Aging in epitaxial ferroelectric PbTiO₃ films

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Ability of epitaxial perovskite oxide ferroelectric films to maintain a poled polarization state on a long-term scale is crucial for advanced devices employing such films. Here polarization relaxation with time, or aging, is experimentally studied in epitaxial capacitor heterostructures of PbTiO₃ sandwiched between SrRuO₃ and Pt electrodes. The relaxation obeys logarithmic time-decay for the time 10²–10⁵ s after poling pulses. The decay is by factor ~10 slower than that reported for polycrystalline films. Our experimental results show that existing models are insufficient for epitaxial films.

Keywords: Ferroelectric; epitaxy; capacitor; aging.

1. Introduction

Perovskite-type oxide ferroelectrics (FE) are known for their spontaneous and switchable polarization, large dielectric permittivity, huge piezoelectric coefficient, strong electro-optic, pyro-electric, photo-voltaic, and other effects. Mainstream applications of bulk FEs are discrete capacitors, numerous electromechanical and optoelectronic devices, and radiation sensors. Progress in technology of single-crystal epitaxial FE films, including growth on Si substrates, opens way to innovative nano- and microscale FE devices.^{1–3} It should be noted that memory devices have long been considered as the main application of thin FE films.^{4–9} The related research has been focused on dynamic polarization, leakage, switching, imprint, fatigue, and fast retention on a time scale of 10^{–7}–1 s in FE thin-film capacitors. However, epitaxial FE films can enable a wider class of advanced devices, which employ FE polarization or effects associated with polarization. An important issue for these devices is the ability of FE film to maintain a poled polarization state on a long-term scale extending to months or years.

As known, bulk FE ceramics exhibit gradual degradation of polarization with time under equilibrium external conditions, or ageing.^{10–12} A characteristic feature of this process is the decreasing dielectric constant. Local depolarizing fields are believed to be responsible for the FE degradation. Importantly, FE ceramics contain grains with random orientation of the crystal lattice of the grains. When electric field exceeding a coercive one is applied, the polarization in each of the grains orients along crystal axes closest to the field direction. Discontinuities of the polarization create bound surface charges at all grain boundaries and, thus, result in

local depolarizing fields. When the external field is removed, mobile charge carriers can migrate and pile up at the grain boundaries to screen the local depolarizing fields. The piling up of the screening space charge can explain ageing in bulk ceramic samples and ceramic-type films.^{13,14}

In contrast to extensive studies of ageing in bulk ceramic samples,¹⁴ a fast polarization decay on a time scale of 10^{–7}–1 s only has been studied in FE films.^{15–20} It has been generally accepted that the main reason for short-time relaxation is a global depolarizing field (in contrast to local fields in ceramics) which exists due to imperfect screening of polarization charges at the electrode-film interfaces. The theoretical concept of depolarizing-field-driven relaxation in thin films has been recently extended for a longer time scale > 100 s.²¹

Compared to bulk and thin-film ceramic FEs, epitaxial FE films are free of ceramics-type grain boundaries, possess a strict uniform orientation of crystal axes, and may experience anisotropic lattice strain. Moreover, epitaxial FE capacitor heterostructures may employ different materials of the top and bottom electrodes, possessing different work functions. Thus besides the global depolarizing field, also internal field of other origin can principally affect FE relaxation. The long-term polarization relaxation and microscopic mechanisms responsible for ageing in epitaxial FE thin-film capacitors are not explored.

Here we experimentally investigate ageing in capacitor heterostructures formed by epitaxial films of PbTiO₃ (PTO) sandwiched between SrRuO₃ (SRO) and Pt electrodes. PTO is chosen as an archetypical well studied perovskite-type ferroelectric. Ageing is followed by measuring capacitance as a function of time. We show that the capacitance relaxation

obeys logarithmic time-decay for time longer than 10^2 – 10^3 s, with the decay rate being much slower than that reported for polycrystalline films.

2. Experiment

Epitaxial heterostructures of the PTO films (thicknesses of 120, 200, and 300 nm as determined by cross-sectional transmission electron microscopy) and SRO bottom electrode layers (thicknesses of 50–100 nm) were grown by pulsed laser deposition onto (001)SrTiO₃ (STO) single-crystal substrates (MTI Corp.). The substrate temperature of 700°C and oxygen pressure of 20 Pa were kept during deposition. Also a 300-nm-thick PTO film was deposited using pre-ablated PTO ceramic target. The procedure is known to induce lead and/or oxygen vacancies in the PTO deposit because of compositional changes on the surface of the ablated PTO target.^{22–25} The sample is denoted as “300*-nm” herein.

Room temperature crystal structure was inspected in the PTO and SRO films by X-ray diffraction on a high-resolution Bruker D8 DISCOVER diffractometer. The Θ -2 Θ scans, ϕ -scans, reciprocal space maps, and ω -rocking curves were acquired in the directions of specular and nonspecular diffractions of the substrates, SRO electrode layers, and PTO films. Typical examples are shown in Fig. 1. The PTO and SRO films are perovskite-type, highly oriented with (001) planes parallel to the (001) surface of the STO substrates and with [100] in-plane

crystal directions parallel to the [100] direction of the STO substrates. The PTO films are tetragonal with the volume fractions of *c*-domains 50–90%. The out-of-plane lattice parameters of the *c*-PTO films are $c = 4.098$ – 4.129 Å. They differ from that of $c_0 = 4.156$ Å in bulk PTO and evidence the presence of anisotropic lattice strain in the PTO films. An out-of-plane strain s_c is calculated as $s_c = (c/c_0 - 1)$. The thicknesses and microstructural parameters of PTO are summarized in Table 1. We notice that X-ray diffraction has not revealed a difference between the 300-nm-thick and 300*-nm-thick films. We also notice that the strain state in the films differs from that in Ref. 26. A detailed study of crystal structure and lattice strain in the epitaxial PTO films has been reported elsewhere.²⁷

The PTO thin film capacitors with Pt circular top electrodes (area of 0.2 mm²) were formed by pulsed laser deposition of Pt using shadow mask. The impedance of the capacitors was measured by an HP 4284 LCR meter at room temperature. The frequency and amplitude of the sinusoidal ac voltage were $f = 10^2$ – 10^6 Hz and $V_{AC} = 10$ mV, correspondingly. The dielectric hysteresis was inspected by sweeping biasing dc voltage V_{DC} superimposed with probing ac voltage. The impedance was analyzed and the capacitance was estimated using equivalent circuit modeling of a leaky capacitor.^{28,29} Ferroelectric properties were evaluated by measuring dynamic polarization and switching current as a function of voltage using TF 2000E Analyzer (aixACCT Systems GmbH) and Precision LCII Ferroelectric Tester (Radiant Technologies, Inc.). Ageing was studied by inspecting capacitance as a function of time after applying poling pulses with magnitude of 8 V, duration 20 s, and of different polarity. In all measurements, the electric field was applied and the response was measured along the out-of-plane $\langle 100 \rangle$ crystal direction of the *c*-PTO films.

3. Results

The PTO capacitors exhibit frequency dispersion of the measured capacitance C and loss factor $\tan D$ (Fig. 2). Such behavior is typical for FE thin-film capacitors using oxide electrodes.^{28,29} The increased C and $\tan D$ in a lower frequency range $f < 1$ kHz are caused by Ohmic resistance of PTO which is relatively small (compared to bulk samples) because of nanometer-scale thickness of PTO. High losses are observed in a broader frequency range in the 300*-nm-thick PTO film (Fig. 2(d)). This behavior can be explained by an additional decrease of the PTO resistance due to formation of lead and/or oxygen vacancies during PLD from pre-ablated target.^{22–25} Assuming that the low-frequency losses are related to the PTO resistance, the dynamic resistance R_F of the PTO films can be estimated as $R_F \approx (2\pi \cdot \tan D \cdot C)^{-1}$.^{28,29} The resistance is approximately 6 kΩ in the 300*-nm-thick PTO and it is larger than 10 MΩ in other films. The small resistance indicates the presence of defects in the specially prepared 300*-nm-thick film.

Fig. 1. Typical X-ray diffraction patterns in the grown heterostructures. (a) Θ -2 Θ scan in the stack with 300-nm-thick PTO. Diffractions from PTO, STO, and SRO are marked by f, e, and s, correspondingly. (b) Reciprocal space map around the (002) reciprocal lattice points in the stack with 200-nm-thick PTO. Here reciprocal lattice units (r.l.u.) of STO substrate are used. (c) ω -rocking curves along the (002) and (200) PTO diffraction peaks in the stack with 200-nm-thick PTO.

Fig. 2. (a)–(d) Capacitance C and (e)–(h) loss factor $\tan D$ as a function of frequency f in the PTO capacitors with the thickness of PTO (a), (e) 120 nm, (b), (f) 200 nm, (c), (g) 300 nm, and (d), (h) 300* nm.

The drop of capacitance and increase of losses in a higher frequency range of $f > 100$ kHz are related to conducting properties of the thin SRO films. A nonzero resistance of the SRO film is mainly responsible for a contact resistor in series to leaky capacitor in equivalent circuit of thin-film capacitor stack.^{28,29} The capacitance weakly changes with frequency and the losses are minimal at frequencies $f = 1$ –100 kHz. Frequency $f = 10$ kHz from this range is selected for a further dielectric characterization of the capacitors.

The dynamic polarization–voltage P – V hysteresis loops (Fig. 3) and the corresponding current–voltage I – V loops (Fig. 4) evidence the presence and switching of FE polarization in all capacitors except the 300*-nm one (Figs. 3(d) and 4(d)). The sloped double P – V loop in the 300*-nm PTO film (Fig. 3(d)) is consistent with the loops typically observed when dopants or defects are introduced into Pb-containing FEs.^{30,31} The fields created by charged and/or dipolar defects are superimposed with external biasing field, resulting in peculiar switching current, too (Fig. 4(d)). This behavior agrees with the high losses and small resistance, and confirms the presence of defects in the 300*-nm-thick PTO film.

The capacitors demonstrate butterfly-type dielectric C – V_{DC} hysteresis loops (Fig. 5). The hysteresis originates from the presence and switching of FE polarization.³² The sharp peaks of capacitance suggest abrupt change of polarization at coercive voltages V_c . Also the observed difference between the dynamic and dielectric coercive voltages agrees with the results in Ref. 32. The dielectric hysteresis loops are clearly asymmetric: the voltages V_c and maxima in capacitance at

positive bias V_{DC} differ from those at negative V_{DC} . The loops are characterized by width $2V_c = |V_c^+| + |V_c^-|$, where V_c^+ and V_c^- are the positive and negative coercive voltages, correspondingly. An offset voltage V_0 is determined as $V_0 = 1/2(|V_c^+| - |V_c^-|)$. The voltage offset is commonly related to an internal electric field. The main source of the field in FE thin-film capacitors with different materials of the top and bottom electrodes is different work-functions of the electrodes. Here, the offset is dominated by a contact potential at the Pt–film interface.³³ The offset $V_0 \approx (0.6$ – $0.8)$ V is approximately similar in all of the PTO capacitors except a smaller $V_0 \approx 0.1$ V in the capacitor with the 300*-nm film. The increased density of charge carriers in the 300*-nm film is mainly responsible for the smaller in-built potential therein. The coercive field is determined as $E_c = 1/2(2V_c)/d$ and it increases from 75 to 145 kV/cm with decreasing thickness d of the PTO films from 300 to 120 nm. Notice that the field is $E_c \approx 183$ kV/cm in the 300*-nm film compared to $E_c \approx 75$ kV/cm in the 300-nm film. The observed very large coercive field in the 300*-nm film can be attributed to pinning of domain walls by defects. Also domains are known to be pinned by the SRO–PTO interface.³⁴ With decreasing PTO thickness, the volume fraction of the interface-pinned domains increases, that leads to the larger coercive fields.

Interestingly, inspections of the virgin unpoled capacitors show that the PTO films are self-polarized (Fig. 6). The initial capacitance is similar to that after sweeping the positive (Figs. 6(a)–6(c)) or negative (Fig. 6(a)) bias. This observation suggests that the fractions of c -domains with the out-of-plane polarization directed towards one of the electrodes (SRO or

Fig. 3. Dynamic polarization-voltage P – V loops measured at frequency $f = 1$ kHz in the PTO capacitors with the thicknesses of PTO (a) 120 nm, (b) 200 nm, (c) 300 nm, and (d) 300* nm.

Pt) exceed those with polarization directed towards the other electrode in the as-deposited films. As shown theoretically in Ref. 35, such factors as film–substrate lattice mismatch, misfit dislocations, surface piezoelectric effect, surface tension, and depolarization field influence self-polarization. All these factors are interconnected and could influence ageing behavior too.

Next we inspect the FE relaxation by applying poling dc pulses and measuring capacitance as a function of time after the end of pulse. The capacitor with the 300*-nm PTO film cannot be poled by the positive pulse of 8 V and the relaxation is shown after the negative pulse only. As seen from Fig. 7, plots of capacitance versus logarithm of time for $t > 100$ s are fitted well by a linear dependence $C = C_0 - \alpha \ln(t)$, where α is the long-term relaxation coefficient. The relaxation coefficients α extracted from the linear fits are summarized in Table 1. In order to compare decay rates of the dielectric permittivity in our PTO films with those previously reported in polycrystalline FE films, the coefficients $\beta = \alpha d/\epsilon_0 S$ were determined in the PTO films and extracted from the data in Refs. 36 and 37, correspondingly. Here d and S are the thickness of the PTO film and the area of the top electrode, respectively. The epitaxial PTO films exhibit decay coefficients of approximately $\beta \approx 0.1$ – 0.5 , i.e., by factor ~ 10 smaller than those of 1.5–5 in the polycrystalline films.^{36,37} The small decay coefficients evidence excellent stability of polarization achieved here.

Fig. 4. Current-voltage I – V loops measured at frequency $f = 1$ kHz in the PTO capacitors with the thickness of PTO (a) 120 nm, (b) 200 nm, (c) 300 nm, and (d) 300* nm.

The relaxation in the PTO capacitors is asymmetric: it depends on polarity of the dc pulses. The logarithmic-type relaxation has been modeled as a result of polarization switching which is driven by a time-dependent depolarizing field in Ref. 21. The depolarizing field has been assumed to originate from incomplete screening of polarization charge by electrodes. Here, different screening properties of the SRO and Pt electrodes are responsible for dependence of relaxation coefficients on polarity of the poling pulses.

The model²¹ predicts that the relaxation should become faster as FE film thickness decreases. However, it is not the case in the PTO capacitors. Although the relaxation coefficients in the 200-nm-thick film are somewhat smaller than those in the 120-nm-thick film, the decay is faster in the 300-nm-thick film. As suggested above, the presence of a -domains additionally contributes to the decay in this film. The presence of domains and their role in ageing are not taken into account in the model.²¹

It is worth mentioning that FE ageing is generally connected with the charge carriers, whose density depends on density of point defects, and with the defects themselves.^{13,14,38} The relaxation rate should increase with increasing density of defects. Here, defects are clearly present in the 300*-nm-thick film, which is thus expected to exhibit a faster relaxation compared with the 300-nm-thick film. However, the experimentally found rate is rather slow in the 300*-nm-thick film. This observation implies that other

Fig. 5. Capacitance C as a function of dc voltage V_{DC} (electric field E) in the PTO capacitors with the thicknesses of PTO (a) 120 nm, (b) 200 nm, (c) 300 nm, and (d) 300* nm.

(than defects) factors dominate ageing in epitaxial films. Again, the model²¹ is insufficient for ageing in epitaxial films.

The presented experimental results suggest that multiple microscopic mechanisms are responsible for the stability and

Fig. 6. Capacitance C as a function of dc voltage V_{DC} in the first dc sweeps in the unpoled PTO capacitors with the thicknesses of PTO (a) 120 nm, (b) 200 nm, (c) 300 nm, and (d) 300* nm. Arrows show directions of the dc sweeps. Solid circles mark the initial states.

Fig. 7. Capacitance C as a function of logarithm of time after poling pulses, $\ln(t)$, in the PTO capacitors with the thicknesses of PTO (a) 120 nm, (b) 200 nm, (c) 300 nm, and (d) 300* nm.

relaxation of FE polarization. It is worth noticing that interfaces between epitaxial ferroelectric and conducting oxides provide specific sites for pinning or nucleation of domains.³⁴ The presence of lattice strain and strain distribution across film thickness, also specific for epitaxial films, favor a certain domain configuration. In particular, as seen from Table 1, the best polarization stability is achieved in the 200-nm-thick PTO film, which possesses the largest volume fraction of c -domains and experiences the smallest lattice strain. Finally, unintentional defects pin domain walls. More detailed and systematic studies in a broader class of epitaxial heterostructures are required in order to specify dominating mechanisms responsible for stabilization of FE domains and for long-term FE relaxation therein. Concurrently, theoretical modeling for ageing in epitaxial films should be developed.

Table 1. Microstructural and electrical characteristics of the PTO films.

Thickness d , nm	120	200	300	300*
Volume fraction of c -domains, %	80	90	50	50
Lattice parameter c , Å	4.097	4.129	4.115	4.115
Out-of-plane strain s_c , %	-1.4	-0.7	-1.0	-1.0
Loss $\tan \delta$ at 10 kHz	0.036	0.018	0.023	4.5
Double coercive voltage $2V_c$, V	3.5	5.5	4.5	11
Voltage offset V_0 , V	0.8	0.6	0.8	0.1
Coercive field E_c , kV/cm	145	138	75	183
Long-term relaxation coefficient α , 10^{-3} nF	1.8/3.0	1.2/1.7	0.4/3.2	2.7
Permittivity relaxation coefficient β	0.12/0.20	0.13/0.19	0.07/0.54	0.46

4. Conclusions

FE relaxation on time scale of $1\text{--}10^5$ s is experimentally studied in capacitors of epitaxial tetragonal *c*-PTO films with thicknesses of 120–300 nm sandwiched between epitaxial SRO bottom electrodes and Pt top electrodes. The FE and dielectric hysteresis loops evidence the presence and switching of FE polarization, and self-poling in PTO. The long-term capacitance decay is proportional to logarithm of time after poling pulses. The decay rate is by factor 5–10 slower than in polycrystalline films. The achieved relaxation properties are discussed in terms of the existing models. Our experimental results show that theoretical models for ageing are insufficient for epitaxial films.

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References

- R. A. McKee, F. J. Walker and M. F. Chisholm, Crystalline oxides on silicon: The first five monolayers, *Phys. Rev. Lett.* **81**, 3014 (1998).
- R. A. McKee, G. J. Walker and M. F. Chisholm, Physical structure and inversion charge at a semiconductor interface with a crystalline oxide, *Science* **293**, 468 (2001).
- S. H. Baek, J. Park, D. M. Kim, V. A. Aksyuk, R. R. Das, S. D. Bu, D. A. Felker, J. Lettieri, V. Vaithyanathan, S. S. N. Bhargava, N. Bassiri-Gharb, Y. B. Chen, H. P. Sun, C. M. Folkman, H. W. Jang, D. J. Kreft, S. K. Streiffer, R. Ramesh, X. Q. Pan, S. Trolier-McKinstry, D. G. Schlom, M. S. Rzchowski, R. H. Blick and C. B. Eom, Giant piezoelectricity on Si for hyperactive MEMS, *Science* **334**, 958 (2011).
- J. F. Scott and C. A. P. De Araujo, Ferroelectric memories, *Science* **246**, 1400 (1989).
- C. P. De Araujo, G. W. Taylor and J. F. Scott, *Ferroelectric Thin Films: Synthesis and Basic Properties* (Gordon and Breach, Amsterdam, 1996).
- O. Auciello, J. F. Scott and R. Ramesh, The physics of ferroelectric memories, *Phys. Today* **51**, 22 (1998).
- N. Setter, D. Damjanovic, L. Eng et al., Ferroelectric thin films: Review of materials, properties, and applications, *J. Appl. Phys.* **100**, 051606 (2006).
- V. Fridkin and S. Ducharme, *Ferroelectricity at the Nanoscale: Basics and Applications* (Springer, Berlin Heidelberg, 2014).
- E. Y. Tsymlal, E. R. A. Dagotto, C. B. Eom and R. Ramesh, *Multifunctional Oxide Heterostructures* (Oxford University Press, Oxford, 2012).
- K. W. Plessner, Ageing of the dielectric properties of barium titanate ceramics, *Proc. Phys. Soc. London Sect. B* **69**, 1261 (1956).
- K. Okazaki, *Ceramics Engineering for Dielectrics* (Gakken Shya, Tokyo, 1969).
- M. Takahashi, Space charge effect in lead zirconate titanate ceramics caused by the addition of impurities, *Jpn. J. Appl. Phys.* **9**, 1236 (1970).
- Y. A. Genenko, J. Glaum, O. Hirsch, H. Kungl, M. J. Hoffmann and T. Granzow, Aging of poled ferroelectric ceramics due to relaxation of random depolarization fields by space-charge accumulation near grain boundaries, *Phys. Rev. B* **80**, 224109 (2009).
- Y. A. Genenko, J. Glaum, M. J. Hoffmann and K. Albe, Mechanisms of aging and fatigue in ferroelectrics, *Mater. Sci. Eng. B* **192**, 52 (2015).
- J. M. Benedetto, R. A. Moore and F. B. McLean, Effects of operating conditions on the fast-decay component of the retained polarization in lead zirconate titanate thin films, *J. Appl. Phys.* **75**, 460 (1994).
- I. G. Jenkins, T. K. Song, S. Madhukar, A. S. Prakash, S. Aggarwal and R. Ramesh, Dynamics of polarization loss in (Pb, La)(Zr, Ti)O₃ thin film capacitors, *Appl. Phys. Lett.* **72**, 3300 (1998).
- O. Lohse, M. Grossmann, U. Boettger, D. Boltz and R. Waser, Relaxation mechanism of ferroelectric switching in Pb(Zr,Ti)O₃ thin films, *J. Appl. Phys.* **89**, 2332 (2001).
- B. S. Kang, J. G. Yoon, T. W. Noh, T. K. Song, S. Seo, Y. K. Lee and J. K. Lee, Polarization dynamics and retention loss in fatigued PbZr_{0.4}Ti_{0.6}O₃ ferroelectric capacitors, *Appl. Phys. Lett.* **82**, 248 (2003).
- A. Q. Jiang, Y. Y. Lin, T. A. Tang and Q. Zhang, Asymmetry of domain forward switching and multilevel relaxation times of domain backswitching in antiferroelectric Pb_{0.99}Nb_{0.02}(Zr_{0.84}Sn_{0.12}Ti_{0.04})_{0.98}O₃ thin films, *Appl. Phys. Lett.* **90**, 142901 (2007).
- P. Gao, C. T. Nelson, J. R. Jokisaari, Y. Zhang, S. H. Baek, C. W. Bark, E. Wang, Y. Liu, J. Li, C. B. Eom and X. Pan, Direct observations of retention failure in ferroelectric memories, *Adv. Mater.* **24**, 1106 (2012).
- X. J. Lou, Polarization retention on short, intermediate, and long time scales in ferroelectric thin films, *J. Appl. Phys.* **105**, 094107 (2009).
- J. S. Horwitz, K. S. Grabowski, D. B. Chrisey and R. E. Leuchtner, In situ deposition of epitaxial PbZr_xTi_(1-x)O₃ thin films by pulsed laser deposition, *Appl. Phys. Lett.* **59**, 1565 (1991).
- D. J. Lichtenwalner, O. Auciello, R. Dat and A. Kingon, Investigation of the ablated flux characteristics during pulsed laser ablation deposition of multicomponent oxides, *J. Appl. Phys.* **74**, 7497 (1993).
- C. G. Tyrrell, T. H. York, L. G. Coccia and I. W. Boyd, Kinetic energy distributions of ions ejected during laser ablation of lead zirconate titanate and their correlation to deposition of ferroelectric thin films, *Appl. Surf. Sci.* **96–98**, 769 (1996).
- C. S. Ma, S. K. Hau, K. H. Wong, P. W. Chan and C. L. Choy, The role of ambient gas scattering effect and lead oxide formation in pulsed laser deposition of lead-zirconate-titanate thin films, *Appl. Phys. Lett.* **69**, 2030 (1996).
- S. Venkatesan, A. Vlooswijk, B. J. Kooi, A. Morelli, G. Palasantzas, J. T. M. De Hosson and B. Noheda, Monodomain strained ferroelectric PbTiO₃ thin films: Phase transition and critical thickness study, *Phys. Rev. B* **78**, 104112 (2008).
- J. Peräntie, M. S. Stratulat, J. Hannu, H. Jantunen, M. Tyunina, Enhancing polarization by electrode-controlled strain relaxation in PbTiO₃ heterostructures, *APL Mater.* **4**, 016104 (2016).
- M. Tyunina and J. Levoska, Application of the interface capacitance model to thin-film relaxors and ferroelectrics, *Appl. Phys. Lett.* **88**, 262904 (2006).

- ²⁹M. Tyunina, M. Plekh, M. Antonova and A. Kalvane, Ferroelectric transitions in epitaxial $\text{Pb}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ films studied by dielectric analysis, *Phys. Rev. B* **84**, 224105 (2011).
- ³⁰M. I. Morozov and D. Djmjanovic, Hardening-softening transition in Fe-doped $\text{Pb}(\text{Zr,Ti})\text{O}_3$ ceramics and evolution of the third harmonic of the polarization response, *J. Appl. Phys.* **104**, 034107 (2008).
- ³¹A. Chandrasekaran, D. Damjanovic, N. Setter and N. Marzari, Defect ordering and defect-domain-wall interactions in PbTiO_3 : A first-principles study, *Phys. Rev. B* **88**, 214116 (2013).
- ³²L. Pintilie, M. Lisca and M. Alexe, Polarization reversal and capacitance-voltage characteristic of epitaxial $\text{Pb}(\text{Zr,Ti})\text{O}_3$ layers, *Appl. Phys. Lett.* **86**, 192902 (2007).
- ³³L. Pintilie, I. Vrejoiu, D. Hesse, G. LeRhun and M. Alexe, Ferroelectric polarization-leakage current relation in high quality epitaxial $\text{Pb}(\text{Zr,Ti})\text{O}_3$ films, *Phys. Rev. B* **75**, 10403 (2007).
- ³⁴M. G. Han, M. S. J. Marshall, L. Wu, M. A. Schofield, T. Aoki, R. Twisten, J. Hoffman, F. J. Walker, C. H. Ahn and Y. Zhu, Interface-induced nonswitchable domains in ferroelectric thin films, *Nat. Commun.* **5**, 4693 (2014).
- ³⁵M. D. Glinchuk, A. N. Morozovska and E. A. Eliseev, Mismatch-induced electric field as reason of self-polarization phenomenon and electret state appearance in the strained ultrathin ferroelectric films, *J. Appl. Phys.* **99**, 114102 (2006).
- ³⁶H. Y. Guo, J. B. Xu, Z. Xie, E. Z. Luo, I. H. Wilson and W. L. Zhong, Ferroelectric relaxation of $(\text{Pb}_{0.76}\text{Ca}_{0.24})\text{TiO}_3$ thin film, *Solid State Commun.* **121**, 603 (2002).
- ³⁷A. L. Kholkin, A. K. Tagantsev, E. L. Colla, D. V. Taylor and N. Setter, Piezoelectric and dielectric aging in $\text{Pb}(\text{Zr,Ti})\text{O}_3$ thin films and bulk ceramics, *Integr. Ferroelectr.* **15**, 317 (1997).
- ³⁸Z. Feng and X. Ren, Striking similarity of ferroelectric aging effect in tetragonal, orthorhombic and rhombohedral crystal structures, *Phys. Rev. B* **77**, 134115 (2008).