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Ferroelectric properties of heterostructure $Sr_{0.5}Ba_{0.5}Nb_2O_6/Ba_{0.2}Sr_{0.8}TiO_3$/Si(001)

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The properties of *c*-oriented thin films of $Sr_{0.5}Ba_{0.5}Nb_2O_6$ grown on a Si(001) (*p*-type) substrate with a pre−deposited $Ba_{0.2}Sr_{0.8}TiO_3$ layer were studied using scanning probe microscopy and dielectric spectroscopy. It is established that the $Sr_{0.5}Ba_{0.5}Nb_2O_6$ films are characterized by low surface roughness (less than 6 nm) and average crystallite size of ~ 93 nm. It is shown that there is spontaneous polarization in the film directed from its surface to the substrate, which causes the manifestation of the field effect for the case of the Si substrate with *p*-type conductivity without the external field effect. Differences in the magnitudes of the surface potential signal for regions polarized by an external electric field of different polarities (+10 and −10 V), as well as in their relaxation to the initial state, are revealed. The reasons for the established patterns are discussed.

Keywords: barium-strontium niobate, SBN, scanning probe microscopy, thin films

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At present, a great attention is paid to heterostructures based on ferroelectrics (FEs) and semiconductors, which is caused by wide opportunities for their application in modern technology [1]. Regardless of a significant progress achieved during recent decades in this field, one has to admit that the potential of heterostructures of this type is not fully discovered, and the problem of searching for a ferroelectric with optimal composition and/or structure whose deposition procedure allows integration into the silicon technology is still topical [2]. Heteroepitaxial deposition of a material of the perovskite−type structure on silicon substrates was for the first time carried out for $SrTiO_3$ [3], which further allowed performing heteroepitaxial growth of a number of other FEs having structures of the perovskite type [4]. In paper [5] we have shown that this approach enables deposition on the silicon substrate a barium-strontium niobate (SBN) film having the structure like that of tetragonal tungsten bronze. Contrary to the case of monocrystals, structure and properties of SBN films grown on, e. g., silicon substrates are still poorly studied, however, just such films are a promising basis for creating novel IR matrices based on the pyroelectric effect [6], electrooptical modulator [7], elements of FeRAM and microelectromechanical systems. The goal of this work was to investigate room−temperature ferroelectric characteristics of the $Sr_{0.5}Ba_{0.5}Nb_2O_6$(SBN-50)/$Ba_{0.2}Sr_{0.8}TiO_3$(BST-20)/Si(001) heterostructure by scanning probe microscopy and dielectric spectroscopy.

Heterostructures SBN-50/BST-20/Si(001) were fabricated according to the procedure of intermittent sputtering by the method of high−frequency cathode sputtering in oxygen [4]. As a substrate, Si(001) (KDB-12, *p*-type, 12 Ω/cm) was used; the SBN-50 layer thickness was ~ 250 nm, that of the BST-20 layer was 35 nm (the thicknesses were estimated based on the sputtering time and pre−determined growth rate of each layer). High−frequency room−temperature CV characteristics (the sample capacity C at frequency $f = 10^5$ Hz with $U = 40$ mV versus the shifting electric field varying from −10 to +10 V) of the capacitor structures were measured using analyzer TF Analyzer 2000E. The topography, domain structure and data on the local switching processes and relaxation of signals of the polarized film regions were obtained with scanning probe microscope MFP-3D SA (Asylum Research, Oxford Instruments, USA) in the piezoresponse force microscopy (PFM) and Kelvin probe force microscopy (KPFM) modes with using cantilever NSG10/TiN (Tipsnano, Estonia). The image processing and analysis were performed using codes Gwyddion and WSxM [8].

During the analysis of the film topography image, grains were clearly seen whose size varied from 10 to 260 nm with the most probable radius of ~ 93 nm. The topography statistical analysis showed that the mean−square roughness of the SBN-50 film was below 6 nm. The absence of pores, cavities and other growth defects evidenced a high quality of the film surfaces. The revealed structure of the film surface directly results from the fact that the crystallite growth was of the oriented type along the substrate normal and of the stochastic type in the plane of conjugation with the substrate. As per data of the X-ray diffraction analysis, SBN-50 films were *c*-oriented (with the texture extent of ~ 8.3 and crystallite misorientation angle with respect to the surface normal of 3.5°). However, in the SBN-50 film

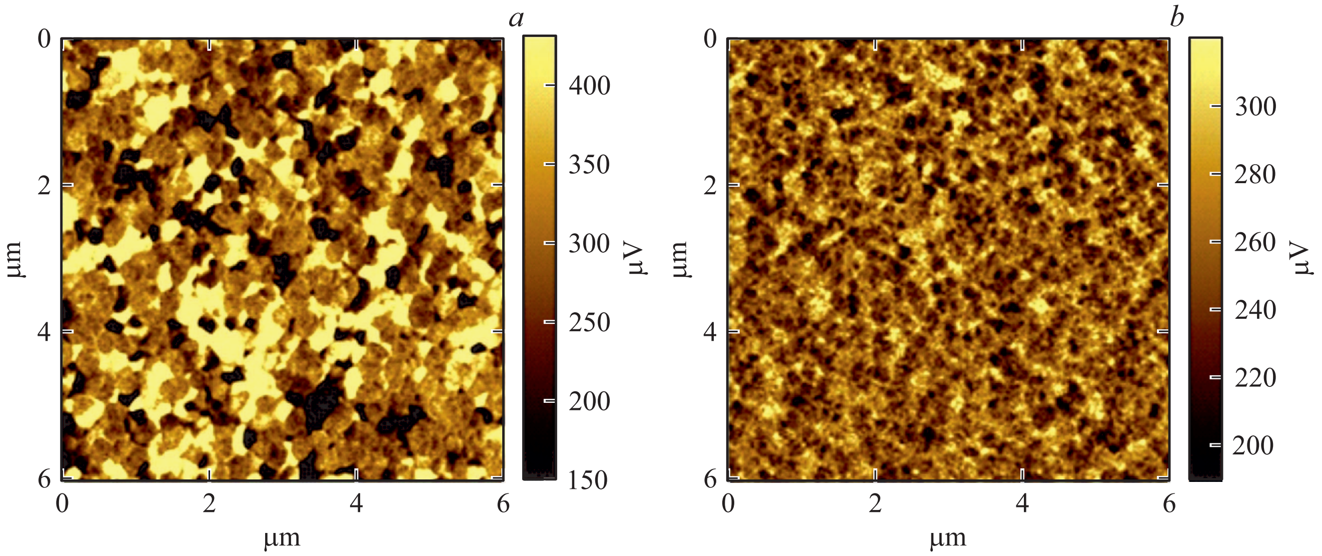

Figure 1. Image of the lateral (*a*) and vertical (*b*) piezoresponse signals of the SBN-50 film.

there was fixed a lateral piezoresponse signal (Fig. 1, *a*) that was more intense than the vertical signal (Fig. 1, *b*). This is characteristic of ferroelectric domains with the polarization component in the plane of conjugation with the substrate.

During the film polarization along the substrate normal, stable regions with different polarization orientations (from the substrate and towards the substrate) were successfully formed, which confirmed ferroelectric properties of the double–layer structure. The initial piezoresponse signal was positive, which means that, contrary to [9], the SBN-50 film peculiar feature is spontaneous polarization directed from the film surface to the substrate. In the KPFM mode, investigation was performed of relaxation of the polarized regions preliminary obtained in the mode of a ± 10 V piezoresponse force microscopy. In Fig. 2, *a*, the light square represents the result of applying the $+10$ V voltage to the cantilever, while the dark square is for the polarization at -10 V. Due to sufficiently low coercive fields in the SBN-50 ($\sim 2-3$ kV/cm [9]) films, just the contactless KPFM mode allows considerable reduction of the effects of the induced region depolarization directly during scanning. The analysis showed that in the KPFM mode the contrast of induced regions remains clearly visible for a long time (for more than 100 min), however, almost fully disappears in 180 min.

Fig. 2, *b* presents profiles of the surface potential signals obtained in 15, 45 and 180 min after polarization in the mode of piezoresponse force microscopy. What calls attention is significant asymmetry of the surface potential signal in the regions polarized at $+10$ and -10 V. Relaxation of the polarized state (in our case, this is ΔSP, namely, the signal of surface potential between positively and negatively charged regions) proceeds quite rapidly, and ΔSP reaches almost the initial value in 180 min (Fig. 2, *c*). Contrary to a similar case for a monocrystalline film SBN-50 [6] , the relaxation process, e.g., the $\Delta SP(t)$ dependence, is well describable by two exponents (Fig. 2, *c*) with the relaxation times of ~ 12 and ~ 32 min, respectively.

The results of studying dielectric characteristic of the SBN-50/BST-20/Si(001)–based capacitor structures are demonstrated in Fig. 3. To exclude the contribution of the memory effects characteristic of FEs, prior to measurements the samples were heated to $T = 570$ K (above the expected Berns temperature), held at this temperature for 60 min, and then cooled to room temperature. If the geometrical arrangement of the layers is taken into account, capacitance of the studied capacitor system is $C = (1/C_{\text{SBN-50}} + 1/C_{\text{BST-20}} + 1/C_{\text{Si}})^{-1}$, where $C_{\text{SBN-50}}$ is the SBN-50 film capacitance, $C_{\text{BST-20}}$ is the BST-20 film capacitance, C_{Si} is the silicon substrate capacitance. Prior to exposure to the field, the studied heterostructure capacitance is ~ 10 pF, which evidences that the *p*-Si substrate surface is in the depletion mode [10]. This takes place also in the case of SBN-50 films 80 nm thick deposited on Si(001) and of structures BST-20 (5 nm)/Si(001) [5]. The reason for this is the field effect manifestation due to the above–mentioned spontaneous polarization in the SBN-50 FE film directed towards the surface. The $C(U)$ dependence shape is similar to that of the high–frequency CV characteristic for the metal–ferroelectric–dielectric–semiconductor [10] and metal–dielectric–semiconductor [11] structures. In this case, the structure capacitance is measured by using a low AC signal with the period considerably shorter than lifetime of minority charge carriers and time of recharging of the semiconductor surface states. Under such conditions, the charge in the semiconductor inversion layer goes behind the AC voltage variation, and capacitance of minority carriers is zero (i.e., capacitance of the spatial charge region in the enrichment mode is defined by the majority charge carriers, while in the depletion and inversion modes it is

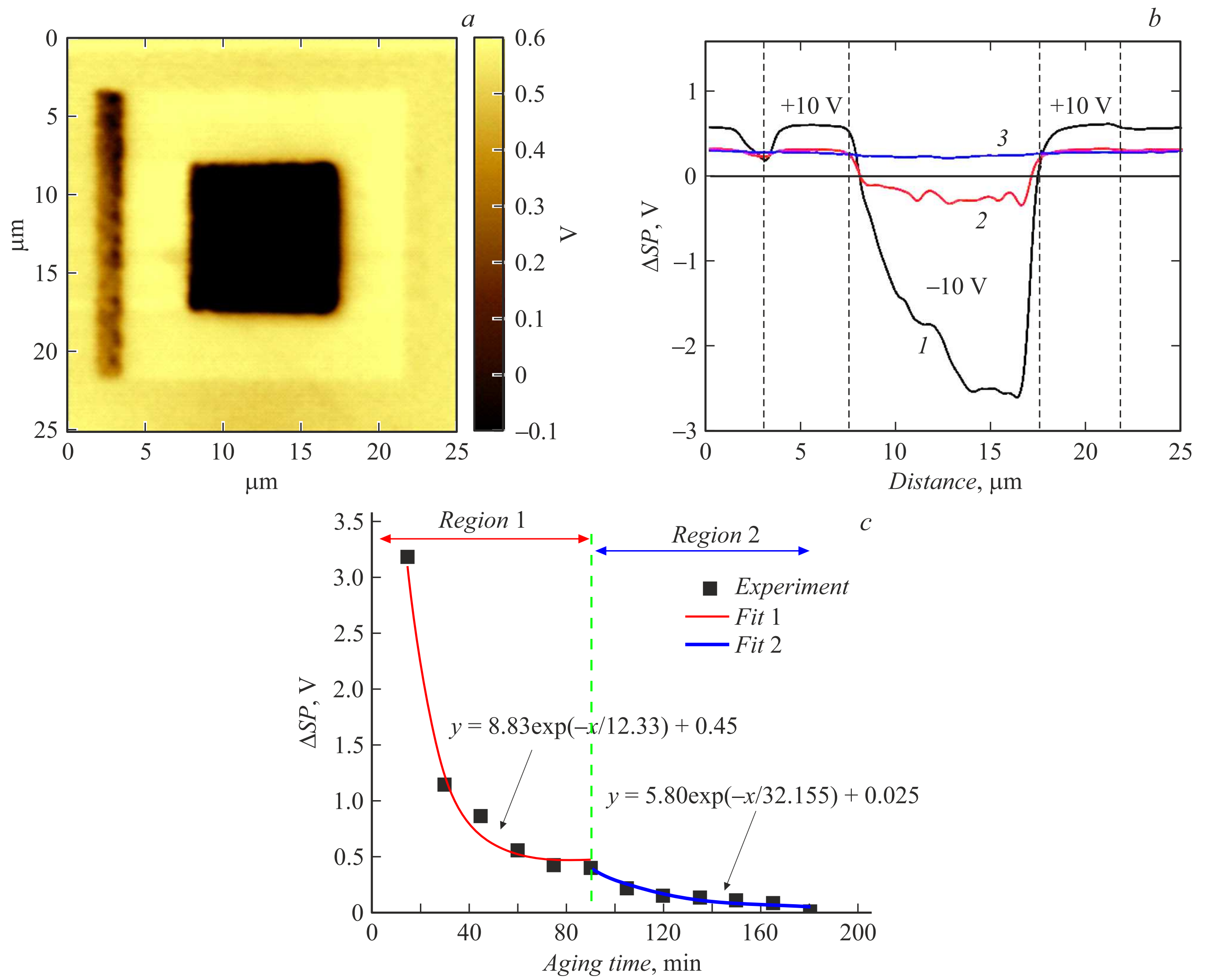

Figure 2. *a* — film SBN-50 surface potential after polarization with DC voltage of ±10 V; *b* — surface potential signal profiles in 15 (*1*), 45 (*2*) and 180 min (*3*) after pre–polarization; *c* — time dependence of the ΔSP signal.

defined only by the depletion layer). After a half–period exposure to the field at $U = 0$ V, the sample is characterized by a new state with $C = 17.5$ pF, which remains stable for more than 30 min and gradually relaxes to the initial one, which is caused by the SBN-50 film polarization. Application of the positive half-period returns the structure to the state with $C \sim 10$ pF. A slight hysteresis in the $C(U)$ dependences ($\Delta U \sim 1$ V) evidences, on the one hand, negligibility of contribution to the observed pattern of long–lifetime charged traps at the BST-20/Si interface, and, on the other hand, sufficiently low SBN-50 coercive fields ($\Delta U \approx 2h_{\text{SBN-50}}E_C$, see [9].

Thus, the paper demonstrates that in *c*-oriented films there forms a poly-domain structure characterized by spontaneous polarization arising in the process of the film synthesis and directed from the film surface to the substrate. This caused variations in the heterostructure dielectric and ferroelectric properties. Since the barium–strontium niobates are single–axis ferroelectrics, the predominance of the horizontal polarization vector component over the vertical one was quite unexpected. It is important to take this into account in experimental investigation of heterostructures based on thin SBN films and in fabricating detectors and sensors based on them. It is known that the domain structure of SBN monocrystals is quite complex (for instance, dimensions of fractal–like near–surface nanodomains depend on the composition, while the polar regions themselves can emerge at $T \gg T_C$ [12]) and significantly varies under the action of the field. It is reasonable to expect that in thin SBN films the above effects may be enhanced and/or manifest themselves in another way due to confinement effects and deformation fields; this is

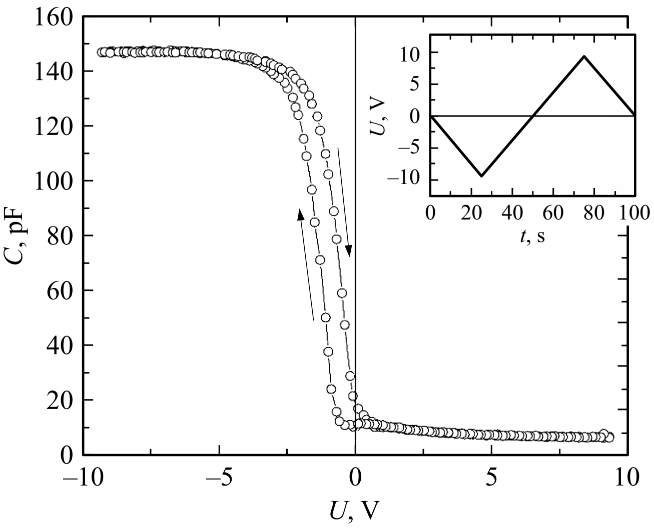

Figure 3. The room−temperature $C(U)$ dependence for heterostructure Al/Cr/SBN-50/BST-20/Si(001)/Cr/Al. The inset presents the $U(t)$ dependence.

just we have revealed. Our preliminary investigations have shown that in the SBN-50/BST-20/Si(001) heterostructure under study signs of spontaneous polarization are observed at $T > 250°C$. This can expand the application area of these materials in the thin−film state.

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Conflict of interests

The authors declare that they have no conflict of interests.

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