Memristive properties of solar cells based on perovskite and polymer composite

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Abstract. Organic-inorganic halide perovskites recently have emerged as a perspective material for using in solar cells. This material has many perspective properties, one of them is the ion migration. Modern ionic memristors, electric circuit elements that can change its resistance depending on the current flowing through it, is based on this phenomenon. In this paper, we present the experimentally obtained memristic properties in the perovskite solar cell, which contains composite of perovskite and polymer as absorbing layer instead of pure perovskite.

1. Introduction

Nowadays, everyone knows three main elements of an electrical circuit: a resistor, a capacitor, and an inductor that bind four physical quantities: electrical current, charge, voltage, and charge flux. The resistor connects the voltage and current; capacitor - charge and voltage; inductor - current and charge flux. In 1971, Leon Chua¹ suggested that there is a fourth element - the “memristor”. Memristor is a nonlinear, bipolar, passive circuit element capable to change its resistance depending on the charge flowing through it. After power off, the memristor remembers its last state, that can be used as a non-volatile memory cell³. In the future, it is possible to implement computing systems using memristors, in which information will be stored and processed by the same device¹.

There are two types of memristors on the principle of operation: ionic thin-film memristors (Titanium dioxide memristors¹, Polymeric (ionic) memristors³, layered memristor³ and others) and memristors based on spin-magnetic interaction (Spintronic Memristors⁴, Spin Torque Transfer (STT)⁵). Ionic memristors are based on the phenomenon of ion migration through the film. The latter rely on the spin separation of electrons due to the change of the external magnetic field. All this leads to the appearance of the hysteresis phenomena of I – V characteristics. Memristors have two distinct states: low- and high-resistance, one of which is called on-state, the second is called off-state¹. Each of these states is characterized by set voltage and reset voltage, respectively. The current voltage (I-V) characteristic of the memristor has clearly pronounced surges at these voltages, forming a hysteresis loop, which is an evidence of the memristive properties.

Usually, ionic memristors (for example TiO₂-based memristors) consists of two layers: with high and low oxygen concentration. The high-resistance state is obtained by moving oxygen ions from its oxygen rich part to the deplete part of the device (Figure 1a) under the electric field. The material doped with oxygen ions has very high-resistance and ensures the “off” state of the memristor. When the applied
voltage is inverse to the previous one, oxygen ions move backward, reducing the sample resistance

![Diagram](image1)

**Figure 1.** Illustration of the oxidation / reduction process of an ionic memristor. 

A) Application of external voltage makes oxygen ions move towards cathode and dope TiO$_{2-x}$ layer and therefore lower the device resistance.

B) Application of reverse bias makes oxygen ions move back and deplete the TiO$_{2-x}$ layer with consequent increase of device resistance.

(Figure 1b) and switching the memristor to the on state.

Organometal halide perovskites (OHP) have emerged 10 years ago as a family of materials prospective for optoelectronics, photovoltaic and photonic applications\(^6\). From this point, OHP attracted tremendous attention from the scientific community since new material demonstrate many interesting properties like high absorption, high exciton energy at room temperature, lasing and many more. But the most important feature of OHP is solution processing which enables smooth band gap tuning and production of low cost and highly efficient solar cells and light emitting diodes\(^2\).

The record efficiency of perovskite solar cells (PSC) reached more than 23%\(^7\) surpassing its senior competitors: organic solar cells (record PCE 17.3%)\(^8\) and dye-sensitized solar cells (record PCE 14.3%)\(^9\). And its characteristics, has already surpassed the record indicators of silicon solar cells (a record PCE of 24.7%)\(^10\). Along with the development of PSC, scientists revealed hysteresis phenomena of the I-V characteristics, which are associated with the phenomenon of ion migration in perovskite. Under applied external electric voltage ions of cations (methylammonium, MA; formamidinium, FA; cesium, Cs) and anions (Cl\(^-\), Br\(^-\), I\(^-\)) migrate towards perovskite interfaces\(^4,5\) (Figure 2). Thus, by maintaining the PSC under voltage, anions and cations dope the interfaces of the perovskite with transport layers, which leads to formation of a p-i-n structure. However, if we turn off the voltage, the ions will migrate back, and the p-i-n structure will disappear.

The presence of ion migration opens the way for the implementation of perovskite-based memristors\(^11\). Perovskite based device in the states with the formed p-i-n structure and without it have different resistances and, thus, IV characteristics will have a hysteresis loop. However, to implement such a

![Diagram](image2)

**Figure 2.** Ion migration in MAPbBr$_3$I-based perovskite solar cell. 

a) Non-biased device. 

b) Device under voltage biasing. Ions of perovskite (MA$^+$, Br$^-$, I$^-$) move towards perovskite interfaces which form a p-i-n structure inside the provskite layer.
device, it is necessary to resolve a number of problems, one of which is the backward ion migration in the absence of an external electric voltage. This leads to absence of fully developed memristor loops since p-i-n structure which was formed under high voltage will disappear. To solve this problem we added a small amount of polyethylene oxide (PEO) into the perovskite layer. PEO is an ion conducting polymer and it is usually used as host for development of polymer batteries. In our case, PEO fills the space between the perovskite grains. Figure 3 demonstrates a SEM image of the MAPbBr$_2$I:PEO film light areas correspond to perovskite covered with PEO since it has high electric resistance and dark areas correspond to pristine perovskite. PEO allows to restrain ions as they move under applied external voltage and slow down their migration. The presence of the PEO can help maintain the p-i-n structure after removal of external voltage.

2. Results

The investigated solar cells had the structure: ITO / PEDOT:PSS / MAPbBr$_2$I:PEO / C$_60$ / LiF / Ag. (Figure 3b). The absorbing layer is a composite of MAPbBr$_2$I and PEO. The mass of the polymer was 0.004% of the perovskite mass. Perovskite precursors (MAI and PbBr$_2$) were dissolved in a DMF:DMSO solvent mixture (1:1) in a molar concentration of 0.8M. PEDOT: PSS was used as a hole transport layer and it was deposited on a glass substrate covered with ITO by spincoating and annealed at 150 C during 10 minutes. On the PEDOT:PSS, a MAPbBr$_2$I:PEO composite was deposited by two-step spincoating technique with pouring of diethyl ether at the tenth second of the second step. Then in a vacuum deposition chamber a 30 nm of fullerene (C$_{60}$), 1.5 nm layer of LiF and 60 nm of Ag were deposited on the perovskite film. The I-V characteristics of the devices were obtained under the AM1.5G irradiation (100mW/cm$^2$). Before measuring the I-V characteristics, the devices were biased at small forward voltage ($V_{bias} \approx 1 – 1.5V$). Measurement of I-V characteristics were conducted from $V_{bias} \rightarrow 0 \rightarrow V_{bias}$.

Figure 4a shows the I-V characteristics of devices with PEO and without it, measured after 1.5 V biasing for 1 minute. In the I-V characteristic of the perovskite-polymer composite device, a hysteresis loop is observed, which is almost absent in the I-V characteristics of the device without the polymer. During voltage biasing the ions in perovskite film gradually migrate to the boundaries, form p-i-n structure and penetrate into the PEO. With the start of measurement and voltage decrease, the perovskite ions try to migrate back to the bulk of the perovskite layer, but the polymer between perovskite grains restrain them, and the ions detach from the boundaries later then in case of with pure perovskite, where nothing can slow down the backward ion migration.

With decreasing the voltage, we observe state switching to high-resistance state (off-state) at 0.7V that is probably associated with backward ion migration in film and p-i-n structure disappearance. At low voltage device is in off state with high resistance. With increasing voltage, at 1.3 V perovskite ions
become able to migrate through PEO to boundaries and form p-i-n structure inside the perovskite layer and switch device to the low-resistance state (on-state). This I-V dependence forms a two hysteresis loop (Figure 4a) that is very similar to I-V of a memristor (Figure 4b).

We demonstrated memristive properties of perovskite devices by introduction of small amount of ion conducting polymer into the perovskite layer and utilization of device biasing for development of p-i-n structure. Finding a ways to control ionic migration and utilization it for development new types of devices are more preferable than just cupping it by introduction of multiple cations, since it can provide a cheap realization of 4th main element of electrical circuit.

Acknowledgments
The work was supported by the Russian Science Foundation (Project 19-73-30023)

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