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Chap. 19 : Dielectric properties and switching processes of ferroelectric superlattices

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Abstract : We review dielectric properties of BaZrO₃/BaTiO₃ (BZ/BT) superlattices deposited on a single-crystal MgO substrate, and having a period of 13.32 nm. These superlattices have specific properties distinguishing them from BZ or BT bulk materials, and from thin films, with a ferroelectric phase transition around 393-395 °C, significantly higher than in bulk samples and thin films of BT, and appearing of second order. The polarization switching occurs in two stages and the precise analysis of experimental data demonstrates that the motion of the domain walls causes the switching processes. We conclude that the mobility of the domain walls decreases on heating. The presence of an internal bias field has been demonstrated and shown to be directed from the superlattice to the substrate, in agreement with an analysis based on the flexoelectric effect. The switching current has been shown to vary in weak fields as $1/E^\mu$ with the exponent μ much smaller than in thin ferroelectric films. The appearance of the power index μ , which is significantly different from unity, may be due to a decrease in the average value of the switched polarization due to the boundaries between layers of different materials.

Keywords : PEROVSKITES, BaTiO₃, BaZrO₃, SUPERLATTICE, FERROELECTRIC, POLARIZATION, SWITCHING, DIELECTRIC PROPERTIES, PHASE TRANSITIONS

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I. Introduction

The successes of modern solid-state electronics are mostly based on the using of high-quality elemental base (in memory devices, control devices in circuitry and electro-optics, as pyroreceivers, micromanipulators, etc.), a significant part of which are nanoscale ferroelectric materials. The avant-garde role of ferroelectrics in many applications is based on their unique features: high performance characteristics, the ability to relatively easily change functional parameters (spontaneous polarization, its dependence on temperature, the value of the dielectric constant, its dependence on the frequency of the applied field, the values of electromechanical coefficients, etc.), a wide operating temperature range, etc. Ferroelectric thin films can be used to create a large number of different devices of micro-, nano-, opto- and microwave electronics due to the fact that they are radiation-resistant, energy-efficient, have the ability to control their parameters using external influences, short switching times, and stable characteristics in a wide temperature range and high dielectric characteristics [1-3]. The use of ferroelectric materials for creating memory devices is described in [4,5]. The work [6] gives an example of the implementation of a ferroelectric memory cell (FRAM) based on lead zirconate titanate PZT, developed by Texas Instruments and Ramtron.

One of the reasons for the attractiveness of ferroelectrics for practical use is the flexibility of their structure, associated with the presence of phase transformations in them, in the vicinity of which the structure of the crystal lattice is substantially softened. And also the presence in them in a certain temperature range of a stable polar state with a polarization vector, the orientation of which can be changed by applying an external electric field. Quantitative indicators of the favorable properties associated with ferroelectrics are such macroscopic parameters as the phase transition temperature, the magnitude of spontaneous polarization and the so-called coercive field, which characterizes its ability to switch. In planar ferroelectric devices as artificially created layered formations - ferroelectric superlattices are characterised by an additional flexibility of variation of parameters such as composition, thickness, and alternation of individual layers.

As separate layers in ferroelectric superlattices, the generally used substances have a perovskite structure, and are organized either in a combination of a ferroelectric — another ferroelectric or a ferroelectric — paraelectric materials [7–9]. The BaTiO_3 / SrTiO_3 combination is known for presenting a significant polarization and dielectric constant in the formed superlattice [10]. In this case, the paraelectric (“virtual ferroelectric”) SrTiO_3 becomes polarized due to mechanical stresses arising in the interface between layers with different unit cell sizes [11, 12].

Superlattices of a different composition, PbTiO_3 / SrTiO_3 , are notable for the fact that they have an almost ideal ratio of crystal lattice parameters of constituent materials. It appears that the ratio of the unit cell sizes of the alternating materials constituting the

layers of the superlattice, is a parameter that plays a decisive role in the formation of the required properties of the material.

Studies [10-12] and similar works confirm the seemingly obvious assumption that by creating suitable mechanical stresses, in particular in a heterogeneous material, it is possible to obtain the required change in the material properties. At the same time, it should be noted that quantitatively this relationship is still far from being refined, and there is certainly no reliable data on the differences in the sizes of unit cells of the mated materials that create the indicated stresses.

In a comprehensive study of ferroelectric superlattices, structural studies and data on the transition temperatures to the polar phase predominate [10-12]. The main applications of ferroelectric superlattices are associated with partial (in weak fields) or complete (switching) polarization changes [13-15], which were carried out also by the authors of this work. This article is a synthesis of data obtained by its authors [16, 17].

II. Materials and methods

BaTiO₃ (BT) and BaZrO₃ (BZ) epitaxial layers were grown on cubic single crystal (001) MgO ($a_{\text{MgO}} = 4.213 \text{ \AA}$) substrates buffered with an oxide conducting layer of La_{1/2}Sr_{1/2}CoO₃ (LSCO) ($a_{\text{LSCO}} = 3.805 \text{ \AA}$) as the lower electrode and platinum as the top electrode, with a radius of 0.5 mm. The samples were grown by pulsed laser deposition (PLD) using a Lambda Physik 248 nm excimer laser in a MECA 2000 UHV chamber. A 50 Å LSCO buffer layer was deposited at a substrate temperature of 750 °C in an oxygen partial pressure of 0.2 mbar. The temperature and oxygen pressure during BT and BZ layers deposition were 750 °C and 0.1 mbar, respectively. A deposition rate of 0.42 Å/pulse and 0.37 Å/pulse was determined from X-ray thickness (Laue) oscillations observed on very thin films of BT and of BZ successively. The growth of samples was controlled by Reflection high-energy electron diffraction (RHEED), which is an efficient in situ technique that allows to study the surface of the sample during deposition. RHEED streaks, produced from the BZ and BT layers and their Azimuthal positions showed a perfect cube-on-cube epitaxial growth [18,19]. The superlattice consists of 32 recurring layers of BZ and BT, with the thickness of individual layers of barium zirconate being 6.65 nm and that of barium titanate being 6.67 nm, and a period $\Lambda = 13.32 \text{ nm}$. The total thickness of the samples was about 400 nm.

The following methods and techniques were used to study the characteristics of samples.

X-ray diffraction studies were carried out using cobalt anode as a source of X-radiation with wavelengths $\lambda_{\alpha} = 1,789 \text{ \AA}$, $\lambda_{\beta} = 1,620 \text{ \AA}$.

The temperature dependence of dielectric permittivity of test samples was found by measuring the sample capacity with the LCR-meter Instek LCR-819. The frequency of the measurement signal was in the range of 1-50 kHz and the measuring voltage was

equal to 0.1 V. To identify the switching patterns of synthesized superlattices, a modified Sawyer-Tower scheme (by conductivity compensation) of studying dielectric hysteresis loops was used. As well as the Merz method, which accounts for the switching currents caused by bipolar rectangular pulses of the electric field. The switching current was measured by the voltage drop due to the resistance in series with the sample and recorded on the screen of a two-channel digital oscilloscope (TDS 2075). For this purpose, periodic voltage pulses of the same duration with an amplitude from 50 mV to 8 V and a frequency of 10 kHz were applied to a ferroelectric capacitor with a sample connected in series with a reference resistance equal to 50 Ω . The equidistant (polarizing and repolarizing) bipolar rectangular pulses were produced with the use of an Arbitrary Waveform Generator 2571 with a time increase of the switching voltage of no more than 10 ns. The pulse duration was from 5 to 80 μ s.

III. Results

X-ray diffraction studies of the investigated BaZrO₃/BaTiO₃ superlattices (cobalt anode as a source of X-ray radiation with wavelengths $\lambda_{a1} = 1.7889$ Å, $\lambda_{a2} = 1.7928$ Å (not used), and $\lambda_{\beta} = 1.6208$ Å) have shown that they are single crystal formations. The interplanar distance was determined to be $a = 4.084$ Å, which corresponds neither to barium titanate nor to barium zirconate: the bulk BT at room temperature has a tetragonal structure with dimensions $a_{BT} = 3.992$ Å and $c_{BT} = 4.036$ Å, and adjacent BZ layer for the bulk material has a cubic structure with the size $a_{BZ} = 4.192$ Å.

It is known that in a free state at room temperature, barium zirconate does not exhibit any polarization, it is paraelectric. The sizes of the elementary cells of barium titanate and barium zirconate along the substrate in the multilayer sample, are different from the bulk. Because of the indicated difference in the size of elementary cells under the action of the mismatch strain stresses in the superlattice, the unit cell BZ is compressed from the direction parallel to the substrate. It is known [20, 21] that with an increase in the uniform pressure in barium zirconate crystals, a phase transition from the cubic phase to the tetragonal phase occurs at a pressure of 17.2 GPa. This transition occurs due to the rotation of the oxygen octahedra ZrO₆ around one of the coordinate axes at an angle of 6°. Under conditions of compression in two mutually perpendicular directions in the plane of the plate and the absence of normal stress perpendicular to the plane of the plate, Poisson expansion of the crystal occurs in this direction.

These changes lead to the loss of stability of the zirconium ion in the symmetric position of the cell of the crystal lattice of barium zirconate and its displacement in the normal direction. As shown in [13-17], as a result of these processes, the BZ layers in the superlattice undergo a phase transition to the ferroelectric phase with the polarization vector directed perpendicular to the substrate, and the lattice BaZrO₃/BaTiO₃ as a whole, in accordance with research of the dielectric hysteresis

loops, demonstrates the presence of polarization in the direction of the normal to the substrate.

In the present work, with a view to revealing the regularities of an influence of the layer material and the dimensional parameters of the layers of the ferroelectric superlattice on its dielectric characteristics and phase transformations, the temperature studies of the dielectric constant and the tangent of the dielectric loss angle of the indicated ferroelectric superlattices were carried out.

Studies of the temperature dependence of the dielectric constant show the presence of a single maximum corresponding to a phase transition in the superlattice with a temperature of 393-395 °C (Fig.1) that is substantially higher than the transition temperature for bulk and film samples of barium titanate. A singular maximum in the temperature dependence of the dielectric constant, together with an absence of lines related to the BT and BZ structures in diffractogram, indicates that a new structure has been synthesized with respect to the original components. The dielectric constant of the synthesized superlattice increases from several dozens at room temperature to about 11000 units at the Curie point. This value of ϵ is higher than that for known ferroelectric films [22].

Figure 1. The temperature dependence of dielectric permittivity of the ferroelectric BaZrO₃/BaTiO₃ superlattice under the measuring field with a frequency of 1 kHz.

The temperature dependence of the inverse dielectric permittivity $1/\epsilon(T)$ for studied samples is presented in Fig. 2. These results show that the investigated superlattice behaves as a material with a second-order phase transition. For this dependence both Curie-Weiss law and the law of "two" are carried out: for BaZrO₃/BaTiO₃ superlattices the permittivity near the Curie point is inversely proportional to the temperature and the ratio of the slopes of the inverse dielectric constant below and above the Curie point is

close to 2 (in reality it is equal about $\sim 1.97 \div 1.83$. Besides, the $\varepsilon(T)$ dependences practically do not exhibit a temperature hysteresis with heating and cooling.

Figure 2. Dependence of the reverse dielectric permittivity on the temperature for BaZrO₃/BaTiO₃ superlattice.

Figure 3. The dependence of dielectric permittivity on temperature for BaZrO₃/BaTiO₃ superlattices with different frequency of measuring field: 1, 2, 3 - 1 kHz, 10 kHz, 50 kHz respectively.

The results of studying the effect of frequency on the values of dielectric response are shown in Fig. 3. From these dependencies, it is seen that the values of dielectric

constant decreases with increasing frequency of measuring field throughout the investigated temperature range. At the same time, the position of the temperature dependence maximum of permittivity remains relatively stable when frequency varies.

This behaviour evidently indicates the presence of areas in the studied materials with different relaxation times, which respond to an applied action with different rates and at different frequencies. Fig. 4 demonstrates dielectric hysteresis loops for studied superlattices at different temperatures. According to these loops of dielectric hysteresis, temperature dependencies of the spontaneous polarization (Fig.5) and the coercive field (Fig.6) can be calculated. The spontaneous polarization of the created structures at room temperature turns out to be $22.0 \mu\text{C}/\text{cm}^2$.

Figure 4. Dielectric hysteresis loops for $\text{BaZrO}_3/\text{BaTiO}_3$ superlattices at the following temperatures: 1,2,3,4 – 20, 340, 380, 395 °C

From Fig. 5 it is clearly visible, that superlattices are characterized by a smoother decrease of the polarization as it approaches the temperature of the transition to a nonpolar phase, compared to the bulk barium titanate material in which the polarization in the corresponding region demonstrates a sharp decrease.

The absence of a polarization jump upon the transition to the polar state in the temperature dependence of spontaneous polarization in comparison with bulk barium titanate, is a characteristic sign of a second-order phase transition in the superlattice.

The coercive field of the superlattice coincides with that characteristic for thin-film ferroelectric objects $E_c \approx 130 \text{ kV}/\text{cm}$. The strong temperature dependence of the coercive field (Fig.6) occurs in a rather wide range of temperatures; the same situation is observed for the temperature dependence of the spontaneous polarization (Fig.5).

Figure 5. The temperature dependence of the spontaneous polarization for the ferroelectric BaZrO₃/BaTiO₃ superlattice.

Figure 6. The temperature dependence of the coercive field for the ferroelectric BaZrO₃/BaTiO₃ superlattice.

Studies have shown that samples of synthesized superlattices have an internal bias field, which could be determined from the displacement of the dielectric hysteresis loop along the field axis. According to the calculations, the internal field in the studied superlattice appears to be small, but it also definitely assumes a non-zero value, equal to 32 kV/cm at room temperature (20 °C) and it slightly goes down as the temperature increases.

A special study was carried out to determine the sign (direction) of the indicated field. To do this, a constant field of predetermined direction was applied to the superlattice and the shifting of the hysteresis loop was registered in the total switching and additionally applied constant field. As it was shown when a positive charge is applied to the substrate, the hysteresis loop shifts to the side opposite to its displacement only under the action of internal bias field in the sample. This means that the initial internal bias field is directed from the surface of the superlattice to the substrate.

Figure 7. Switching currents of the BaZrO₃/BaTiO₃ superlattice for different values of the switching fields: 1,2,3,4 correspond to 22, 117, 187, and 235 kV cm⁻¹, respectively

The alternative to hysteresis loops way for studying the processes of polarization switching is the Merz method. In this method the value of the switching current is determined by subtracting the discharge of the linear component of the capacitance from the total current pulse. In this method the values used for the analysis are the integral switching characteristics: the maximum value of the switching current pulse $i_{\max}$ and the total switching time τ_s . The switching time τ_s is defined as the interval between the start of the current pulse and the time at which the switching current falls to 10% of the maximum value $i_{\max}$.

Figure 7 displays the switching current pulses of the studied superlattice as a function of the total switching time τ_s for different values of the switching fields. From these data it is possible to deduce the dependence of the maximum values of the switching currents as a function of the applied field strength. Results presented in Figure 8 show that these dependencies generally have the same characteristics as for switching ferroelectrics.

According to this picture, the full switching curve, similar to ferroelectric films [23], has two sections: the initial, so-called "activation" area or the "weak" fields area, where the indicated switching current dependence on the applied field is close to the exponent, and the subsequent linear section, namely the "strong" fields area or the "slip" area, where the dependence of the maximum switching current is proportional to the field $i_{\max} \approx \mu P E / d$ (P – polarization, μ – mobility of domain walls, d – sample thickness).

The boundary between the areas of the activation and nonactivation switching regimes, the so-called threshold or critical field E_{th} , determined by the switching currents as a field corresponding to the transition of an exponential dependence to a linear one, approximately corresponds to the coercive field determined by the dielectric hysteresis loop. According to experimental results, this threshold field decreases when approaching the ferroelectric phase transition temperature.

Figure 8. Characteristic dependence of the switching current on the external electric field strength for the BaZrO₃/BaTiO₃ superlattice at a temperature of 100 °C

A more detailed examination shows that the behaviour of the switching current in the weak fields areas differs from the usual activation mode. The activation switching regime in the area of "weak" fields is usually described by an exponential law:

$i_{\max} = i_{\max \infty} \exp(-\alpha/E)$, where α is an activation field that depends on the temperature. A plot of $\ln(i_{\max})$ versus the reverse field strength $1/E$ for the studied structures shows that this dependence for the BaTiO₃/BaZrO₃ superlattice is not a straight line.

This means that the simple activation dependence indicated above no longer describes the real dependence of the switching current on the field strength. In this case, it can be described by a more complicated formula in which the power-law exponent is introduced into the above activation dependence: the maximum value of the switching current is proportional to $\sim \exp(-\alpha/E^\mu)$ [23].

The selection of the power-law exponent μ introduced into the indicated dependence makes it possible to determine its values corresponding to the model function that are most consistent with the experimental dependence. Table 1 shows the values of the matched index μ for different temperatures. In comparison with ferroelectric films [23], the stated index at room temperature has a much lower value and is practically independent of the temperature.

Table 1 : Value of the matched index μ for the BaZrO₃/BaTiO₃ superlattice for weak fields at different temperatures

Temperature	24 °C	65 °C	120 °C	200 °C	250 °C	300 °C	350 °C
μ BaZrO ₃ / BaTiO ₃	0.21	0.21	0.20	0.20	0.196	0.19	0.19

To determine the "effective activation field" (constant α in the formula $i_{\max} \sim \exp[-\alpha/E^\mu]$, which describes the so-called "creep" (i.e. a slow but steady movement), the dependence of the logarithm of the maximum value of the switching current $\ln(i_{\max})$ is constructed as a function of $1/E^\mu$ the inverse field strength raised to the power μ .

Figure 9. Dependence of the logarithm of the maximum switching current on the inverse field strength, raised to the power of μ , for the $\text{BaZrO}_3/\text{BaTiO}_3$ superlattice for weak fields at different temperatures: 1,2,3 and 4 correspond to 65 °C, 120 °C, 230 °C and 350 °C, respectively.

Table 2: Value of the activation fields for the $\text{BaZrO}_3/\text{BaTiO}_3$ superlattice in the weak fields area at different temperatures

Temperature	24 °C	65 °C	120 °C	200 °C	250 °C	300 °C	350 °C
α (kVcm ⁻¹)	11.0	10.1	8.8	7.6	6.2	6.1	5.6
$\text{BaZrO}_3/\text{BaTiO}_3$							

As seen from Figure 9, these dependences are already straight lines, the slope of which can help one determine the values of the activation field at different temperatures.

The results are presented in Table 2. As expected, when the superlattice approaches the Curie point, the value of the effective activation field decreases with increasing temperature.

After the termination of the "activation" stage, the dependence of the maximum switching current as a function of the applied field is a straight line under fields larger than the threshold (the area of "strong" fields). The performed studies show that in this

region (Fig. 10), the slope of the switching current versus external field decreases with increasing temperature. This fact can be connected with a decrease in the mobility of the domain walls near the temperature of the phase transition in non-polar phase due to the growth of the switching time here.

According to the conducted studies, the samples of synthesized superlattices have an internal bias field, which can be determined by two methods:

- from the shift of the dielectric hysteresis loop
- from the point of intersection between the extrapolation of the linear section of $i_{\max}(E)$ dependence and the field axis.

Determined values of internal bias field by the two indicated methods approximately coincide. At the temperature of 20 °C, the internal bias field is 32 kV cm⁻¹ and slightly decreases with increasing temperature. From here, the internal displacement field is directed from the superlattice to the substrate, which can be explained by the flexoelectric deformations of the material deposited on the lower electrode (occurrence of polarization due to strain gradient).

Figure 10. Dependence of the switching current on the external field strength for the BaZrO₃/BaTiO₃ superlattice at various temperatures: 1,2,3,4,5,6 and 7 correspond to 20 °C, 100 °C, 200 °C, 250 °C, 300 °C, 350 °C and 400 °C, respectively

IV. Discussion

It stands to reason that ferroelectricity in the barium zirconate layer in a synthesized superlattice is induced by the mechanical stresses caused by the adjacent layers of barium titanate. The general increase of the Curie point in the superlattice in comparison to barium titanate in the bulk or film samples may be related with the mutual elastic action of the barium titanate and barium zirconate layers on each other.

These stresses significantly change the main characteristics of the thermodynamic potential of the superlattice, as a result of which metastable states disappear in its structure, which are the basis for a "jump-like" change in polarization with temperature; i.e. a first-order phase transition turns into a second-order transition. At the same time, the temperature of the loss of stability of the polar state of the superlattice increases significantly.

Figure 11 Schematic representation of the mechanism at the origin of the internal bias field: (a) free, undistorted cell, (b) distorted cell at interface with the substrate

At the interface between the deposited layer and the substrate, there is a stress due to smaller lattice parameter of the substrate ("electrode") that leads to a distortion of BaZrO_3 unit cells and to a symmetry lowering that induces a shift of Zr ions (see text) represented by the red arrow.

To explain the direction of the internal biasing field obtained in the investigated structures, one can use the representations of the flexoelectric effect. According to the technology of superlattice preparation, a layer of barium zirconate is in contact with the lower electrode. The unit cell size of the lower electrode, which is located near the substrate, is smaller than the barium zirconate cell size it makes contact with. This fact creates compressive stresses acting on the barium zirconate cell in the direction which is parallel to the substrate plane (Fig. 11). As a result of these stresses, the elementary

cells of barium zirconate contacting this electrode take the shape of a trapezoid the short base of which contacts the electrode. Due to the change in the shape of the unit cell, that lowers the local site symmetry, the positively charged ferroactive zirconium ion located in its center is extruded to the side opposite to the substrate, which means the appearance of the opposite negative charge at the interface with the electrode. The main factors determining the properties of ferroelectric superlattices and the possibility of their change in comparison with its constituent bulk materials are mechanical stresses arising from the mismatch of the sizes of the elementary cells of the various components of the superlattice which are in contact with each other and with the substrate. The stretching of BaTiO₃ layers in BaTiO₃/BaZrO₃ superlattices, as a result of epitaxial conjugation with BaZrO₃ layers, having a higher lattice parameter, should stabilize polarization in BaTiO₃ along the substrate. However, as shown in [24], the situation in the superlattice is qualitatively changed by the presence of a structural instability in BaZrO₃ relative to rotations of octahedra and by its competition with ferroelectric instability.

In biaxially compressed BaTiO₃/BaZrO₃ ferroelectric superlattices with the strain in the layer plane within 1–3%, the tilting of the octahedra leads to an improper ferroelectric phase transition¹ and, as a result, to the appearance of a nonzero z-component of polarization. This polarization evidently is manifested in the experiment when registering hysteresis loops in samples with electrodes that create a field along the normal to the [001] surface of the growth of the ferroelectric lattice. As a result in the BTO / BZO superlattices, high dielectric constant values are observed along this direction.

In principle, repolarization can be carried out by switching the material as a whole or by using the movement of domain boundaries [25-28]. To answer the question about the possibility of realization in this case of the switching of the material as a whole, it is necessary to compare the values of the coercive field actually detected in the experiment with the theoretical estimates of the material switching field as a whole.

The coercive field corresponding to the switching of the material as a whole, is determined, in thermodynamic theory, from the condition of the extremum of the dependence of the applied electric field versus polarization [28]:

$$E_c = \frac{2}{3\sqrt{3}} \alpha \sqrt{\frac{\alpha}{\beta}} = \frac{4}{3\sqrt{3}} \frac{\pi}{\epsilon} \frac{P_0}{\epsilon} \quad (1)$$

where α and β are the coefficients in the expansion of the thermodynamic potential in a series in terms of the polarization, P_0 is the spontaneous polarization, and ϵ is the dielectric permittivity of the material. Substituting into (1) the registered value of the spontaneous polarization $P_0 \sim 22.0 \mu\text{C cm}^{-2}$ and the value of the dielectric constant at room temperature $\epsilon \sim 10 \div 50$, we obtain a coercive field to switch the observed material as a whole that is equal to 2000 kV cm^{-1} , which exceeds the experimentally

¹ It is a phase transition where the polarization is a secondary order parameter, i.e. an order parameter coupled to the primary order parameter which is not of polar nature.

observed coercive field in the material under study (see Fig.6, the maximum value of coercive field is 150 kV/cm).

The weak value of experimentally observed coercive field in comparison with the estimated value of the indicated field for switching the material as a whole means that the switching process cannot be carried out by a simultaneous reversal of polarization in the entire sample, but occurs through the formation and growth of nuclei of the switched phase. The formation of such nuclei in the bulk of a homogeneous substance would require a too high stimulating energy. As a consequence, in reality, switching of superlattices, like other ferroelectrics, obviously occurs through the formation and growth of nuclei at domain boundaries. This is also confirmed by the estimations of the switching field in the domain mechanism presented below.

From the point of view of the domain mechanism, the threshold or critical field for switching of the perfect (defect-free) sample is determined as the field that makes it possible to overcome the Peierls barrier. This barrier is the difference between the energies of the main and saddle configuration of the domain wall, arising from the coordinate dependence of the energy of the domain wall in the discrete material. The specified field is equal to [28]

$$E_c = \frac{V_0}{aP_0} \quad (2)$$

where V_0 is the Peierls barrier, P_0 is the spontaneous polarization, and a is the size of the unit cell.

Substituting in eq.(2), the value of the lattice constant $a = 4.084 \text{ \AA}$ found experimentally, the spontaneous polarization equal to $22.0 \text{ \mu C cm}^{-2}$, and introducing a tentative value of the lattice barrier of the order of 1 erg cm^{-2} , typical for crystals of the barium titanate family [29], we obtain $E_c = 100 \text{ kV cm}^{-1}$.

This theoretical value of the threshold field calculated on the basis of a domain mechanism, is close to the experimentally observed value. The coincidence of the experimentally observed and estimated values of the threshold field is an additional argument in favour of the domain mechanism of switching of the studied superlattices.

V. Conclusions

Summarizing the results of research on dielectric and switching properties of ferroelectric barium zirconate /barium titanate ferroelectric superlattices deposited on a single-crystal magnesium oxide substrate, and consisting of 32 single-crystal layers with a period of $\Lambda = 13.32$ nm, the following can be noted. The investigated superlattices have a ferroelectric phase transition at the temperatures approximately equal to 393-395 °C which is significantly higher than the Curie point in bulk samples and thin films of barium titanate. Implementation of the "two" law, the absence of temperature hysteresis of the dielectric constant, smooth changes in the polarization and coercive field with a temperature near the Curie point indicate that the observed transition is a second-order phase transition.

The study of polarization switching in these superlattices has shown that the switching processes are carried out in two stages: the "creeping" stage and the sliding stage. The threshold field separating these stages corresponds to the coercive field and decreases with increasing temperature as the temperature approaches the Curie point of the superlattice.

The presence of the activation stage, the theoretical estimates of the coercive field switching of various mechanisms, and their comparison with experiments for the actually observed switching processes indicate that the motion of the domain walls causes the switching processes in the studied superlattices. At the pre-threshold stage, the activation process is the nucleation of a new phase on a moving domain wall. Here, the energies of the applied field are still insufficient to overcome the barrier that deters the switching, and an activation fluctuation on the temperature side (lattice vibrations) assists the switching process.

When the applied field reaches a value equal to the coercive field, the lattice barrier no longer affects the domain wall, and its motion is under the control of the corresponding processes of energy dissipation accompanying the movement of the domain boundaries (phonon inhibition, interaction with defects accompanying the motion of the domain wall, etc.).

In the region where the switching current varies linearly as a function of the field, the slope of the stated current dependence decreases with increasing temperature, which can be explained by a decrease in the mobility of the domain wall due to critical deceleration of the polarization relaxation near the Curie point.

In the studied structures, the presence of an internal bias field has been demonstrated. This field could be estimated from the displacement of the dielectric hysteresis loops and from the intersection point of the linear

section of the switching current with the field axis. Its value is approximately 32 kV/cm at room temperature and slightly decreases with increasing temperature. The specified internal field for the studied heterostructure substrate, i.e., the multilayer superlattice, is directed from the superlattice to the substrate. The action of the flexoelectric effect explains the emergence of the internal field of the stated direction.

Integral switching characteristics, and hence the speed of the motion of the domain walls in fields less than the threshold value, do not obey a strictly exponential dependence on the field strength. This leads to the appearance of a power-law exponent for the applied electric field μ in the dependence of the switching current (the velocity of the domain walls) on the electric field strength, which is much smaller in comparison with that of thin ferroelectric films and changes insignificantly when approaching the phase transition point.

In our opinion, the appearance of the power index μ , which is significantly different from unity, in the exponent of the switching current may be due not to a change in the switching mechanism, but, for example, to a decrease in the average value of the switched polarization due to a decrease of polarization near the boundaries of the layers of various materials.

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