Systematic electrical characterization study of a hybrid organic-inorganic semiconductor heterojunction at different illumination conditions

Oscar H. Salinas[a,b], M.C. Arenas[c], M.E. Nicho[d], and Hailin Hu[b]
[a]*Universidad Tecnológica Emiliano Zapata del Estado de Morelos,*
Av. Universidad Tecnológica No. 1, Col. Palo Escrito, C.P. 62760, Emiliano Zapata, Morelos,
e-mail: oscarsalinas@utez.edu.mx
[b] *Centro de Investigación en Energía, Universidad Nacional Autónoma de México,*
Apartado Postal 34, Temixco 62580, Morelos, México.
[c]*Centro de Física Aplicada y Tecnología Avanzada, Universidad Nacional Autónoma de Mexico,*
Apartado Postal 1-1010, Santiago de Querétaro, Querétaro, 76000, México,
e-mail: mcaa@fata.unam.mx
[d]*Centro de Investigación en Ingeniería y Ciencias Aplicadas, Universidad Autónoma del Estado de Morelos,*
Av. Universidad 1001, Col. Chamilpa, 62209, Cuernavaca, Morelos, México.

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Electrical characterization study of hybrid heterojunctions (HHJs) based on CdS and poly(3octylthiophene) (P3OT) is performed in order to know the process repeatability and materials homogeneity that may influence on power conversion efficiency (PCE) of CdS/P3OT photovoltaic (PV) solar cells. Basic statistical and numerical techniques for solving linear equations were used for systematic analysis of PV performance of those HJs. Adjustment curves were calculated from experimental data with the adjustment factor equal to almost 99.9 %, which means that the model has a high confidence level. They also were combined with theoretical models to establish a mathematical model that can describe the electrical performance of the mentioned junctions. PV response was analyzed under different illumination conditions, 23, 40, 124 and 285 mW/cm^2 of I_{rr} level. The relationships between short circuit current (J_{SC}) and open circuit voltage (V_{OC}) with irradiance level (I_{rr}) were determined with high confidence level too. The dependence of J_{SC} on I_{rr} is linear, whereas V_{OC} depends logarithmically on I_{rr} and on J_{SC}. For spectral response a 100 Watts halogen lamp and light filters from 400 nm to 689 nm of wavelength were used. The maximum incident photon converted to electron efficiency (IPCE) was experimentally determined at 2.75 eV of photon energy. This value corresponds to the optical forbidden gap of the inorganic semiconductor material. The obtained results are in agreement with the theoretical concepts of PV devices.

Keywords: Photovoltaic effect; short circuit current; open circuit voltage; irradiance.

En este trabajo se realiza un estudio sistemático de la caracterización eléctrica de heterouniones híbridas con la finalidad de conocer la repetitividad del proceso y la homogeneidad de materiales que se utilizan para preparar dispositivos electrónicos semiconductores para aplicación fotovoltaica. La caracterización eléctrica de dispositivos fotovoltaicos se realiza para saber su eficiencia de conversión de energía. Para el análisis sistemático de los resultados eléctricos, se utilizaron técnicas básicas estadísticas y de métodos númericos para resolver ecuaciones lineales que involucran parámetros eléctricos del dispositivo. Las curvas de ajuste obtenidas a partir de los datos experimentales presentaron un factor de ajuste del 99.9 %, lo que significa un alto nivel de confianza en el modelo. Estas curvas de ajuste fueron combinadas con modelos teóricos para obtener un modelo matemático que describe el comportamiento eléctrico de este tipo de uniones específicas. La relación entre la corriente de corto circuito (J_{SC}) y el voltaje de corto circuito (V_{OC}) con el nivel de irradiancia (I_{rr}) se determinaron con un alto nivel de confianza. Las curvas demuestran que J_{SC} depende linealmente con I_{rr}, mientras que el V_{OC} depende logarítmicamente. Por otro lado, V_{OC} depende logarítmicamente de J_{SC}. La respuesta fovoltaica fue analizada a 23, 40, 124 y 285 mW/cm^2 de nivel de irradiancia. Se utilizaron filtros de 400 a 689 nm de longitud de onda y una lámpara de halógeno de 100 Watts para obtener la respuesta espectral. La máxima eficiencia de conversión de fotones incidentes (IPCE) se determinó experimentalmente en 2.75 eV de energía de los fotones, valor que corresponde con el ancho de banda prohibida del material semiconductor inorgánico. Los resultados obtenidos concuerdan con los conceptos teóricos básicos de dispositivos fotovoltaicos.

Descriptores: Efecto fotovoltaico; corriente a corto circuito; voltaje a circuito abierto; irradiancia.

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1. Introduction

Electrical characterization of a semiconductor electronic device is an effective way to get knowledge about the physical behavior of each component layer as well as that of the whole junction. Test conditions depend on the device application, and in the case of PV semiconductor devices electrical characterization under dark and illumination conditions are required. The common procedure is to get the current versus voltage curves, called I-V curves, for both test conditions. Parameters gotten directly from the I-V curves, are open circuit voltage (V_{OC}) and short circuit current (J_{SC}). The first one has been related mainly with energy differences levels at the interface of the electron-acceptor and electron-donor materials according to a flat energy band analysis [1]. On the other hand, the J_{SC} value depends on the generation and

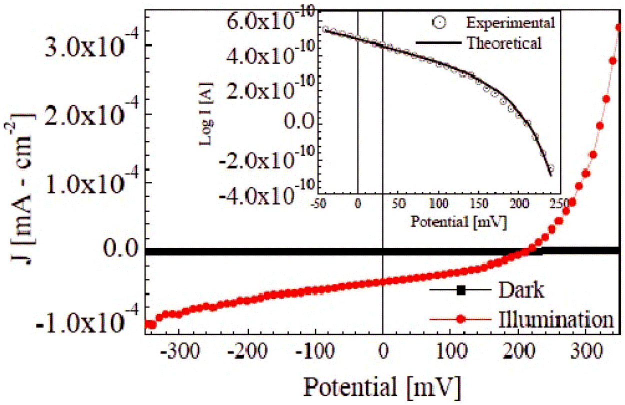

FIGURE 1. I-V curves of CdS/P3OT hybrid HJ in dark (solid line) and under illumination conditions (circles) at 88 mW/cm^2 of I_{rr} level.

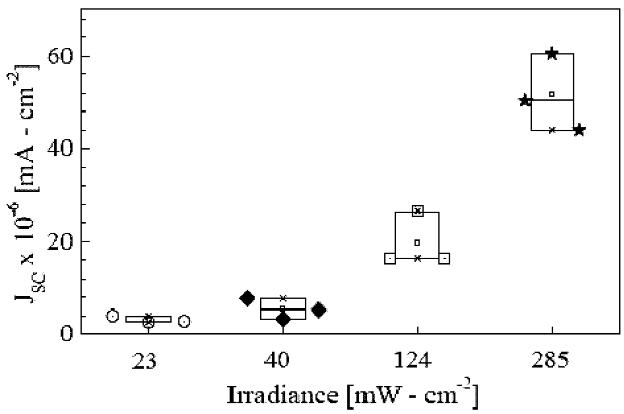

FIGURE 2. Distributions of J_{SC} data at different I_{rr} levels.

collection of the two free charge carriers, electrons and holes. Charge carrier generation could be done by different sources, for instance light and heat. When light is the source there are two principal parameters that impact on this free charge carriers generation, light intensity and light wavelength. The first is related to the I_{rr} and can be analyzed from the power conversion efficiency (PCE) results. The second one is analyzed by calculating the incident photon converted to electron efficiency (IPCE), which is also called internal quantum efficiency [2]. Since the amount of available photons varies with the photon wavelength [3], reaching to maximum values at visible region, the IPCE depends on the absorption coefficient and band-gap of absorbing material in a solar cell. Collection of free charge carriers depends on the materials properties like mobility, lifetime carrier recombination issues, resistivity, and so on [4]. Another two parameters, PCE and fill factor (FF) are calculated based on V_{OC} and J_{SC} levels [4]. PCE is the ratio between the output power and the incident power of the PV devices. Output power, also called maximum power, is straightly related to the electrical performance of the photovoltaic devices; it is calculated as the product of J_{SC} and V_{OC}. It is also related with the FF, which depends on the I-V curve shape. Incident power is the I_{rr} level applied on the front or back surface of PV devices. Based on extracted and calculated PV parameters, the device performance can be evaluated for its PV application. Physical phenomena occurred in PV devices are so-called photovoltaic effects, and the conversion from solar energy into electrical energy is well described in literature [1-5]. Statistical analysis is useful to know process repeatability, semiconductor thin layer homogeneity, and device reliability about its electrical performance. Following this kind of analysis, mathematical models describing the experimental behavior can be gotten based on experimental data and simple correlation and regression analysis.

Organic or polymer PV devices can be prepared using different types of device structures [6-8]. Heterojunctions (HJs) are one of them. They can be prepared either planar [1,9] (separated electron donor and acceptor layers), or bulk structure (mixed electron donor and acceptor materials to form a single PV active layer) [10]. There are technological differences between them, but the main one is the interfacial area [4]. About PV cell preparation process, planar heterojunction (HJ) is easier to prepare and to analyze than bulk HJ. In the organic materials family a bulk HJ has been shown higher PCE than the planar one. In previous works [9,11], we have developed planar HJs based on poly(3octylthiophene)-cadmium sulfide for photovoltaic application. A statistical study about the photovoltaic performance of organic/inorganic HJ is presented in this work.

2. Experimental

Hybrid HJs based on planar structures ITO/CdS/P3OT/Cu, were prepared for this statistical study. Transparent conductive ITO substrates were cleaned before CdS layer deposition following the procedure described in Ref. 6. Layers of CdS were deposited by chemical bath deposition (CBD) [12,13]. The obtained CdS layers had a thickness of 200 nm and they were used as-prepared without any further heat or chemical treatment. P3OT in toluene solution was drop-cast on CdS film, as described in previous reports [1,14]. The thickness of deposited P3OT films were about 200 nm, measured on an Atomic Force Microscope (AFM, NanoScope Multimode Scanning Microscope) [14]. P3OT and CdS optical band gap (Eg) is about 1.8 eV and 2.4 eV, respectively [1,12]. The Highest Occupied Molecular Orbital (HOMO) level and the electron affinity (χ) of P3OT are 5.4 eV and 3.4 eV, respectively [1].

The top contact of HJs was Cu [1,15]. Cadmium sulfide (CdS) is the electron acceptor and poly(3octylthiopene) (P3OT) is electron donor in this HJ. The electrical contact between CdS and ITO was ohmic behavior [11]. Electrical characterization of CdS/P3OT hybrid HJs at 25°C in air was done with an automatic data acquisition system which consists in a Keithley 230 programmable voltage source and a Keithley 619 electrometer/multimeter, both coupled each other and connected to a personal computer. Illumination of HJ devices was through ITO layer by using a 100 Watts

TABLE I. Estimated electrical parameter values of different hybrid HJs.

I_{rr} (mW/cm^2)	V_{OC} (mV)	J_{SC} 10^{-6} (mA/cm^2)	J_0 10^{-6} (mA/cm^2)	FF	R_{shunt} 10^8 (Ω)	n	ϕ_B (eV)
285	211	44.00	0.0884	0.34	8.2	1.53	1.02
124	200	16.40	0.0884	0.422	27	0.71	1.02
40	156	3.40	0.0884	0.398	130	0.79	1.02
23	134	2.63	0.0884	0.327	85	0.83	1.02
285	183	60.6	0.115	0.381	6.0	0.54	1.01
124	164	26.6	0.115	0.338	12	0.57	1.01
40	148	7.74	0.115	0.39	50	0.65	1.01
23	152	4.01	0.115	0.412	140	0.77	1.01
285	117	50.40	0.177	0.291	2.8	0.43	1.00
124	233	16.40	0.177	0.357	28	1.00	1.00
40	196	5.30	0.177	0.388	100	1.10	1.00
23	164	2.84	0.177	0.378	200	1.08	1.00

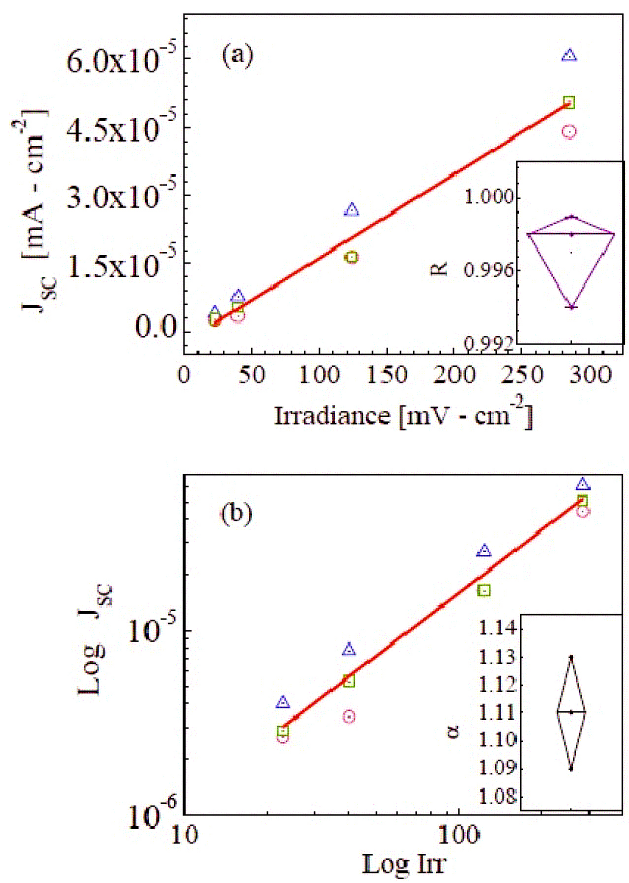

FIGURE 3. J_{SC} vs. I_{rr}, linear (a) and logarithmic scale (b).

halogen lamp. The I_{rr} level was 88 mW/cm^2, close to 84 mW/cm^2 corresponding to AM1.5 spectrum [1]. The measurement was done at three different zones of each sample in order to get information about the sample homogeneity. Statistical analysis was performed using free software. Correlation and regression analysis was done to get mathematical

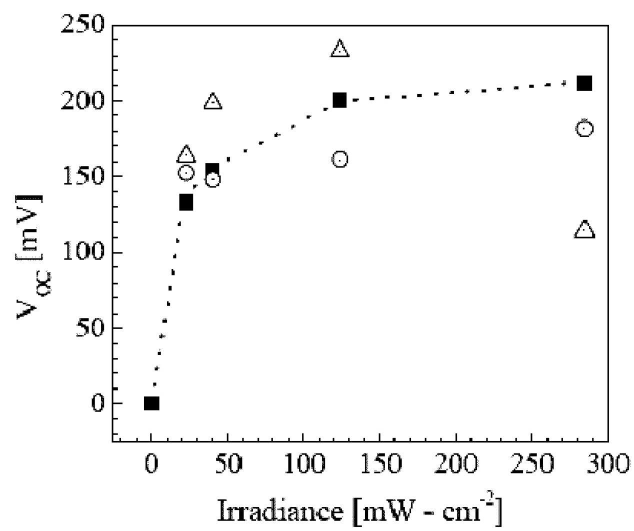

FIGURE 4. V_{OC} dependence on the I_{rr} level.

models based on experimental data. These models describe electrical behavior of hybrids HJs with a high confidence level.

3. Results

The current through PV devices increases significantly when the cell samples are under illumination conditions, as showed in Fig. 1. When HJ is in dark there is no electric energy generation (solid line). The I-V curve shows soft trace under illumination conditions, the kind of the trace impacts on the Fill Factor (FF) of the PV devices [6]. Higher values of FF are expected for soft traces, while resistive traces have lower FF values. Experimental I-V curve can be modeled using the following mathematical model [1]:

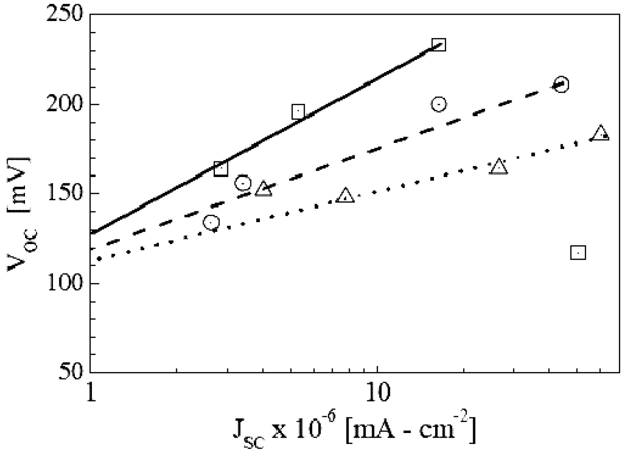

FIGURE 5. Logarithmic correlation between V_{OC} and J_{SC}.

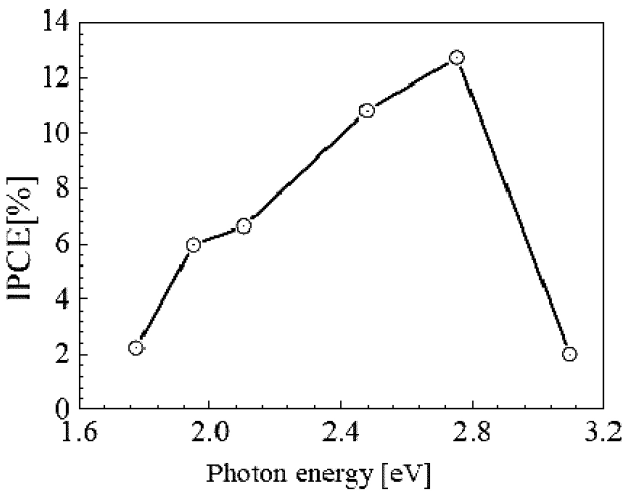

FIGURE 6. IPCE of the hybrid HJ at different photon wavelength values.

$$I = I_L - \left[I_o \left[\exp\left(\frac{qV - R_s I}{nkT} \right) - 1 \right] + \frac{V - R_s I}{R_{\text{shunt}}} \right] \quad (1)$$

This model is obtained from a basic electrical circuit including an ideal diode, a series resistance (R_S) and a parallel resistance (R_{shunt}) [1]. As shown in the inset of Fig. 1 the theoretical and experimental curves match very well. Therefore values of important parameters of HJs can be extracted and estimated, that are listed in Table I. The procedure to get the barrier height (ϕ_B) is explained in literature [1,4]. In this case, its value is estimated at 1.0 eV approximately. According to the energy flat band diagram, the energy difference between Lowest Unoccupied Molecular Orbital (LUMO) of P3OT and Conduction Band (EC) of CdS is 1 eV approximately [1]. It means that thermionic emission mechanism is dominating in the current transport. It shows in Table I that the higher the I_{rr} the higher the influence of the R_{shunt}. The ideality factor (n) has not a clear correlation with the I_{rr}, and in the best of the cases it is 1, which is the ideal case. The reverse saturation current density (J_0) does not depend on the I_{rr} level but on the zone of the sample, which is expected. According to the results showed in Table I, there is a dependence of the J_{SC} and V_{OC} values on the I_{rr}. The J_{SC} dependence on the I_{rr} level is shown in Fig. 2. It is clear that the highest J_{SC} is obtained at higher I_{rr} levels. Also at higher I_{rr} levels, the J_{SC} data distribution is more open. According to the experimental data, the relationship between the J_{SC} and I_{rr} is linear (Fig. 3). The different symbols (triangles, squares and circles) correspond to the measurements taken from three different zones of the samples. Solid line corresponds to the line of better adjustment of the experimental data. The adjustment factor (R) has a value close to one (0.998 average, inset of Fig. 3a), which means a very good agreement between the linear adjustment with experimental data. Based on that, the relationship between J_{SC} and I_{rr} can be written as follows:

$$J_{SC} = (0.182 I_{rr} - 2.3) 10^{-6} \quad (2)$$

It can be seen in Fig. 3b that the dependence of J_{SC} on I_{rr} follows the power law, J_{SC} vs. I_{rr}^{α}. Values of α close to one are expected for PV devices where bimolecular recombination has no impact and therefore transport of hole and electron can be done with comparable efficiency [2]. In this case α is 1.11, in average, therefore we can declare that bimolecular recombination is present. It is also reported that for high I_{rr} levels the J_{SC} magnitude is limited by this mechanism or tends to be saturated.

If the Eq. (1) is analyzed at zero current conditions (open circuit) and no R_S influence, the following equation is obtained,

$$V_{OC} = \frac{nkT}{q} \ln\left(\frac{J_{SC}}{J_O} + 1 \right) \quad (3)$$

Combining Eq. (2) and Eq. (3),

$$V_{OC} = \frac{nkT}{q} \ln\left(\frac{(0.182 I_{rr} - 2.3) 10^{-6}}{J_O} + 1 \right) \quad (4)$$

Therefore a logarithmic dependence between V_{OC} and I_{rr} level is expected, which can be corroborated in Fig. 4. The use of Eq. (4) to calculate expected values of V_{OC} based on I_{rr} measurements could introduce calculate errors, because it does not take into account resistive effects. In order to get more accurate estimated values of V_{OC} based on experimental data the following equation is used,

$$I_L = I_O \left(\exp\left(\frac{qV_{OC}}{nkT} \right) - 1 \right) + \frac{V_{OC}}{R_{\text{shunt}}} \quad (5)$$

Solving Eq. (5), by numerical methods, it is possible to estimate V_{OC}. A comparison between experimental data (different symbols) and estimated V_{OC} values is shown in Fig. 4. The maximum mismatch values is around 3 mV, which means the experimental-theoretical model is very accurate.

On the other hand, the Eq. (4) also indicates a logarithmic correlation between V_{OC} and J_{SC}, which can be corroborated in Fig. 5. The analysis of the electrical response with light of different wavelength is done by calculating the IPCE as follows,

$$IPCE(\%) = \frac{1240}{\lambda}\frac{J_{SC}}{I_{rr\lambda}}10^2 \quad (6)$$

where λ and $I_{rr\lambda}$ are the light wavelength and the irradiance level at that wavelength, respectively. Units of J_{SC} could be A (or mA)/m^2 and for $I_{rr\lambda}$ could be W (or mW)/cm^2. Experimental results are shown in Fig. 4. It can be seen that the maximum IPCE value occurs at the energy of 2.75 eV approximately. This value is close to the band gap value of CdS , which is around 2.4 eV. It means the light is traveling thorough CdS layer and is being absorbed by the P3OT layer. Both layers met the objective for they were chosen as materials for PV applications.

4. Conclusions

A systematic analysis of electrical characterization lets us get mathematical models to describe hybrid HJs electrical behavior. With this systematic study it was demonstrated that I_{rr} level plays an important roll over the PV performance of CdS/P3OT hybrid HJs. Physical and electrical parameters involved in the mathematical models, describe HJ electrical behavior with high confidence level. The obtained experimental-theoretical models are a very useful and powerful simulation tool, which can be used to a continuous improvement. The internal photon to electron conversion efficiency depends on the wavelength of the incident light. Physical, optical and mechanical characteristics of P3OT and CdS materials are highly compatible to prepare devices for PV application.

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