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Research Article

Asymmetry of Polarization Reversal and Current-Voltage Characteristics of Pt/PZT-Film/Pt:Ti/SiO_2/Si-Substrate Structures

S. L. Bravina,[1] N. V. Morozovsky,[1] J. Costecalde,[2] C. Soyer,[2] D. Remiens,[2] and D. Deresmes[2]

[1] *Institute of Physics, NASU 46, Prospect Nauki, 03680 Kyiv, Ukraine*
[2] *IEMN-DOAE-MIMM Team, CNRS, UMR 8520, Bat. P3, Cité Scientifique USTL, 59652 Villeneuve d'Ascq, France*

Correspondence should be addressed to S. L. Bravina, bravmorozo@yahoo.com

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The characterization of the asymmetries of bipolar charge-voltage and current-voltage loops of polarization reversal and unipolar current-voltage curves for Pt/PZT-film/Pt:Ti/SiO_2/Si-substrate systems was performed in the dynamic mode. The asymmetry of local deformation-voltage loops was observed by piezoresponse force microscopy. The comparison of the dependences of introduced asymmetry factors for the bipolar charge-voltage and current-voltage loops and unipolar current-voltage curves on drive voltage indicates the interconnection of ferroelectric and electrical space charge transfer asymmetries.

1. Introduction

At present, lead zirconate titanate (PZT) film on silicon structures are considered among the best ones for creating elements of Si-integrated converters of various types. However, the practically important electrical characteristics of "metal-PZT film-metal-Si-substrate" systems manifest the well-known set of natural and technological asymmetries.

Earlier [1–3], we reported the results of investigations of polar and poling asymmetries of the set of pyroelectric and related characteristics of Pt/PZT-film/Pt:Ti/SiO_2/Si-substrate sandwich type structures.

In this paper, we concentrate our attention on the characterization of the complex of the asymmetries of dynamic bipolar charge-voltage (Q-V-) and current-voltage (I-V-) loops and unipolar current-voltage (J-V-) curves as well as bipolar deformation-voltage (X-V-) loop asymmetry. We present the results of investigation of interrelated polarization reversal and current-voltage dynamic asymmetries of Pt/PZT-film/Pt:Ti/ SiO_2/Si-substrate systems.

2. Experiment

2.1. Samples. The samples under investigation were PZT films prepared by the radiofrequency magnetron sputtering method. The bottom Pt electrode of 150 nm of thickness with Ti adhesive layer of 10 nm of thickness was deposited on the 350 nm SiO_2 layer on a 350 μm (100) n-type Si wafer. $Pb(Zr_xTi_{1-x})O_3$ film with $x = 0.54$ of 1-2 μm of thickness was deposited on the Pt/TiO_x/SiO_2/Si-substrate structure just after its stabilization by annealing treatment at 650–700°C.

The perovskite ferroelectric phase of PZT was obtained by annealing at 625°C for 30 min. Then, a top Pt (150 nm) electrode of $\approx 1\ mm^2$ of area was deposited by sputtering.

The sputtering conditions and the results of X-ray and microstructure characterization were described in details in [4].

2.2. Measurements. For the investigations of polarization reversal (PR) and current-voltage characteristics, the measuring set for complete ferroelectric characterization [2] was used. The examination of PR characteristics was performed in two actual modes, namely, ferroelectric hysteresis loops of charge (Q-V-loops) and current (I-V-loops) were registered.

The measurements were performed by Sawyer-Tower like circuit [5] in the multicycle mode under applied a.c. triangular drive voltage V_d of 1 Hz of frequency in the amplitude range of $0 \leq V_{da} \leq 11$ V.

To eliminate PR-current contribution, the examination of dynamic current-voltage characteristics (J-V-curves) was performed at unipolar saw-tooth drive voltage V_d with 0.5 s of durability and 1 Hz of repetitive frequency in the amplitude range of $0 \leq V_{da} \leq 10$ V.

Drive voltage was applied to the circuits of series connection of tested sample with reference resistor for I-V-loops and J-V-curves and with reference capacitor for Q-V-loops. The corresponding characteristics were observed by means of two-beam digital storage oscilloscope YB 54060 operating in I-V-mode. The voltage on the reference elements was monitored and plotted versus drive voltage.

Piezoelectric response force microscopy (PFM) observations of deformation-voltage (X-V-) loops were carried out with a commercial AFM Veeco "Dimension 3100" using the probe of *App-Nano* ANSCM-PA type with cantilever spring constant of ≈40 N/m (resonance frequency ≈300 kHz). The probe was equipped by Si tip with double layer of chromium and platinum/iridium5 (Pt/Ir5) coating of 23 nm thick. After localization of the top Pt electrode by AFM imaging, the PFM measurements were performed in the contact mode with PFM tip located over the PZT grain (1–3 μm) visible through the top Pt electrode.

A modulation ac voltage of 2 kHz of frequency and 1.5 V of amplitude was applied to the conductive PFM tip, and dc driving voltage V_d cycled in the range $-10\,\text{V} \leq V_d \leq +10\,\text{V}$ was applied to the bottom Pt electrode of the film. The amplitude of V_d was chosen to be higher than the coercive voltage for polarization reversal in the examined PZT film.

PFM response amplitude hysteresis loops were recorded as a function of V_d by demodulating photoelectrically transformed cantilever deflection signal with a lock-in amplifier Signal Recovery 7270.

3. Results and Discussion

3.1. Polarization Reversal Characteristics. The obtained Q-V-loops and I-V-loops of polarization reversal are presented in Figures 1 and 2, respectively. Under increasing V_{da}, the start of saturation of Q-V-loops (Figure 1(a)) is accompanied by appearance of maxima on I-V-loops (Figure 2(a)). The main characteristics of Q-V- and I-V-loops are changed after several minutes of cycling under $V_{da} = 10$ V that can be considered as forming.

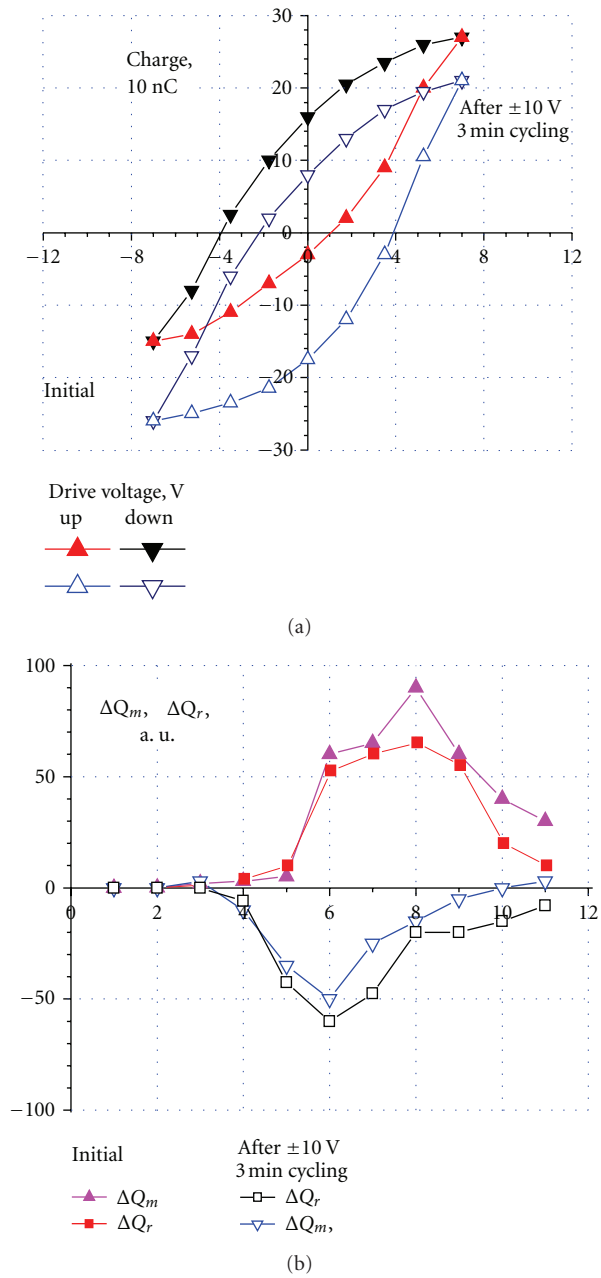

Figure 1: Bipolar charge-voltage loops of polarization reversal (a) and drive voltage dependences of charge asymmetry factors (b).

3.1.1. The Peculiarities of Bipolar Charge-Voltage Loops. Under increasing V_{da}, the tendency of Q-V-loops for saturation is accompanied by vertical (along Q-axis) shift (Figure 1(a)), which reaches the maxima and starts to decrease under subsequent V_{da} increasing. At $V_{da} = 10$ V, the coercive voltages V_c obtained from Q-V-loop are $V_c^- = -3.4$ V and $V_c^+ = +5.2$ V. The vertical shift changes its sign (see Figure 1(a)) under decreasing V_{da} after forming at $V_{da} = 10$ V.

Figure 1(b) presents the V_{da} dependences of charge asymmetry factors $\Delta Q_i = (Q_i^+ + Q_i^-)/2$ considered as a measure of the vertical shift of Q-V-loop ($i = m, r$ correspond to maximal ($V_d = V_{da}$) and remanent ($V_d = 0$) polarization, resp.). Under V_{da} increasing the positive ΔQ_m and ΔQ_r appear in V_c^+ vicinity. After forming under subsequent V_{da} decreasing the negative ΔQ_m and ΔQ_r disappear in V_c^- vicinity. This behaviour of $\Delta Q_m(V_{da})$ and $\Delta Q_r(V_{da})$ shows that the vertical shift of Q-V-loops is connected with PR processes in the coercive V_c^- and V_c^+ vicinities.

3.1.2. The Peculiarities of Bipolar Current-Voltage Loops. The observed I-V-loops are noticeably asymmetrical (Figure 2(a)). The absolute value of the voltage V_m^+ of positive current maximum I_m^+ is higher than that of the voltage V_m^- of the negative current maximum I_m^-. At that, I_m^+ value is significantly

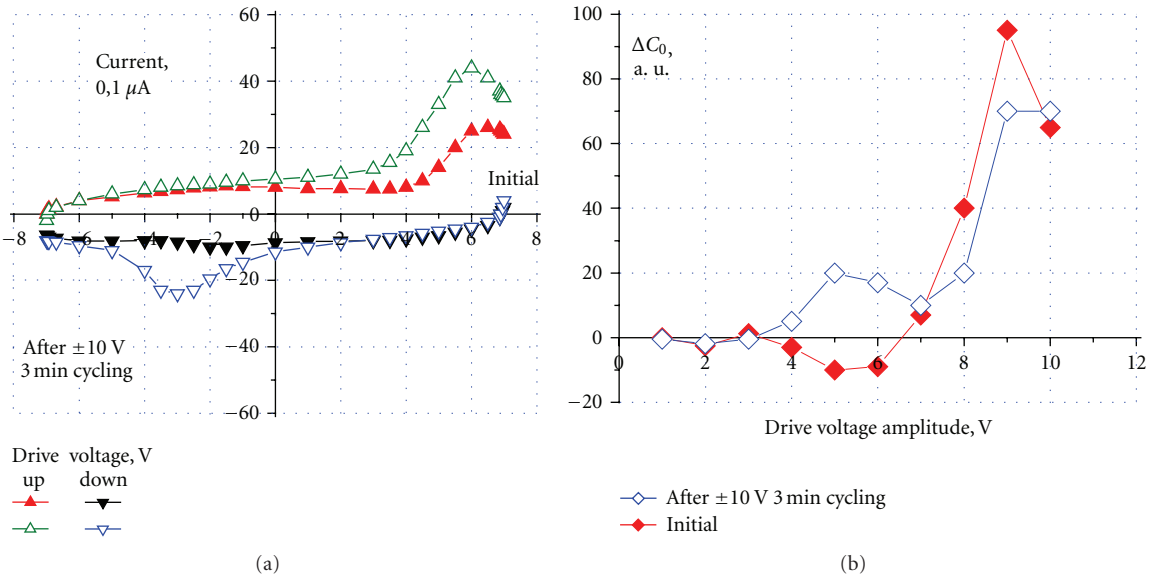

Figure 2: Bipolar current-voltage loops of polarization reversal (a) and drive voltage dependence of capacitive asymmetry factor (b).

higher than that of I_m^-. At $V_{da} = 10$ V, the voltages V_m obtained from I-V-loop are $V_m^- = -3.7$ V and $V_m^+ = +6.7$ V.

The forming under $V_{da} = 10$ V results in the change of V_m^+ and V_m^- values and increase of I_m^+ and I_m^- values under subsequent V_{da} decrease (see Figure 2(a)).

Because the vertical (along I-axis) size of I-V-loop is proportional to the sample capacity C [6], the value of $\Delta I_0 = (I_0^- + I_0^+)/2\ V_{da}$ (where I_0^- and I_0^+ are the currents at $V_d = 0$) can be considered as a measure of the capacitive asymmetry $\Delta C_0 = (C_0^- - C_0^+)$ of I-V-loop.

Figure 2(b) presents V_{da} dependences of capacitive asymmetry factor $\Delta C_0 \propto \Delta I_0$. Under V_{da} increasing and its subsequent decreasing after forming the values of ΔC_0 are near the same at $V_{da} < V_m^-$ and at $V_{da} > V_m^+$. However, in the range $V_m^- < V_{da} < V_m^+$ not only the behaviour of $\Delta C_0(V_{da})$ but also ΔC_0 signs are different before and after forming. At that, the maximal ΔC_0 difference before and after forming is observed at $V_{da} \approx |V_c^+| = 5.2$ V. This behaviour of $\Delta C_0(V_{da})$ shows that the current asymmetry of I-V-loops is connected with PR processes in V_m^- and V_m^+ vicinities.

Direct modelling by means of the electrical circuit that includes inversely connected Zener diodes divided by parallel RC circuit [7] demonstrates the possibility of controlling the value of vertical shifts of Q-V-loops and peculiarities of I-V-loops by adjusting Zener voltages.

3.2. Unipolar Current-Voltage Characteristics. For the observed unipolar J-V-curves (Figure 3(a)) under V_{da} increasing and its subsequent decreasing after forming is characteristic of the change of asymmetry degree and the shape of the positive and negative branches and also the change of the voltages V_t^+ and V_t^- of transition between sublinear and superlinear J-V-regions.

As a measure of J-V-curve asymmetry the ratio $A_R = J_m^+/J_m^-$ of the maximal (index "m") current values of positive $J_m^+(V_{da})$ and negative $J_m^-(V_{da})$ branches was taken.

The V_{da} dependences of A_R and also V_t^-/V_{da} and V_t^+/V_{da} for initial and formed J-V-curves are presented in Figure 3(b). The values of A_R for initial and formed J-V-curves are different at $V_{da} < V_m^+$ and became near equal at $V_{da} \geq V_m^+$. Under increasing V_{da} the dependence $A_R(V_{da})$ reaches the maximum at $V_{da} \approx |V_c^-|$. After forming $A_R(V_{da})$ dependence has the smooth step with the start at V_m^-, the centre near $V_{da} \approx V_c^+$, and the finish at V_m^+.

The difference in $V_t^+(V_{da})$ and $V_t^-(V_{da})$ behaviour is displayed by V_{da} dependences of V_t^+/V_{da}, and V_t^-/V_{da} ratios (see Figure 3(b)). The equality of V_t^+/V_{da} and V_t^-/V_{da} is observed up to $V_{dm} \approx |V_c^-|$ and the value of $(V_t^+ - V_t^-)/V_{da}$ reaches maximum at $V_{da} \approx V_m^+$.

This behaviour of asymmetry ratio $A_R(V_{da})$ and also transition voltages $V_t^+(V_{da})$ and $V_t^-(V_{da})$ of unipolar J-V-curves manifests the peculiarities in the coercive V_c^- and V_c^+ vicinities as bipolar Q-V-loops and in V_m^+ and V_m^- vicinities as bipolar I-V-loops.

3.3. Deformation-Voltage Loops. Figure 4 presents the local deformation-voltage (X-V-) loops (PFM-amplitude) studied on the same Pt/PZT/Pt:Ti/SiO_2/Si-substrate structure as were examined integral charge Q-V- and current I-V-loops of polarization reversal.

As it is seen from Figure 4(a), the initial X-V-loop is remarkably asymmetrical. An apparent approach of the loop shape to a near symmetrical butterfly-like one (Figure 4(b)) was achieved by cycling under V_d sweeping with a decreasing from 10 V to zero amplitude (local forming procedure).

So, the forming procedure results in similar symmetrization of corresponding characteristics related to integral and local PR processes.

4. Conclusion

The developed conception of asymmetry factors clearly shows the interconnection of polarization reversal asymmetry and

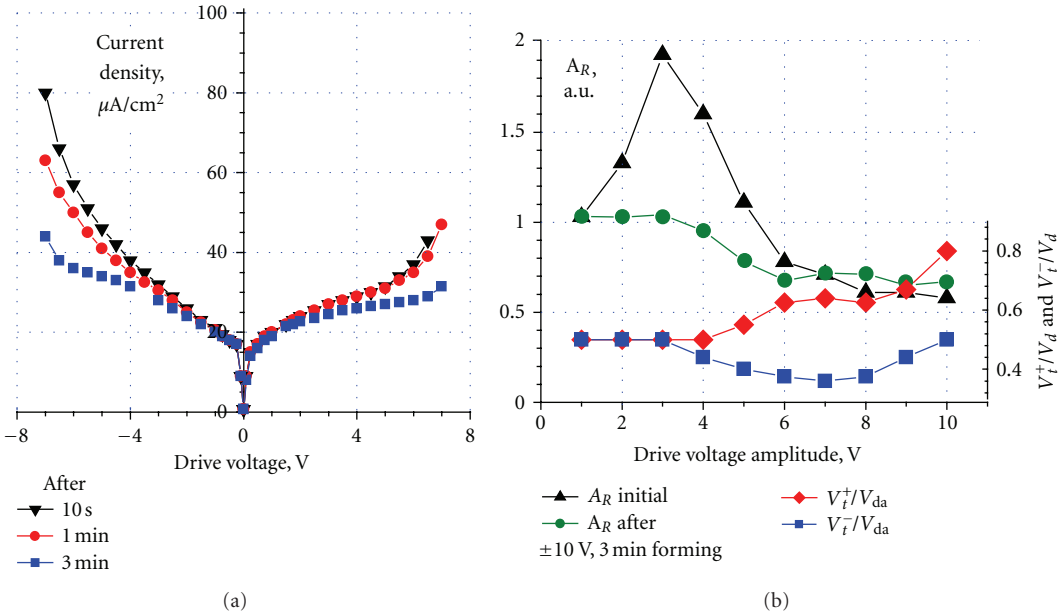

Figure 3: Unipolar current-voltage curves (a) and drive voltage dependences of transition voltages and asymmetry ratio (b).

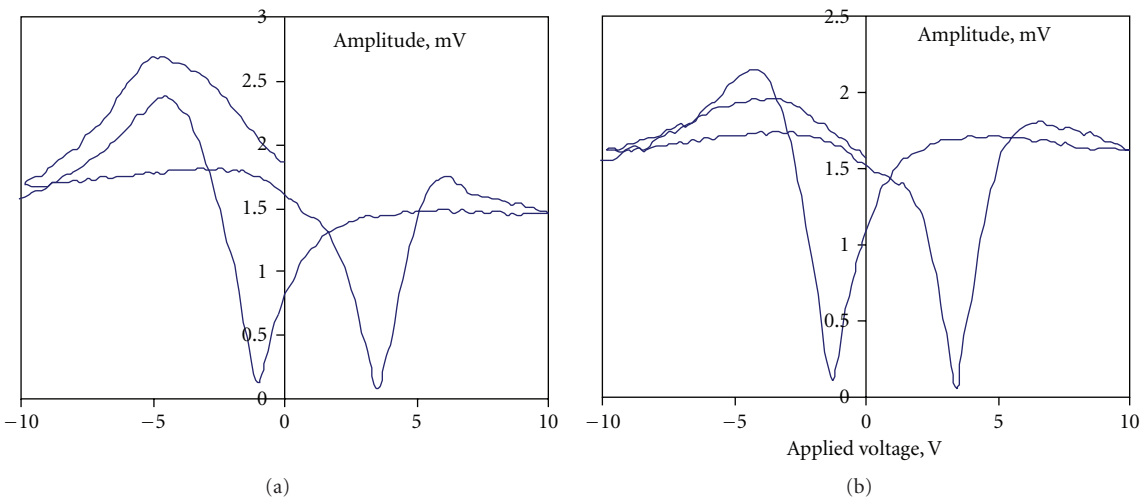

Figure 4: PFM amplitude-voltage loops initial (a) and after forming by drive voltage sweeping with decreasing amplitude (b).

asymmetry of electrical space charge transfer in ferroelectric Pt/PZT-film/Pt:Ti/SiO_2/Si-substrate structures.

The obtained results evidence the interrelation of charge transfer and polarization reversal processes in PZT-film on Si structures. It is assumed that charge transfer-polarization reversal interplay takes place at least in the case of polarization reversal assisted by charged domain wall displacement proper to PZT films [8].

The physical reason of the observed consequences of the electrical treatment is the space charge transfer symmetrization through the film thickness under alternative voltage forming.

The observed asymmetry of the investigated polarization reversal and current-voltage characteristics is developed in the conditions of the space charge transfer in time.

References

[1] S. L. Bravina, E. Cattan, N. V. Morozovsky, D. Remiens, and G. Wang, "Pyroelectric characterization of hysteresis phenomena asymmetry in PZT film on silicon structures," *Integrated Ferroelectrics*, vol. 73, no. 1, pp. 27–35, 2005.

[2] S. L. Bravina, E. A. Eliseev, N. V. Morozovsky, D. Remiens, A. Grosman, and C. Soyer, "Pyroactive PZT-film/Si, PZT-film/Por-Si/Si and P(VDF/TrFE)-film/Si structures for integrated IR-sensorics," in *Pyroelectric Materials and Sensors*, D. Remiens, Ed., pp. 1–23, Research Signpost, Kerala, India, 2007.

[3] S. L. Bravina, N. V. Morozovsky, D. Remiens, and C. Soyer, "Examination of operation of PZT-film-Si-substrate structures as pyroactive memory elements," *Ferroelectrics*, vol. 353, no. 1, pp. 193–201, 2007.

[4] T. Haccart, E. Cattan, and D. Remiens, "Dielectric, ferroelectric and piezoelectric properties of sputtered PZT thin films on Si

substrates: influence of film thickness and orientation," *Semiconductor Physics, Quantum Electronics and Optoelectronics*, vol. 5, no. 1, pp. 78–88, 2002.

[5] B. Jaffe, W. R. Cook, and H. Jaffe, *Piezoelectric Ceramic*, Academic Press, London, UK, 1971.

[6] S. L. Bravina, N. V. Morozovsky, E. Dogheche, and D. Remiens, "Fast humidity sensing and switching of $LiNbO_3$ films on silicon," *Molecular Crystals & Liquid Crystals*, vol. 535, no. 1, pp. 196–203, 2011.

[7] S. L. Bravina and N. V. Morozovsky, "Pyroelectric effect in switching systems metal-ferro-semiconductor-metal based on proustite-pyrargyrite," *Phys & Techn Poluprov*, vol. 18, pp. 1944–1949, 1984.

[8] D. Fu, K. Suzuki, K. Kato, M. Minakata, and H. Suzuky, "Investigation of domain switching and retention in orientated $PbZr_{0,3}Ti_{0,7}O_3$ thin film by scanning force microscopy," *Japanese Journal of Applied Physics*, vol. 41, no. 11B, part 2, pp. 6724–6729, 2002.