop is not yet well pronounced as the onset of the pulsed AFE–FE transition needs higher electric fields, thus determination of the relaxation field from Fig. 3b is less reliable.

5. Phase transition in PZT of different ratio Zr/Ti

Pulse phase transition in PZT was determined for different Zr/Ti ratio near the ferroelectric–antiferroelectric structural transition, which is shown in Fig. 5, also comparing to the 50 Hz hysteresis loops. The structural phase change from the (almost) ferroelectric simple hysteresis for PZT (92/8) to a well pronounced double hysteresis loop is clearly visible for both switching methods. As the Zr-content increases, the two minor cycles drift to higher electric fields.

The phase transition fields and the maximum polarization of the PZT thin films are shown in Fig. 6a and b for PZT (92/8) to PZT (100/0), respectively. The characteristic shift to higher transition fields for compositions more far from the structural phase boundary is well visible. The width of the hysteresis loops and the maximum polarization remain rather constant for all antiferroelectric compositions (except

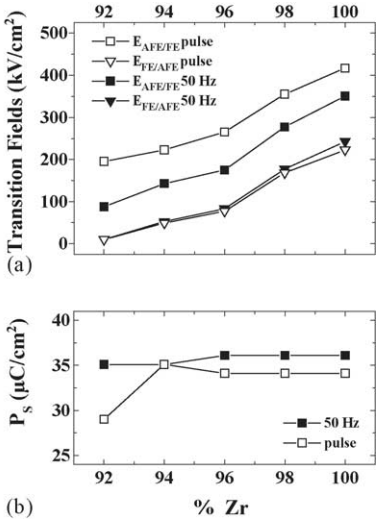

Fig. 6. 50 Hz and pulse phase transition fields $E_{AFE–FE}$ and $E_{FE–AFE}$ (a) and the corresponding maximum polarization (b) for different Zr/Ti ratio.

PZT (92/8) which is at the structural phase boundary) and is very comparable for the 50 Hz and the pulse phase transition measurements.

6. Conclusion

We have investigated the electric field induced phase transitions in antiferroelectric PZT thin films and compared the dynamic behavior of the 50 Hz and the pulse phase transition process. From the voltage and current waveform signals, the

AFE–FE transition field can be deduced, showing an onset of the transition almost independent from the applied voltage, and a phase transition time which is mainly determined by the circuit parameters. The spontaneous FE–AFE relaxation does not depend on the initially effectuated forwards transition. “Pulse hysteresis loops” may be established from the voltage and current signals, showing that at high frequencies almost the same polarization may be induced as in the case of a 50 Hz transition. The AFE–FE forwards transition field, however, is higher in the case of the fast transition. Polarization values for unipolar pulse sequences are slightly smaller than these for bipolar sequences, reflecting an existing remanent polarization value by a shift of the zero polarization level.

References

1. Pan, W. Y., Gu, W. Y. and Cross, L. E., Transition speed on switching from a field-induced ferroelectric to an antiferroelectric upon the release of an applied electric field in (Pb,La)(Zr,Ti,Sn)O_3 antiferroelectric ceramics. *Ferroelectrics*, 1989, **99**, 185–194.
2. 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.
3. 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**, 593–595.
4. Seveno, R. and Gundel, H. W., Preparation of antiferroelectric PZT thin films on bare and RuO_2 coated steel substrates. *Integrated Ferroelectrics*, 2001, **33**, 185–197.
5. Seveno, R., Averty, D. and Gundel, H. W., Preparation and characterization of antiferroelectric PZT thin films on steel substrates using intermediate oxide layers. *Ferroelectrics*, 2002, **271**, 241–246.
6. Fatuzzo, E. and Merz, W. J., *Ferroelectricity*. North Holland Publishing Company, Amsterdam, 1967.
7. Gundel, H. W., Limousin, P., Seveno, R. and Averty, D., Pulse polarization inversion and phase transition in ferroelectric and antiferroelectric thick films. *J. Eur. Ceram. Soc.*, 2001, **21**, 1619–1623.