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Exciton dynamics characterization by electrochemical impedance spectroscopy of CsPbBr₃(I₃) perovskite nanocrystals for photovoltaic application

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Abstract. 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). We present the results of studies of impedance spectroscopy (IS) in operating sandwich structures based on films of nanocrystals (NC) of inorganic perovskites of lead halides CsPbI₃ and CsPbBr₃. These last are characterized by the presence of extensive phonon disorder in the former. This phonon disorder gives rise to unique electron–phonon coupling and dielectric responses. The perovskite material is deposited on the surface of a solar cell based on crystalline silicon (*c*-Si). The IS results show that under identical conditions, the Nyquist plots for both structures are in good agreement with the equivalent circuit model represented in continued line as a fit curve. It represents series resistance, recombination resistance and geometric capacitance, respectively, which arise due to charge accumulation, charge transfer resistance and/or additional interfacial electronic states. It is found, that adding of the CsPbI₃ layer enhances the photo response under bias, but such a photo response leads to a decrease in dc conductivity. On the contrary, adding of the CsPbBr₃ layer blocks the photo response under bias but slightly improves the photo response for the zero bias. The obtained results provide the way to improve the performance of next generation of tandem *c*-Si SCs with perovskite NCs upper layers.

Keywords: impedance spectroscopy, perovskites, nanocrystals, crystalline silicon

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Материалы конференции

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Характеризация экситонной динамики методом электрохимической импедансной спектроскопии нанокристаллов перовскита CsPbBr₃(I₃) для фотовольтаического применения

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Аннотация. Нанесение дополнительного слоя наночастиц является широко используемым методом улучшения оптических и электрических характеристик полупроводниковых солнечных элементов (СЭ). Представлены результаты исследований импедансной спектроскопии (ИС) в действующих сэндвич-структурах на основе

пленок нанокристаллов (НК) неорганических перовскитов галогенидов свинца CsPbI₃ и CsPbBr₃. Характеризуется наличием у первого обширного фононного беспорядка. Этот фононный беспорядок приводит к уникальному электрон-фононному взаимодействию и диэлектрическим откликам. Результаты ИС показывают, что при одинаковых условиях диаграммы Коул-Коула для обеих структур хорошо согласуются с моделью эквивалентной схемы и представляют соответственно последовательное сопротивление, рекомбинационное сопротивление и геометрическую емкость, которые возникают из-за накопления заряда, сопротивления переносу заряда и/или дополнительные межфазные электронные состояния. Обнаружено, что добавление слоя CsPbI₃ усиливает фотоотклик при смещении, но такой фотоотклик приводит к снижению проводимости на постоянном токе. Напротив, добавление слоя CsPbBr₃ блокирует фотоотклик при смещении, но немного улучшает фотоотклик при нулевом смещении. Полученные результаты позволяют улучшить характеристики следующего поколения tandemных СЭ *c*-Si с верхними слоями перовскитных НК.

Ключевые слова: импедансная спектроскопия, перовскиты, нанокристаллы, кристаллический кремний

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Introduction

Recently, extensive research is carried out in the world aiming to the improvement of efficiency of heterostructure-based tandem crystalline silicon solar cells (*c*-Si SC) by applying films of organic-inorganic perovskites to increase efficiency and decrease optical loss. Modification of *c*-Si SC surface with films of organic-inorganic perovskites is considered one of the most promising directions [1] due to high absorption coefficient of 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. From another side optical resonance nanostructures such as inorganic perovskite nanocrystals (NC) can also improve the same properties of *c*-Si SC [5].

Impedance spectroscopy (IS) is a versatile characterization technique to monitor electrical and electrochemical processes operando, as well as profile the electronic structure in solid-state devices [6]. In most works, the impedance spectroscopy was used to characterize solar cells based on *c*-Si or perovskites separately [6–9]. In this paper we present the results of studies of IS in operating sandwich structures based on films of NCs of inorganic perovskites of lead halides CsPbI₃ and CsPbBr₃ deposited on the surface of a SCs based on *c*-Si. (Electrical and optical characteristics of CsPbI₃ and CsPbBr₃ lead halide perovskite nanocrystal films deposited on *c*-Si SCs were studied in our previous work [5].) The IS results show that under identical conditions the Cole-Cole plots for both structures as well as for pure *c*-Si SC are in good agreement with the equivalent circuit model and represents series resistance, recombination resistance and geometric capacitance, respectively, which arise due to charge accumulation, charge transfer resistance and/or additional interfacial electronic states.

Experimental details

We used SCs made of single-crystalline silicon, *c*-Si, provided by the Research Center of Thin-Film Technology in Power Industry at Ioffe Institute. The basic structure of SC shown in Fig. 1. *a*. This last is a combination of multi junctions shown in Fig. 1, *a*. The double junction solar cell used as the main substrate for the thin perovskite Ncs. Its efficiency has enhanced in another research [9] from 11% to 23% by using the deposition technic PECVD

(plasma-enhanced chemical vapor deposition). This last allows the possible facility of variation of electronic properties in thin films evaporated.

A crystalline substrate of n-type silicon, *c*-Si, (100)-oriented, this substrate is sandwiched with 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. And with an undoped layer of amorphous hydrogenated silicon with a thickness of 2–5 nm. Then, on the front side, a p-doped layer of amorphous hydrogenated silicon with a thickness of 5–20 nm is deposited and it finishes with a layer of tin-oxide ITO with a thickness of 90–110 nm. On the back side of the sandwiched crystalline substrate, 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 are successively applied. The crystalline substrate thickness is around 80–250 μm . *c*-Si is considered as a material where main light absorption takes place in the SC. Absorbance and PL spectra of pure CsPbBr_3 and CsPbI_3 NCs thin films deposited on the form of suspension were synthesized similarly to our precedent studies. Absorbance and PL spectra of pure CsPbBr_3 and CsPbI_3 NCs films on quartz substrates are shown in Fig. 1, *b*.

In the following work impedance spectroscopy (IS) measurements were carried out. IS is used to study and to examine the dynamics of transport mechanism and interface resistance in our heterostructures and further understand the roles of perovskites Nps CsPbBr_3 and CsPbI_3 in the solar cell device under a range of operating biases and illumination intensities.

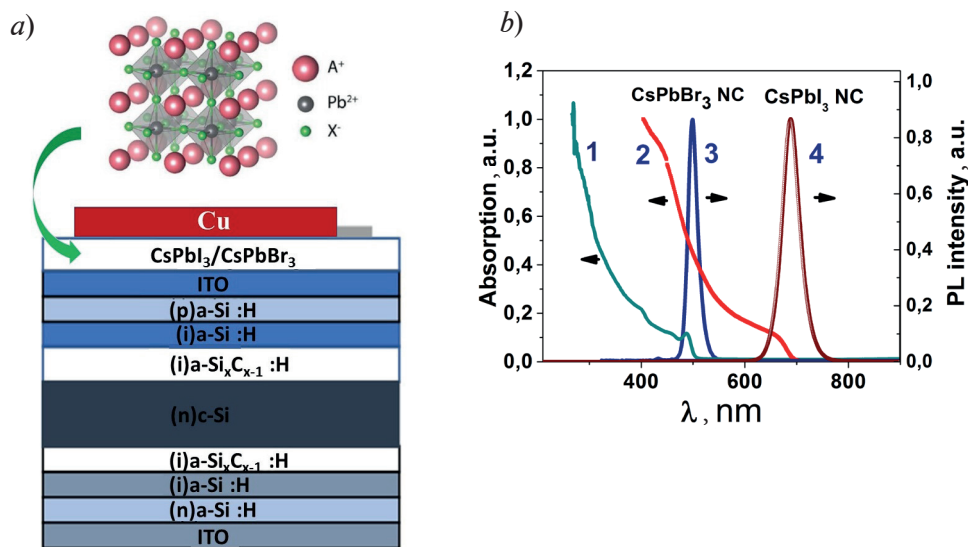


Fig. 1. Tandem structure coated with A+Pb+X- perovskite NCs. (*b*) Absorbance spectra of pure CsPbBr_3 NCs (curve 1), and CsPbI_3 NCs (curve 2) films on Si substrates; the same graph shows the PL spectra of pure CsPbBr_3 NCs (curve 3) and CsPbI_3 NCs (curve 4)

Results and discussion

To investigate the features of the charge carrier processes in the composite samples, we conducted an impedance spectroscopy study under the same conditions (in the dark and under illumination). The y-intercept on the horizontal axis is related to the serial resistance (represented R1), which represents the ohmic resistance of the contacts that collect the current and it corresponds to a shift from zero to the intersection of the semicircle with the Re axis at high frequencies. A smaller intercept means a lower series resistance. In Fig. 2, *a, c* without illumination and under applied bias for *c*-Si/ CsPbBr_3 and *c*-Si (reference substrate) a similar behavior is noticed the intercept is very small comparing it to the intercept without an applied voltage, which means the resistance due to the contact is almost negligible. Under light, the same behavior the intercept is decreasing with decrease of applied bias. It's also interpreted by the recombination resistance (R2) which is related to the arc.

For *c*-Si/ CsPbI_3 , Fig. 2, *b*, the Nyquist plot show an inverse results recombination resistance is the dominant factor contrary to the serial resistance. In comparison with the sample *c*-Si,

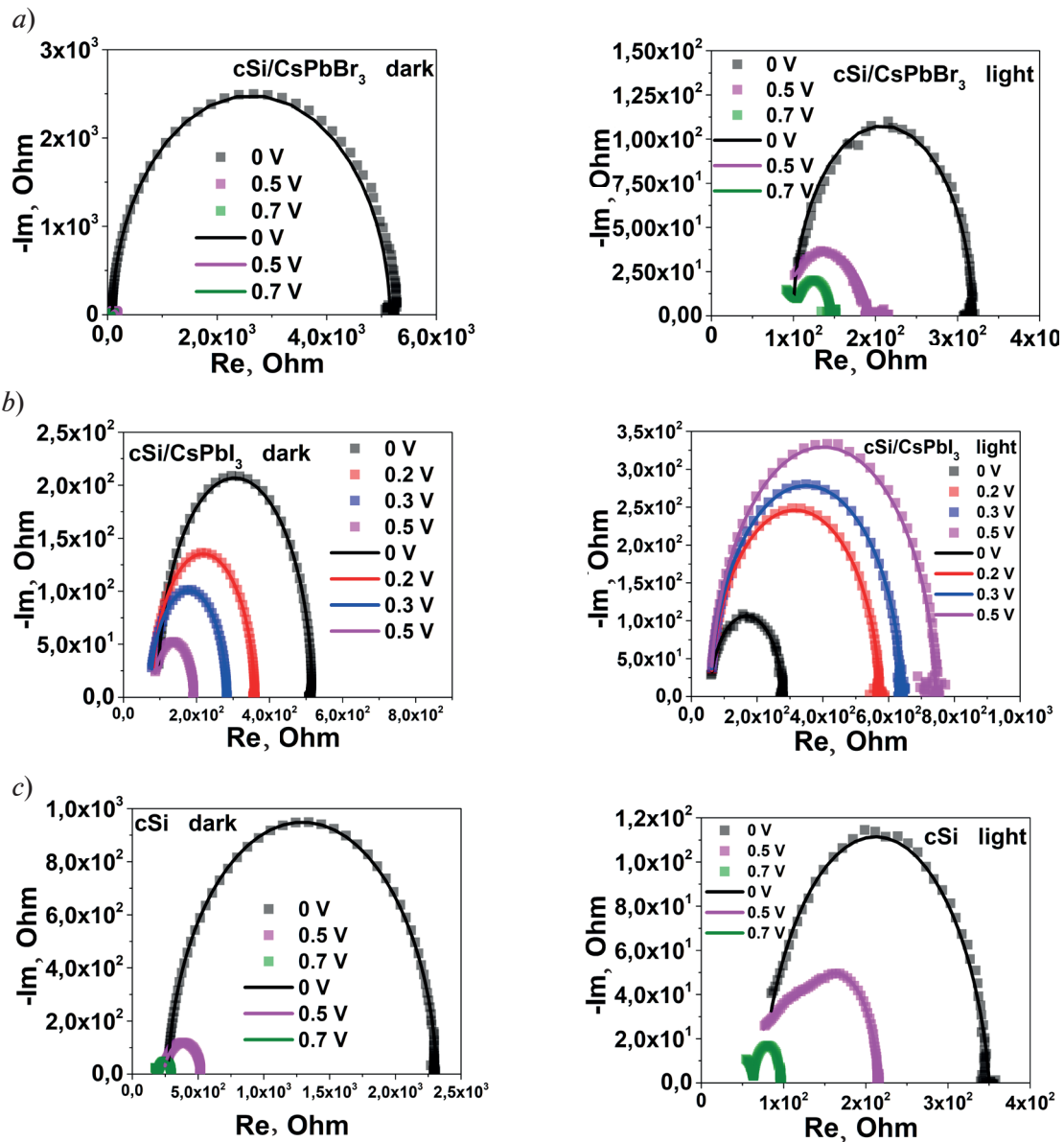


Fig. 2. Representative impedance response for (a) – *c*-Si/CsPbBr₃ under illumination and in dark at different biases (insert: smaller scale in the frequency region without illumination). (b) – *c*-Si/CsPbI₃ under illumination and in dark. (c) *c*-Si under illumination and in dark at different biases (insert: smaller scale in the low frequency region)

demonstrates a less significant change in the impedance response in the dark, but significantly better conductivity. Exposure to light on *c*-Si/CsPbI₃ sample leads to the appearance of a negative photo response, effect see Fig. 2, *b*.

In the Nyquist plot, a high frequency signature is observed with a line which is related to the element R1, see circuit table1, represents the parasitic inductive tail in the Cole-Cole plots at high frequencies is ascribed to stray inductance originating from the cables and electrodes. The relative contribution from this component becomes non negligible under high bias as the cell resistance decreases with increasing DC bias. The CPE1 element is a non-ideal capacitor and associated with the p⁺-n junction in the Si layer and the non-uniform distribution of dielectric relaxation time exhibited by inhomogeneity in the perovskite layer.

Cole-Cole plots at various biases were modeled by an equivalent circuit for all samples, which consists of resistor R1 in series with the parallel combination of a constant phase element CPE1 and resistance R2. This equivalent circuit provides an excellent fit for the data over a

range of applied biases. Summarizing, it can be noted that the CsPbI₃ film enhances the photo response upon displacement, but such a photo response leads to a decrease in conductivity. On the contrary, the CsPbBr₃ film blocks the photo response under bias but slightly improves the photo response for the zero bias.

Conclusion

We report on the results of investigations of IS in operating sandwich structures based on films of NCs of inorganic perovskites of lead halides CsPbI₃ and CsPbBr₃ deposited on the surface of a SCs based on *c*-Si. The IS results show that under identical conditions the Cole-Cole plots for both structures fit with the equivalent circuit model and represents series resistance, recombination resistance and geometric capacitance, respectively, which arise due to charge accumulation, charge transfer resistance and/or additional interfacial electronic states. It was found, that adding of the CsPbI₃ layer enhances the photo response under bias, but such a photo response leads to a decrease in conductivity. On the contrary, adding of the CsPbBr₃ layer blocks the photo response under bias but slightly improves the photo response for the zero bias. The obtained results provide the way to improve the performance of next generation of tandem *c*-Si SCs with perovskite NCs upper layers.

REFERENCES

1. **Chen Q., De Marco N., Yang Y., Song T.-B., Chen C.-C., Zhao H., Hong Z., Zhou H., Yang Y.**, Under the spotlight: The organic-inorganic hybrid halide perovskite for optoelectronic applications, *Nano Today*, 10 (2015) 355–396.
2. **Noh J.H., Im S.H., Heo J.H., Mandal T.N., Seo S.I.**, Chemical Management for Colorful, Efficient, and Stable Inorganic-Organic Hybrid Nanostructured Solar Cells, *Nano Lett.* 13 (2013) 1764–1769.
3. **Oga H., Saeki A., Ogomi Y., Hayase S., Seki S.**, Improved Understanding of the Electronic and Energetic Landscapes of Perovskite Solar Cells: High Local Charge Carrier Mobility, Reduced Recombination, and Extremely Shallow Traps, *J. Am. Chem. Soc.* 136 (2014) 13818–13825.
4. **Boudjemila L., Aleshin A.N., Malyshkin V.G., Aleshin P.A., Shcherbakov I.P., Petrov V.N., Terukov E.I.**, Electrical and Optical Characteristics of CsPbI₃ and CsPbBr₃ Lead Halide Perovskite Nanocrystal Films Deposited on *c*-Si Solar Cells for Photovoltaic Applications, *Physics of the Solid State*, 64 (2022) 1670.
5. **Hauff E., Klotz D.**, Impedance spectroscopy for perovskite solar cells: characterisation, analysis, and diagnosis, *J. Mater. Chem. C*, 10 (2022) 742–761.
6. **Shehata M.M., Truong T.N., Basnet R., Nguyen H.T., Macdonald D.H., Black L.E.**, Impedance spectroscopy characterization of *c*-Si solar cells with SiO_x/Poly-Si rear passivating contacts, *Solar Energy Materials & Solar Cells*, 251 (2023) 112167.
7. **Hailegnaw B., Sariciftci N.S., Scharber M.C.**, Impedance Spectroscopy of Perovskite Solar Cells: Studying the Dynamics of Charge Carriers Before and After Continuous Operation, *Phys. Status Solidi A*, 22 (2020) 2000291.
8. **Terukov E., Kosarev A., Abramov A., Malchukova E.**, From 11% Thin Film to 23% Heterojunction Technology (HJT) PV Cell: Research, Development and Implementation Related 1600×1000 mm² PV Module in Industrial Production, *IntechOpen, Solar Panels and Photovoltaic Materials* (2018), ch. 5.
9. **Masuko K., Shigematsu M., Hasiguchi T., Fujishima D., Kai M., Yoshimira N., Yamaguchi T., Ichihashi Y., Mishima T., Matsubara N., Yamanishi T., Takahama T., Taguchi M., Maruyama E., Okamoto S.**, Achievement of more than 25% conversion efficiency with crystalline silicon heterojunction solar cell. *IEEE Journal of Photovoltaics*. (11) (2014) 1433–1435.
10. **Aleshin A.N., Shcherbakov I.P., Chikalova-Luzina O.P., Matyushkin L.B., Ovezov M.K., Ershova A.M., Trapeznikova I.N., Petrov V.N.**, Photo- and electroluminescence features of films and field effect transistors based on inorganic perovskite nanocrystals embedded in a polymer matrix, *Synthetic Metals*, 260 (2020) 116291.



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