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Light-emitting and light-detecting perovskite electrochemical cell on silicon

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Abstract. Here we report on a novel architecture of inorganic perovskite light-emitting and light-detecting electrochemical cell formed on silicon substrate. The cell's active material layer consists of a composite material made: halide perovskite ($CsPbBr_3$) microcrystals, polymer support matrix (poly(ethylene oxide)), and added mobile ions (Li^+). The proposed device emits light of 7000 cd/m^2 and electroluminescence efficiency of $1.3 \cdot 10^5$ lm/W at 523 nm. The light-detecting property of the device is characterized by sensitivity up to 0.75 A/W, specific detectivity of $8.56 \cdot 10^{11}$ Jones, and linear dynamic range of 48 dB. Moreover, since the device fabricated is fabricated on a silicon substrate it exhibits 40% lower Joule heating compared to the perovskite optoelectronic devices fabricated on conventional ITO/glass substrates.

Keywords: composite inorganic halide perovskite, silicon, light-emitting electrochemical cell, photodetector

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Перовскитная электрохимическая светоизлучающая ячейка на кремнии для детектирования света

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Аннотация. В статье сообщается о новой архитектуре неорганической перовскитной светоизлучающей электрохимической ячейки на кремниевой подложке для детектирования света. Слой активного материала ячейки состоит из композитного материала, состоящего из микрокристаллов галогенидного перовскита ($CsPbBr_3$), полимерной поддерживающей матрицы (поли(этиленоксид)) и добавленных подвижных ионов (Li^+). Устройство излучает свет на длине волны 523 нм яркостью 7000 кд/м^2 и эффективностью электролюминесценции в $1{,}3 \cdot 10^5$ лм/Вт. Фотодетектирующее свойство устройства характеризуется чувствительностью до 0,75 А/Вт, удельной обнаружительной способностью в $8{,}56 \cdot 10^{11}$ Джонса и линейным динамическим диапазоном в 48 дБ. Кроме того, поскольку изготовленное устройство изготовлено на кремниевой подложке, оно демонстрирует на 40% меньший Джоулев нагрев по сравнению с перовскитными

оптоэлектронными устройствами, изготовленными на обычных подложках из ITO/стекла.

Ключевые слова: композитный неорганический галогенидный перовскит, кремний, электрохимическая светоизлучающая ячейка, фотодетектор

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Introduction

Halide perovskites are a type of semiconductor material that has many unique photoactive, optoelectronic and photonic properties. They have a general stoichiometry of ABX3, where A is usually either Cs, methylammonium (MA), or formamidinium (FA), and B is usually either Cl, Br, or I. The conventional perovskite light-emitting device is a perovskite LED (PeLED), which typically consists of number of different material layers that must be carefully selected and fabricated in a substantial number of technological steps [1–5]. On the other hand perovskite light-emitting electrochemical cells (PeLECs) are feasible alternative to PeLEDs. PeLEC consists of a single multifunctional layer [6] – composite perovskite material, i.e., the mixture of inorganic halide perovskite (e.g. $CsPbBr_3$) nanocrystals acting as an electroluminescent component embedded into polymer matrix (poly(ethylene oxide) (PEO) which aids ion transport and passivates crystal grains, and mobile ions (Li^+ from LiTFSI). In such a device, the dynamically formed intrinsic p-i-n structure is responsible for charge injection, facilitation of ion transport, enhanced photoluminescence quantum yield (PLQY) and efficient electroluminescence [7]. One of the significant issues in PeLEDs and PeLECs application for display design is Joule heating poor endurance of conventional substrates (soda-lime glass, polyethylene terephthalate (PET), etc.) [8–10]. Finally, expanding the functionalities of halogen perovskite devices [11–16] by e.g. combining light-detection (or photovoltaic) regime of operation with light-emitting regime is still an ambitious challenge.

Here we demonstrate PeLEC device consisting of a single layer of composite inorganic perovskite material, i.e. $CsPbBr_3$:PEO:LiTFSI mixture. Owing to the fact that silicon thermal conductivity is substantially higher than that for the ITO/glass structure, our device sustains a much higher level of Joule heating during operation. Our device emits light at bias applied in forward direction and detects light when reversed bias is applied.

Materials and Methods

Si++(111) substrate patterning.

The phosphorous-doped single-crystal silicon substrate <100> (n^{++}-Si(100)) was used for device fabrication, see Fig. 1, *a* top panel. A thermally oxidated 200 nm thick SiO_2 layer was covered in a positive photoresist. Next, the photoresist was patterned, developed and washed away. After that the SiO_2 uncovered 2×2 mm^2 square areas were etched away with hydrofluoric acid (HF). The residual photoresist photoresist was removed using the organic solvent dimethyl sulfoxide (DMSO) and the substrate was then washed in deionized water. Finally, bottom aluminum (Al, thickness ~ 200 nm) contact was deposited on the back side of n^{++}-Si(100) substrate by vacuum thermal evaporation.

Perovskite Solution Preparation.

The $CsPbBr_3$ solution of 0.2 mmol/ml concentration was prepared by adding CsBr and $PbBr_2$ salts in a 1:1 molar ratio to anhydrous DMSO solvent and stirring the mixture overnight at 60 °C

at 300 rpm. To mix a composite perovskite solution the prepared $CsPbBr_3$ DMSO solution, poly(ethylene oxide) (PEO, $M_W = 10^6$ g/mol, concentration 20 mg·mL^{-1}) DMSO solution, and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) DMSO solution (concentration 10 mg·mL^{-1}) were mixed in 1:0.1:0.01 dry components wt. ratio, respectively, with subsequent overnight stirring at 60 °C and 300 rpm.

Device fabrication.

The device fabrication work-flow schematically presented in Fig. 1, *a* middle and bottom panels. First, the patterned n^{++}-Si(100) substrates surface was activated in O_2 plasma ($P = 10$ W) for 2 mins. Then, the perovskite active region was fabricated through spin-coating process in dry N_2 filled glovebox. After that, a ~ 40 nm thick layer of entangled SWCNt network was placed on top of the patterned structure and densified with anhydrous diisopropyl ether (DIPE).

Device Characterization.

The device cross-section SEM imaging was performed using Zeiss Supra 25 SEM. The device's *J-V* curves were acquired with a Keithley 2401 source meter. The device luminance measurements were carried out using Telescopic Optical Probe 150 of CAS 120 Instrument Systems spectroradiometer. For photodetector behavior measurements, a continuous-wave (CW) laser diode of 450 nm wavelength with the maximum output optical power density of 405.85 mW/cm^2 was used as an excitation source. Photodetector external quantum efficiency (EQE) spectra were obtained using a 200 W halide lamp, monochromator Solar Laser Systems M266, and calibrated reference Si solar cell. Heat distribution imaging was acquired with a commercially available IR-imaging camera "Seek Thermal".

Results and Discussion

According to cross-section (CS) SEM measurements the perovskite film thickness constitutes ~ 140 nm with average grain size of ~ 150...200 nm, see SEM images in Fig. 1, *b*. Our light emitting device is a light-emitting electrochemical cell, see images of electroluminescent pixel in Fig. 1, *c* and spectrum of electroluminescence in Fig. 2, *a*, which provides light electroluminescence

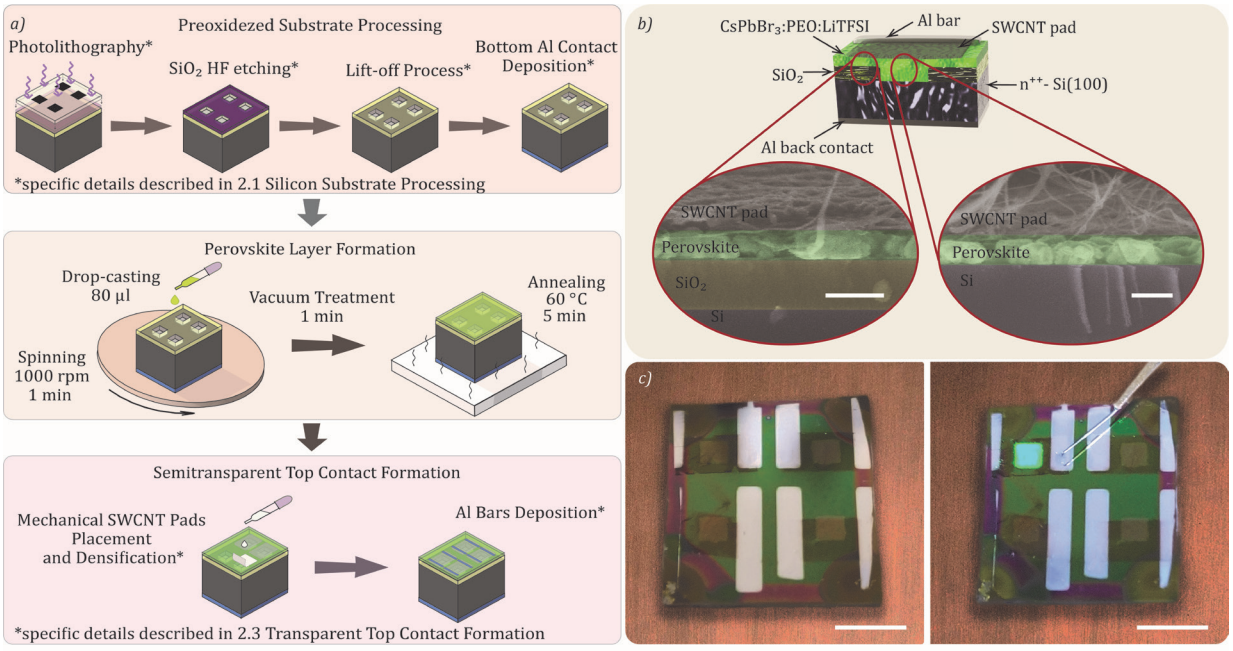

Fig. 1. Dual-function device processing scheme (*a*); Device cross-section 3D illustration and SEM images, scale bars – 200 nm (*b*); Final device photos: left panel – without applied bias, right panel – with applied positive bias to one of the pixels, scale bars – 5 mm (*c*)

efficiency $1.3 \cdot 10^5$ lm/W, see J-L curve in Fig. 2, *c*, and luminance (L) more than 7000 cd/m^2, see J-L curve in Fig. 2, *b*.

In the light-detecting regime of operation, sensitivity of our device reaches 0.75 A/W with specific detectivity $8.56 \cdot 10^{11}$ Jones and LDR 48 dB, see Fig. 3. U_{ch} is characteristic bias below which the device exhibits apparent photocurrent growth.

For the device on ITO/glass the consumed power was equal to 139.3 mW at applied 3.5 V (ITO based device does not endure $V > 3.5$ V, shunting at higher biases) and 0.0398 A current (device $T = 33$ °C), as for n^{++}-Si(100) 207.0 mW of electrical power was consumed at 4.5 V and 0.046 A current (device $T = 24$ °C). Hence, our device on n^{++}-Si(100) substrate withstands 32.7% higher applied power with 40% lower thermal heating, compared to the ITO/glass-based device.

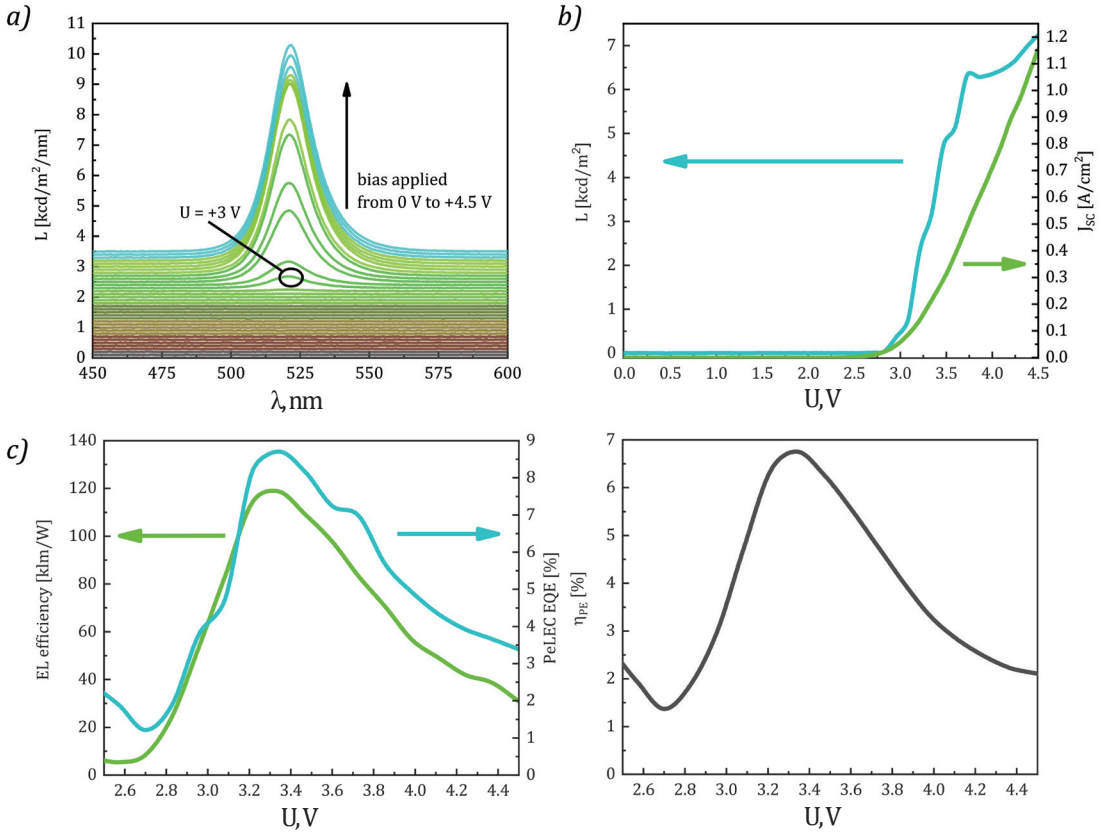

Fig. 2. Composite perovskite PeLEC key figures-of-merit: the device EL spectra under applied bias offset relative to each other (*a*); measured device's *J-V* curve plot in one axis with L-V curve (*b*); left panel – the device's EL efficiency curve and PeLEC EQE characteristic on applied voltage; right panel – the device's power efficiency curve (*c*)

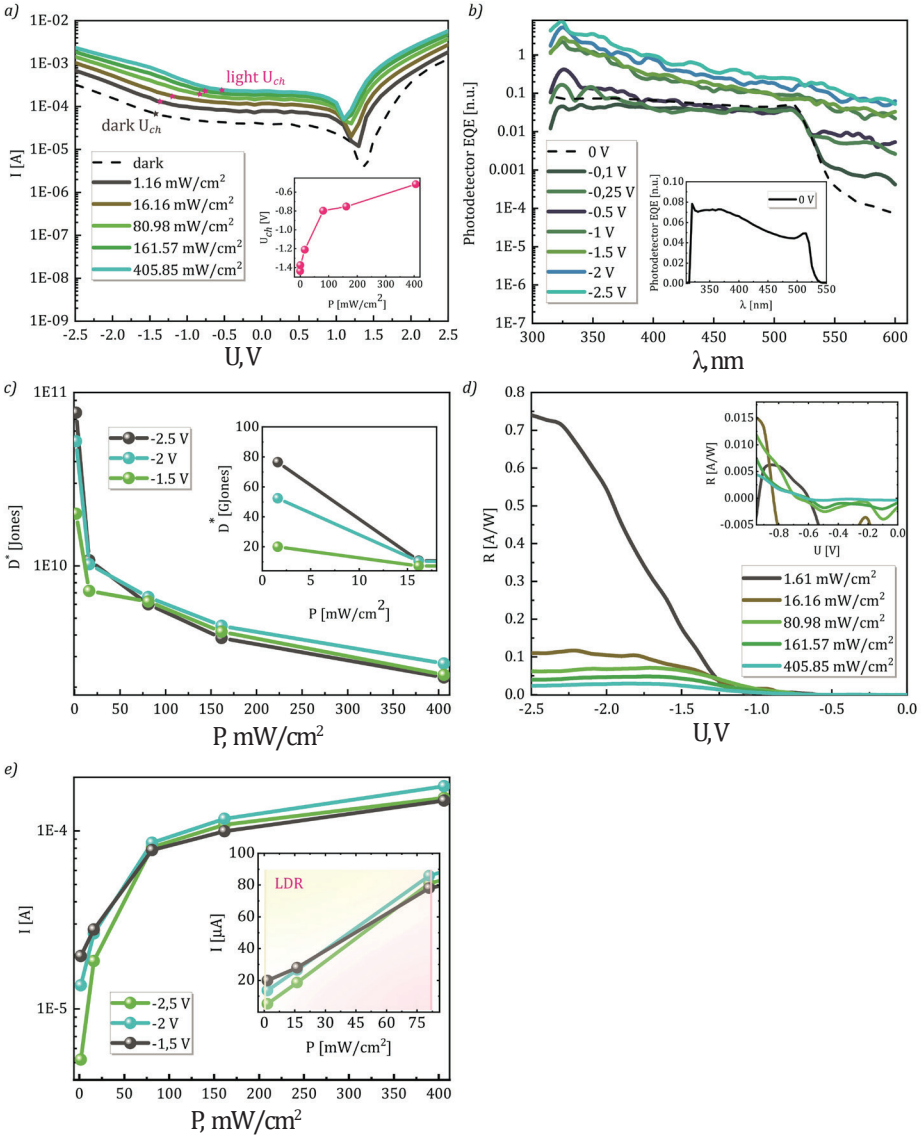

Fig. 3. Composite perovskite photodiode key figures-of-merit: (*a*) *J-V* curves at different laser incident radiant power densities, insert – U_{ch} values on incident radiant power density; (*b*) photodetector EQE on the electrical bias, insert – the device's EQE at $U = 0$ V in linear axis; (*c*) the device's specific detectivity curves for different laser incident radiant power densities, insert – zoomed-in section of the graph for maximal D^* in linear axis; (*d*) the device's responsivity for different laser incident radiant power densities, insert – zoomed-in section of the graph from $U = 0$ V to U_{ch} (*e*) the device's LDR curves for three different biases, insert – LDR region for three biases in linear axis

Conclusion

We have demonstrated dual-function PeLEC (light-emitting ang light-detecting device) consisting of a single layer of composite inorganic perovskite material with improved Joule heating endurance.

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