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Effects of resistive switching in films based on inorganic perovskite nanocrystals $CsPbBr_3(I_3)$, conjugated polymer P3HT and [60]PCBM

© M.K. Ovezov, A.N. Aleshin

Ioffe Institute,
St. Petersburg, Russia

E-mail: strontiumx94@gmail.com, aleshin@transport.ioffe.ru

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The development of reliable optoelectronic memristors is crucial for the successful development of neuromorphic systems, however, existing devices suffer from uncontrolled dynamics of ion migration resulting in the unpredictable resistive switching parameters. Structures were obtained in this paper using nanocrystals of inorganic perovskites — quantum dots $CsPbBr_3(I_3)$, films of conjugated polymer poly(3-hexylthiophene) (P3HT) and a fullerene derivative [60]PCBM. The morphology and optoelectronic properties of the sandwich structures obtained were studied. It was found that the obtained samples demonstrate a memory effect at 300 K consisting in switching from a high- to a low-resistive state when voltage is applied. The nature of the memory effect observed in such structures associated with the capture of charge carriers by traps is discussed, as well as the prospects for using such materials in neuromorphic interfaces and for the manufacture of memory cells — memristors.

Keywords: inorganic perovskites, transport mechanisms, resistive switching, memristors, conductive polymers.

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1. Introduction

The development of digital technologies sets new urgent tasks for the associated electronic component base. Rapidly evolving virtual ecosystems connected to the Internet, in particular, with the Internet of Things, require an increase of the speed of devices and devices into which they are integrated. The currently generally accepted von Neumann architecture has long been capable to meet the increasing demand for hardware characteristics, but the development of technologies reveals the limitations imposed on it [1–3]. One of the main such limitations is the difference in performance between the processor and the computer's memory, which creates an imbalance in the exchange of data between them, which, in turn, limits the speed of the computer. The development of reliable optoelectronic memristors is crucial for the successful solution of this task for development of neuromorphic systems. The range of materials used for creation of memristors has been significantly expanded in recent years for the improvement of memristor performance [4,5]. Memristors based on perovskite [6], silicon oxides (mainly SiO_2) [7], metal oxides [8], graphene and its derivatives [9] and other materials were developed. Most such materials improve the stability of the characteristics of memristors, but they contain oxygen vacancies that limit the memristor effect. An important area of research is the use of materials that do not contain oxides, such as inorganic nanocrystals of perovskites, as memristors. Switching effects in such systems and the effect of layers of semiconductor polymers and fullerene derivatives on them are currently insufficiently studied.

Sandwich structures were obtained in this paper using nanocrystals (NC) of inorganic perovskites — quantum dots — $CsPbBr_3(I_3)$, conjugated semiconductor polymer poly(3-hexylthiophene) (P3HT) and a fullerene derivative [60]PCBM. The morphology and optoelectronic properties of the obtained structures were studied. It was found that the obtained samples demonstrate the memory effect at 300 K, which consists in switching the structure from a high to a low-resistive state when voltage is applied. The nature of the memory effect observed in such structures associated with the capture of charge carriers by traps is discussed, as well as the potential of usage of such materials in neuromorphic interfaces.

2. Subjects of the study and methods of investigation

The studied structures were made by applying appropriate solutions to glass substrates with 5 mm wide conductive layers of tin-doped indium oxide (ITO). A layer of conductive polymer —poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT : PSS) (Sigma Aldrich) was applied to the ITO layer to coordinate the work function of the hole layers and then it was dried at 60°C for 30 min. PEDOT : PSS films were applied by centrifugation using Chemat Technology spin-coater KW-4A centrifuge at speeds of 1000 rpm and 3500 rpm for 10 and 30 s, respectively. Layers of $CsPbBr_3(I_3)$ nanocrystals (details of NC synthesis were described earlier in [10]) were applied to PEDOT : PSS and dried for 10 min at a temperature of 100°C. Layers of semiconductor polymer P3NT and fullerene derivative [60]PCBM (both — Sigma Aldrich) were applied to the NC layer for more efficient absorption of light by the structure and these layers were dried for 10 min at a temperature of

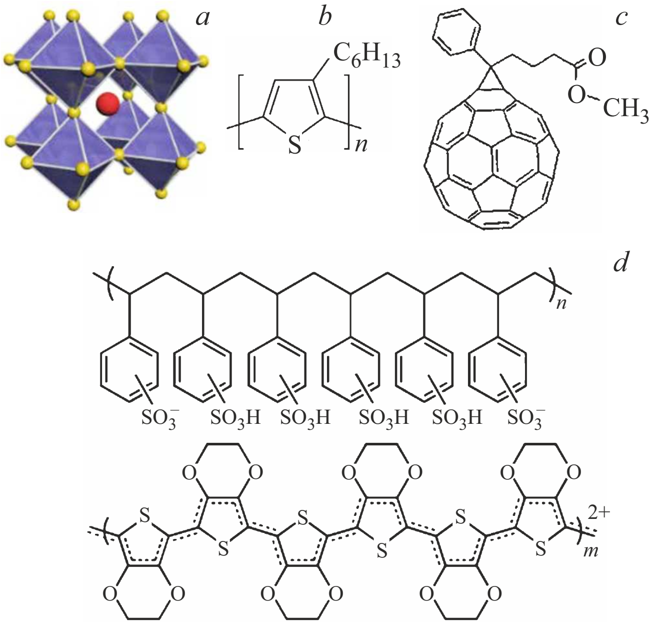

Figure 1. Structural formula *a*) $CsPbX_3$, where X — I, Br, *b*) P3HT, *c*) [60]PCBM, *g*) PEDOT : PSS.

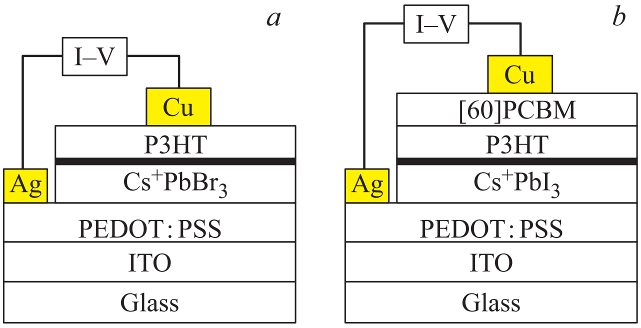

Figure 2. The structure of the studied structures.

60°C in an inert box in a nitrogen atmosphere. The obtained samples were stored before measurements in a vacuum desiccator MB „SANPLATEC Corp.“. The structure of the molecules of the materials used in this paper, as well as the structure of the samples studied in this paper, are shown in Figure 1 and 2, respectively. The morphology of the surface of the deposited layers of NC was studied using atomic force microscopy (AFM) using SOLVER P47 PRO NT-MDT. Photoluminescence (PL) of films of $CsPbI_3$ and $CsPbBr_3$ nanocrystals was excited by an ultraviolet LED UVTOP280TO39HS with radiation wavelength of 285 nm.

The current-voltage curve (CVC) of the samples were measured in planar geometry using a two-probe pattern at room temperature in darkness and with illumination by a sunlight simulator using an automated setup based on Keithley 6487 picoammeter. The applied voltage varied from -2 to 2 V with variable pitch. The contacts to the ITO (PEDOT : PSS) electrodes were attached with silver wire using carbon paste. Contacts with P3HT were implemented in the form of clamping copper electrodes.

3. Results and discussion

The results of AFM studies of the morphology of films of $CsPbBr_3$ nanocrystals deposited on *c*-Si substrate, shown in Figure 3, indicate that samples have a developed surface with a relatively heterogeneous morphology. As can be seen from Figure 3, globules consisting of arrays of NC

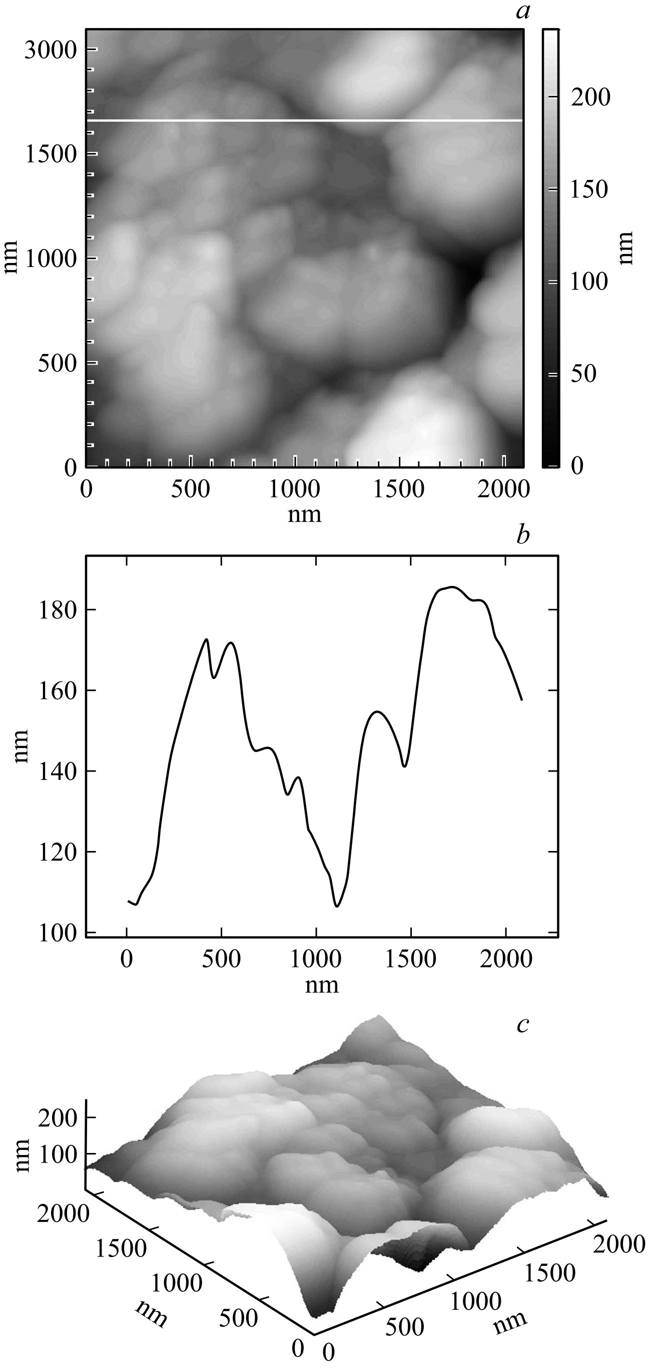

Figure 3. The results of AFM studies of the morphology of films of $CsPbBr_3$ nanocrystals deposited on *c*-Si.

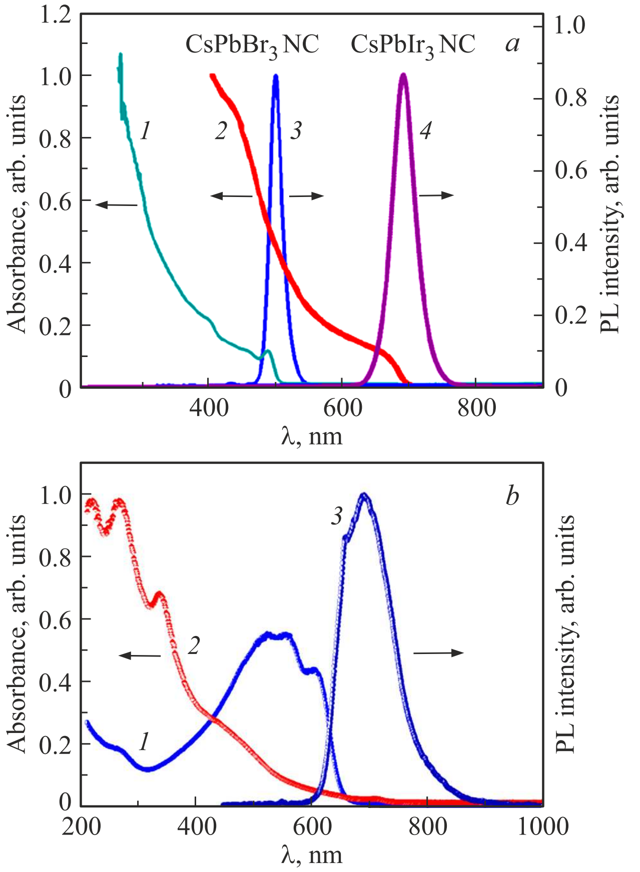

Figure 4. *a*) Absorption spectra of pure films of CsPbBr$_3$ nanocrystals (line *1*) and CsPbI$_3$ nanocrystals (line *2*) on quartz substrates; PL spectra of pure CsPbBr$_3$ nanocrystals (line *3*) and CsPbI$_3$ nanocrystals (line *4*); *b*) Absorption spectra of (*1, 2*) and PL (*3*) of films: P3HT (*1, 3*) and [60]PCBM (*2*) respectively.

CsPbBr$_3$ with pronounced boundaries are observed in the studied films, while the average grain diameter varies within $\sim 500-700$ nm, and their height is $\sim 60-80$ nm. The studied films of CsPbBr$_3$ nanocrystals are characterized by significant roughness (Root Mean Square, Rq), which in the field $2 \times 2\,\mu$m was $Rq \sim 33.6$ nm (Average Roughness = 26.7 nm) (Figure 3, *b, c*).

The absorption and PL spectra of films of CsPbBr$_3$ nanocrystals and CsPbI$_3$ nanocrystals, as well as P3HT and [60]PCBM films are shown in Figure 4, *a* and *b* respectively. Figure 4, *a* shows that the absorption edge and peak PL of films of CsPbBr$_3$ and CsPbI$_3$ nanocrystals correspond to wavelengths of 510 nm and 680 nm, respectively, and the absorption edge of the P3HT film is 640 nm. Thus, CsPbBr$_3$ nanocrystals absorb light in the range of about 500 nm, while the absorption edge of CsPbI$_3$ nanocrystals is shifted to the red region of the spectrum (680–690 nm). The use of P3HT and [60]PCBM films also allows shifting the absorption edge of the entire structure to a longer wavelength region and expanding the spectral absorption range. A similar effect with respect to films of organometallic perovskites is widely used in solar cell manufacturing.

Figure 5, *a, b* shows the CVC structures based on CsPbBr$_3$ nanocrystals and films of P3HT: ITO/PEDOT : PSS/CsPbBr$_3$/P3HT/Cu. The structure demonstrates pronounced diode properties with a forward and reverse bias current ratio reaching four orders of magnitude, as well as the resistive switching effect observed in case of application of a forward bias of $\sim 0.2-0.3$ V. The presence of reverse switching is observed with a decrease of voltage, while the switching effect is more pronounced during subsequent passages, as shown in Figure 5, *b*, and CVC before and after switching is ohmic in nature, which is consistent with the results of previous studies [11]. The observed character of the CVC is in many ways similar to the CVC of films of organometallic perovskites [11,12], which, taking into account their reproducibility, makes the studied structures perspective with a view of their use in memristor and RRAM — instrument structures.

Typical CVC of composite film of ITO/PEDOT : PSS/CsPbI$_3$/P3HT/[60]PCBM/Cu is shown in Figure 6, *a, b*. The effect of switching from a low-conducting to a high-

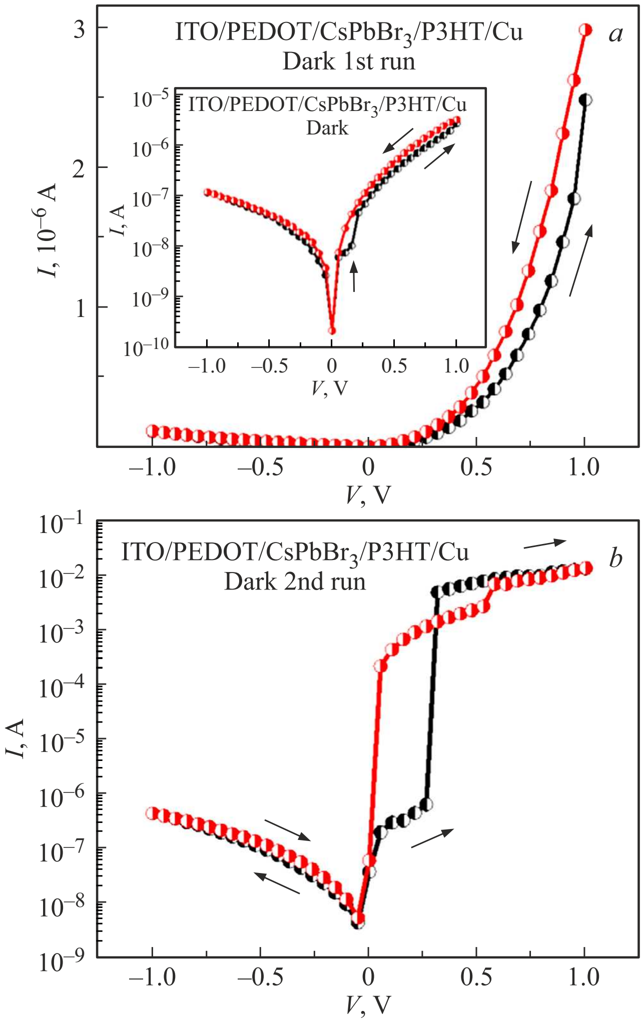

Figure 5. CVC of ITO/PEDOT : PSS/CsPbBr$_3$/P3HT/Cu structure, measured in the darkness, on a direct and semi-logarithmic scale, at the first (*a*) and second (*b*) passage.

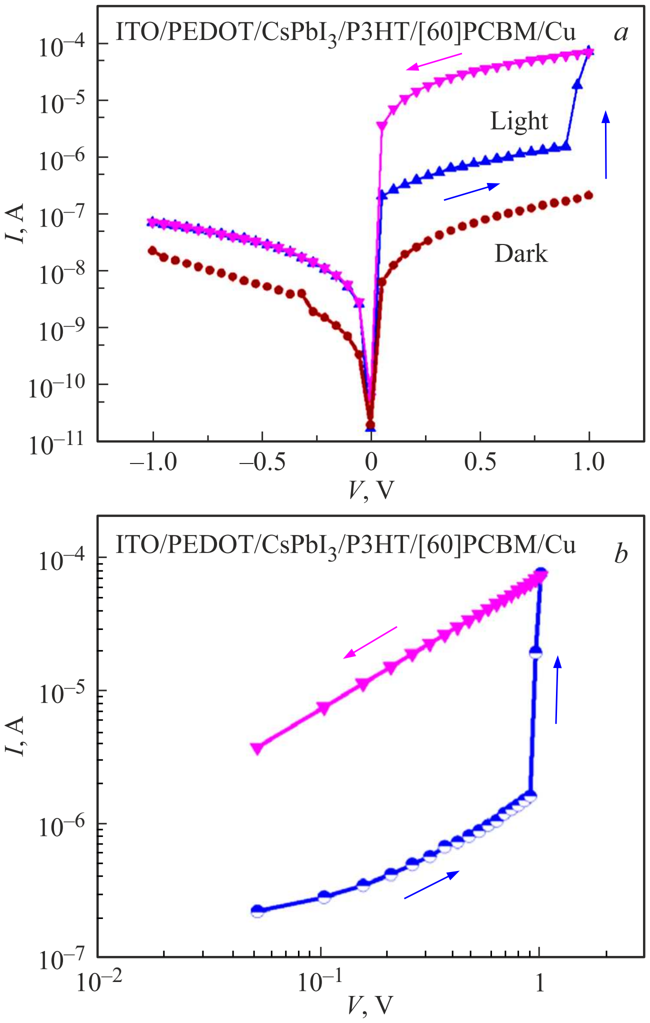

Figure 6. CVC of ITO/PEDOT : PSS/$CsPbI_3$/P3HT/[60]PCBM/Cu structure, measured in the darkness and with illumination, at the semi-logarithmic (*a*) and double logarithmic (*b*) scale.

conducting state in these samples takes place when a bias of the order 0.9−1 V is applied to the electrodes with illumination by a sunlight simulator. It should be noted that both before and after switching, the CVC obey the Ohm's law, while the current ratio in high- and low-conducting states differed by 150−200 times. The samples remained in the photoinduced switched state as long as they were exposed to the bias, no switching was observed when the reverse bias was applied, at the same time the samples demonstrated diode properties with a forward and reverse bias current ratio of 10.

Figure 7, *a, b* shows diagrams of energy levels of sandwich structures of ITO/PEDOT : PSS/$CsPbBr_3$/P3HT/Cu (*a*) and ITO/PEDOT : PSS/$CsPbI_3$/P3HT/[60]PCBM/Cu (*b*). The subject structures absorb photons, and then free carriers are generated at the P3HT/$CsPbBr_3$(I_3) interfaces after exciton dissociation. Consequently, the built-in electric field at the interfaces, induced by accumulated electrons, results in good photosensitivity of the samples irradiated with a sunlight simulator.

Thus, the effect of resistive switching is observed not only in structures based on films of organometallic perovskites [11,12], but also in sandwich structures based on nanocrystals of inorganic perovskites — $CsPbBr_3$(I_3) and semiconductor polymer P3HT — both in the darkness and with the illumination.

The memory phenomenon in such materials can be explained by the capture and subsequent release of the charge by traps. Optical programming capabilities allow memristors in both studies to simulate synaptic plasticity with light stimulation, which provides a cost-effective solution for creating artificial synaptic devices with photoelectric operations in the field of memory architecture designing using nanocrystals. Reconfigurable devices that can switch between volatile and non-volatile states have recently attracted a lot of attention.[12,13]. Reconfigurable memristors [14] were demonstrated in 2022 that implemented switching between diffusion/volatile and drift/non-volatile modes while maintaining high performance.

Devices based on thin films of perovskite nanocrystals have a wider band gap and higher stability than 3*D* films of halide perovskites because of the suppression of migration of ions Cs and halogens. These properties make them suitable for memristor applications requiring tunable

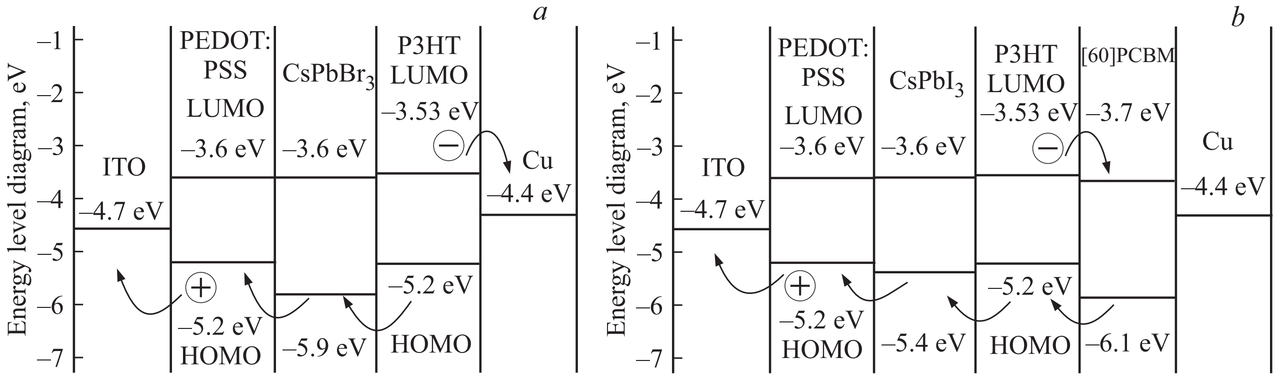

Figure 7. Energy band diagrams of structures of ITO/PEDOT : PSS/$CsPbBr_3$/P3HT/Cu (*a*) and ITO/PEDOT : PSS/$CsPbI_3$/P3HT/[60]PCBM/Cu (*b*).

conductance states, low power consumption, and fast response. We have recently proposed a special mechanism for resistive switching in memristors based on organometallic perovskites, associated with the splitting of the film volume into vortex movements of ions and vacancies of the Benard cell type [15]. It was demonstrated that such cells may act as a preparatory stage for splitting the volume of halide perovskites into a multitude of closely spaced filaments which are formed by neutral halogen vacancies and support the electronic gap conduction in addition to the ionic one. We believe that this mechanism can also manifest itself in the structures studied in this paper.

At the same time, it should be noted that structures based on nanocrystals of halide perovskites also have certain problems, such as structural complexity and the presence of barriers for carrier transfer. For this reason additional studies are needed to optimize their characteristics and overcome the limitations for memristor applications.

4. Conclusion

Sandwich structures were obtained in the study using perovskite nanocrystals of $CsPbBr_3(I_3)$, conjugated polymer P3HT and fullerene derivative [60]PCBM. The morphology and optoelectronic properties of the obtained structures were studied. It was established that the obtained structures demonstrate a memory effect at 300 K consisting in switching from a high to a low-resistive state when bias is applied and with illumination, while a current change of 2 orders of magnitude is observed in samples obtained using [60]LSWM and a current change of 4 orders of magnitude in observed in samples without it. The nature of the memory effect observed in such structures is associated with the capture of charge carriers by traps. The studied materials are perspective in view of the use in neuromorphic interfaces.

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Conflict of interest

The authors declare that they have no conflict of interest.

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