Electrophysical parameters of P3HT:PCBM solar cells

D A Onishchuk, P S Parfenov, A P Litvin, D P Shcherbinin, A V Baranov, A V Fedorov

Center of Information Optical Technologies, ITMO University, Saint Petersburg 197101, Russia

onishchuk.dmitry@gmail.com

Abstract. Using the dark capacitance–voltage and current–voltage characteristics we analyzed the electrophysical parameters of P3HT:PCBM solar cells with addition of PbS nanocrystals. The influence of the device architecture on the built-in potential value and ideality factor are considered. The process of space-charge limited current characterizing is also described.

1. Introduction

Nowadays, optoelectronic devices based on colloidal semiconductor nanocrystals (NCs) obtain a widely application. The considerable attention is paid to the solar cells (SCs) and light emitting diodes development. However, the efficiency of NCs devices is influenced by many factors, and to improve their efficiency we need a full understanding of processes taking place in heterojunction and bulk material of the devices. The purpose of our work is analysis of the electrophysical parameters of P3HT:PCBM SCs, and analysis of addition of PbS NCs [1]. Paper discusses methods, based on dark capacitance–voltage and current–voltage characterization.

2. Experimental

The main parameters of the SCs are: short circuit current (Isc) (or short circuit current density (Jsc)), open circuit voltage (Voc), Fill Factor (FF), shunt (Rsh) and series (Rs) resistances, and power conversion efficiency (PCE). These parameters make it possible to rate efficiency of the SCs, but provide minimum information about the processes taking place in heterojunction and bulk material. To fully characterize these processes we need to calculate dark shunt (Rsh) and series (Rs) resistances [2], as well as the built-in potential (Vb) [3], ideality factor, density and mobility of the charge carriers. We investigated some devices with different contact layers (Au, Al, Ag) and different active and transport layer materials (PEDOT:PSS, ZnO) (Table 1). The J–V characteristics were measured by Ossila Solar Cell I-V Test System.

| Device | Structure |
|--------|-----------|
| Au_1   | ITO / ZnO / P3HT-PbS / PEDOT:PSS / Au |
| Au_2   | ITO / ZnO / P3HT-PbS-PCBM / PEDOT:PSS / Au |
| Al_1   | ITO / PEDOT:PSS / P3HT-PCBM / ZnO / Al |
| Al_2   | ITO / PEDOT:PSS / P3HT-PCBM / Al |

Table 1. Samples of SCs
2.1. **Dark $R_{SH}$ and $R_s$ analysis**

Due to $R_s$, only part of the applied bias is applied to the heterojunction. Therefore to obtain reliable data, the losses caused by $R_s$ should be taken into account. The voltage at heterojunction can be described by the following expression:

$$V_D = V - JR_s.$$  (1)

While the light characteristics $R_{SH}$ and $R_s$ are determined by intersection of J-V curve with axes, the dark $R_{SH}$ and $R_s$ are determined the graph of differential resistance ($R_{diff}$). We found that the light parameters are different from light. For example, device Ag-2 demonstrates 39 Ohm⋅cm$^2$ and 2.8 Ohm⋅cm$^2$ $R_{SH}$ and $R_s$ for dark characteristic, and 22 Ohm⋅cm$^2$ and 15 Ohm⋅cm$^2$ $R_{SH}$ and $R_s$ for light characteristic.

2.2. **Built-in potential**

The $V_{bi}$ value was determined in the point of intersection C$^2$ vs V curve extrapolation with X-axis, and the density of charge carriers $N_0$ was calculated by the extrapolation's slope (Table 2), in accordance with the Mott–Schottky law [3]. Capacitive characteristics were measured by Keysight E4980A LCR Meter. However, we couldn’t determine $V_{bi}$ value from C$^2$ vs V curves for Ag-1 and Ag-2 devices; therefore, we investigated C–V characteristics. In this case, the capacitance peak shows the voltage slightly smaller than $V_{bi}$ [4]. For comparison, for all device’s values of $V_{bi}$ were determined from C–V characteristics (Table 2). To obtain more accurate results for NCs SCs, you can apply modified Mott – Schottky model [5].

| Device | Light | $R_{SH}$ (dark) $R_{SH}$ (Ohm⋅cm$^2$) | Light $R_s$ (dark) $R_s$ (Ohm⋅cm$^2$) | $V_{bi}$ (V) | C$^2$-V | C-V | $N_0$ (cm$^3$) | PCE (%) | n |
|--------|-------|---------------------------------|---------------------------------|-------------|-------|-------|--------------|--------|----|
|        |       |                                 |                                 |             |       |       |              |        |    |
| Al-3   | ITO / PEDOT:PSS (thin) / P3HT-PCBM / ZnO / Al | 154 | 140 | 145 | 150 | 235 | 437 | 245 | 264 | 627 | 1830 | 26.4 | 39.8 | 20.2 | 34.6 |
| Ag-1   | ITO / PEDOT:PSS / P3HT-PCBM / ZnO / Ag | 71 | 2 | 25 | 28 | 242 | 11 | 246 | 9.2 | 698 | 30.2 | 14.1 | 3.4 | 14 | 2.9 |
| Ag-2   | ITO / PEDOT:PSS / P3HT-PCBM-PbS / ZnO / Ag | 2.5 - 3.5 | 0.41 | 1.6 | 0.35 | 0.7 | 0.5 - 0.7 | 1.25 | >1 | 3 - 6 | 0.03 | 0.01 | 5.3⋅10$^{17}$ | 3.0⋅10$^{17}$ | 5.7⋅10$^{18}$ | 9.1⋅10$^{18}$ | 6.7⋅10$^{18}$ | 0.2 |

The $V_{bi}$ obtained by two different methods had a large divergence. In that regard we measured the C–F characteristics of samples, having the same structure as Au-2 and Ag-2 devices (Fig. 1 (a)). There are several regions in these plots. Device with Ag-2 structure has three regions: in the first (up to 10 kHz) capacitance decrease with increasing frequency, which indicates a gradual decline in the contribution of the trap states; in the second region (10–70 kHz) capacitance almost unchanged, which indicates the smallest contribution of traps and the presence of almost constant number of charge carriers [6]; in the third region (above 70 kHz) a decrease in the capacitance is observed again, which is due to a decrease in the contribution of the main charge carriers whose time of transfer in the device is became longer than the applied frequency. Therefore, the frequency 10–70 kHz can be considered suitable for determining $V_{bi}$. Device with the same as Au-2 structure has only two regions, probably traps states
here is deeper and suitable for determining $V_{bi}$ frequency is less than 1 kHz. The figure 1 (b) shows an example of $V_{bi}$ determination, measured at the correct frequencies.

![Figure 1](image1.png)

**Figure 1.** (a) C–F characteristics of Au$_2$ and Ag$_2$ devices; (b) $V_{bi}$ determination by $C^2$ vs V plot of Au$_2$ (left scale) and Ag$_2$ (right scale) devices. $V_{bi}$ is 0.42 V for Au$_2$, and 0.1 V for Ag$_2$ devices.

2.3. **Space Charge Limited Current (SCLC) and ideality factors**

The slope of the dark J – V characteristic inherent SCLC is achieved only under the bias voltage is greater than 10 V. Therefore we used Keithley SourceMeter 2636B. In addition to the voltage drop on serial resistance we take into account the build-in potential. The corrected dark J–V characteristic of Au$_2$, adjusted for the voltage drop and $V_{bi}$, is presented in Fig. 2 (a). This characteristic was measured specially to get the SCLC mode, which is achieved at relatively high voltages. The mobility of charge carriers was calculated in accordance with the Mott-Gurney law [7,8] and in zero field was $2 \cdot 10^{-5}$ cm$^2$/V·s.

![Figure 2](image2.png)

**Figure 2.** The dark J–V characteristic of Au$_2$: (a) – double logarithmic scale, the straight lines denote the slope 1 and 2; (b) – logarithmic scale, the straight lines show an ideality factor of 4.5 and 8.

According to the ln(J)–V plot (Fig. 2 (b)), we determining the exponential regions and calculated the ideality factors "n" using the equation that follows from equation 2:

$$m = \frac{1}{n\kappa T},$$

where m is a slope of the approximate straight lines. Ideality factors characterize the recombination processes in the device. Usually their value varies from 1 to 2 [9], and they can change with the applied voltage.
3. Results
The deviation of the dark resistances from the light's characteristics are linked to the uneven light absorption by the active layer [10] and can be caused by large number of defects, which, under illumination, contribute to the leakage current, as evidenced by decreasing R_{SH}. However, the transport of charges to the electrodes under illumination is impeded, as evidenced by the increase in R_S.
The V_{bi} values for Al_2 and Al_3 were much higher than for Al_1, which, in the case of Al_2, may be due to the absence of a leveling ZnO layer. In the case of Al_3, this also can be associated with the formation of structural defects of thinner layer of PEDOT:PSS. But the common reason may be in oxidation of aluminum, which changes the aluminum work function from 4.3 to 1.4 eV. The V_{bi} value of Ag_1 and Ag_2 may also be associated with the contact layer oxidation. Silver oxidation can slowly change the working function from 4.3 to 5.0 eV [11], which corresponds to the working function of ITO.

High ideality factors are associated with charge recombination in heterojunction [12] and formation of nonohmic contacts [13]. An increase value of the ideality factors correlates with a decreasing in the efficiency of devices; therefore, a high value indicates a large number of defects. It correlated with the fact that measured charge carriers concentration increases when the efficiency of devices is decrease, which is probably due to the fact that the contribution of trap states is added to the desired concentration of main charge carriers [14]. All investigated devices are characterized by a high value of the ideality factor, which indicates the dominant influence of trap states, which make a large contribution to the N_D values. Ideality factor correlates well with efficiency of devices, which indicates the main role of defects in limiting the efficiency of the derives.

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