ITO-free Perovskite Light-Emitting Electrochemical Cell

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Abstract. Since Complementary metal–oxide–semiconductor technology is the conventional technology for micro- and optoelectronics, integration of emerging materials, such as halide perovskites, into the process is an important branch of perovskite technologies development. In this regard ITO free device research becomes increasingly important. The Perovskite Light-Emitting electrochemical cells are a promising alternative to conventional Perovskite Light Emitting Diodes. In this work we demonstrate green (λEL = 523 nm) CsPbBr₃ Perovskite Light-Emitting electrochemical cells with luminescence intensity of 50 kd/m² integrated with Si⁺⁺(111) substrate.

1. Introduction
Since first reported [1] in the early 90’s PeLEDs research has been the staple research path for perovskite optoelectronic applications. Even though PeLEDs demonstrate some of the most impressive optical characteristics out of all devices based on emerging materials [2] some of the efficiency issues (low EQE) alongside with the complicated design hinder the technology introduction into industry.

Specifically, a typical PeLED device consists of photoactive perovskite layer enclosed between charge injection layers and electrodes in order to provide efficient charge injection from the low charge mobility perovskite film. Hence, while PeLED is a multilayer structure, that requires sophisticated balanced components in terms of their electrophysical and optical properties, PeLEC device is formed with a single multifunctional layer, that combines properties of high ion mobility and enhanced PLQY [3]. Due to the ion migration the p-i-n structure is formed, which makes for much simpler design. In addition, lowered work function requirements decrease demand for intricate electrode selection, which paves the way for novel electrode materials, such as carbon nanotubes, graphene, etc. [4] The simplicity of the design provides for scalable and cost-efficient technological solutions [5,6].

Likewise, flexibility of PeLECs processing and design opens a juncture to CMOS technology and microelectronics industry. Fabricating PeLECs directly on chip is a huge step into two technologies
integration. Here, we report PeLEC manufactured directly on the Si(111) substrate with semitransparent Single Walled Carbon Nanotubes (SWCNt) top electrode [7].

Our PeLECs architecture, see Figure 1, consists of a patterned n-doped Si**(111) substrate (n~10\(^{19}\) cm\(^{-3}\)) with thermally evaporated Al back contact (w~300 nm), single layer of photoactive perovskite material and SWCNt top contact with 80% transparency at 550 nm [7]. The CsPbBr\(_3\) (\(E_g = 2.5\) eV, \(\lambda_{EL} = 523\) nm) perovskite was chosen as the photoactive material due to its enhancement ambient atmosphere and thermal stability [8] in addition to the high PLQY [2]. The SWCNt entangled network is the perfect candidate to use as a top semitransparent contact for PeLECs due to their chemical inertness, low resistivity in combination with high transparency [7].

![Figure 1. CsPbBr\(_3\) LEC architecture scheme.](image1)

2. Experimental section

2.1 Si**(111) substrate patterning

The device pattern from the Figure 1 was obtained from masking Si**(111) surface area with dielectric epoxy-based negative photoresist. The Si**(111) substrates with preliminary deposited back Al contact were cleaned in a series of organic solvents (Acetone, IPA) and DI water to remove polar organic residues. Next, the samples were annealed at 200 °C for 2 h to remove water residues. After that, the SU8 epoxy-based resin was spin-coated onto the samples surface at 2000 rpm (thin film thickness calibrated to be 150 nm). In order to remove solvent from the thin film Si** substrates were annealed at 95 °C on a hot plate for 2 min. The photoresist exposure was done by UV source (\(\lambda = 365\) nm) through a mask with the square pattern of a size 3x3mm, see Figure 2. Exposure dose was set to 1.5 J/cm\(^2\). The post-bake was done at 95 °C for another 2 min. The photoresist developing was done by 20 sec propylene glycol methyl ether acetate (PGMEA) treatment. In order to provide the samples chemical inertness, they were cured at 200 °C for 5 min.

![Figure 2. The Si**(111) patterned sample.](image2)
2.2 Perovskite solution preparation
The CsPbBr$_3$ solution was prepared by adding CsBr (0.3 mmol/ml) and PbBr$_2$ (0.2 mmol/ml) in anhydrous DMSO solvent. The salts were left dissolving with moderate stirring (300 rpm) overnight without heating. The polyethylene oxide (PEO, $M_w = 1000000$ g/mol) DMSO solution (concentration 10 mg/ml) was stirred overnight at 60 °C, 200 rpm. Right before device fabrication the two pre-made solutions were mixed in a clean vial with the mass ratio CsPbBr$_3$:PEO = 1.25:1 and stirred for 1 hour without heating.

2.3 Device fabrication
First, the patterned Si**(111) substrates surface was treated in O$_2$ plasma ($P = 10$ W) for 2min. Then, the perovskite active region (thickness ~100 nm) was fabricated through spin-coating process (10 μl, 60 sec) 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 dry IPA. The final device can be seen in the Figure 3,a).

Figure 3. (a) The PeLEC on Si**(111) device; (b) Our PeLEC device visible EL.

3. Results and discussion
The CsPbBr$_3$ thin film surface morphology was investigated with Atomic Force Microscopy (AFM) NT-MDT NTegra Aura set-up in tapping regime. In the Figure 4 the surface microstructure can be clearly seen: the overall homogeneous phase distribution indicates perovskite material uniformity with evident PEO inclusions only at the crystal grain boundaries. The mean perovskite composite crystal grain size is estimated to be ~230 nm.

In order to measure key PeLEC characteristics, the device was connected to a Keithley 2401 source meter and a voltage of 0V to 3V was applied to the electrodes, see Figure 3,b). As can be seen from the
J-V curve in the Figure 5, our PeLEC opens at ~2.5 V, which corresponds well to the active material bandgap energy.

![J-V curve graph](image)

Figure 5. CsPbBr$_3$ LEC J-V characteristic (red curve) and LEC EL characteristic (green curve).

The visible electroluminescence (EL) curve of our device can be seen in the Figure 5. The EL signal emerges at voltage greater than $V_{th} \sim 2.8$ V. The luminescence characteristic of CsPbBr$_3$ LEC were measured using a spectroradiometer Spectrascan PR650. Our LEC demonstrates $50 \text{ kd/m}^2$ at 12 mA.

4. Conclusion
We have demonstrated green bright PeLEC device integrated with the key microelectronics material – silicon. The exceptional device design puts our work on the CMOS map and opens a whole route for Si and perovskites integration.

Acknowledgments
This work was supported by the Russian Science Foundation (project № 19-73-30023).

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