Micro- and nanoelectronics. Condensed matter physics

Микро- и наноэлектроника. Физика конденсированного состояния

UDC: 537.226
https://doi.org/10.32362/2500-316X-2022-10-2-28-34

RESEARCH ARTICLE

Local piezoelectric properties of perforated ferroelectric barium–strontium titanate films

Natalia E. Sherstyuk @

MIREA – Russian Technological University, Moscow, 119454 Russia
@ Corresponding author, e-mail: nesherstuk@mail.ru

Abstract
Objectives. Focused ion beam etching remains one of the most common methods for fabricating 2D photonic crystals and structures based on functional materials. This technique is quite well developed for semiconductors. But at the same time, the change in the properties of ferroelectric materials under the action of a focused ion beam, including parameters of distribution and switching of the polarization state under the action of an electric field, remains poorly studied. The purpose of this work is to determine the local piezoelectric parameters in perforated ferroelectric films of barium strontium titanate ($Ba_{0.8}Sr_{0.2}TiO_3$) with ordered vertical air channels fabricated by focused ion beam etching.
Methods. Experimental studies were conducted using piezoresponse force microscopy under applied electric field in planar geometry.
Results. It is shown that the perforation of a ferroelectric film leads not only to the formation of significant inhomogeneities in the piezoelectric response distribution in the structure, but also to the noticeable increase in the magnitude of both the vertical and lateral components of the piezoresponse near the perforation holes. The calculation results showed that the greatest enhancement is observed for the lateral component of the piezoresponse: from 5 pm/V for a nonperforated film to 65 pm/V in the perforated area.
Conclusions. The most probable mechanism for such a change in properties is the influence of a disturbed layer that occurs at the boundary and the inner surface of vertical air channels. The properties of this layer are due to two factors: amorphization of the structure as a result of the focused ion beam etching and the appearance of pinned domain states near the hole, leading to the formation of the complex piezoresponse distribution both at the hole boundary and in the gap between the perforations. The information obtained is important for understanding the peculiarities of the formation of local piezoelectric and ferroelectric responses in photonic crystals fabricated by focused ion beam etching, as well as for finding ways to control their state when an external electric field is applied.

Keywords: ferroelectrics, photonic crystals, piezoresponse force microscopy, focused ion beam etching

• **Submitted:** 04.08.2021 • **Revised:** 18.10.2021 • **Accepted:** 02.03.2022

For citation: Sherstyuk N.E. Local piezoelectric properties of perforated ferroelectric barium–strontium titanate films. *Russ. Technol. J.* 2022;10(2):28–34. https://doi.org/10.32362/2500-316X-2022-10-2-28-34

Financial disclosure: The author has no a financial or property interest in any material or method mentioned.

The author declares no conflicts of interest.

НАУЧНАЯ СТАТЬЯ

Локальные пьезоэлектрические свойства перфорированных сегнетоэлектрических пленок титаната бария-стронция

Н.Э. Шерстюк @

МИРЭА – Российский технологический университет, Москва, 119454 Россия
@ *Автор для переписки, e-mail: nesherstuk@mail.ru*

Резюме
Цели. Методика травления фокусированным ионным пучком остается одной из наиболее востребованных для изготовления двумерных фотонных кристаллов и структур на основе функциональных материалов. Данная методика достаточно хорошо отработана для полупроводников. Но в то же время изменение свойств сегнетоэлектрических материалов под действием фокусированного ионного пучка, в т.ч. параметров распределения и переключения поляризационного состояния под действием электрического поля, остается слабоизученным. Цель работы – определение локальных пьезоэлектрических параметров в перфорированных сегнетоэлектрических пленках титаната бария-стронция ($Ba_{0.8}Sr_{0.2}TiO_3$) с упорядоченными вертикальными воздушными каналами, изготовленными методом травления фокусированным ионным пучком.
Методы. Экспериментальные исследования проведены методом силовой микроскопии пьезоотклика при приложении электрического поля в планарной геометрии.
Результаты. Показано, что перфорация сегнетоэлектрической пленки приводит не только к формированию значительных неоднородностей в распределении пьезоэлектрического отклика в структуре, но и к заметному росту величины как вертикальной, так и латеральной компоненты пьезоотклика вблизи отверстий перфорации. Результаты расчета показали, что наибольшее усиление наблюдается для латеральной компоненты пьезоотклика: от 5 пм/В для неперфорированной пленки до 65 пм/В в области перфорации.
Выводы. Наиболее вероятным механизмом подобного изменения свойств является влияние нарушенного слоя, возникающего на границе и внутренней поверхности вертикальных воздушных каналов. Свойства этого слоя обусловлены двумя факторами: аморфизацией структуры в результате травления фокусированным ионным пучком и возникновением вблизи отверстия закрепленных доменных состояний, приводящих к формированию сложного распределения пьезоотклика как на границе отверстий, так и в промежутке между отверстиями перфорации. Полученная информация имеет значение для понимания особенностей формирования локальных пьезо- и сегнетоэлектрических откликов фотонных кристаллов, изготовленных травлением фокусированным ионным пучком, а также для поиска путей управления их состоянием при приложении внешнего электрического поля.

Ключевые слова: сегнетоэлектрики, фотонные кристаллы, силовая микроскопия пьезоотклика, травление фокусированным ионным пучком

• **Поступила:** 04.08.2021 • **Доработана:** 18.10.2021 • **Принята к опубликованию:** 02.03.2022

Для цитирования: Шерстюк Н.Э. Локальные пьезоэлектрические свойства перфорированных сегнетоэлектрических пленок титаната бария-стронция. *Russ. Technol. J.* 2022;10(2):28–34. https://doi.org/10.32362/2500-316X-2022-10-2-28-34

Прозрачность финансовой деятельности: Автор не имеет финансовой заинтересованности в представленных материалах или методах.

Автор заявляет об отсутствии конфликта интересов.

INTRODUCTION

The practical application of ferroelectric thin films is due to the peculiarities of the formation of the domain structure and its change under the action of an external electric field. At film thicknesses below 100 nm the average domain size becomes close to the film thickness, and the distribution of domains per unit volume is significantly affected by defects of various nature, surface topology, and properties of interfaces. These factors lead not only to noticeable distortions of the switching parameters (for example, the magnitude of the coercive field changes, the asymmetry of the hysteresis loop arises, etc.), but also to changes in the optical and nonlinear optical properties of the ferroelectric film due to its polarization state [1, 2]. Nevertheless, this approach opens up the possibility of creating, within the framework of one technology, a wide range of functional elements of integrated electronics and photonics with a controllable change in parameters due to the formation of ordered structures with certain geometry on the surface or in the volume of a functional material—superlattices and photonic crystals (PCs).

With the evolution of integrated photonics and the development of new principles for the functioning of its elements, systems, based on a combination of PCs of several types (for example, one-dimensional–two-dimensional) or on a combination of PCs of the same type, but with different geometric parameters, are of particular relevance, which ensures the implementation of various processes within a chip. This approach is already used in the design of hybrid electron-photonic chips based on semiconductor materials. Similar devices based on two-dimensional ferroelectric photonic crystals (FEPCs) are obviously not so common, but the fundamental possibility of creating tunable devices controlled by an electric field with their help maintains the interest of researchers in these materials [3–6].

Focused ion beam (FIB) etching is one of the most common methods for fabricating two-dimensional FEPCs, which, compared with lithography methods, has a number of advantages. It is easier to adapt to various materials and makes it possible to fabricate structures with different geometries within one technological cycle, while providing relatively low energy consumption at the sufficiently high spatial resolution, up to 5 nm [7].

Based on numerical simulations, it was shown in [8] that the domain structure of two-dimensional FEPCs, which are an ordered array of submicron holes, is quite complex even in simplified model that does not take into account defects in the structure and surface layer. In this case, the polarization distribution depends on the number and mutual arrangement of the channels, as well as on the depolarizing field that appears on the inner surface of the channels. In particular, it was shown that periodic perforation of a homogeneous ferroelectric film by cylindrical vertical air channels leads to the formation of polarization vortices at the edge of the holes, which, in turn, significantly increase the electric field in the region between the holes. This statement was partially confirmed by the method of electric force microscopy and optical second harmonic generation (SHG) in [9−11]. However, the results obtained by the SHG method, due to the spatial resolution of the technique, which is limited by the wavelength of the radiation used, make it possible to obtain only a qualitative agreement with the results of [8].

Despite the significant number of studies, the influence mechanism of the manufacturing method and geometric parameters of FEPC elements on the polarization distribution in the perforated region and, consequently, on the ability to control the state and properties of the material when an external electric field is applied, remains poorly understood. This paper presents the results of the experimental study by piezoresponse force microscopy (PFM) of the ferroelectric polarization state in the edge region of holes in perforated ferroelectric films of barium strontium titanate when an electric field is applied in planar geometry. Such a structure makes it possible to carry out local studies of the switching process both in the film and in the near-electrode region; in this case, in contrast to the z-geometry, the recorded piezoresponse is not averaged over the entire film thickness.

RESEARCHED STRUCTURES AND EXPERIMENTAL DETAILS

Thin barium–strontium titanate films $Ba_{0.8}Sr_{0.2}TiO_3$ (BST) of 1 μm thick were epitaxially grown on a MgO(001) substrate by high-frequency sputtering of ceramic targets [12]. An external electric field was formed in the film plane using an aluminum interdigital electrode (IDE) system with a gap between the electrodes of 1 μm and a period of 2 μm; the electrode height was 200 nm. Using the FIB method, a system of ordered vertical air channels with a hole diameter of about 880 nm was formed in the gaps between the electrodes. A Quanta 3D microscope (FEI Technology, United States) was used for etching; etching was performed with gallium ions; the etching current was 0.5–0.7 nA (Fig. 1a). The hole depth estimated by the etching time was about 1 μm.

The local piezoelectric properties of the obtained structure were studied by the PFM method using the contact mode of an Ntegra Aura scanning probe microscope (NT-MDT, Russia) in the vertical and

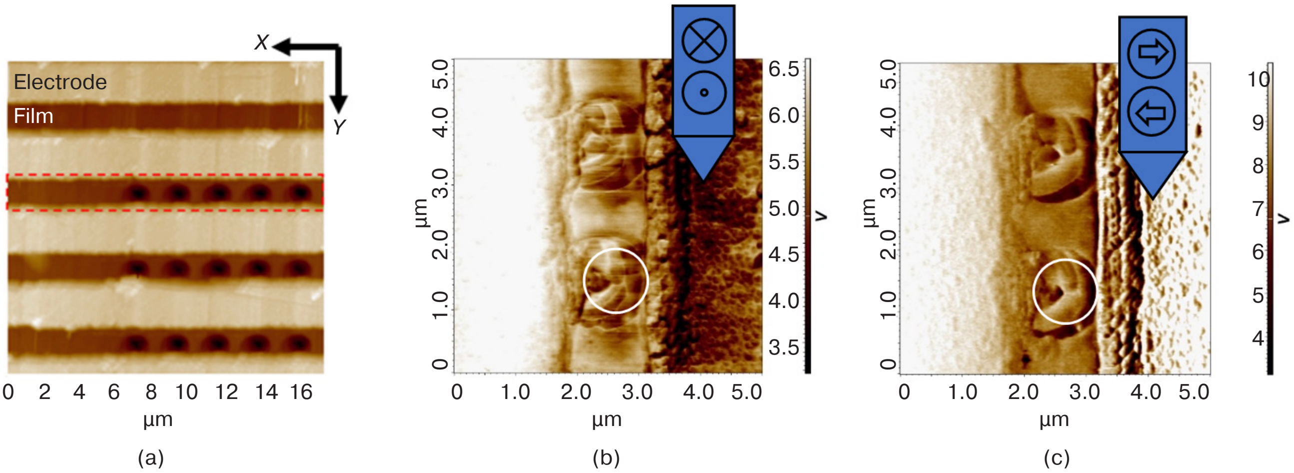

Fig. 1. Topography of the studied structure in the perforation area obtained by atomic force microscopy (a) and the distribution of the vertical (b) and lateral (c) components of the piezoresponse obtained by the PFM method for two adjacent perforation holes in the area marked by a dotted line at position (a). The white circle marks the vertical channel boundary

horizontal planes (Figs. 1b and 1c), respectively. During the scan, the movement of the cantilever was severely limited by the complex structure of the connecting electrodes and significant fluctuations in the sample topography. Therefore, scanning was carried out only in one direction perpendicular to the electrodes (along the *Y* axis in Fig. 1a). Cantilevers of the PPP-EFM series (resonant frequency 45–115 kHz; force constant 0.5–9.5 N/m, NANOSENSORS, Switzerland) were used for measurements; the voltage applied to the IDE system was in the range of 5–30 V. PFM measurements were carried out with alternating voltage applied with a frequency of 50 kHz and an amplitude of 5 V.

RESULTS AND DISCUSSION

Examples of PFM images of the vertical (vertical piezoresponse force microscopy, VPFM) and lateral (lateral piezoresponse force microscopy, LPFM) components of the piezoresponse at the edge of the air channel (region 1) and in the region located approximately in the middle between the two channels (region 2) are shown in Fig. 1b and Fig. 1c, respectively. It can be seen that the distributions of the piezoresponse in these regions are distinctly different. In the nonperforated region between the electrodes, the distributions of both components of the piezoresponse are more or less uniform. When voltage is applied to the electrodes in a nonperforated structure, the maximum value of the piezoresponse is localized in the near-electrode region. This agrees with the results of [13], in which it is shown that both components of the electric field sharply increase at the electrode boundary. In our measurements, the decrease in intensity from the maximum to the average value in the gap is observed at a distance of approximately 250 nm for both the lateral and vertical components. When a field of the opposite sign is applied, the near-electrode peak of the piezoresponse has a different value: the maximum intensity of the piezoresponse, when a constant voltage of +10 V is applied, significantly (by a factor of 2.8 for the lateral and about 1.7 times for the vertical component of the piezoresponse) exceeds the same value when a constant voltage of −10 V is applied. One of the reasons for this difference may be the nonswitchable polarization, which usually occurs at the film/substrate interface due to mechanical stress caused by the lattice period mismatch. However, at a film thickness of 1 μm the effect of this polarization on the lateral component of the piezoresponse near the surface can be considered insignificant. Another explanation for this difference in the piezoresponse may be the contribution to the recorded signal due to a change in the profile of the entire structure caused by the piezoelectric effect in the film under the electrodes. Previously, we showed [9] that an electric field can lead to a change in the structure profile within a few hundred nanometers. When a voltage of +10 V is applied, the change in the profile does not exceed 50 nm, but this may be sufficient for a noticeable shift of the laser beam in the recording system of an atomic force microscope, which, as a result, manifests itself in the asymmetry of the piezoresponse. This issue requires clarification.

On the perforated structure hole boundary, there are points at which a change (switching) of polarization is observed when an opposite potential difference is applied to the electrodes (for example, region 1) and points that retain their state at any value of the applied field (Fig. 2a). This distribution is explained by the influence of not only the features

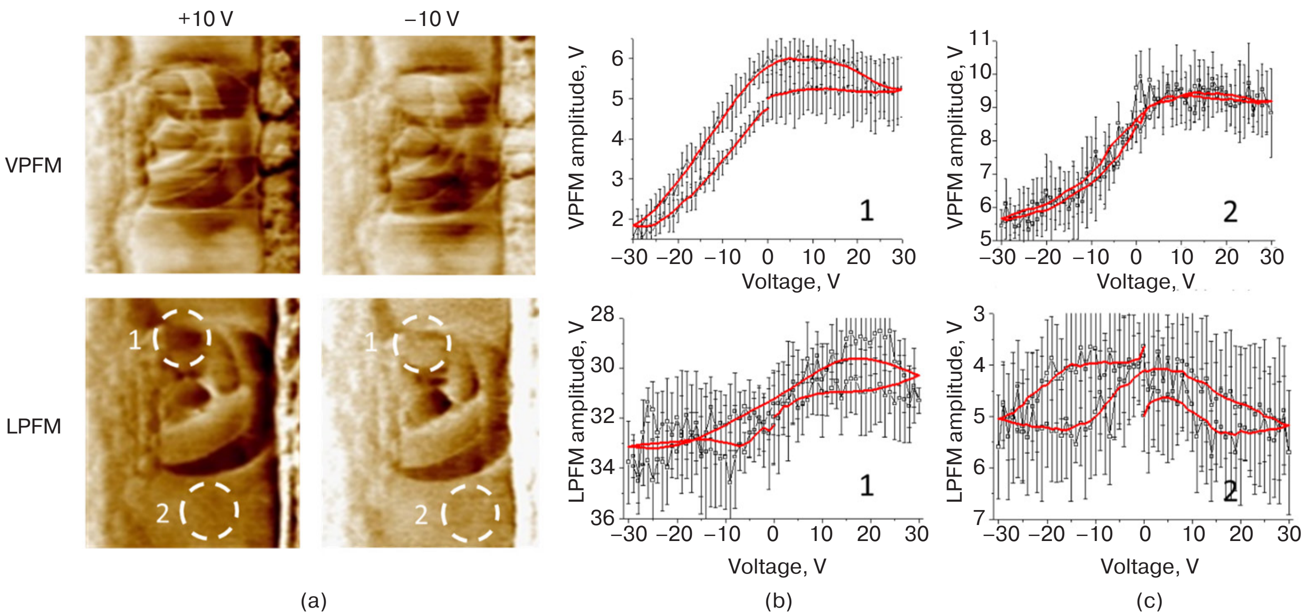

Fig. 2. Maps of the distribution of the piezoresponse in the area of one hole of the perforated structure when an external field is applied to the interdigital electrodes (a) and the dependence of the amplitude of the vertical (upper panels) and lateral (lower panels) piezoresponse on the voltage at the electrodes of the interdigital system of electrodes measured in regions 1 (Fig. 2b) and 2 (Fig. 2c). The red line is the result of averaging over 5 measurements for each cycle

of the topography, but also several mechanisms. The distribution of the piezoresponse is affected by structural defects that appear on the inner surface and on the hole edge as a result of etching. Firstly, the impact of high-energy ions is manifested in the implantation of high-energy Ga^+ ions into the material structure, and secondly, in the formation of a large number of microdamages on the surface and, as a result, in the amorphization of the near-surface layer. These factors create a defective layer on the structure surface (on the hole edge and on the air channel inner surface), which properties may differ significantly from those of the base material [14, 15]. It was also shown in [15] that the damaged region is not limited by the structure specified by the electronic template but extends no less than 1 μm from its edge into the depth of the region not subjected to etching. These damages and related distortions of properties are all the more significant, the more complex and more dependent on local polarization properties is the structure of PC elements. A rough estimate of the grains parameters in the hole region, performed using the NT-MDT Ntegra Aura scanning probe microscope software, showed that most of the grains in the holes have an average size of less than 100 nm, which corresponds to an amorphous structure.

Another factor affecting the inhomogeneity of the resulting distribution of the piezoresponse is the pinning of domains to the inner surface of the air channel, which interact with the side surface of the conducting needle of the cantilever. As a result, the overall piezoresponse in the hole region has a much greater intensity and inhomogeneity than the typical response of an amorphous structure.

To study the effect of a defective layer on the piezoresponse parameters, piezoelectric hysteresis loops were measured in the region containing the switched domain (region 1 in Fig. 2a) and in the gap between two air channels (region 2 in Fig. 2a). Details of the measurement technique are given in [9]. Since the structure has a significant number of defects, 5 measurements for each cycle were averaged. The results of individual measurements, the averaged value, and the errors for the vertical and lateral piezoresponse are shown in Figs. 2b and 2c, respectively. During the measurements, the external bias voltage changed from the initial state (0 V) to a positive value and back.

The vertical piezoresponse loop in region 1 is not symmetrical and has a relatively low saturation state at +10 V and a large, about 3 GV/m, saturation field at a negative value of the applied field (Fig. 2). The vertical piezoresponse loop in region 2 (in the gap between the holes) is more symmetrical and slightly shifted to the negative part. The nonswitchable polarization caused by mechanical stresses at the interface with the substrate does not affect the formation of the piezoresponse. Therefore, such a shift can be explained by the influence of pinned domain states near the boundary of the air channel opening. The possibility of the formation of short-range mesoscale domains in a perforated ferroelectric structure is confirmed in a number of works (e.g., [16]).

The field dependences of the lateral piezoresponse recorded in region 1 show a more complex piezoelectric behavior compared to that observed in the gap between holes (region 2). This behavior is consistent with the relaxation of mechanical strain near the holes, where the film material is removed by ion etching [17]. However, an important feature of these results is that the perforated structure showed a high response in the LPFM signal even with hysteresis behavior. The increase in the PFM signal and the different loop termination tendencies can be explained by the assumption that the LPFM domains formed a closed structure around the hole with the opposite orientation of the spatial domains. In accordance with this assumption, the LPFM signal in the second region is formed under the influence of two 180-degree domains from adjacent holes, resulting in the formation of 90-degree domains between the holes, which are visualized by measuring VPFM. This mechanism partly agrees with the simulation results presented in [8] and requires further detailed study.

Based on the measured piezoelectric hysteresis, the piezoelectric coefficients in regions 1 and 2 were estimated in accordance with the approach described in [9, 10], in which it is assumed that the effective piezoelectric coefficients of the vertical d_V and lateral response d_L are: $d_V \approx d_{33}$, $d_L \approx d_{15} \pm d_{31}$.

The calculation results showed that perforation of a ferroelectric film leads to an increase in the lateral component of the piezoresponse from d_L = 5 pm/V for a nonperforated film to 65 pm/V in the region of perforation. The VPFM tensor also increased but not as sharply, from 11 to 40 pm/V.

CONCLUSIONS

When an ordered structure of vertical air channels is formed in an epitaxial film of the $Ba_{0.8}Sr_{0.2}TiO_3$ ferroelectric by etching with a focused ion beam, a damaged layer is formed on the inner surface of the air channel, the properties of which are due to two factors: amorphization of the structure and the appearance of pinned domain states near the channel boundary. This, in turn, leads to the formation of a complex piezoresponse distribution in the area of the perforation hole. If the vertical component of the piezoresponse dominates in the nonperforated structure, then in the perforated structure the contribution of the lateral component increases due to the formation of a complex structure with opposite domain orientations in the region adjacent to the hole boundary. Perforation leads to an increase in both the vertical and lateral components of the piezoresponse compared to the nonperforated film. The results obtained must be taken into account when calculating and modeling the distribution of the piezoelectric properties of two-dimensional photonic crystals based on ferroelectric films.

ACKNOWLEDGMENT

The author thanks M.S. Ivanov (University of Aveiro, Portugal) for the help in conducting PFM studies.

REFERENCES

1. Scott J.F., Paz de Araujo C.A. Ferroelectric memories. *Science*. 1989;246(4936):1400–1405. https://doi.org/10.1126/science.246.4936.1400
2. Wang Y.G., Zhong W.L., Zhang P.L. Surface and size effects on ferroelectric films with domain structures. *Phys. Rev. B*. 1995;51(8):5311–5314. https://doi.org/10.1103/PhysRevB.51.5311
3. Lin P.T., Yi F., Ho S.-T., Wessels B.W. Two-dimensional ferroelectric photonic crystal waveguides: simulation, fabrication, and optical characterization. *J. Lightwave Technol*. 2009;27(19):4330–4337. https://doi.org/10.1109/JLT.2009.2023808
4. Matveev O., Morozova M., Romanenko D. Concept of using composite multiferroic structure magnonic crystal – ferroelectric slab as memory unit. *J. Phys.: Conf. Ser*. 2019;1389(1):012041(1–5). https://doi.org/10.1088/1742-6596/1389/1/012041
5. Hu X., Gong Q., Feng S., Cheng B., Zhang D. Tunable multichannel filter in nonlinear ferroelectric photonic crystal. *Opt. Commun*. 2005;253(1–3):138–144. https://doi.org/10.1016/j.optcom.2005.04.056
6. Takeda H., Yoshino K. Tunable photonic band gaps in two-dimensional photonic crystals by temporal modulation based on the Pockels effect. *Phys. Rev. E*. 2004;69(1Pt2):016605(1–5). https://doi.org/10.1103/PhysRevE.69.016605
7. Ferri A., Rémiens D., Desfeux R., Da Costa A., Deresmes D., Troadec D. Evaluation of damages induced by Ga+-focused ion beam in piezoelectric nanostructures. In: Wang Z. (Ed.). *FIB Nanostructures. Lecture Notes in Nanoscale Science and Technology*. Cham: Springer; 2013. V. 20. P. 417–434.
8. Levanyuk A.P., Misirlioglu I.B., Mishina E.D., Sigov A.S. Effects of the depolarization field in a perforated film of the biaxial ferroelectric. *Phys. Solid State*. 2012;54(11):2243–2252. https://doi.org/10.1134/S1063783412110170
9. Sherstyuk N.E., Ivanov M.S., Ilyin N.A., Grishunin K.A., Mukhortov V.M., Kholkin A.L., Mishina E.D. Local electric field distribution in ferroelectric films and photonic crystals during polarization reversal. *Ferroelectrics*. 2016;503(1):138–148. https://doi.org/10.1080/00150193.2016.1217143
10. Ivanov M.S., Sherstyuk N.E., Mishina E.D., Khomchenko V.A., Tselev A., Mukhortov V.M., Paixao J.A., Kholkin A.L. Enhancement of local piezoelectric properties of a perforated ferroelectric thin film visualized via piezoresponse force microscopy. *J. Phys. D: Appl. Phys*. 2017;50(42):425303(1–6). https://doi.org/10.1088/1361-6463/aa8604

11. Mishina E., Zaitsev A., Ilyin N., Sherstyuk N., Sigov A., Golovko Yu., Muhortov V., Kolesnikov A., Lozovik Yu., Yemtsova M., Rasing Th. Switchable nonlinear metalloferroelectric photonic crystals. *Appl. Phys. Lett.* 2007;91(4):041107(1–6). https://doi.org/10.1063/1.2762284
12. Mukhortov V.M., Golovko Y.I., Tolmachev G.N., Klevtzov A.N. The synthesis mechanism of complex oxide films formed in dense RF – plasma by reactive sputtering of stoichiometric targets. *Ferroelectrics*. 2000;247(1):75–83. https://doi.org/10.1080/00150190008214943
13. Brekhov K.A. Electric field intensity in a planar capacitor based on thin $BaSrTiO_3$ Ferroelectric Film. *Nano- i Mikrosistemnaya Tekhnika = Nano- and Microsystems Technology*. 2018;20(9):555–561 (in Russ.). https://doi.org/10.17587/nmst.20.555-561
14. Volkert C.A., Minor A.M. Focused ion beam microscopy and micromachining. *MRS Bulletin*. 2007;32(05):389–399. https://doi.org/10.1557/mrs2007.62
15. Morelli A., Johann F., Schammelt N., Vrejoiu I. Ferroelectric nanostructures fabricated by focused-ion-beam milling in epitaxial $BiFeO_3$ thin films. *Nanotechnology*. 2011;22(26):265303(1–6). https://doi.org/10.1088/0957-4484/22/26/265303
16. Kholkin A.L., Kalinin S.V., Roelofs A., Gruverman A. *Scanning Probe Microscopy: Electrical and Electromechanical Phenomena at the Nanoscale.* Kalinin S., Gruverman A. (Eds.). New York: Springer; 2006. 988 p.
17. Nagarajan V., Roytburd A., Stanishevsky A., Prasertchoung S., Zhao T., Chen L., Melngailis J., Auciello O., Ramesh R. Dynamics of ferroelastic domains in ferroelectric thin films. *Nat. Mater*. 2003;2(1):43–47. https://doi.org/10.1038/nmat800

About the author

Natalia E. Sherstyuk, Cand. Sci. (Phys.-Math.), Associate Professor, Department of Nanoelectronics, Institute for Advanced Technologies and Industrial Programming, MIREA – Russian Technological University (78, Vernadskogo pr., Moscow 119454 Russia). E-mail: nesherstuk@mail.ru. Scopus Author ID 6602267129, ResearcherID A-3460-2014. https://orcid.org/0000-0002-7068-4028

Об авторе

Шерстюк Наталия Эдуардовна, к.ф.-м.н., доцент кафедры наноэлектроники Института перспективных технологий и индустриального программирования, ФГБОУ ВО «МИРЭА – Российский технологический университет» (119454, Россия, Москва, пр-т Вернадского, д. 78). E-mail: nesherstuk@mail.ru. Scopus Author ID 6602267129, ResearcherID A-3460-2014. https://orcid.org/0000-0002-7068-4028

Translated by E. Shklovskii
Edited for English language and spelling by L. Daghorn, Awatera