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An influence of mechanical stresses on the magnitude of the internal field in lead zirconate titanate thin films

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Received April 7, 2022

Revised June 9, 2022

Accepted June 23, 2022

In self-polarized lead zirconate titanate thin films formed on platinized silicon substrates, a significant increase in the internal electric field was observed as a result of long-term aging. To explain this phenomenon, a mechanism is proposed for the formation of the internal field associated with the diffusion of charged oxygen vacancies, which, in turn, is due to the action of a mechanical stress gradient. The diffusion coefficient of charged oxygen vacancies was estimated to be $\sim 3 \cdot 10^{-16} \text{ cm}^2/\text{s}$.

Keywords: thin films, lead zirconate titanate, internal field, Gorsky effect.

DOI: 10.21883/TPL.2022.08.55058.19218

Most recently, thin ferroelectric films of lead zirconate-titanate (PZT) are increasingly used in microelectromechanics as acoustic emitters and receivers, various sensors, harvesters, IR devices, magnetoelectric converters, etc. [1–3]. The most effective are self-polarized thin films, in which macroscopic polarization occurs during their growth (formation of the perovskite phase) and for which no subsequent polarization procedure is required [4,5].

The physical mechanisms leading to the appearance of self-polarization in thin ferroelectric layer due to the appearance of the internal electric field are still controversial. The influence of mechanical stresses arising in polycrystalline films due to the difference in the temperature coefficients of linear expansion of the substrate (mostly silicon) and thin film on the formation of macroscopic polarization is of maximum interest [6–12]. The gradient of mechanical stresses in the ferroelectric film leads to the flexoelectric effect, which is considered in a number of papers as one of the main causes of self-polarization [10–12]. Calculations of the internal field based on the flexoelectric effect show that it is several orders of magnitude smaller than actually observed [8,12]. High-temperature annealing of thin-film capacitor PZT structures at temperatures above the Curie temperature, which leads to the disappearance of the internal field and macroscopic polarization, also states against the flexoelectric effect as the driving force for the appearance of self-polarized state [13]. In this regard, it is necessary to develop a new approach to identify the role of mechanical stresses. For this purpose, in the present paper, we studied the ferroelectric properties of both freshly prepared thin PZT films and those subjected to aging.

Thin PZT films were formed using a two-stage technology [7,14]. Films were deposited in a sputtering chamber of a radio-frequency magnetron. The composition of the sputtered PZT perovskite target corresponded to the region

of the morphotropic phase boundary with the elemental ratio of atoms $\text{Zr/Ti} \approx 54/46$. The substrate was a platinized silicon wafer $375 \mu\text{m}$ thick. The platinum layer 150 nm thick was characterized by $\langle 111 \rangle$ -growth orientation. The thickness of the PZT films was $\sim 500 \text{ nm}$. At the second stage of films formation, to obtain a single-phase perovskite structure, they were annealed in air at 580°C for an hour. Platinum contact pads $100 \times 100 \mu\text{m}$ served as the upper electrodes.

To determine the magnitude of the internal field, we studied the reversible dependences of the permittivity and dielectric losses on an E7-20 immittance meter (measuring field 40 mV , bias voltage $0 - \pm 10 \text{ V}$), as well as dielectric hysteresis loops on a modified Sawyer–Tower unit in alternating electric field (in the range $0 - 600 \text{ kV/cm}$) at a frequency of 1 kHz .

According to the phase analysis results, all the films obtained after high-temperature annealing were characterized by a single-phase perovskite structure with a predominant growth $\langle 110 \rangle$ orientation. Studies of the dielectric properties of thin films were carried out both on freshly prepared capacitor PZT-structures and on those subjected to long-term aging (~ 4 years, i.e. 10^8 s). Fig. 1, *a* shows the dielectric hysteresis loops measured on freshly produced films upon application of the alternating voltage $U_{\text{ext}} = 10$ and 30 V (i.e., electric field E_{ext} values of 200 and 600 kV/cm , respectively), and in Fig. 1, *b* — similar loops obtained on the same samples subjected to long-term aging.

In weak fields ($E_{\text{ext}} = 200 \text{ kV/cm}$) the asymmetry (shift along the abscissa axis) of the hysteresis loops, expressed by the value of the internal field (E_{int}), reached the value $\sim 28 \text{ kV/cm}$. Amplitude increasing of the applied voltage ($U_{\text{ext}} = 30 \text{ V}$ or $E_{\text{ext}} = 600 \text{ kV/cm}$) led to a significant decrease in E_{int} , i.e. to the fact that the hysteresis loop became more symmetrical (Fig. 1, *a*). Significant

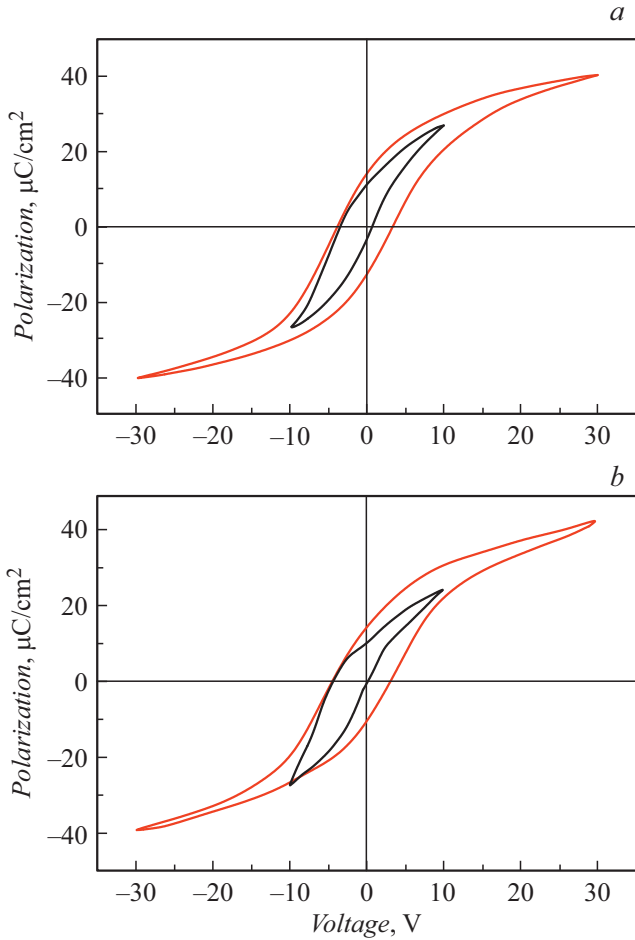


Figure 1. Loops of the dielectric hysteresis of thin PZT films immediately after structure formation (a) and after long-term aging (b) when alternating voltage with amplitude of 10 and 30 V is applied.

changes occurred in the shape of the hysteresis loops as a result of sample aging (Fig. 1, b). When the external field $E_{ext} = 200$ kV/cm was applied, the value of the internal field reached $E_{int} \sim 41$ kV/cm. In strong field ($E_{ext} = 600$ kV/cm), the value of E_{int} was also higher than in freshly prepared films and reached the values $E_{int} \sim 22\text{--}24$ kV/cm.

Based on the fact that self-polarization in the first approximation is proportional to the value of the internal field E_{int} [4], we can conclude that long-term aging led both to increase in the internal field and self-polarization, and to increase in the stability of the macroscopic polar state. We believe that the increase in E_{int} is due to the displacement of charged oxygen vacancies [15] through the film thickness, caused by the action of bending mechanical stresses (Gorsky effect) [16–19]. The Gorsky effect (also called the upward diffusion effect) is often observed in metal alloys subjected to bending mechanical stresses. It means that heavy atoms diffuse in the direction of the gradient of mechanical stresses (i.e., towards the expansion of the volume of the structure), and light atoms — in

the opposite direction (toward the compression of the structure) [16]. This mechanism was later used by Kosevich to describe the diffusion of vacancies in a solid state (Fig. 2) [17]. Subsequently, the effect was used to estimate the diffusion of charged oxygen vacancies in complex oxide dielectrics [18].

In ferroelectric thin films the appearance of a significant internal field and self-polarization are caused by negative (electronic) space charge localized in deep traps near the lower interface [4,5,14], and doubly charged oxygen vacancies are uniformly distributed in the film volume (Fig. 3, a). It is assumed that the action of mechanical stresses acting on the film from the side of the silicon substrate leads to the diffusion of oxygen vacancies towards the free surface of the film and redistribution of the space charge (Fig. 3, b).

The formation of additional space charge ($\Delta\sigma$) in the film due to the vacancies diffusion as a result of aging can be estimated based on the increase in the internal field ($\Delta E_{int} \sim 13$ kV/cm) using the relation $\Delta\sigma \sim \epsilon\epsilon_0\Delta E_{int}$, where ϵ is the relative permittivity, which at room temperature has a value of about 700, and ϵ_0 — dielectric constant. Calculations show that $\Delta\sigma$ is ~ 0.8 $\mu\text{C}/\text{cm}^2$. Assuming that the concentration of oxygen vacancies is $N^V \sim 10^{18} \text{ cm}^{-3}$, and the electron activation energy is $E_e \sim 0.22$ eV [16], the concentration of doubly charged oxygen vacancies can be estimated as $N^{V^{2+}} \sim 1.3 \cdot 10^{16} \text{ cm}^{-3}$. Then the average distance over which the space charge moved through the thickness during aging is estimated by the value $d \sim 10^{-11}$ cm, and the average speed of charge movement $u \sim 10^{-19}$ cm/s.

Under conditions of gradient of mechanical stresses, the speed of vacancy motion (u) is expressed as

$$u = (D_v/kT)f_v, \quad (1)$$

where $f_v = \omega_0 \text{grad}P$ — elastic force acting on the vacancy, k — Boltzmann constant, T — temperature, ω_0 — vacancy

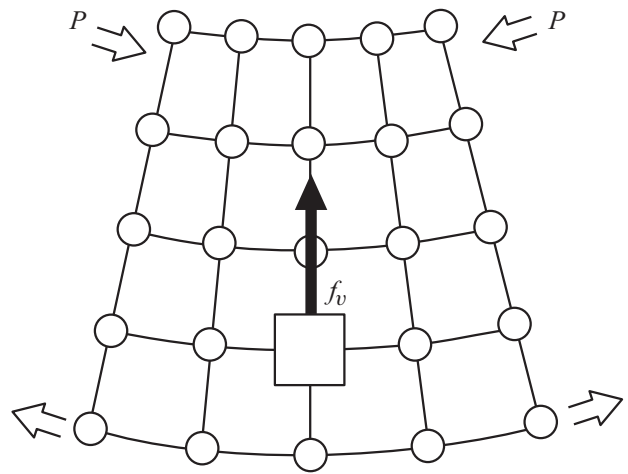


Figure 2. Schematic representation of the movement of charged oxygen vacancy under a gradient of mechanical stresses in thin film.

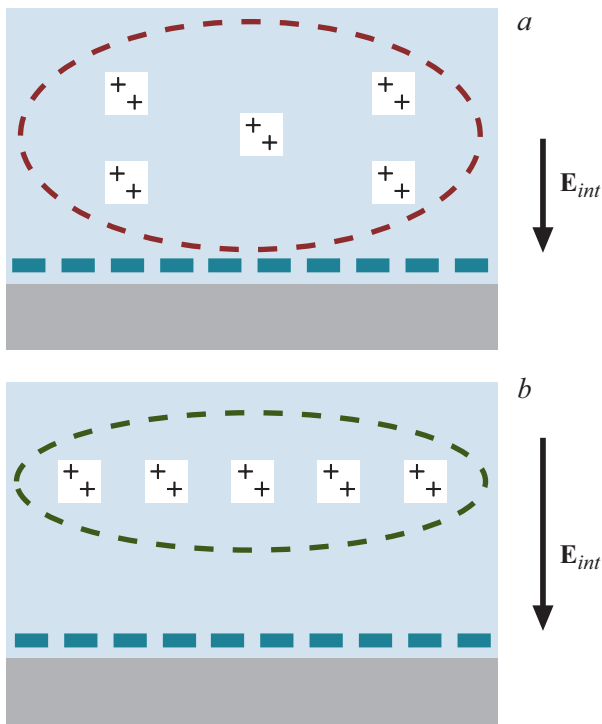


Figure 3. Schematic representation of the space charge distribution and the internal field value E_{int} . *a* — in freshly formed thin PZT film, *b* — after its long-term aging.

volume, D_v — vacancy diffusion coefficient, $\text{grad}P$ — mechanical stress gradient [17]. From this expression one can estimate the diffusion coefficient of oxygen vacancies

$$D_v = u\omega_0 \text{grad}P / kT. \quad (2)$$

The mechanical stress gradient can be expressed as $\text{grad}P = c \text{grad}\eta = c \text{grad}(a/R)$, where c is the elastic constant for the PZT film, η is the strain gradient equal to the ratio of the lattice parameter (a) to the radius of curvature (R) of the PZT film/Si substrate structure. The value of the curvature radius, calculated by the Stoney formula, was calculated based on the condition that a thin film at room temperature is subject to tensile stresses ~ 60 MPa, caused by the difference in the temperature coefficients of linear expansion of the film and the substrate [7]. Based on the calculation result $R \sim 130$ m and literature data for $a \sim 0.4$ nm, $\omega_0 \sim (0.08)^3 \text{ nm}^3$, $c \sim 75$ GPa, $T \sim 300$ K the value D_v is estimated as $\sim 3 \cdot 10^{-16} \text{ cm}^2/\text{s}$.

Among the data on D_v given in the literature, note those obtained in the paper [20], where the values in the absence of applied field were about $5 \cdot 10^{-16} \text{ cm}^2/\text{s}$, which is close enough to the values determined in this paper. Also note that similar (rather high) values of the diffusion coefficient at room temperature can be associated with increase in the diffusion coefficient upon the activation energy decreasing due to mechanical stresses (Zhurkov relation). To determine the quantitative contribution of mechanical stresses and the Gorsky effect to the formation of internal field, it is

necessary to carry out additional more thorough studies, including the use of substrates that differ in the value of the temperature coefficient of linear expansion.

Conflict of interest

The authors declare that they have no conflict of interest.

References

- [1] Y. Ma, J. Son, X. Wang, Y. Liu, J. Zhou, *Coatings*, **11** (8), 944 (2021). DOI: 10.3390/coatings11080944
- [2] L. Song, S. Glinsek, E. Defay, *Appl. Phys. Rev.*, **8** (4), 041315 (2021). DOI: 10.1063/5.0054004
- [3] A.A. Bukharaev, A.K. Zvezdin, A.P. Pyatakov, Yu.K. Fetisov, *Phys. Usp.*, **61** (12), 1175 (2018). DOI: 10.3367/UFNe.2018.01.038279.
- [4] A.L. Kholkin, K.G. Brooks, D.V. Taylor, S. Hiboux, N. Setter, *Integr. Ferroelectrics*, **22** (1-4), 525 (1998). DOI: 10.1080/10584589808208071
- [5] V.P. Afanasjev, A.A. Petrov, I.P. Pronin, E.A. Tarakanov, E.Yu. Kaptelov, J. Graul, *J. Phys.: Condens. Matter*, **13** (39), 8755 (2001). DOI: 10.1088/0953-8984/13/39/304
- [6] T. Ogawa, A. Senda, T. Kasanami, *Jpn. J. Appl. Phys.*, **30** (9S), 2145 (1991). DOI: 10.1143/JJAP.30.2145
- [7] I.P. Pronin, E.Yu. Kaptelov, A.V. Gol'tsev, V.P. Afanas'ev, *Phys. Solid State*, **45** (9), 1768 (2003). DOI: 10.1134/1.1611249.
- [8] A. Gruverman, B.J. Rodriguez, A.I. Kingon, R.J. Nemanich, A.K. Tagantsev, J.S. Cross, M. Tsukada, *Appl. Phys. Lett.*, **83** (4), 728 (2003). DOI: 10.1063/1.1593830
- [9] P.V. Yudin, A.K. Tagantsev, *Nanotechnology*, **24** (43), 432001 (2013). DOI: 10.1088/0957-4484/24/43/432001
- [10] E. Sviridov, I. Sem, V. Alyoshin, S. Biryukov, V. Dudkevich, *Mater. Res. Soc. Symp. Proc.*, **361**, 141 (1994). DOI: 10.1557/PROC-361-141
- [11] L.M. Garten, S. Troler-McKinstry, *J. Appl. Phys.*, **117** (9), 094102 (2015). DOI: 10.1063/1.4913858
- [12] L.A. Delimova, N.V. Zaitseva, V.V. Ratnikov, V.S. Yuferev, D.S. Seregin, K.A. Vorotilov, A.S. Sigov, *Phys. Solid State*, **63**, 1145 (2021). DOI: 10.1134/S1063783421080060.
- [13] S. Okamura, S. Miyata, Y. Mizutani, T. Nishida, T. Shiosaki, *Jpn. J. Appl. Phys.*, **38** (9S), 5364 (1999). DOI: 10.1143/JJAP.38.5364
- [14] I.P. Pronin, E.Yu. Kaptelov, E.A. Tarakanov, V.P. Afanas'ev, *Phys. Solid State*, **44** (9), 1736 (2002). DOI: 10.1134/1.1507258
- [15] D.M. Dolgintsev, V.P. Pronin, E.Yu. Kaptelov, S.V. Senkevich, I.P. Pronin, *Tech. Phys. Lett.*, **45** (3), 246 (2019). DOI: 10.1134/S1063785019030258.
- [16] W.S. Gorsky, *Phys. Z. Sow.*, **8**, 457 (1935).
- [17] A.M. Kosevich, *Sov. Phys. Usp.*, **17**, 920 (1975). DOI: 10.1070/PU1975v017n06ABEH004405.
- [18] V.I. Barbashov, Yu.A. Komysa, *Phys. Solid State*, **47** (2), 238 (2005). DOI: 0.1134/1.1866400.
- [19] I.P. Pronin, S.A. Kukushkin, V.V. Spirin, S.V. Senkevich, E.Yu. Kaptelov, D.M. Dolgintsev, V.P. Pronin, D.A. Kiselev, O.N. Sergeeva, *Mater. Phys. Mech.*, **30** (1), 20 (2017). https://www.ipme.ru/e-journals/MPM/no_13017/MPM130_02_pronin.pdf
- [20] G. Holzlechner, D. Kastner, C. Slouka, H. Hutter, J. Fleig, *Solid State Ionics*, **262**, 625 (2014). DOI: 10.1016/j.ssi.2013.08.027