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Simulation of *I-V* Curves for Inverted Planar Structure Perovskite Solar Cells using Equivalent Circuit Model with Inductance

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Physical modeling of hysteretic behavior in *I-V* curves of perovskite solar cells (PSCs) is necessary for further improvements of their power conversion efficiencies (PCEs). Reduction of the hysteresis in inverted planar structure PSCs (p-PSCs) has been achieved by the use of PCBM layer. In the cases, the *opposite trend of the I-V hysteresis* has been observed where the forward scan shows slightly higher efficiency than the reverse scan. In this paper, an equivalent circuit model with inductance was newly proposed. This model consists of Schottky diode involving parasite inductance focusing PCBM/Al(Ca) interface and well represents the opposite trend of the *I-V* hysteresis of the p-PSC with the inverted structure.

Organic-inorganic hybrid perovskite materials were found to show semiconductor behavior with excellent optical properties by D. Mitzi in 1998.[1,2] The perovskite materials have been used for photovoltaic devices recently,[3,4] and the power conversion efficiency (PCE) of perovskite solar cells (PSCs) have been improved over 21.0%.[5,6] However, it has been often noticed that the PSCs exhibit *I-V* hysteresis, especially in the case of planar structure perovskite solar cells (p-PSCs). Therefore, understanding of the hysteresis in the *I-V* curves of p-PSC has been given to improve the PCE.[7-10] Origin of the hysteresis investigated through several studies has been discussed based on ion migration, ferroelectric polarization, capacitive effect of the interfaces, carrier dynamics at the interfaces and so on. Although it is considered that the iodides accumulate at the interfaces under external field and cause the *I-V* hysteresis,[11-15] the existence of large capacitance should be attributed to remarkable mismatch at the interfaces. The weak contact between the layers is critical in p-PSC,[16,17] and the magnitude of hysteresis strongly depends on the contacts. A typical planar structure, where perovskite layer is sandwiched between hole conducting layer (spiro-OMeTAD) and electron conducting layer (TiO_2), suffers from strong hysteresis.[17-19] In some cases, the PCE estimated from forward scan (scan from short circuit, / J_{sc} side to open circuit/ V_{oc} side) is less than half of that from the reverse scan (scan from V_{oc} to J_{sc}). Inefficient electron extraction due to the charge traps at the $TiO_2/CH_3NH_3PbI_3$ interface is possibly responsible for creating the large hysteresis in the *I-V* curves. In order to reduce the hysteresis, several contact engineerings have been proposed such as modification of compact TiO_2 layer by PCBM or fullerene.[20]

On the other hand, inverted p-PSC employing n- and p-type organic semiconductors show negligible *I-V* hysteresis.[21,22] This also indicates that hysteresis is most likely coming from the interfacial contact between these layers. The organic layer such as PCBM gives better contacts with $CH_3NH_3PbI_3$ that passivate or inhibit the formation of trap states at the interface.[20] Interestingly, several reports have shown negligible hysteresis with higher PCE for forward scan in the inverted planar structure cells with PEDOT:PSS and PCBM as the hole and electron transporting materials, respectively.[23,24] Due to the small difference in the PCE estimated from both direction of the scans, further investigation on this opposite trend of hysteresis was not done yet. In order to understand the above phenomenon (i.e. higher PCE in forward scan), we simulated the *I-V* response of p-PSC using an equivalent circuit model that employs one opposite diode to represent some interfacial properties in the p-PSC. The device structure considered in this work is a typical inverted structure, ITO/PEDOT:PSS/$CH_3NH_3PbI_3$/PCBM/Al which has been reported in a literature (Figure 1 a).[24] It is known that two semiconductors with different energy levels form a junction or a diode. A similar junction forms when a metal with high work function is in contact with an n-type semiconductor with lower work function and known as Schottky junction.

The electron injection from $CH_3NH_3PbI_3$ to PCBM is possible due to the suitable difference of the conduction band edge of the PCBM which forms the diode. Hence, two interfaces in the given device structure (Figure 1 b), PEDOT:PSS/$CH_3NH_3PbI_3$, $CH_3NH_3PbI_3$/PCBM can be considered as simple diodes while the PCBM (semiconductor)/Al(Ca)(metal) interface may have another Schottky barrier diode (SBD) with opposite direction (Figure 1 b). When the semiconductor is in the contact with a metal, band bending happens at the interface. Metal/semiconductor contacts in electronic devices behave as Schottky junctions and have been extensively studied in the fields of inorganic contacts as well as organic light emitting diodes.[25-28]

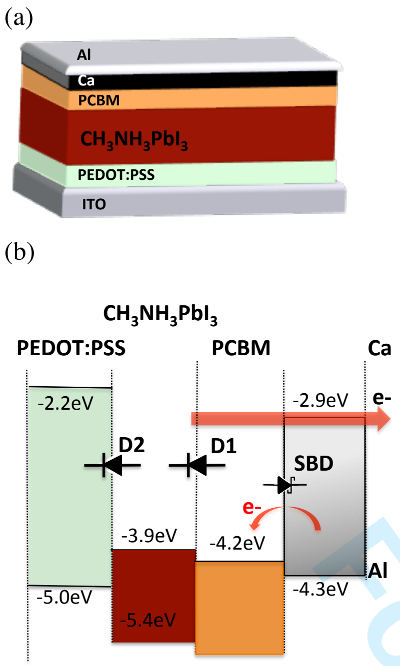

Figure 1. (a) Typical structure and (b) band diagram of the inverted perovskite solar cell Al(Ca)/PCBM/$CH_3NH_3PbI_3$/PEDOT:PSS.

In our previous report,[17] the simulated *I-V* curves of an equivalent circuit model with two diodes in a series, two shunt capacitors, two shunt resistances and single series resistance reproduce the experimentally observed curves quite well with the large hysteresis. These capacitive components at interfaces create the hysteresis due to the charge trapping/detrapping and/or charge accumulation caused by the defects at the interfaces related to the lattice mismatch and thermal expansion coefficient of the $CH_3NH_3PbI_3$.[16] In order to check the reverse trend of *I-V* hysteresis found in the inverted p-PSCs we constructed an equivalent circuit (Figure 2) having three diodes, corresponding to three interfaces. The *I-V* curve was calculated by using this equivalent circuit to simulate the reported one (Figure S1).

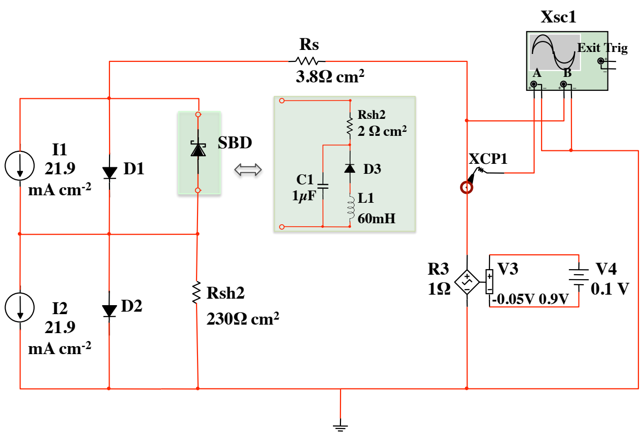

Figure 2. Equivalent circuit model for simulation of the I-V curves for inverted p-PSC.

Here in our model, series and shunt resistance (Rs and Rsh) values were fixed as an initial parameter from experimental result.[24] Then D3 and L1 (60mH) and C1 (1μF) block was added in series with Rsh1 to accomplish higher current behavior for forward scan. The L1 value changed systematically to minimize the difference between experiential and simulated curves. All parameters for three diodes are included in the Table S1.

The D2 represents the interface PEDOT:PSS/$CH_3NH_3PbI_3$, D1 and SBD represent the interface of $CH_3NH_3PbI_3$/PCBM and PCBM/Al(Ca), respectively. In our equivalent circuit SBD was equipped in parallel with D1 to simulate opposite current flow from Al(Ca) to PCBM because of non- uniform contact or incomplete coverage of the metal over the PCBM surface.[29]

The combination of the electrical parts consisting of resistance (Rsh2), capacitance (C1) and/or inductance (L1) can represent the Schottky diode (SBD) as shown in Figure S2. This type of configuration has already been reported as a definition of circuit containing SBD.[30,31] The secondary effect of slow traps in an organic Schottky diode is named apparent inductance.[32] There also have been frequently reported that in the impendence spectroscopy of organic semiconductor devices, inductor-like behavior "negative capacitance" is observed, which has been recently suggested to originate from self-heating effect of transient current.[33] Behavior of hysteresis in the *I-V* curves with different inductance L1 (500mH, 50mH and 0mH) is shown in Figure S3. At 0 mH the simulated *I-V* curves showed no hysteresis. For inductance equal 500 mH and 50 mH, (Figure S1) the simulated *I-V* curves showed a very good agreement with the experimental curves, forward scan showing higher PCE.

The aging effect of PCBM and subsequent metal penetration into the layer of PCBM produces deep traps and slow filling of these traps can be described as an apparent inductance.[32] Moreover, in the case of solar cells and organic light-emitting diodes, inductive element is associated with complex multistep dynamics such as surface states.[34] Another possibility may be the self-heating effect,[33] although we have no immediate evidence to support these hypotheses.

Based on the equivalent circuit (Figure 2) we have constructed physical real device composed of two Si photo diodes and one diode, an inductor and resistor (Figure 3).

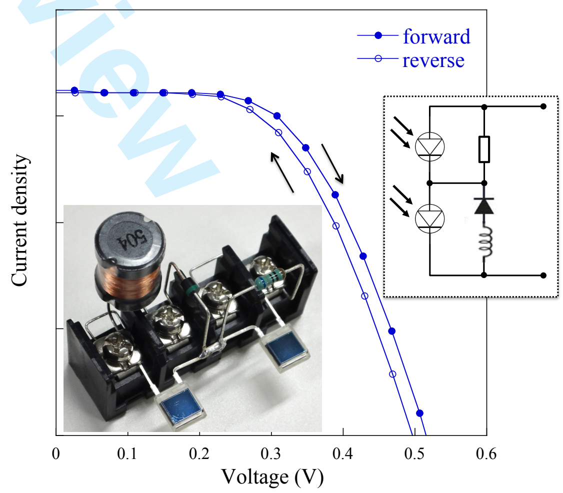

Figure 3. Photovoltaic response for modeled perovskite solar cells based on equivalent circuit with 2 Si photo diodes, a diode, an inductor and resistor (light intensity 0.1mW·cm^{-2}, holding time 1 ms, scan speed 2135mV·s^{-1}).

The *I-V* curves for this device well supported our equivalent circuit (Figure 2) having two Si photodiode and one SBD diode, and conclude that the inverted trend of hysteresis is coming from the inductance originating from the interface PCBM/Al(Ca).

In conclusion, the *I-V* hysteresis of inverted p-PSC can be reproduced by an equivalent circuit model that consists of two photo diodes representing two interfaces of PEDOT:PSS/$CH_3NH_3PbI_3$ and PCBM/$CH_3NH_3PbI_3$, as well as of one Schottky type diode representing the interface PCBM/Al(Ca). The latter of which is composed of inductance and small capacitance. We believe that the inductance is the sign for change of PCBM/Al(Ca) interface, charge accumulation or/and traps at this interface. The simulated *I-V* curves by our model match the experimental *I-V* curves quite well. Based on the equivalent circuit model the inverted trend of hysteresis has been also proved by newly constructed real device having two Si photo diodes, one diode with an inductor.

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Graphical Abstract

Textual Information

A brief abstract (required)

Planar structure perovskite solar cells (p-PSCs) generally show remarkable hysteresis in *I-V* curves. However, the several p-PSC devices with inverted structure show very small hysteresis. In the small hysteresis of the inverted p-PSC, *opposite trend of the I-V hysteresis* has been observed where the forward scan shows higher efficiency than the reverse scan. In this paper, an equivalent circuit model which reproduce the opposite trend of *I-V* hysteresis of the inverted p-PSC has been reported focusing the PCBM/Al(Ca) interface, which behaves like a Schottky contact including inductance.

Title(required)

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Authors' Names(required)

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