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Electrical and Optical Characteristics of CsPbI₃ and CsPbBr₃ Lead Halide Perovskite Nanocrystal Films Deposited on *c*-Si Solar Cells for Photovoltaic Applications

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Received July 4, 2022

Revised July 4, 2022

Accepted July 6, 2022

The deposition of an additional layer of nanoparticles is a widely used method for improving the optical and electrical characteristics of semiconductor solar cells (SCs). In this work, films of nanocrystals (NC) of inorganic perovskites of lead halides CsPbI₃ and CsPbBr₃ are deposited on the surface of a solar cell based on crystalline silicon (*c*-Si). It is shown that the optical properties of such NC films are in good agreement with the optical properties of *c*-Si. It has been found that the absorption coefficient of solar cells with NC layers of inorganic perovskites is much higher in the visible region of the spectrum, which increases the photocurrent generation in the SC in the range of 370–900 nm. A significant effect of surface roughness on the photoelectric properties of solar cells has been found. CsPbI₃ NC films have a textured surface and higher photocurrent than CsPbBr₃ NC films, which are rougher. Enhanced photovoltaic properties of photoelectric structures with a CsPbI₃ NC layer compared to CsPbBr₃ NC films due to their lower degree of roughness were observed.

Keywords: perovskite nanocrystals, silicon solar cells, reflection spectra, photoluminescence, electrical conductivity.

DOI: 10.21883/PSS.2022.11.54189.418

1. Introduction

The development of solar power engineering requires continuous improvement of characteristics of photovoltaic devices — solar cells (SC). An important development direction of SC efficiency improvement technology is the use of heterojunctions between amorphous hydrogenated and crystalline silicon (*a*-Si:H/*c*-Si), that possess all advantages of SC based of crystalline silicon, but can be produced at lower temperatures, that decreases their cost. In recent years an extensive research activities are carried out in the world related to the improvement of efficiency of these heterostructure-based tandem SC by applying films of metal-organic perovskites to further increase efficiency and decrease optical loss. Modification of *c*-Si SC surface with films of metal-organic perovskites is considered one of the most promising directions [1]. This is due to high absorption coefficient in these materials in the visible spectrum [2], the ability to form multilayer heterostructures based on them [3], quite high mobility of charge carriers [4], as well as relatively low cost of their production. At the same time an assumption was made that optical resonance nanostructures (perovskite nanocrystals, NC) can make possible the transition from optical scale to nanometer scale decreasing light absorption due to the excitation of strongly

localized optical modes. This will allow for a decrease in the number of required optical devices, such as waveguides, lasers, photosensors and so on, as well as open the way to effective control of light in subwave range [5].

This work presents results of studies focused on the modification of optical and electrical properties of *c*-Si SCs by applying on them films of NCs of CsPbI₃ and CsPbBr₃ inorganic perovskites. It is found that optical properties of NC provide good matching with crystalline *c*-Si SC, as well as that they have strong absorption and intensive photoluminescence (PL). NCs of perovskites are characterized by high bonding energies of excitons and lifetimes, as well as high diffusion distances of charge carriers as compared with polycrystalline films of perovskites [1]. NCs of CsPbI₃ and CsPbBr₃ were applied on a substrate made of crystalline silicon, *c*-Si, coated with a conductive layer of ITO. NCs are characterized by a wide bandgap, from 1.75 to 2.13 eV [1] and 2.34 eV [6] for CsPbI₃ and CsPbBr₃, respectively, while *c*-Si has a bandgap of 1.2 eV, which cumulatively results in the creation of a heterostructure with a wide bandgap.

2. Research targets and methods

In this study we used SCs made of single-crystalline silicon *c*-Si provided by the Research Center of Thin-Film

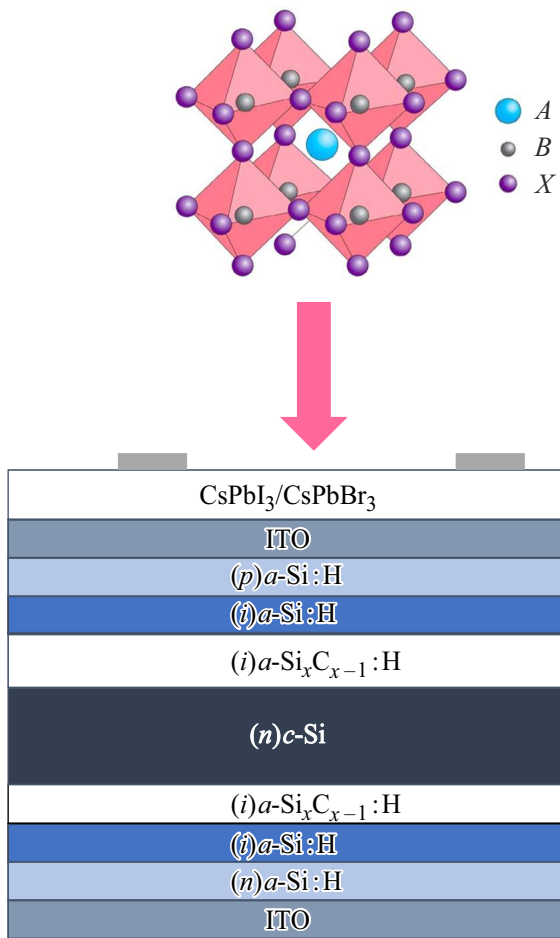


Figure 1. Structure of SC and NCs of A^+BX^- perovskites, where $A^+ = \text{Cs}$, $B = \text{Pb}$, $X^- = \text{I}_3, \text{Br}_3$.

Technology in Power Industry at Ioffe Institute. The basic SC shown in Fig. 1 includes a crystalline substrate of n -type silicon, c -Si, (100)-oriented, on both sides of which are successively applied a layer of amorphous hydrogenated silicon carbide in the form of a solid solution of $\text{Si}_x\text{C}_{x-1}:\text{H}$, with $0.8 < x < 0.90$ with a thickness of 0.5–2 nm, an undoped layer of amorphous hydrogenated silicon with a thickness of 2–5 nm, on the front side (the side of radiation) a p -doped layer of amorphous hydrogenated silicon is applied with a thickness of 5–20 nm, a layer of tin-oxide ITO with a thickness of 90–110 nm. On the back side of the crystalline substrate there are successively applied a n -doped layer of amorphous hydrogenated silicon with a thickness of 10–20 nm, a layer of tin-oxide, ITO, with a thickness of 40–80 nm. The crystalline substrate with a thickness of 80–250 μm is a material where main light absorption takes place in the SC.

The goal of this work was to apply films of perovskite NCs of CsPbI₃ and CsPbBr₃ onto the frontal part of the above-described SCs and to study electrical and optical characteristics of such structures. Two types of NCs of CsPbI₃ and CsPbBr₃ in the form of suspension were

synthesized in Saint Petersburg Electrotechnical University „LETI“ similar to our previous studies [7]. NC solutions were applied on substrates of c -Si by spin-coating using a Chemat Technology spin-coater KW-4A at 2000 rpm for 30 s. In the process of depositing the perovskite NCs were synthesized by means of molecular-crystalline synthesis, during which the structure was self-organized while the solvent was evaporating. Then the top ITO electrode with a thickness of 80 nm was applied onto the film of perovskite NCs by the thermal spraying method. The structure of the samples under examination is shown in Fig. 1. The morphology of the surface of the applied NC layers was studied by atomic force microscopy (AFM) using SOLVER P47 PRO NT-MDT. It is known that perovskite NCs are highly efficient light-emitting materials, and studying the character of their PL makes it possible to study the quality of the prepared samples. PL of films of CsPbI₃ and CsPbBr₃ NCs was excited by ultraviolet LED UVTOP280TO39HS with a wave length of 285 nm, which radiation was focused to a point with a diameter of 2 mm on the surface of samples using a quartz lens at an angle of 10° from the normal orientation to the sample surface. Reflection spectra were measured in the Research Center of Thin-Film Technology in Power Industry at Ioffe Institute using the CARY5000 scanning spectrophotometer in the spectral range from 200 to 2500 nm. Current-Voltage characteristics (IV curves, I-Vs) of samples were measured in sandwich-geometry using a two-probe scheme. IV curves of photoelectric current ($I_{\text{ph}}\text{-V}$) of SCs under study were measured using the Keithley 6487 picoammeter with illumination by a xenon lamp calibrated at a solar simulator with a power of 50 mW/cm², at a room temperature in a voltage range from +0.5 V to –0.5 V, with a variable step. Contacts to the samples were made of silver and copper wire.

3. Results and discussion

The morphology of films of CsPbI₃ and CsPbBr₃ NCs applied from solutions by spin-coating at 290 K was studied by AFM. Fig. 2 (I — a, b, c) and (II — a, b, c) shows AFM-images that illustrate the difference in surface textures for the film of CsPbI₃ NCs, which is less rough and contains shapes of spherical structure of different sizes with random distribution, with root-mean-square roughness, RMS: $S_q = 12.1$ nm, which nature, perhaps, is related to the formation of NC agglomerates. In contrast to the film of CsPbI₃ NCs, films of CsPbBr₃ NCs are characterized by the absence of explicit spherical shapes, while their RMS is: $S_q = 47.7$ nm, which is considerably higher than that of films of CsPbI₃ NCs. Such significant difference in RMS and mean value of roughness can be explained by the formation of agglomerates due to an increase in the size and density of CsPbI₃ NCs. The last fact can result in the growth of light absorption and modification of optical losses.

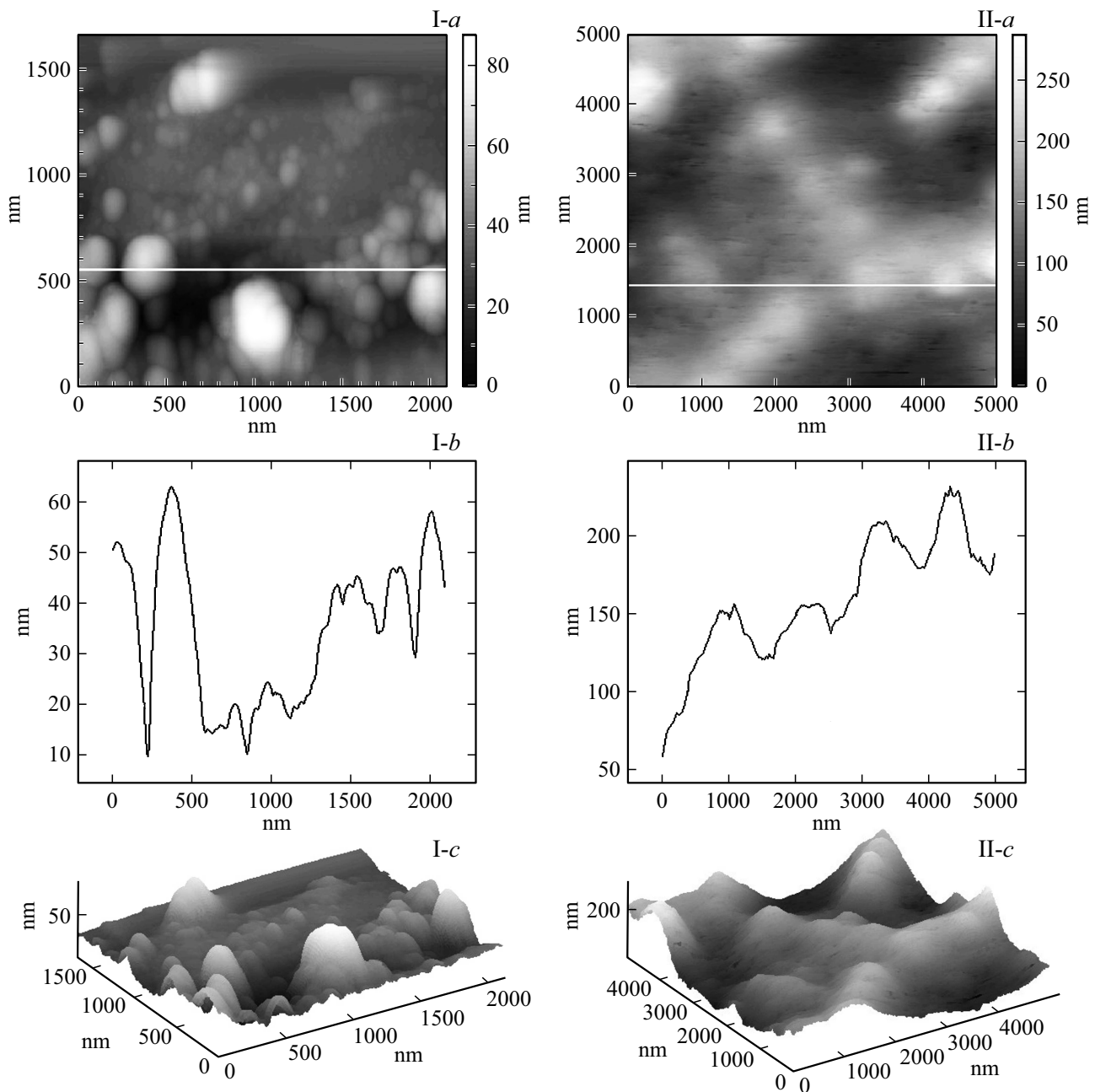


Figure 2. Morphology of the film surface of CsPbI₃ (I — *a, b, c*) and CsPbBr₃ (II — *a, b, c*), respectively, studied by the AFM method.

Fig. 3 shows reflection spectra of *c*-Si films, as well as CsPbI₃ and CsPbBr₃ NCs. As can be seen from Fig. 3, the absorption coefficient (α) of SC with applied layers of NCs of perovskites are considerably higher in some ranges of visible spectrum as compared with initial *c*-Si SC, that results in an increase in the generation of photoelectric current in a range of 370–900 nm. A decrease in the absorption coefficient results in the shift of the reflection spectrum towards short-range infrared region, which is connected with the increase in effective refraction indices, that changes depending on the concentration of NCs inside the layer. Also, it is worth noting, that samples of *c*-Si

and NCs of CsPbI₃ are characterized by the presence of similar reflectance bands in the same range of wave lengths. While the reflection coefficient of CsPbBr₃ is different from the last two substances. The intensity of reflection remains quite high in all three samples, that was quite unexpected and, probably, attributable to the absence of an antireflection layer, that significantly reduces the index of reflection. Films of *c*-Si and CsPbBr₃ NCs demonstrate similar results, while in the case of CsPbI₃ NCs the coefficient of reflection has a moderate value, not greater than 40%. As it follows from the presented results, the interaction of CsPbI₃ NCs with *c*-Si is very weak, while the film of CsPbBr₃ NCs has abso-

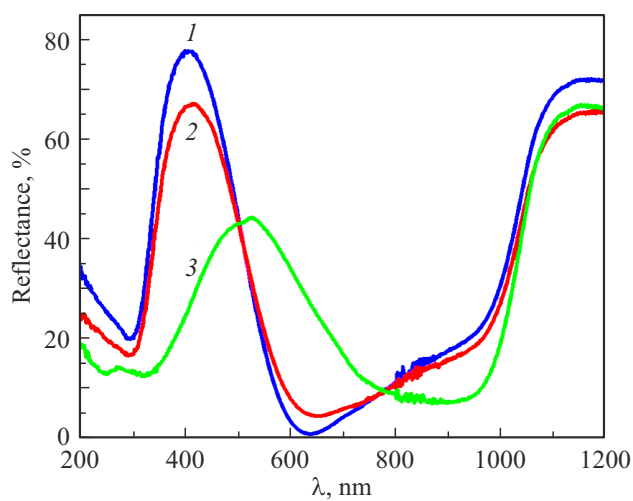


Figure 3. Reflection spectra of films of NCs of perovskites and *c*-Si: 1 — *c*-Si SC; 2 — NCs of CsPbI₃; 3 — NCs of CsPbBr₃.

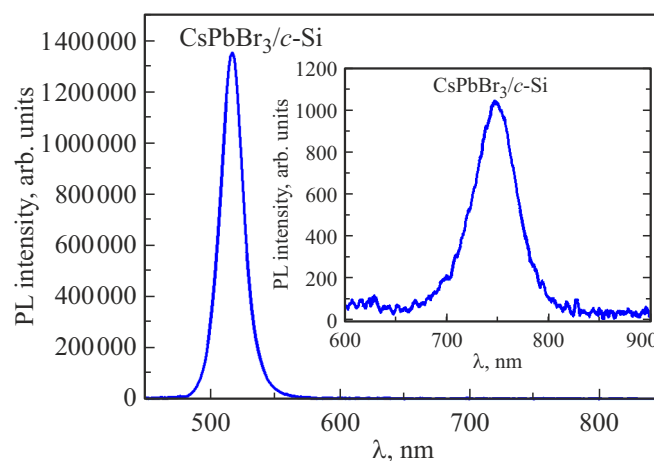


Figure 4. PL spectra of films of CsPbBr₃ NCs and CsPbI₃ NCs (inset) measured at 290 K.

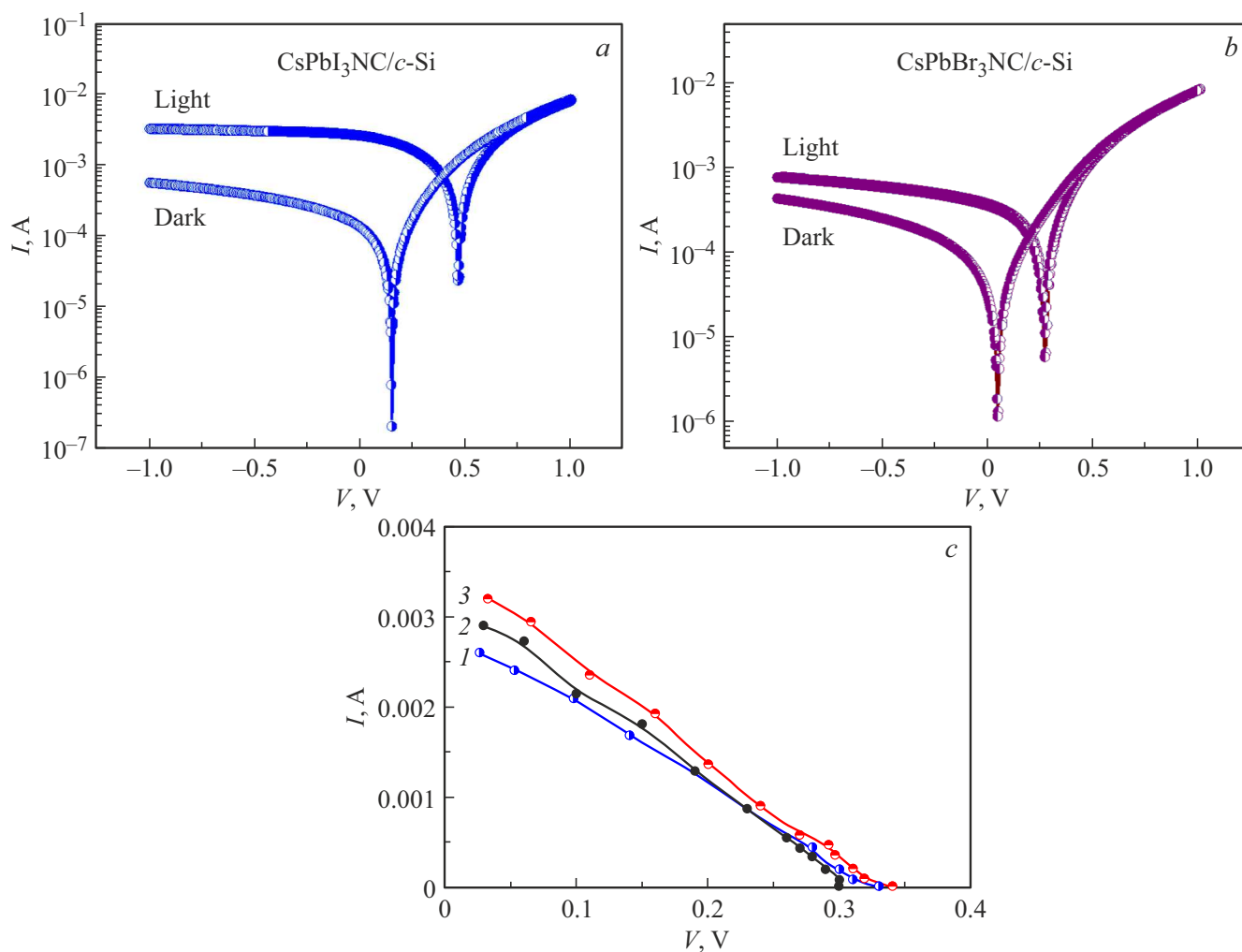


Figure 5. IV-curve of photoelectric current of films of CsPbI₃ (a) NCs and CsPbBr₃ (b) NCs in darkness and under illumination, photovoltaic characteristics of structures of CsPbI₃ NCs, CsPbBr₃ NCs, and *c*-Si SC (c).

lutely different behavior than *c*-Si. For CsPbI₃ NCs the intensity of absorption is high in a range of 710–980 nm, while for CsPbBr₃ NCs it is lower, but in another spectral range — 580–970 nm. This is, probably, related to different roles the perovskite NCs under study as indirect energy converters in the tandem with *c*-Si. In addition, as it follows from Fig. 3, the studied structures demonstrate unusual absorption in the UV-range.

Fig. 4 and inset in Fig. 4 show PL spectra of thin films of CsPbBr₃ NCs and CsPbI₃ NCs, respectively, applied on substrates of crystalline silicon, measured at 290 K (PL was excited using LED with maximum electroluminescence at 285 nm). As it follows from Fig. 4, PL peak for the film of CsPbBr₃ NCs was observed at 2.47 eV, while for the film of CsPbI₃ NCs it was at 1.67 eV. It is worth noting, that the PL intensity at 290 K of the film of CsPbBr₃ NCs with the maximum at 550 nm was 100 times higher than the PL intensity of the film of CsPbI₃ NCs with the maximum at 740 nm, that confirms the results of [8]. It can be assumed, that the observed peaks of PL has an exciton nature, at the same time no peaks connected with possible defects were observed in the measured spectra, thus the spectra represent inherent PL of thin films of CsPbI₃ and CsPbBr₃ NCs.

Typical IV curves of photoelectric current of films of CsPbI₃ NCs (*a*) and CsPbBr₃ NCs (*b*) measured in sandwich — geometry in darkness and under illumination using solar simulator with radiation spectrum close to the AM1.5 spectrum, are shown in Fig. 5, *a, b*. As can be seen from Fig. 5, the amplitude of photoelectric current in films of CsPbI₃ NCs is higher than that in films of CsPbBr₃ NCs, that makes CsPbI₃ NCs preferable option for the use in SC. Photovoltaic characteristics of structures of CsPbI₃ NCs, CsPbBr₃ NCs, and *c*-Si of SC are shown in Fig. 5, *c*. A particularly important parameter is short-circuit current, *J*_{sc}. Measured *J*_{sc} current for films of CsPbI₃ NCs is higher than that of CsPbBr₃ NCs, and in general films of CsPbI₃ NCs and CsPbBr₃ NCs have higher current than basic samples of *c*-Si SC. The analysis of obtained dependencies shows that currents are identical in the region of increased voltage. Currently the cause of the difference between IV curves is not completely clear, however, further studies are in progress in order to optimize parameters of such structures.

4. Conclusion

In this work we studied electrical and optical characteristics of films of NCs of lead halide perovskite, CsPbI₃ and CsPbBr₃, applied on *c*-Si SC. Results of morphology study have shown that the spherical shape of NCs forms a textured surface, that can provide control of optical characteristics of perovskite and composite SCs. It is found that NCs of CsPbI₃ and CsPbBr₃ interact with *c*-Si in different ways, that results in different peaks of absorption in different regions of visible range, which, in general, improves the absorption of the entire heterostructure: for CsPbI₃ —

in a range of 350–450 nm, while for CsPbBr₃ — in a range of 530–850 nm. The study of reflection spectra shows that spectra of CsPbBr₃ NCs have more complex and promising for SC structure as compared with NCs of CsPbI₃. The IV curve of structure with a layer of CsPbI₃ NCs demonstrates higher photoelectric current, that is indicative of the fact that NCs of CsPbI₃ have better electrical properties than NCs of CsPbBr₃. The observed better photovoltaic characteristics of SCs of structures with a layer of CsPbI₃ NCs as compared with SCs with a layer of CsPbBr₃ NCs probably are attributable to their lower roughness.

Acknowledgments

The authors would like to thank V. Levitsky for the help in measurements of reflection spectra of composite layers of NCs of perovskites and *c*-Si, as well as A. Belorus for the help in the synthesis of NCs of perovskites.

Conflict of interest

The authors declare that they have no conflict of interest.

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