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### High Detectivity ITO/Organolead Halide Perovskite Schottky Photodiodes

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#### Abstract

Schottky photodiode, which is based on metal-semiconductor junction, is one of the most widely used technology for low cost image sensor arrays. Here, we fabricate a hole transport layer free organolead halide perovskite diode (ITO/ CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/PCBM/BCP/Ag), and explore its Schottky diode behavior. A Schottky barrier is identified between the transparent conductor ITO and the solution processed perovskite (CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>), with a barrier height of ~0.97eV measured by capacitance-voltage (C-V) measurements. The Schottky barrier at the ITO/ CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> junction is found to effectively suppress electron injection from ITO to the perovskite under reversed biased, leading to a surprising low dark current of  $1.9 \times 10^{-9}$ A/cm<sup>2</sup> when biased at -0.1V. When functioned as a photodetector, the ITO/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> schottky diode outperforms the conventional perovskite photodiode with PEDOT:PSS layer in terms of detectivity, reaching a high specific detectivity (D\*) of  $8.9 \times 10^{12}$  Jones. Moreover, by tuning the band gap of perovskite with the content of Bromine (Br), i.e. CH<sub>3</sub>NH<sub>3</sub>Pb (I<sub>1-x</sub>Br<sub>x</sub>)  $_3(0 \le x \le 1)$ , the Schottky barrier height at the ITO/Perovskite junction is raised, further lowering down the dark current of the perovskite photodiode. This work provides fundamental investigation on the device physics of perovskite Schottky diode, as well as a low cost approach for designing high sensitivity of photodetectors.

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Photodetectors are key components for realizing a wide range of industrial and scientific applications, such as optical communication, medical diagnosis and industrial inspection. Various photodetectors based on inorganic materials, such as ZnO, a-Si:H and GaAs, for applications ranging from UV to NIR detection have been developed in the past.[1-3] For example, a-Si:H photodiode with intrinsic layer sandwiched between p-doped and n-doped layer (p-i-n structure) is frequently used in flat panel X-ray image.[4] Recently, hybrid organic-inorganic perovskite (MAPbX<sub>3</sub>, MA short for CH<sub>3</sub>NH<sub>3</sub>, X=I, Br or Cl) has also become a promising alternatives for photodetector applications, due to their outstanding optoelectronic properties, such as tunable bandgap, high absorption coefficient, high charge carrier mobility, and long carrier diffusion length.[5-7] The bandgap of perovskite can be tuned by mixing halide elements in the perovskite [8], usually denoted as MAPb  $(I_{1-X}Br_X)_3(0\leq x\leq 1)$ , which enables the design of photodetector for specific wavelength range. What makes perovskite materials more attractive is their low temperature solution process ability, which would potentially bring down manufacturing cost and offer flexibility for electronic product design. [9, 10]

In general, the photodetectors based on organolead halide perovskite can be divided into two types: photodiode structure (such as p-i-n structure), and photoconductor structure.[11, 12] Photoconductor type diode offers high photocurrent gain with short channel design.[13] Nonetheless, this type of photodetector is not suitable for application where low dark current is required. As for the photodiode structure, most of the reported devices adopted a p-i-n structures similar to its solar cell counterpart (ITO/PEDOT: PSS/Perovskite/PCBM/ Bathocuprione (BCP) /Ag), which has been reported with a remarkable power conversion efficiencies of above 20%[14-16]. In the photodiode configuration, it is important to create asymmetric electrode or electrode interfacial layer at the two terminal for selective carrier transportation. Under dark condition, the asymmetric electrode arrangement could help reduce the dark current by blocking the thermal activated free carriers. To improve the device performance, several groups have developed different types of hole/electron blocking layers for photodetector applications, including PEDOT:PSS, PTAA and OTPD.[17, 18] An alternative low cost effective way to achieve low dark current is to adopt Schottky diode structure. For Schottky contact, the Schottky barrier created at the semiconductor side of the metal-semiconductor interface can block the injection of carrier under reversed bias, and effectively reduce the dark current of photodetectors. In fact, typical ITO/a-Si:H schottky diode gives a reasonably low dark current density of 10<sup>-8</sup>~10<sup>-9</sup> A/cm<sup>2</sup> when biased at -2V, and a fair on/off rectification ratio of  $10^3$  at  $\pm 2V$ .[19] Nonetheless, the Schottky diode based on perovskite materials is rarely reported. The band bending at the metal/perovskite or ITO/perovskite interface is usually overlooked in previous studies.

Here, hole transport layer (HTL) free type device with ITO/Perovskite/PCBM/ BCP/Ag structure (Figure 1a) is fabricated, and its photodetection performance is compared to a conventional perovskite photodiode with p-type PEDOT: PSS layer. A schematic band diagram of each layer in the device before contact is shown in Figure 1b, with energy levels similar to previous reports. [20, 21] Our investigation identifies that a Schottky barrier is formed at the ITO/perovskite interface, which effectively suppresses the electron injection from ITO to the perovskite under reversed biased in the dark, leading to a satisfactory low dark current for photodetection applications. As a result, the photodiode without PEDOT:PSS layer shows much lower dark current  $(1.9 \times 10^{-9} \text{A/cm}^2)$ , leading to a higher specific detectivity  $(1.8 \times 10^{12} \text{Jones})$  when compared to the device with PEDOT:PSS layer. We further investigated the Schottky barrier height of the

#### ITO/MAPb (I<sub>1-X</sub>Br<sub>X</sub>) 3 interface by using capacitance-voltage (C-V) measurements.

In experiments, patterned ITO glass substrates (2 cm in length and width, 1mm in height, with a piece of 2mm in width, 2cm in length patterned ITO in the middle) were cleaned in deionized water, acetone, and ethanol orderly in an ultrasonic bath for 15 min, and dried under nitrogen flow, followed by ultraviolet ozone treatment for 10 min. For device with PEDOT:PSS layer, PEDOT: PSS (Clevios 4083) was spin-coated on the substrates under 2000 rpm for 60 s and annealed at 150°C for 20 min in air. Otherwise, the substrates were transferred directly to glove box for device fabrication. The perovskite precursor (see supplementary for experiment) was spin-coated on the substrate at 3000 rpm for 40 s, with 200  $\mu$ l chlorobenzene added added on the substrate after the speed reaches to 3000 rpm during the spin-coating process to decrease the crystallization time of perovskite to obtain smooth compact perovskite thin films.[22] The substrates were heated on a hot plate at 100 °C for 10 min to convert the spin coated film into polycrystalline perovskite. Details of the perovskite material characterizations can be found in Figure S1. The PCBM solution was then spin-coated on the substrate at 2000 rpm for 40 s, followed by annealing at 100 °C for 10 min. Next, the BCP solution was spin-coated on the substrate at 2000 rpm for 60 s. Finally, the Ag electrode (80 nm) was thermally evaporated on the substrates through a shadow mask.



**Figure1.** (a)Schematics of MAPbI<sub>3</sub> photodetector. (b) Schematic band diagram of each layer in the device before contact, and the proposed electron-hole recombination mechanism in the dark.

To investigate the performance of photodiodes, typical current density-voltage (J-V) curves of our best perovskite photodetectors with and without PEDOT: PSS layer under dark and under illumination (0.45 mW/cm<sup>2</sup> at 500 nm) conditions were plotted in Figure 2(a). The photocurrent of both photodetectors, with or without PEDOT: PSS layer, is almost equivalent to each other, which is around  $1.2 \times 10^{-4}$ A/cm<sup>2</sup> at -0.1V. Notably, the dark current of the device without hole transporting layer is about one order magnitude lower than that of the device with PEDOT: PSS layer, reaching  $1.9 \text{ nA/cm}^2$  at -0.1V. As a result, the rectification ratio of the HTL free device reaches  $10^5$  when biased at  $\pm 1$ V. The dark I-V characteristics of the fabricated photodetectors are quite reproducible. A statistics of the dark current densities of ten photodiode devices with and without PEDOT:PSS layer were presented in Figure 2(b), showing an average of dark current of the PEDOT:PSS. To access the

(2)

photodiode's performance, the responsivities and detectivity were calculated. The responsivities (R) of the photodiode at 500nm is ~0.22 A/W, which is consistent with previously reported value. [23] The specific detectivity (D\*) is also evaluated according to the following equation[24]  $\blacktriangle$ 

$$D^* = \frac{R}{(2qJ_d^{-1})^{/2}}$$

where R is the responsivity and q is the elementary charge. Due to the dark current difference, the HTL free device shows a much higher D\* while the two devices have similar R. The D\* of the devices are calculated to be  $8.9 \times 10^{12}$  Jones, which is very close to the previously reported value found in electron transport layer modified perovskite photodiode evaluated by the same method. [17] It is worth to note that PEDOT: PSS is still favorable for solar cell application, as shown in Figure S2. The power conversion efficiency (PCE) of the device with PEDOT: PSS is higher than the device without PEDOT: PSS layer. It suggests, that under light biased, PEDOT:PSS acts as an effective hole transporting layer for extracting photo-generated holes from the perovskite layers, yet, when operated under dark, the PEDOT:PSS could not block the electron injection from the ITO electrode, leading to a high reverse saturation dark current at the PEDOT:PSS/Perovskite interface.



**Figure 2.** (a) J-V characteristics of devices in the dark and under light illumination at 500 nm with an intensity of  $0.4 \text{mW/cm}^2$ . (b) Statistics of the dark current density of ten photodiode devices with

and without PEDOT:PSS layer when baised at -0.1V. (c) Linear dynamic range of the devices. (d) Photocurrent rise and delay time of the devices.

The linear dynamic range (LDR), which shows how linear a response that the detector have for different light intensity, is given by:

$$LDR = 20Log \frac{J_{ph \max}}{J_d}$$

where  $J_{ph max}$  is maximum photocurrent within a linear range. The LDR of the device without PEDOT: PSS layer is measured to be 101 dB, which is much higher than the LDR (69dB) of the device with PEDOT: PSS layer as shown in Figure 2c. In contrast, the LDR of some inorganic photodetectors, such as InGaAs photodetectors can only achieve 66dB[25], and the LDR of the traditional Si photodetectors is around 120 dB. It is worth to note our LDR is currently limited by the maximum light source intensity, which is not the intrinsic limit of perovskite photodetector device.

Transient photocurrent behavior of both devices were also investigated and plotted in Figure 2d, which shows five-cycle curves of photocurrent time response under an interval of 10 s illumination. Both the device with or without PEDOT: PSS layer switch in a fast speed, with rise time and delay time are less than 50 ms as indicated in Figure S3. The transient behavior is currently limited by the sampling time of test equipment, which is not the ultimate switching speed of perovskite photodetector. The ON/OFF ratio of photodetectors without PEDOT: PSS layer is  $6.06 \times 10^4$ , which is one order higher than the ON/OFF ratio ( $1.51 \times 10^3$ ) of the traditional structure at the bias of -0.1V. The high photosensitivity value from the device without PEDOT:PSS layer originated from its low dark current. Generally speaking, the origination of dark current in a diode is mainly composed of the recombination and injection of carriers under reverse biased. In order to reveal the origin of the lower dark current in the HTL free photodiode, we further perform EIS measurements to investigate the recombination of carriers in the dark.



**Figure 3**. (a) Electrochemical impedance spectroscopy of the device, (b) Plot of ln(Jsc+J) vs (V-RsJ) and the linear fitting for reverse saturation current extraction.

An electrochemical workstation (CHI660E) with a frequency range from 0.1 MHz down to 1

 Hz at bias potentials 0.8 V (with a 5 mV sinusoidal AC perturbation) was employed for electrochemical impedance spectroscopy at room temperature in dark condition. The Nyquist plot of the EIS measurement results was shown in Figure 3a. Considering the device structure, the equivalent circuit shown in the inset in Figure 3a is used as a model. The series resistance component in the circuit model, R1, is associated with ITO resistance, and R2 indicates the parallel resistance of the device, which is related to its leakage current. By fitting the circuit model in Figure 3a, we can derived the R1 and R2 values. The results show that the device with PEDOT: PSS layer has a smaller R1 (176.6 ohms) than that of the device without PEDOT: PSS layer (230.2 ohms), suggesting that the PEDOT:PSS contact layer allows faster charge transfer at the interface than the ITO/Perovskite interface. Nonetheless, it is worth to note that R2 obtained from the device without PEDOT: PSS layer,  $2.47 \times 10^4$  ohms, is larger than that of the device with PEDOT; PSS,  $1.246 \times 10^4$ ohms. This suggests that PEDOT:PSS would induce more charge recombination under dark in the device. As the perovskite layer is fabricated in the same manner, the main recombination pathway is suspected to be at the interface rather than in the bulk. We conclude that although PEDOT:PSS is beneficial for hole transportation, however, it does not serve as an good electron blocking layer probably due to the indium defect in the PEDOT:PSS layer, which leads to charge recombination at the PEDOT:PSS/Pervoskite interface. A possible dark current generation mechanism for device with PEDOT:PSS is shown in Figure 1b. It is suspected that the acidic nature of PEDOT:PSS, with a pH value of ~2, will lead to the corrosion of ITO, causing In ion diffusion into PEDOT:PSS layer. [26] The defective In in the PEDOT:PSS would give rise to the intermediate states in the PEDOT:PSS which act as recombination centers for injected hole and electrons. In the dark and under reversed biased condition, the thermal generated holes from the perovskite will be transported to the PEDOT:PSS layer, where they recombine with the electron injected from ITO with the assist of In defect at the PEDOT:PSS/ITO interface. The injected holes and electron recombination then leads to the high dark current in devices with PEDOT:PSS, as shown in Figure 1b.

For the device without PEDOT:PSS, the injection of electrons is suspected to be mainly suppressed by the barrier height of Schottky contact between ITO and perovskite. The Schottky junction at the ITO/Perovskite interface should follow a typical Schottky diode equation

$$J = J_0 \left[ exp\left(\frac{qV}{nkT}\right) - 1 \right], \text{ and } J_0 = A^* T^2 \exp\left(\frac{-q\phi_b}{kT}\right)$$
(2)

where  $J_0$  is the dark reverse saturation current, a parameter that is directly related to the recombination rate in semiconductors [17], A is the Richardson constant, n is the ideality factor, V is the applied voltage and  $\Phi_b$  is the Schottky barrier height. The dark J–V curve of the solar cells is then extrapolated to extract the dark saturation current density,  $J_0$ . As shown in Figure 3(b), the HTL free device has a pretty low  $J_0$  of  $2.2 \times 10^{-13}$ A/cm<sup>2</sup>, which implies that the leakage current is successfully suppressed by the Schottky junction.

To further reveal the relationship between the dark current and the Schottky barrier height, Schottky type devices based on perovskite with different amount of Bromine (Br) substitution were fabricated. It is well known that the band gap of perovskite could be widened by increasing Br content, which would in return affect the Schottky barrier height at the ITO/perovskite junction. The J-V curves of the fabricated devices with increasing Br content is presented in Figure 4a, with an inset plot highlighting the dark current values obtains at -1V bias. It clearly shows that, when

biased at -1V, the dark current of the ITO/Perovskite Schottky photodiode decreases from  $10^{-7}$  A/cm<sup>2</sup> to  $3 \times 10^{-8}$  A/cm<sup>2</sup> as the Br content in the perovskite increases from x=0 to x=0.4. To evaluate the schottky barrier height of the ITO/ MAPb (I<sub>1-x</sub>Br<sub>x</sub>) <sub>3</sub>(0≤X≤1) contact, capacitance-voltage (C-V) measurements were then carried out by an electrochemical workstation (CHI660E) with a frequency of 1000 Hz and bias potentials range from -1.2 V to 1.2 V (with a step of 0.05V) at room temperature in dark condition. In Schottky diodes, the capacitance of depletion layer can be expressed as Eq. (3) [27, 28]

$$C^{-2} = \frac{2[V_1 + V]}{q\varepsilon_s A^2 N}$$

where A is the area of the diode,  $\varepsilon_s$  is the dielectric constant, N is the doping concentration value of semiconductor materials, V<sub>1</sub> is the diffusion potential at zero bias and is determined from the extrapolation of the linear C<sup>-2</sup>-V plot (Figure 4b) to the V axis. Therefore, the value of the barrier height can be obtained by the following equation:

$$\phi_b = V_1 + V_2 \tag{4}$$

(3)

where  $V_2$  is the potential difference between the Fermi level and the bottom of the conduction band. As judged from Figure 4b, with a positive slope from the C<sup>-2</sup>-V plots, the perovskite films fabricated in our research were found to be n-type[31]. Then, the  $V_2$  can be obtained from the following relation:

$$V_2 = kTLn(\frac{N_L}{N})$$
(5)

where k is Boltzmann constant, T is the absolute temperature,  $N_L$  is effective density of states at the conduction band edge[29, 30] and N is the doping concentration. The doping concentration values (N) of the perovskite layer can be derived from the slope of the linear C<sup>-2</sup>-V plot (Figure 4b), which gives a value of  $5.21 \times 10^{16}$  cm<sup>-3</sup> for the MAPbI<sub>3</sub>, in agreement with previous report[31]. Using the Eq. (4) and Eq. (5), we are able to calculate the barrier height of ITO/MAPb (I<sub>1-X</sub>Br<sub>X</sub>)<sub>3</sub>. The calculated results are summarized in Table 1. Based on these results, the energy diagrams of the ITO/MAPb (I<sub>1-X</sub>Br<sub>X</sub>)<sub>3</sub> junction can be sketched, as shown in Figure 4c-e. The barrier heights at the ITO/Perovskite junction increased from 0.967 eV to 1.124 eV when the Br content x increased from 0 to 0.4, leading to the a lower reversed dark current for devices with higher Br content in Figure 4a. All the above results suggest that there is a schottky contact between the ITO and perovskite for the device without PEDOT: PSS.



Figure 4. (a) Dark current of the device with different Br content. (b)C-V characteristics of the device measured at 1kHz. (c)- (e) The energy diagram of ITO/ MAPb ( $I_{1-x}Br_x$ ) <sub>3</sub> contact (x=0, 0.2, 0.4)

Items	X=0	X=0.2	X=0.4
$N_L(cm^{-3})$	6.89×10 <sup>18</sup>	7.16×10 <sup>18</sup>	7.35×10 <sup>18</sup>
N(cm <sup>-3</sup> )	$5.21 \times 10^{16}$	7.91×10 <sup>16</sup>	1.33×10 <sup>17</sup>
V <sub>1</sub> ( eV )	0.127	0.117	0.104
V <sub>2</sub> ( eV )	0.84	0.95	1.02
$\Phi_{b}(eV)$	0.967	1.067	1.124

**Table 1.** The ITO/ MAPb ( $I_{1-x}Br_x$ ) <sup>3</sup> Schottky diode device parameters extracted from C-V measurements with different Br content (x)

In summary, the ITO/ CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> junction effectively suppresses electron injection from ITO to the perovskite under reversed biased, leading to a surprising low dark current of  $1.9 \times 10^{-9}$  A/cm<sup>2</sup>. When functioned as a photodetector, the ITO/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> schottky diode outperforms the conventional p-i-n perovskite photodiode with PEDOT:PSS layer in terms of detectivity, reaching a high photosensitivity of  $6.06 \times 10^{4}$  and a specific detectivity (D\*) of  $8.9 \times 10^{12}$  Jones. Moreover, the Schottky barrier height at the ITO/Perovskite junction can be further adjusted by tuning the

band gap of perovskite with the content of Bromine (Br). This work reveals fundamentally the device physics of Schottky diode based on perovskite and transparent conductor, and provides a low cost technology solution for high sensitivity photodetectors.

# **Supplementary Material**

See supplementary material for the complete device fabricate process, and for the characterization of the MAPbI<sub>3</sub> thin film by UV-Vis, SEM and XRD instruments. The current-voltage curves under light, and the transient response of the photodetectors are also included in the supplementary material.

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