

PACS: 78.20.-e

Peculiarities and asymmetry of polarization reversal in Pt/PZT-film/Pt:Ti/SiO₂/Si-substrate structures in pyroelectric response investigations

S.L. Bravina, E. Cattan*, N.V. Morozovsky, D. Remiens*

Institute of Physics NASU, 46, prospect Nauky, 03028 Kyiv, Ukraine

E-mail: bravina@iop.kiev.ua

** IEMN-DOAE- MIMM CNRS-UMR 8520, Universite de Valenciennes et du Hainaut- Cambresis, 9, Le Mont Houy, 59313 Valenciennes Cedex, France*

E-mail: denis.remiens@univ.valenciennes.fr

Abstract. By RF magnetron sputtering method the Pt/PZT-film/Pt:Ti-sublayer/SiO₂/Si-substrate structures were prepared and pyroelectric response amplitude and phase behaviour under external voltage application was investigated by photopyroelectric modulation method.

The results of investigation of pyroelectric response – external voltage loops of polarization reversal, pyroelectric response – voltage poling curves and pyroelectric response – time repolarization curves and also dynamic current-voltage characteristics of Pt/PZT/Pt:Ti/SiO₂/Si-substrate structures are presented.

From variation of pyroelectric response in the current and voltage modes the capacity-voltage loops of polarization reversal and poling curves were derived. From asymmetric pyroelectric response – time repolarization curves the voltage behaviour of characteristic times of zero response and saturation was analyzed. Observed transformations of current-voltage characteristics display the considerable voltage and time dependent variation of charge transfer conditions.

The performed investigation has shown the strong correlation between the poling pyroelectric and so ferroelectric and electrical asymmetries. Presented data on the polar and time asymmetry of the conditions of polarization reversal are discussed in the terms of influence of dynamics of space charge asymmetry on pinning conditions under the different polarity of applied voltage in the course of polarization reversal.

Keywords: PZT-film/Si structures, pyroelectric response hysteresis loops, polar and poling asymmetry.

Paper received 20.05.04; accepted for publication 21.10.04.

1. Introduction

Polar PZT ceramics are known as materials with excellent piezoelectric and pyroelectric properties [1, 2], which are retained in PZT films [3, 4]. A good technological compatibility with Si-base of modern electronics makes PZT films be a leader in creation of elements of high-density dynamic random access memories (DRAM's), non-volatile random access memories (NV-RAM's), micro-electro-mechanics (MEM's) and infrared sensorics (IRS's) [3–5].

The practically important electrical characteristics of “metal-PZT-film-metal on Si-substrate” system as those of other systems of such type manifest the well-known set of natural and technological asymmetries connected with

specificity of reversing the poling state in the electroded ferroelectric film on the substrate [3–5].

The asymmetries of ferroelectric hysteresis loops and current-voltage characteristics were found not only for strongly asymmetric Au/PZT/Si heterojunction structures [6] and also for weak asymmetric Ni/PZT/Pt/Si structures, which also possess the pyroelectric asymmetry [7].

Pyroelectricity is well known not only as important applicable effect [2] but also as a high informative method of the polar state investigation [8], especially when pyroelectric response amplitude and phase behaviour was investigated by photopyroelectric modulation method [8]. In this method the sample is investigated in the operation modes of pyroelectric detector of radiation (PDR).

In this paper we present the results of investigations of polar and poling asymmetries of the set of pyroelectric

characteristics of Pt/PZT-film/Pt:Ti/SiO₂/Si-substrate systems obtained by photopyroelectric modulation method.

2. Experimental

2.1. Samples

The samples of PZT films were prepared by radio frequency magnetron sputtering method on platinized SiO₂/Si substrate.

The bottom Pt:Ti-bilayer was formed by platinum bottom electrode with a titanium adhesive layer (150 nm of Pt and 10 nm of Ti) deposited on 350 nm SiO₂ layer on (100) *n*-type Si substrate.

For substrate stabilization the annealing treatment of the Pt:TiO_x/SiO₂/Si-substrate structure just before of PZT deposition was performed at 350–400°C. Then PZT film was deposited on the bottom electrode. The sputtering target obtained by uniaxially cold pressing includes the mixture of PbO, TiO₂ and ZrO₂ in the stoichiometric composition. The polar perovskite phase of the PZT-film was obtained by post-annealing treatment at 600–650°C during 0,5–1 hour. The top Pt-electrodes were deposited through a shadow mask by sputtering procedure, which was followed by a lift-off, and have ≈1 mm² of area. The details of the sputtering conditions were described elsewhere [9, 10].

The obtained PZT-films with Zr/Ti ratio 54/46 are near the morphotropic phase boundary, which corresponds to better performances for bulk PZT ceramics.

The thickness of the main components are the following: 150 nm for the top Pt-electrode, 1.9 μm for layer for PZT layer, 350 μm for Si substrate.

Each element has a current-carrying thin stripe with a circle current electrode of 1 mm of diameter on the stripe end.

2.2. Measurements

For the investigations of pyroelectric and ferroelectric characteristics the measuring set for complete pyroelectric and ferroelectric characterization [8] was used.

The measurements of amplitude U_{π} and phase φ_{π} of pyroelectric response were carried out by photopyroelectric modulation method in the current and voltage modes. In the current mode $U_{\pi} = U_{\pi 1} \propto \gamma c_1$, and in the voltage mode $U_{\pi} = U_{\pi 2} \propto \gamma c_1 \varepsilon f_m$, (here γ is the pyroelectric coefficient, c_1 is the volume heat capacity, ε is the dielectric permittivity, f_m is the modulation frequency) [2, 8]. Since $U_{\pi 1} \propto \gamma$ and $U_{\pi 2} \propto \gamma \varepsilon$, the dielectric ratio $D_{\pi} = U_{\pi 1} / U_{\pi 2} f_m \propto \varepsilon_{\pi}$ reflects the behaviour of dielectric permittivity obtained by pyroelectric measurements.

Under examination of loops of pyroelectric response hysteresis (U_{π} - V -loops and φ_{π} - V -loops) the Pt/PZT/Pt:Ti/Si structure was investigated in the operating mode of ferroelectric bolometer, at that applied d.c. voltage V_{dc} was varied stepwise $\pm(0,25-1)$ V cyclically in the range

of $-10 \text{ V} \leq V_{dc} \leq +10 \text{ V}$. The same mode was used under investigations of variations of transient pyroelectric response in due course under application of d.c. voltage (U_{π} - t - and φ_{π} - t -curves). The $U_{\pi 1,2}$ - V -curves were obtained after previous pulse depoling of the samples up to zero response, which remains during a long period without poling voltage application. The U_{π} - t -curves were obtained after previous 11 V d.c. poling of the samples up to saturated U_{π} value, which remains during a long period without poling voltage application.

For minimization of polarization reversal contribution under dynamic current-voltage characterization (I - V -curves) the unipolar saw-tooth drive voltage V_d with 0,5 s of durability and 1 Hz of repetitive frequency in the amplitude range of $0 \leq V_d \leq 10 \text{ V}$ was used.

During pyroelectric measurements the structure under investigation was irradiated by modulated IR-probe from IR LED supplied by generator of sinusoidal voltage through the matching stage [8].

The matching stage for sensitive elements (SE) of PDR, based on FET impedance transformer with using dynamic load and changeable impedance in the input circuit was applied [11, 12]. It successively operates in the current mode (power measurement) and voltage mode (energy measurement) in the range from infrasound up to low ultrasound frequencies. So, the investigated Pt/PZT/Pt:Ti/Si structures were placed in the conditions of operation of the real SE of PDR.

3. Results and comments

3.1. Pyroelectric response characteristics

3.1.1. Pyroelectric response – modulation frequency characteristics

The dependences $U_{\pi 1,2}(f_m)$ and $\varphi_{\pi 1,2}(f_m)$, obtained for the investigated samples of Pt/PZT film/Pt:Ti/Si after positive (“+”) and negative (“-”) d.c. poling are presented in Figures 1a and 1b.

The shapes of $U_{\pi 1,2}(f_m)$ and $\varphi_{\pi 1,2}(f_m)$ are near identical for “+” and “-” poled SE (compare Figs 1a and 1b). Consecutive repolarization of SE gives 180°-addition to $\varphi_{1,2}$ which corresponds to the change of sign of pyroelectric reaction of PZT film and only insignificant variations of shape of $U_{\pi 1,2}(f_m)$ and $\varphi_{\pi 1,2}(f_m)$ dependences. This indicates the almost complete pyroelectric reversibility of reorientation of polarization direction in inter-electrode space of Pt/PZT/Pt:Ti structure. A small scatter of $U_{\pi 1,2}$ values can be explained by the difference in the degree of unipolarity of PZT film under the top Pt electrode and the bottom Pt:Ti one.

3.1.2. Pyroelectric response – voltage poling curves

Figure 1c presents the dependences of pyroelectric response value on the poling voltages lower than the coer-

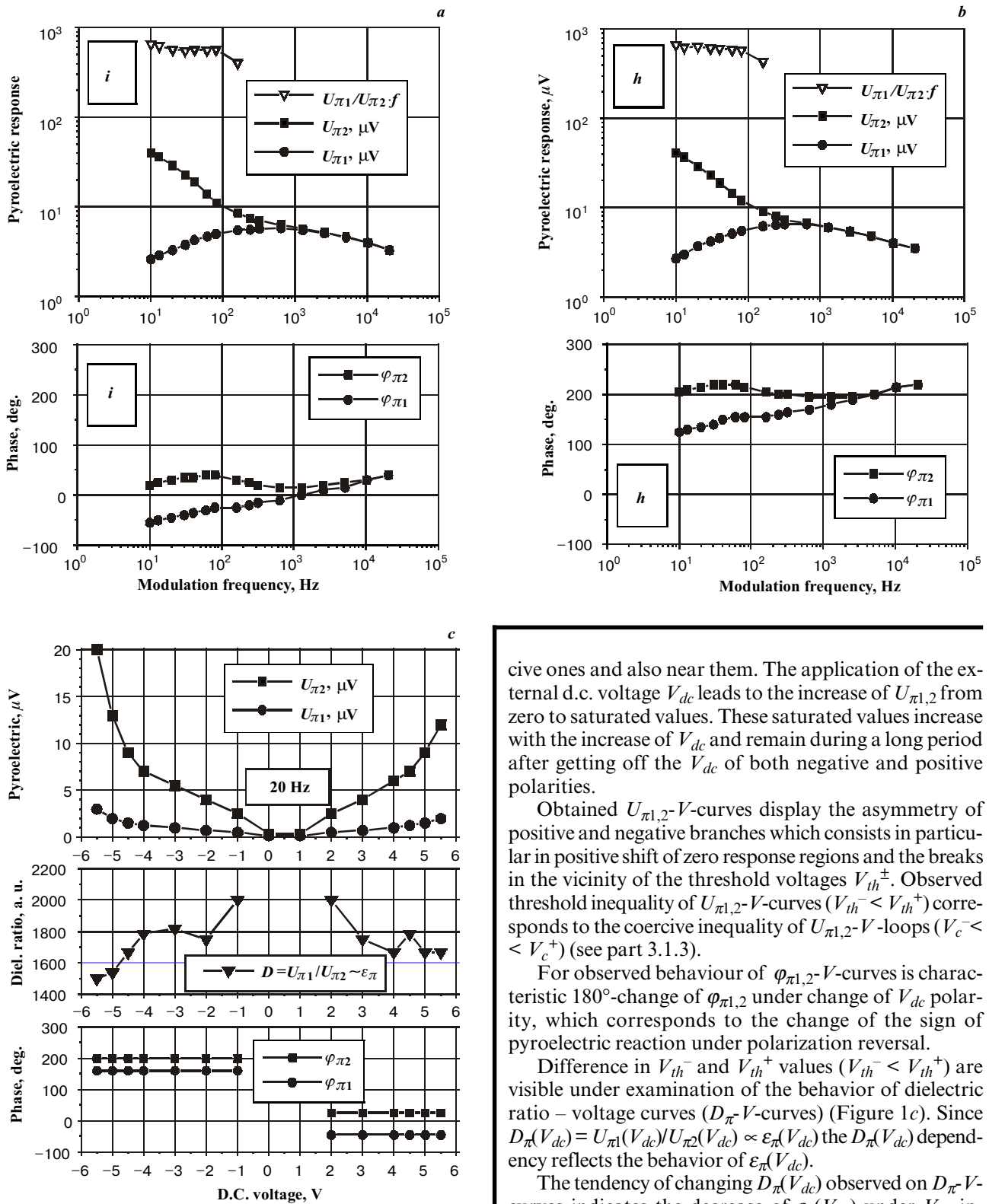


Fig. 1. Modulation frequency dependences (a, b) and poling curves (c) of pyroelectric response amplitudes $U_{\pi 1,2}(f_m)$, dielectric ratio $D_{\pi} = U_{\pi 1}/U_{\pi 2}$ fm and phases $\varphi_{\pi 1,2}(f_m)$:
 a – after +35 V, 5 min d.c. poling;
 b – after -35 V, 5 min d.c. poling.
 c – under d.c. poling after complete depoling.

cive ones and also near them. The application of the external d.c. voltage V_{dc} leads to the increase of $U_{\pi 1,2}$ from zero to saturated values. These saturated values increase with the increase of V_{dc} and remain during a long period after getting off the V_{dc} of both negative and positive polarities.

Obtained $U_{\pi 1,2}-V$ -curves display the asymmetry of positive and negative branches which consists in particular in positive shift of zero response regions and the breaks in the vicinity of the threshold voltages V_{th}^{\pm} . Observed threshold inequality of $U_{\pi 1,2}-V$ -curves ($V_{th}^{-} < V_{th}^{+}$) corresponds to the coercive inequality of $U_{\pi 1,2}-V$ -loops ($V_c^{-} < V_c^{+}$) (see part 3.1.3).

For observed behaviour of $\varphi_{\pi 1,2}-V$ -curves is characteristic 180°-change of $\varphi_{\pi 1,2}$ under change of V_{dc} polarity, which corresponds to the change of the sign of pyroelectric reaction under polarization reversal.

Difference in V_{th}^{-} and V_{th}^{+} values ($V_{th}^{-} < V_{th}^{+}$) are visible under examination of the behavior of dielectric ratio – voltage curves ($D_{\pi}-V$ -curves) (Figure 1c). Since $D_{\pi}(V_{dc}) = U_{\pi 1}(V_{dc})/U_{\pi 2}(V_{dc}) \propto \epsilon_{\pi}(V_{dc})$ the $D_{\pi}(V_{dc})$ dependency reflects the behavior of $\epsilon_{\pi}(V_{dc})$.

The tendency of changing $D_{\pi}(V_{dc})$ observed on $D_{\pi}-V$ -curves indicates the decrease of $\epsilon_{\pi}(V_{dc})$ under V_{dc} increase, which corresponds to decrease of the number of domain walls in the film under poling. The peculiarities of positive and negative branches of $D_{\pi}-V$ -curves around of V_{th}^{\pm} are more diffused for V_{th}^{-} than for V_{th}^{+} . This reflects some differences in rearrangements of domain structure of the Pt/PZT film/Pt:Ti/SiO₂/Si systems under different polarities of external voltage.

3.1.3. Pyroelectric response – external voltage poling – repoling loops

In Figures 2a and 2b the obtained loops of pyroelectric response amplitude $|U_{\pi 1,2}(V_{dc})|$ and phase $\varphi_{\pi 1,2}(V_d)$ and also their combination into real signal $U_{\pi 1,2}(V_{dc})$ are presented.

The $|U_{\pi 1,2}|$ - V -loops have the typical “butterfly”-like shape, which is often observed for strain-electric field response loops of PZT films [13].

The behaviour of $|U_{\pi 1,2}(V_{dc})|$ is characterized by the regions of saturation at the front of the “wings” where $V_d > V_c$ and sharp changes with pronounced minima on the “tails” of the “wings” in the vicinity of $V_d = V_c$.

The $\varphi_{\pi 1,2}$ - V -loops have the characteristic parallelogram-like shape with the regions of $\varphi_{\pi 1,2}$ -change on 180° in the vicinity of $V_{dc} = V_c$ and $\varphi_{\pi}(V_{dc}) = \text{const}$ outside the range of $V_d = V_c$.

Symmetry of the front parts of both positive and negative $|U_{\pi 1,2}(V_{dc})|$ – “wings” reflects the pyroelectric identity of both polarized states of investigated PZT film. Asymmetry of the “tails” of the $|U_{\pi 1,2}(V_{dc})|$ – “wings” and inequality $V_c^- < V_c^+$ indicates the difference on the earlier stage of repolarization processes.

The shapes of obtained $U_{\pi 1,2}$ - V -loops and inequality $V_c^- < V_c^+$ in general are similar to that known for P - V -loops of metal/PZT-film/Si-substrate system [3, 4, 7, 9, 13].

The analysis of $U_{\pi 1}$ - V -loops and $U_{\pi 2}$ - V -loops shows earlier and more complete saturation of $U_{\pi 1}(V_{dc})$ poling curves comparatively with undersaturated $U_{\pi 2}(V_{dc})$ poling curves for the both of V_{dc} polarities. Since $U_{\pi 1} \propto \gamma$ and $U_{\pi 2} \propto \gamma \varepsilon$, we can conclude that the saturation of γ value starts just before V_c^\pm and finishes just after V_c^\pm , which is earlier than that of $\gamma \varepsilon$ value. So this is the ε value which remains undersaturated under $V_{dc} > V_c^\pm$.

The behavior of dielectric ratio $D_{\pi}(V_{dc}) \propto \varepsilon_{\pi}(V_{dc})$ is reflected by D_{π} - V -loop presented in Figure 2c. Observed asymmetry of D_{π} - V -loop corresponds to the same of the $U_{\pi 1,2}(V_{dc})$ -loops.

The general view of obtained $D_{\pi}(V_{dc})$ changes under poling-repoling cycle reflects the general tendency of decreasing ε_{π} value in the poling run under V_{dc} increase and conservation of lower value of ε_{π} under subsequent decrease of V_{dc} . Also the step-like jumps of $D_{\pi}(V_{dc})$ in vicinity of $V_{dc} = 0$ with the maxima around of $V_{dc} = 0$ are observed.

The sharp peculiarities of $D_{\pi}(V_{dc})$ around of $V_{dc} = V_c$ are visible and the first one at V_c^+ is more pronounced than the second one at V_c^- . These peculiarities of $D_{\pi}(V_d)$ reflect the variations of $\varepsilon_{\pi}(V_d)$ and so the states of the domain structure of PZT film with the near zero unipolarity degree.

The behaviour of $\varepsilon_{\pi}(V_{dc})$ in the vicinity of $V_{dc} = 0$ and $V_{dc} = V_c^\pm$ can be connected with the peculiarities of rearrangement of domain structure of PZT film which consists in mutual transformations of interconnected 180° - and non- 180° - (in particular, 90° -) domain groups [5, 14].

3.1.4. Pyroelectric response – time repolarization transient curves

Figure 3 presents the changes of pyroelectric response amplitude and phase in the course of repolarization of Pt/PZT film/Pt:Ti structure by application of d.c. voltage V_{dc} less and near the coercive ones.

Under application of fixed external repoling d.c. voltage V_{dc} the decrease of U_{π} value up to zero followed by subsequent increase of U_{π} value up to saturated one is observed. This saturated value remains during a long period after V_{dc} getting off.

Observed behaviour of $\varphi_{\pi}(t)$, namely 180° -change under transition of $U_{\pi}(t)$ through its zero value, corresponds to the change of the sign of pyroelectric reaction due to polarization reversal in time induced by V_{dc} application.

For positive and for negative V_{dc} the similar tendency in the $U_{\pi}(t)$ behaviour but at different time scales is observed. So the strong asymmetry in the time scale of repolarization process development is clearly evident.

Figure 4 presents repolarization transient curves $U_{\pi}(t)$ combined from amplitude and phase time dependences from Figure 3.

For positive and for negative poling voltages the regions of $U_{\pi}(t) \sim U_{\pi}(0)(1 - \eta \log(t/\tau))$ are observed and the slope η increase with V_{dc} value increase. For negative V_{dc} on the both sides from zero response time the view of $U_{\pi}(t)$ is different at low V_{dc} and similar at high V_{dc} . So under negative V_{dc} the characteristics of domain walls motion before and after repolarization are different at low V_{dc} values and are similar at high V_{dc} values. For positive V_{dc} on the both sides from zero response time the slopes of $U_{\pi}(t)$ are different at both low and high V_{dc} . So, under positive V_{dc} the characteristics of domain walls motion before and after repolarization are different at low and high V_{dc} values.

In Figure 5 the voltage dependences of zero-response time t_0 and saturation time t_s are presented.

Increase of negative V_{dc} value leads to strong decrease of t_s and t_0 values, which remain near constant when V_{dc} value reaches and exceeds the V_c^- value. Under positive V_{dc} value the same tendency of t_0 changing but in more narrow time scale is observed. At low V_{dc} the values of t_0 are 1–2 orders of value higher at negative V_{dc} than at positive ones but at high V_{dc} for the both polarities the values of t_0 are near the same. Under increase of negative V_{dc} the t_s value decreases similar to t_0 but under increase of positive V_{dc} the t_s value noticeably increases. So, for negative V_{dc} the similar tendencies and for positive V_{dc} the different tendencies in the behaviour of t_0 and t_s are observed.

3.2. Dynamic unipolar current-voltage characteristics

Figure 6 presents the set of dynamic unipolar current-voltage characteristics obtained under different amplitudes and polarities of drive voltage.

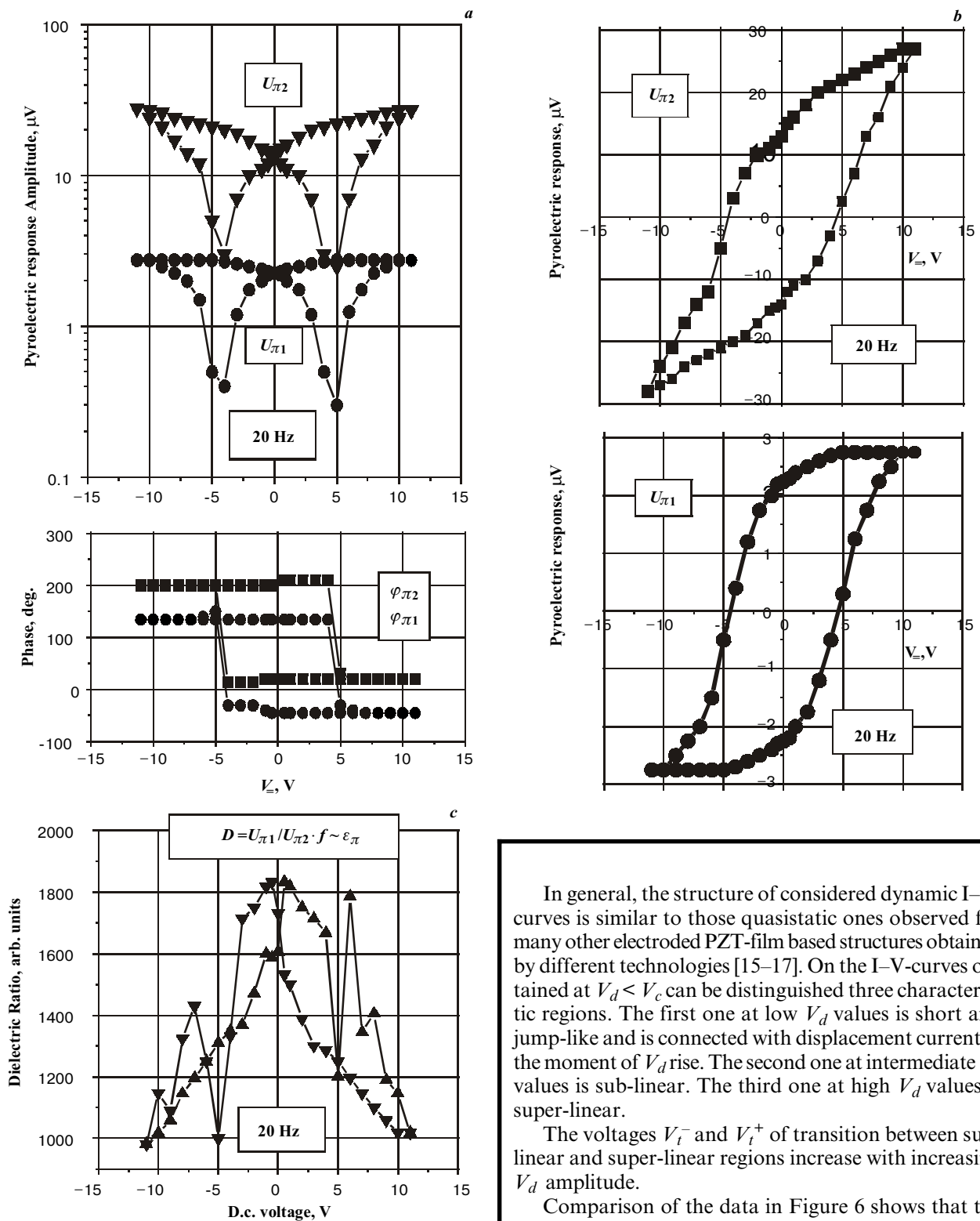


Fig. 2. Pyroelectric response – d.c. voltage loops: *a* – “butterflies” of amplitudes $U_{\pi 1,2}(V)$, and parallelograms of phases $\varphi_{1,2}(V)$; *b* – hysteresis loops of responses $U_{\pi 2}(V)$ (top) and $U_{\pi 1}(V)$ (bottom); *c* – dielectric ratio $D_{\pi}(V)$ loop.

In general, the structure of considered dynamic I–V-curves is similar to those quasistatic ones observed for many other electroded PZT-film based structures obtained by different technologies [15–17]. On the I–V-curves obtained at $V_d < V_c$ can be distinguished three characteristic regions. The first one at low V_d values is short and jump-like and is connected with displacement current in the moment of V_d rise. The second one at intermediate V_d values is sub-linear. The third one at high V_d values is super-linear.

The voltages V_t^- and V_t^+ of transition between sub-linear and super-linear regions increase with increasing V_d amplitude.

Comparison of the data in Figure 6 shows that the differences of positive and negative branches which increase with the rise of V_d values are rather high at short times of V_d application and decrease after forming under long term repetitive action of V_d saw-pulses. So observed dynamic I–V-curves shows a pronounced dynamic character of polar asymmetry.

For unformed I–V-curves the development of super-linear region with the rise of V_d is characteristic. The forming during several minutes leads to the changes of

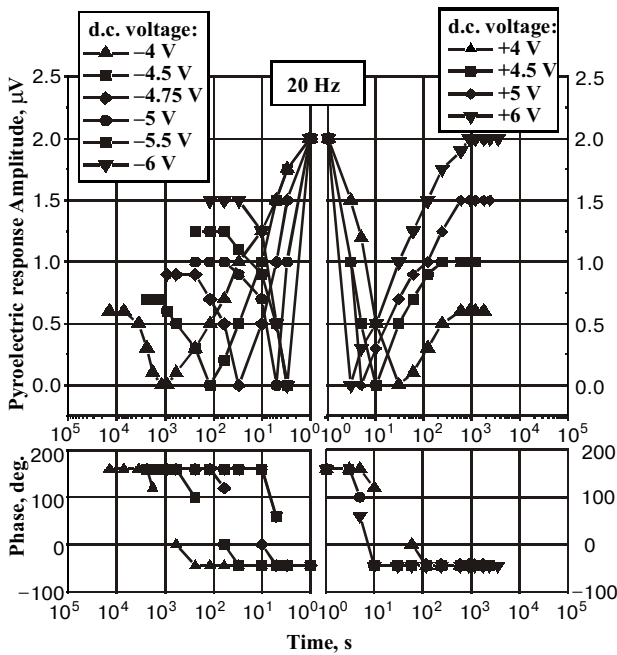


Fig. 3. Pyroelectric response amplitude-time and phase-time repolarization curves: top – pyroelectric response amplitude; bottom – pyroelectric response phase; left – for negative d. c. voltages; right – for positive d. c. voltages.

parameters of the I–V-curves. These changes are more significant under increasing the drive voltage value (compare the data in Figure 6). The expansion of sub-linear region at the expense of super-linear one are observed. Under V_d increase the slope of sub-linear region decreases. Under $V_d > V_c$ the appearance of region with the diffuse maximum and subsequent negative slope is characteristic and more pronounced for the positive branch. These regions are connected with currents of polariza-

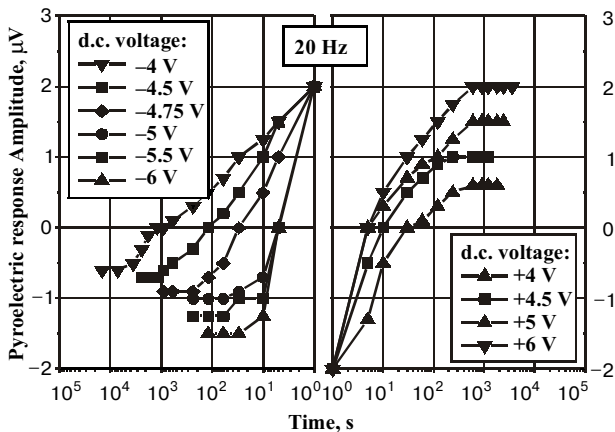


Fig. 4. Pyroelectric response signal – time repolarization transient curves: left – for negative d. c. voltages; right – for positive d. c. voltages.

tion reversal in the definite group of domains (“stubborn domains”) which spontaneously return in the initial state under $V_d = 0$. Taking into account the complex character of mixed 90°- and 180°- domain structure in PZT films [5] and the data [14] concerning the contribution of 180°- and non-180°-domain groups into remanent polarization in PZT films we can suppose that the stubborn domain group in a significant degree consists of non-180°-domains.

4. Discussion

The obtained results show that the investigated systems possess polar asymmetry of pyroelectric parameters, poling time and current-voltage characteristics, which correspond to coexistence of interrelated ferroelectric asymmetry and asymmetry of charge transport.

Indeed, processes of polarization reversal in the Pt/PZT/Pt:Ti/TiO₂/SiO₂/Si structures are developed in the condition of asymmetry of injection properties of Pt-top and Pt:Ti-bottom contacts due to the difference in the conditions of their manufacturing. Besides, there is an asymmetry of profile of the space charge connected with the profile of mobile and immobile point and expanded defects. In PZT films these are V_{Pb}^+ and V_O^- vacancies, domain walls, boundaries of separate micro-regions of PZT film, and also various types of distortions in under-electrode regions of the film.

In the case of investigated Pt/PZT/Pt:Ti structures, because of the complex configuration of the space charge, the charge transport on the different stages of repolarization process can be realized by so called relay-race alternation of different mechanisms (see their list in Ref [17]). The complex structure of observed I–V-curves and its changes in time are in accordance with this interpretation.

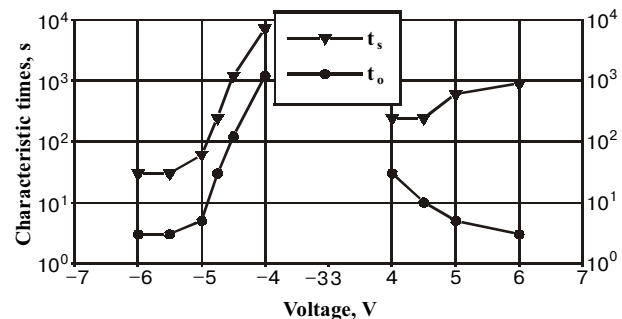


Fig. 5. Voltage dependences of pyroelectric response characteristic times under d. c. voltage repolarization: left – for negative d. c. voltages; right – for positive d. c. voltages.

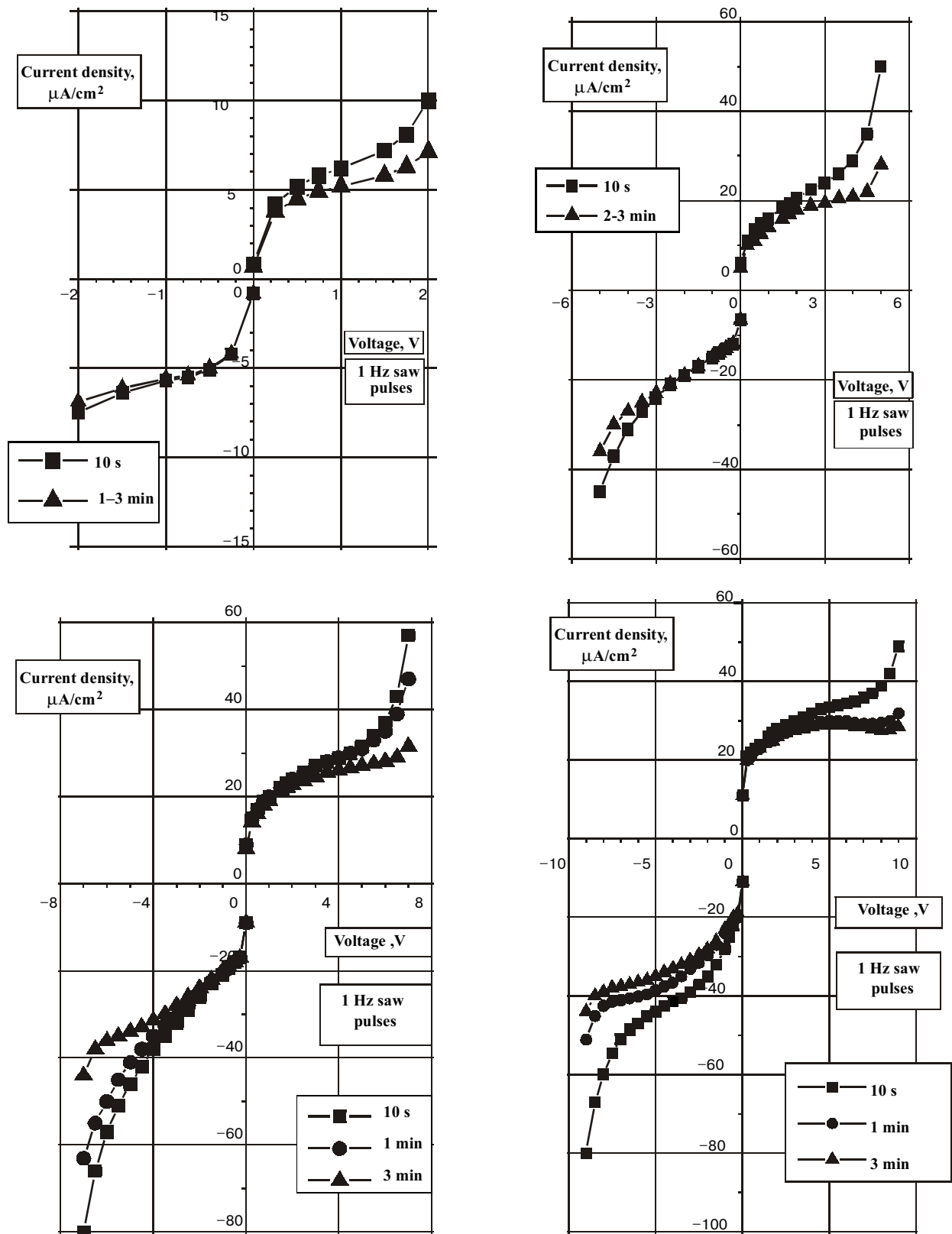


Fig. 6. Dynamic unipolar current-voltage characteristics under different drive voltage amplitudes.

A super-linear region of I–V curves is usually associated with enrichment with charge carriers of near-contact region with metal and discussed in terms of injection mechanisms connected with the existence of currents limited by space charge [18], Schottky emission [19] and Pool-Frenkel ionization [20]. A sub-linear region of I-V-curves can be connected with depletion of contacting regions of essentially different degree of doping due to exclusion and extraction of charge carriers [21]). The formation of such structure is characteristic for the case of diffusion of metal in semiconductor in the region of their contact as the result of thermal treatment and is quite possible in the course of manufacturing the investigated Pt/PZT/Pt:Ti structures.

Dynamic character of observed current asymmetry points to the change of conditions of charge transport with time. So, the observed pyroelectric asymmetry is developed in the conditions of changing the space charge profile with time.

The changes of pyroelectric response under reversing polarization are connected with domain structure reconstruction. That is why the time of such changes is determined in a high degree with processes of nucleation of new domains and displacement of domain walls.

The peculiarities of domain structure behaviour under polarization direction reversal in the perovskite crystalline ferroelectrics [22] and in PZT films [5, 14, 23] are similar in many details. For initially non-polarized or depolarized crystals and PZT films, contained a number of disordered domains of non-180°- (in particular, 90°-) and 180°- orientation the polarization process occurs under action of external voltage by simultaneous displacement of non-180°- and 180°- domain boundaries, and reorientation of 180°-domains. The process of polarization reversal in PZT films starts from the nucleation and growth of opposite domains (OD) of wedge-like shape from the surface into the depth of the film and finishes by broadening the domains spreading through the film by side displacement of domain walls (DW).

The role of processes of charge transport under polarization reversal in thin layer structures of metal-ferroelectric-metal type by means of formation OD and displacement of charged DW was considered earlier in [24, 25]. Facilitation of the conditions of domain nucleation and growth in film structures due to presence of dielectric non-uniformity was considered recently in [26, 27]. To provide the displacement of charged DW it is necessary to supply the certain value of mobile electric charges, which is necessary for compensation of changeable bounded charge. The peculiarities of this DW displacement define the peculiarities of U_{π} -V- and U_{π} -t-curves.

Under registration of U_{π} -V- poling curves the increase of $U_{\pi}(V_{dc})$ from zero value to the maximal one at given V_{dc} value starts in the system of mutually pyroelectrically compensated OD and occurs in the system of rearranged OD. At that the value $V_{dc} = V_{th}$ corresponds to the beginning of sharp change of U_{π} under V_{dc} increase and so the start of fast rearrangement in the system of OD.

Under registration of U_{π} -t-curves of repolarization the variation of $U_{\pi}(t)$ reflects the trend of compensation process in the preliminary arranged OD system. The moment $t = t_0$ when $U_{\pi}(t_0) = 0$ corresponds to pyroelectrically compensated state of OD system. So the time $t = t_0$ corresponds to transport of such value of electrical charge, which is necessary for creation of number of OD required for compensation.

The fact of vanishing U_{π} values at $V_d = V_c^{\pm}$ under U_{π} -V-loops cycling and also at $t = t_0^{\pm}$ under U_{π} -t-curves registration permits to consider some analogies between the coercive voltages V_c^{\pm} and zero response times t_0^{\pm} .

Starting from the definition of the effective degree of unipolarity $\xi = (c^+ - c^-)/(c^+ + c^-)$, where c^+ and c^- are the concentrations of the domains with the opposite directions of the components of polarization vector P_s along the thickness of the film, we can conclude that at $V_d = V_c^{\pm}$ and at $t = t_0^{\pm}$ the value $\xi = 0$. Since the values $V_d = V_c^{\pm}$ and $t = t_0^{\pm}$ correspond to the similar states of the domain structure, namely those just balanced between two inversely poled states, we can consider t_0 as the coercive times. Indeed, from the standpoint of transport of charge value necessary for vanishing the value of integral polarization, the coercive voltage is the necessary voltage value under given time of its action, and the coercive time is the necessary time under given voltage value.

5. Conclusions

The performed investigation has shown the strong correlation between the poling pyroelectric and so ferroelectric and electrical asymmetries.

Observed behaviour of U_{π} -V- and U_{π} -t-curves and also U_{π} -V-loops displays the considerable polar and time asymmetry of polarization reversal.

Observed transformation of I–V-curves is the evidence of considerable V- and t- dependent variation of charge transport conditions.

Changes of pinning conditions, domain wall motion characteristics, charge and mechanical state of the point (immobile and mobile) and extended (domain wall) defects is the reason of observed complex asymmetry.

For the investigated PZT thin films on Si systems with complex composition and asymmetric space charge profile is characteristic its change with time under the action of applied external voltage.

The consequence of contact asymmetry and space charge asymmetry is the difference in the conditions of electric charge transport under the different polarity of applied voltage. It results, in particular, in different time of space charge accumulation necessary for reversing the polarization direction and also in different spread of this process in time. It leads to the difference in coercive times for U_{π} -t-curves obtained under different polarity of poling voltage, and also to the difference in coercive voltage values obtained for $U_{\pi 1}$ -V- and $U_{\pi 2}$ -V-loops under different polarity of drive voltage.

For as more complete as possible examination of polarization reversal processes in PZT thin films on Si struc-

tures it is necessary to perform the investigation of the complex of their electrophysical characteristics including not only ferroelectric but at the least pyroelectric and current-voltage characteristics.

Acknowledgements

Authors gratefully acknowledge Ministry of Science of France and the University of Valenciennes for financial support.

References

1. B. Jaffe, W. R. Cook, H. Jaffe, *Piezoelectric ceramics*, Acad. Press., London, 1971.
2. L.S. Kremenchugsky and O.V. Roitsina, *Pyroelectric Detectors of Radiation*, Naukova Dumka, Kiev, 1979 (in Russian).
3. Y. Ishibashi, *Ferroelectric Thin Films: Synthesis and Basic Properties*, Gordon and Breach, Amsterdam, pp. 135-152, 1996.
4. V.Y. Shur, *Ferroelectric Thin Films: Synthesis and Basic Properties*, Gordon and Breach, Amsterdam, pp. 153-169, 1996.
5. R. Waser, Modeling of electroceramics – application and prospects // *J. Europ. Ceram. Soc.*, **19**, pp. 655-664 (1999).
6. Y. Xu, C. J. Chen, R. Xu, J. D. Mackenzie, Self biased heterojunction effect of ferroelectric thin film on silicon // *Ferroelectrics*, **108**(1-4), pp. 47-52 (1990).
7. W. Liu, J. Ko, W. Zhu, Asymmetric switching behavior of Ni/Pb_{1-x}(Zr_{0.3}Ti_{0.7})O₃/Pt thin films // *Material Letters*, **49**, p. 122 (2001).
8. S.L. Bravina, N.V. Morozovsky, A.A. Strokach, Pyroelectricity: Some Physical and Application Aspects // *Proceedings of SPIE*, **3182**, pp. 85-99 (1997).
9. G. Velu, D. Remiens and B. Thierry, Ferroelectric properties of PZT thin films prepared by sputtering with stoichiometric single oxide target: comparison between conventional and rapid thermal annealing // *J. Europ. Ceram. Soc.*, **17**, p. 1749 (1997).
10. T. Haccart, E. Kattan, D. Remiens, Dielectric, ferroelectric and piezoelectric properties of sputtered PZT thin films on Si substrates: influence of film thickness and orientation // *Semicond. Phys., Quant. Electron. and Optoelectronics*, **5**(1), pp. 78-88 (2002).
11. N.V. Morozovsky, V.B. Samoilov, I.A. Stoyanov, *Investigation of matching stages for pyroelectric detectors of radiation*, in book *Thermal Detectors of Radiation*, GOI, Leningrad, pp. 104-105 (1980).
12. S.L. Bravina, L.S. Kremenchugsky, N.V. Morozovsky et al., *Investigation of Phase Transitions in Ag₃AsS₃ and Ag₃SbS₃ by Method of Dynamic Pyroelectric Effect*, Preprint No. 26, Inst. of Phys. of Acad. Sci. of Ukraine, Kiev, 1982 (in Russian).
13. P. Pertsch, M.-J. Pan, V. R. Vedula, S. Yoshikawa, S.-E. Park, T.R. Shrout, Characteristics of electromechanical solid state multilayer actuators // *IEEE*, pp. 571-574 (1998).
14. K. Saito, T. Oikawa, T. Kurosawa, T. Akai and H. Funakubo, Role of non-180° domain switching in electrical properties of Pb(Zr_{0.35}Ti_{0.65})O₃ thin films // *Jpn. J. Appl. Phys.*, **41**, Part 1, No 11B, pp. 6730-6734 (2002).
15. H. Miki, K. Kushida-Abdelghafar, K. Torii, Y. Fujisaki, Hydrogen related degradation and recovery phenomena in Pb(Zr,Ti)O₃ capacitors with a platinum electrode // *Jpn. J. Appl. Phys.*, **36**, Part 1, No. 3A, pp. 1132-1135 (1997).
16. M. Brazier, M. McElfresh, S. Mansour, Origin of anomalous polarization offsets in compositionally graded Pb(Zr,Ti)O₃ thin films // *Appl. Phys. Lett.*, **74**(2), pp. 299-31 (1999).
17. Stolichnov and A. Tagantsev, Space-charge influenced-ingection model for conduction in Pb(Zr_xTi_{1-x})O₃ thin films // *J. Appl. Phys.*, **84**(6), pp. 3216-3225 (1998).
18. M. A. Lampert and P. Mark, *Current Injection in Solids*, Academic, New-York, 1970.
19. W. Monch ed., *Electronic Structure of Metal-Semiconductor Contacts*, Kluwer Academic, Dordrecht, 1990.
20. F.F. Volkenshtein, *Electrical Conductivity of Semiconductors*, Tehteorizdat, Moscow-Leningrad, 1947 (in Russian).
21. V.L. Bonch-Brujevitch, S.G. Kalashnikov, *Physics of Semiconductors*, Nauka, Moscow, 1977.
22. E.G. Fesenko, V.G. Gavriiliatshenko, A.F. Sementshev, *Domain structure of multi-axes ferroelectrics*, Ed. of Rostov. Univ., Rostov-on-Don, 1990 (in Russian).
23. D. Fu, K. Suzuki, K. Kato, M. Minakata, H. Suzuki, Investigation of domain switching and retention in oriented PbZr_{0.3}Ti_{0.7}O₃ thin film by scanning force microscopy // *Jpn. J. Appl. Phys.*, **41**, Part 2, No. 11B, pp. 6724-6729 (2002).
24. G.M. Guro, I.I. Ivanchik, N.F. Kovtoniuk, C-Domain Crystal BaTiO₃ in the Short Circuited Capacitor // *Sov. Sol. St. Phys.*, **11**(7), pp. 1956-1964 (1969).
25. V. F. Krapivin and E. V. Chensky, Space Charge Limited Currents in the system Metal-Ferroelectric-Metal // *Sov. Sol. St. Phys.*, **12**(2), pp. 597-604 (1970).
26. A. M. Bratcovsky, A. P. Levaniuk, Abrupt appearance of the pattern and fatigue of thin ferroelectric films // *Phys. Rev. Lett.*, **84**(14), pp. 3177-3180 (2000).
27. A. M. Bratcovsky, A. P. Levaniuk, Ease polarization switching in ferroelectrics // *Phys. Rev. Lett.*, **8**(1), pp. 4614-4617 (2000).