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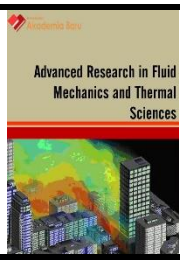

Hybrid Bilayer Heterojunction Al/ZnPc/ZnO /ITO Thin Films Solar Cell Prepared by Pulsed Laser Deposition

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ABSTRACT

Hybrid bilayer heterojunction Zinc Phthalocyanine (ZnPc) thin-film P-type is considered as a donor active layer as well as the Zinc Oxide (ZnO) thin film n-type is considered as an acceptor with (Electron Transport Layer). In this study, using the technique of Q-switching Nd-YAG Pulsed Laser Deposition (PLD) under vacuum condition 10^{-3} torr on two ITO (Indium Tin Oxide) and (AL) electrodes and aluminum, is used to construct the hydride bilayer photovoltaic solar cell heterojunction (PVSC). The electrical properties of hybrid heterojunction Al/ZnPc/ZnO/ITO thin film are studied. The results show that the voltage of open circuit (V_oc=0.567V), a short circuit (I_sc=36 μA), and the fill factor (FF) of 0.443. In addition, the conversion efficiency of (η=3.4%) is recorded with Xenon lamp with an intensity 235mw/cm^2.

1. Introduction

Semiconductors can be classified into two groups as inorganic and organic semiconductors. Conception inorganic semiconductors like silicon and germanium are used extensively in electronic industry, now it is expectant that organic semiconductors shortly. Similar to the valence band and conduction band was the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) on organic semiconductors. The electrons will move from molecular to molecular (Hopping Mechanism) in the case of semiconductors of organic, while in the case of semiconductors of inorganic in the conduction and valence band move through the material as if they are free. When compared to the semiconductor of inorganic the hopping transport mechanism provides organic semiconductor rather low mobility. For tiny molecular organic semiconductors, mobility of the hole is obtained up to $\sim 1.5 \times 10^{-3}\ m^2$ / v.s [1,2]. Whereas silicone will have the mobility of up to$\sim 4.5 \times 10^{-2}\ m^2$/ v.s [3,4]. On the other side, electron mobility reaches $\sim 1 \times 10^{-5} m^2$ /v. s for some tiny molecular materials [5,6]. While silicon does have a significantly

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higher electron mobility of 0.1 m^2/v.s. Low mobility is a significant disadvantage for organic semiconductors compared to inorganic semiconductors [7]. Zinc Phthalocyanine (ZnPc) is the most used organic compounds as an effective layer in photovoltaic solar cells (PSCs) owing to its multiple maximum absorptions in the visible part of the solar spectrum (less than 700 nm) [8-10]. ZnO was the most frequently used as electron transport layer (ETL) products for inverted solar cells owing to the elevated optical transparency in the visible and near-infrared area, as well as the elevated mobility of carriers [11]. In this study we used, the (ZnPc) p-type organic semiconductor is served as an electron donor while the (ZnO) n-type semiconductor is served as an electron acceptor to prepared hybrid Al/ZnPc/ ZnO/ITO thin films solar cell. Compared to the acceptor, donor materials have greater LUMO and HOMO. But the donor is the material transporting the hole and ideally makes ohmic contact with the anode while electrons are transported by the acceptor materials and the cathode contact. Figure 1 demonstrates the donor and acceptor electronic power rates in this study in a ZnPc / ZnO scheme. ZnPc / ZnO absorption band covers the range from 410 to 730 nm, which that means the photons with energy ranging from 1.7 to 3 eV can be absorbed by the active layer and excitons form. Active layer materials with a wide absorption band are needed to make better use of sunlight, and for this purpose, increasingly low band gap (LBG) materials have been created and excellent accomplishments have been made over the previous century. Because ZnPc LUMO and HOMO are greater than ZnO, the exactions at the ZnPc stage and ZnO stage interface will separate into positive and negative charges. Transported the negative charge was by LUMO of ZnO and transported the positive charge was by HOMO of ZnPc and then the charges can be gathered by the ZnPc / ZnO scheme of electrodes. HOMO and LUMO of the donor material should be 0.2–0.3 eV higher than that of the acceptor material, respectively, to achieve effective load segregation. Where is the LUMO of ZnPc and ZnO is -3.6 and - 4.3 eV respectively [12-14]. If the offset is too tiny, effective charge separation would be difficult; if the offset is too large, a lot of energy loss would occur. The open-circuit voltage (V_{oc}) of organic photovoltaic machines is determined by the difference between the donor HOMO energy level and the acceptor LUMO energy level ($V_{OC} = E^{D}_{HOMO} - E^{A}_{LUMO}$) [15,16]. Thus, to minimize donor and acceptor energy loss, HOMO and LUMO concentrations should be carefully tuned.

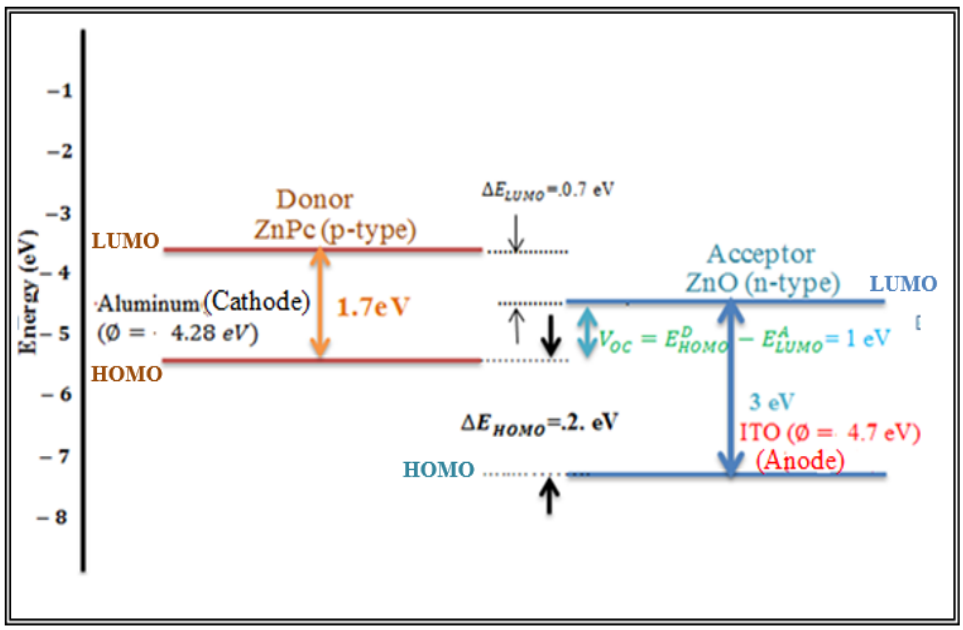

Fig. 1. Energy levels diagram of bilayer Heterojunction solar cell

2. Experimental Measurements

2.1 Measurements of Atomic Force Microscope

SPM-AA3000 contact mode spectrometer, Angstrom Advanced Inc., an American company, conducted surface morphological measurements for ZnPc thin films with distinct thicknesses. Roughness was obtained computerize, grain size and 3D images for all studied samples were getting.

2.2 D.C Conductivity Measurements for ZnPc/ZnO Thin Films

The electrical resistance for ZnPc / ZnO thin movies in the range 300–420 K was measured as a function of temperature. The measurements were performed using a delicate Keithley 616 digital electrometer and electric oven.

2.3 Hall Impact Measurements for ZnPc/ ZnO Thin Films

The Hall Effect Measurements are performed using a Hall Effect System (HIMS-3000) provided by the Ecopa Company to estimate the Hall Effect Coefficient (RH), the type of charge carriers and estimate their mobility and concentration of charge carriers for ZnPc and ZnO thin films. The Hall coefficient and The Hall mobility are obtained.

2.4 Preparation of Solar Cell Devices

Bilayer hybrid organic-inorganic semiconductor photovoltaic solar cell consisting of Zinc Phthalocyanine (ZnPc) as an electron donor (p-type) and Zinc Oxide (ZnO) as an acceptor (n-type) was prepared (which prepared from two layer 50 to match between lattice martial (ZnO) and the substrate (ITO) and 200 nm). Also, the two electrodes Aluminum (Al) as a Cathode and ITO as an Anode were deposited for different thicknesses to contain the devices of the bilayer photovoltaic solar cells are shown in the Figure 2.

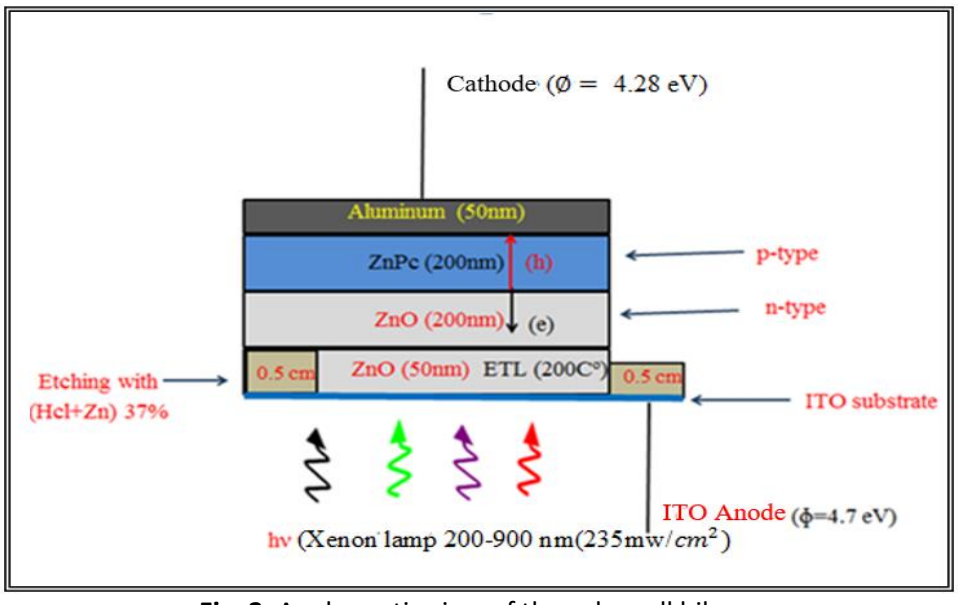

Fig. 2. A schematic view of the solar cell bilayer

3. Results and Discussion

3.1 Optical Energy Band Gap

The absorbance spectrum for both ZnPc and ZnO thin film with an optical energy gap at (1.7 & 3eV) is illustrated in Figure 3 and Figure 4 respectively. At Figure 3(a), The optical energy gap E_g magnitude decreases with increasing in wavelength, this behaviour is resulting from the increasing of grain size and the defect states near the bands at Figure 3(b) it is observed from the figure that there are two bands, One in UV region which is named B-band (transition of $a_{2u} \rightarrow e_g$ type) at the range between 300 mm and 350 mm, and the other in the visible region which is known Q-band (transition of $a_{1u} \rightarrow e_g\, type$) at the range of about 600-650 nm. It can be seen that a flat area in the range 400-550 nm for ZnPc thin films spectrum and Q-band consist of two close peaks. For Figure 4(a). The direct energy gap of thin film ZnO was estimated in 3(eV), this means that the amount of wavelength is around 415 nm i.e. that the visible portion of sunlight is allowed to pass through for ZnO thin film only. For Figure 4(b) demonstrates that the thin film has a very great absorption in the region of ultraviolet and the absorption of UV reduced significantly with increasing the wavelength, which illustrates that ZnO has a great response in the ultraviolet region. The absorbance spectra of the ZnO thin film from 700nm down to about 400nm was low, and then increasing quickly at around 330nm is approached, this behaviour is typically for several semiconductors because of the internal electric field within the flexible and non-flexible photon transport dispersion.

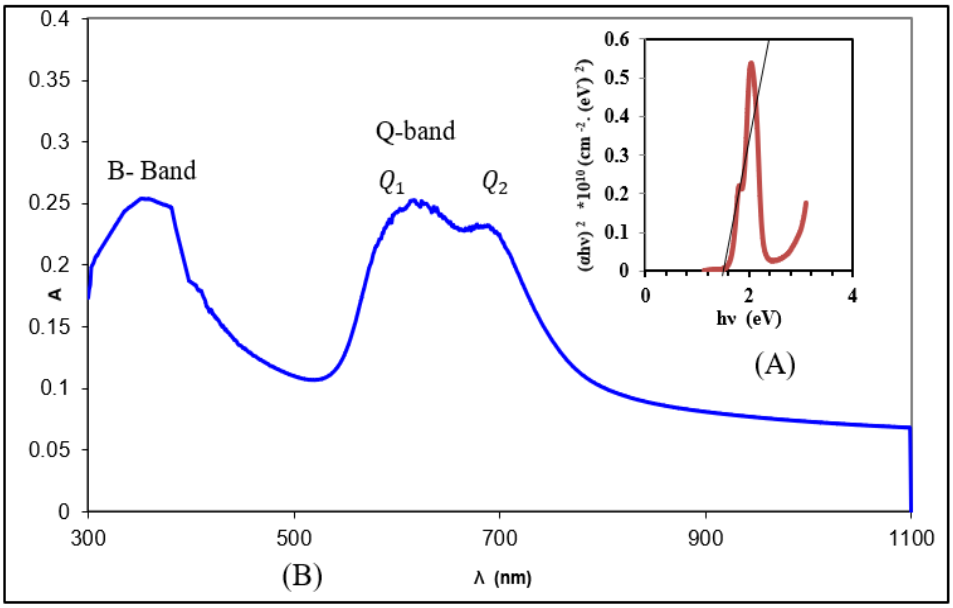

Fig. 3. (a) $(\alpha h\upsilon)^2$ versus photon energy of incident radiation for ZnPc thin film at 150nm thickness, (b) Absorbance as a function of wavelength for ZnPc thin films at room temperature with a thickness 150nm

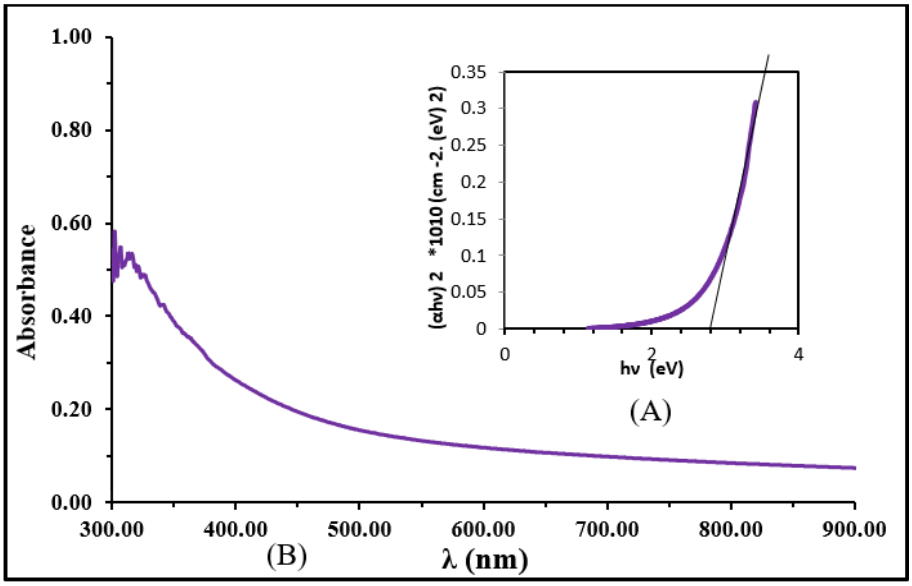

Fig. 4. (a) $(\alpha h\upsilon)^2$ versus photon energy of incident radiation for ZnO thin film at 200nm thickness, (b) The absorbance spectra for ZnO at thickness 200nm

3.2 Atomic Force Microscope

Atomic Force Microscope determined the surface morphology of ZnPc thin film, average roughness was tabulated in Table 1 which shows the roughness decreases with thickness increase, the highest roughness at 150 nm thickness. The Roughness increase with the decrease of the grain size, which means largest surface area, the best choice for solar cell making. While Grain size increase with thickness increasing, because of the degree of crystallinity also increased, while increasing film thickness leads to a decrease in the full width at half maximum (FWHM). This decrease reflects the decrease in the lattice imperfections concentration because the crystallite size increases as well as the decrease in the internal micro strain within films. The same result was achieved from XRD measurements. 3D AFM images with different thicknesses show in Figure 5.

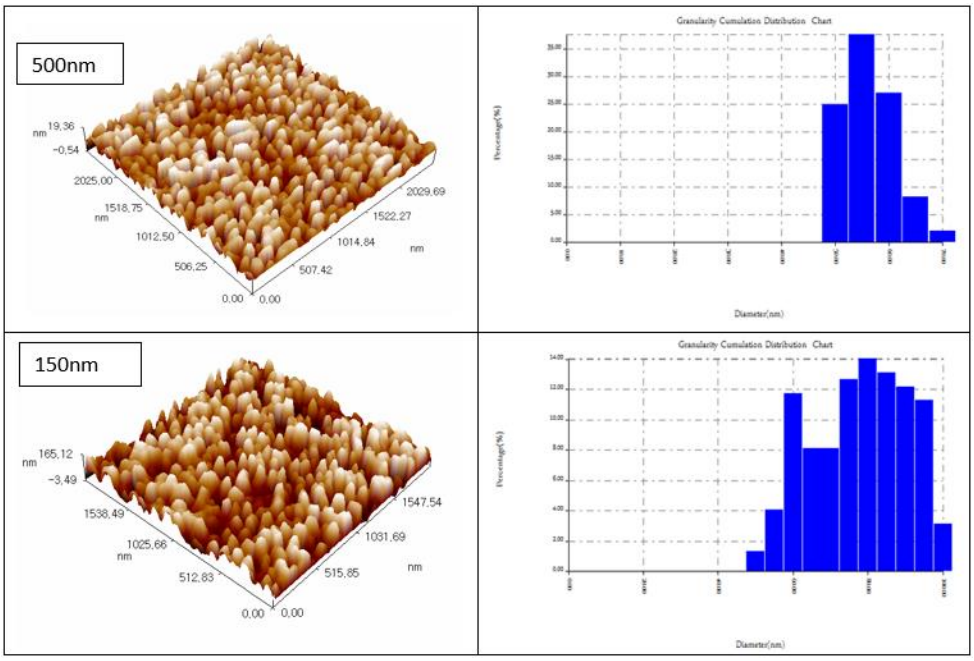

Fig. 5. 3-D AFM pictures of ZnPc thin films with different thicknesses

Table 1
Grain size and average roughness of thin films ZnPc at various thicknesses determined by AFM method

Thickness (nm)	Roughness Average (nm)	Grain Size (nm)
150	6.32	53.84
500	3.84	75.46

3.3 D.C Conductivity Results for ZnPc/ZnO Thin Films

The electrical conductivity (σ_{DC}) behavior was investigated for ZnPc and thin films of ZnO that were deposited at room temperature on glass substrates with various thicknesses prepared by PLD. Film (σ_{DC}) conductivity can be determined using the relationship [18,19].

$$\sigma_{DC} = \frac{1}{\rho} \tag{1}$$

Activation energy $E_a$ts needed for the charge transport from V.B. to C.B. The E_a for the metals can be Calculated according to the Arhenian equation from the plot of $ln\sigma$ versus 1000/T.

$$\sigma = \sigma_o exp\left(\frac{-E_a}{K_B T}\right) \tag{2}$$

where σ_o is the minimum electrical conductivity at 0 K, E_a is the activation energy corresponding to $E_g/2$ for inherent conductivity, T is the absolute temperature and KB is the constant equal to Boltzmann 8.617 buffered (8.617×10^{-5} eVK^{-1}).

The DC electrical conductivity for ZnPc films was calculated. Figure 6 shows the natural logarithm of the conductivity (Lnσ) as a function of 1000/T for ZnPc thin film deposited by the PLD technique at 150nm at room temperature. The electronic transport mechanism in thin films strongly depends on their structure (i.e. grain size). It is observed from this figure that, there are two activation energies within the range 303– 473 K. The first activation energy at 303-433 K, ($E_{a1} = 0.121eV$) represents transition process for carriers within localized states in the energy gap and this suggests the existence of high density of localized. The second activation energy at 433-473 K, ($E_{a2} = 0.6eV$) represents the carriers transport across the grain boundaries by thermal excitation. As a result, the intrinsic defects that are resulting from the thermal fluctuations specify the film samples electrical conductance only at high temperature. It is obvious that the activation energy in the low and high temperature range get to change in same sequence of that of optical energy gap i.e. reduce in the first stage and then increases with further addition of dopant atoms. This ascribed to creation of new states in the band gap hence low energy will demand for charge carrier to pass from Fermi level to the either the valence band or the conduction band, in the E_{a1} case, to pass from Fermi level to localized stated on the valence band top or on the conduction band bottom in case of E_{a2}.

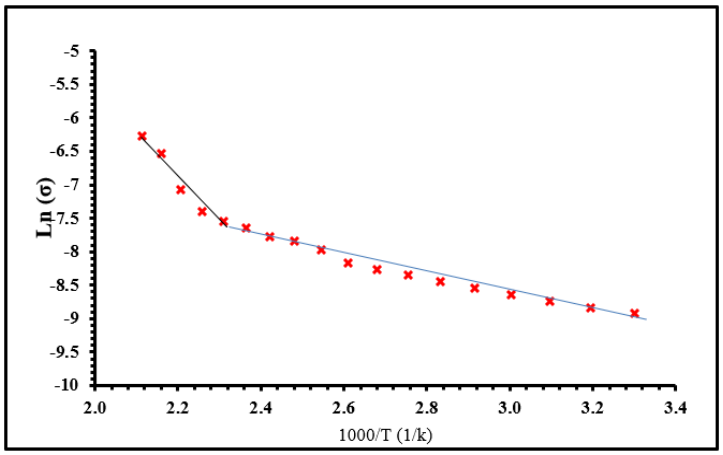

Fig. 6. Ln σ as a function of 1000/T for ZnPc thin film with thickness 150nm

3.4 D.C. Conductivity of ZnO Thin Film

DC electrical conductivity was calculated at a thickness of 200 nm for ZnO films. By plotting the electrical conductivity temperature reliance as shown in Figure 7, the activation energy of the electrical conduction can be determined. The electronic transport mechanism in thin films strongly depends on their structure (i.e. grain size, grain boundaries, structure defects). It is observed from Figure 7 that there are two activation energies within the range 300 – 423 K for 200nm thickness. The first activation energy, at 303-383 K, ($E_{a1} = 0.017eV$) represents a transition process for carriers within localized states in the energy gap and this suggests the existence of a high density of localized**.** The second activation energy at 373-423 K, ($E_{a2} = 0.2eV$) represents the carriers transport across the grain boundaries by thermal excitation. For Figure 6 and Figure 7, It is noted that with increasing temperature the conductivity of ZnPc and ZnO increases and this is the semiconductor conduct and we find that ZnPc thin films have two activation energies and for ZnO thin film has two activation energy, i.e. two activation energies corresponds a polycrystalline structure and one activation energy correspond to single crystal structure, so if the material has three activation energies, then the structure of this material is amorphous, we can conclude that the activation energy is a measure of the amorphousness for this material.

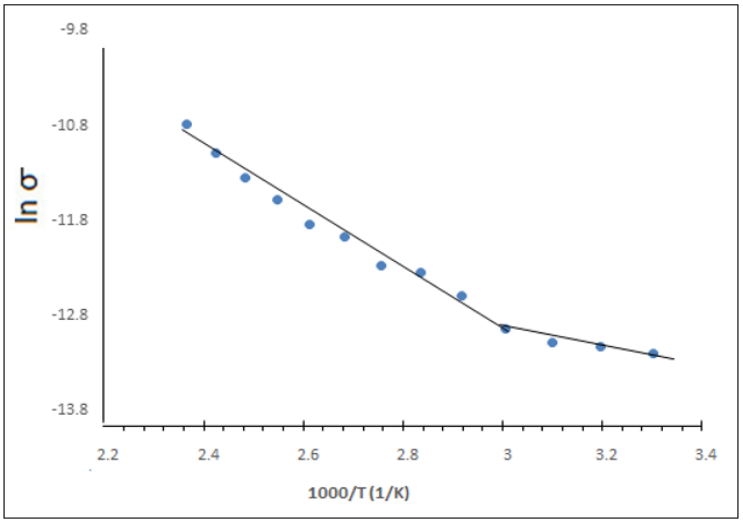

Fig. 7. Ln σ as a function of 1000/T for ZnO thin film with thickness 200nm

3.5 Hall Results for ZnPc and ZnO Thin Films

Carrier concentration and Hall mobility were defined from Hall measurements for thin films ZnPc and ZnO with thicknesses 150 and 200 nm, which were deposited at room temperature on glass substrates using the PLD technique. The Hall coefficient shows that the ZnPc thin film was p-type and ZnO was an n-type semiconductor. It can be inferred from the table that carrier mobility increases with the decrease of the carrier concentration and vary with the increase of film thickness. All these parameters are shown in Table 2.

Table 2
Carrier Concentration Values and Carrier Mobility with different thicknesses for ZnPc / ZnO Thin Films

Sample	Thickness (nm)	Carrier Concentration*10^{12} (cm^{-3})	Carrier Mobility cm^2/v. s.	R_H (cm^3/C)
ZnPc	150	8	73	8×10^6
ZnO	200	0.5	4000	-2×10^6

3.6 Current-Voltage Characteristics Results for ZnPc /ZnO Hybrid Bilayer Heterojunction

Specifying the solar cell device performance and its electrical behaviour, current-voltage (I-V) measurements under illumination and dark were done for ZnPc / ZnO hybrid bilayer heterojunction, prepared using (PLD) of laser with 1064 nm and energies 240 and 500 mJ for ZnPc and ZnO thin films respectively, the cell were irradiated with 235 mW/cm^2 using Xenon lamp for area 1 cm^2. In Figure 8 open-circuit voltage (V_{oc}) and short circuit current (I_{sc}) was determined by the intersect of the photocurrent curve with x and y-axis. Also, maximum voltage (V_m) and current (I_m) for solar cells were found; full factor (FF) and efficiency (η**)** had been calculated. Also, the Series Resistance (R_s) and Shunt Resistance (R_{sh}) have been calculated with the values (R_s= 0.05 kΩ and R_{sh}= 0.026 kΩ). As shown from Figure 8 the variation of the current with forward and reverse bias voltage are approximately a typical of ohmic conduction. The solar cell parameters were measured from Figure 8 as shown in Table 3.

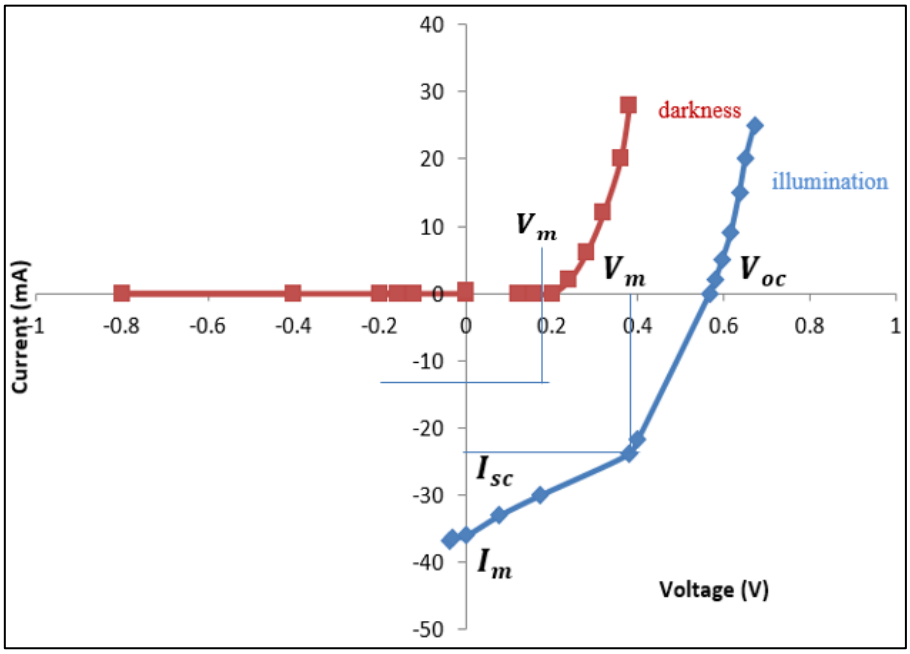

Fig. 8. The photocurrent for AL/ZnPc/ZnO/ITO solar cell

Table 3
Values of V_{oc}, I_{sc}, V_m, I_m, FF and η for ZnPc/ZnO heterojunction

V_{oc}(v)	I_{sc}(mA)	V_m(v)	I_m(mA)	Fill Factor	η%
0.567	36	0.375	24	0.443	3.4

4. Conclusions

Zinc Phthalocyanine (ZnPc) thin film with increase thickness cause, the degree of crystallinity also increased. The Roughness increase with decrease grain size, which means the largest surface area, the best choice for solar cell making. There are two activation energies for ZnPc and ZnO. It is observed that the conductivity of ZnPc and ZnO increases with temperature increment and this is the semiconductor behaviour. Hall effect measurements show that the thin film of ZnPc is p-type and ZnO is an n-type semiconductor. Bilayer heterojunction photovoltaic solar cell device manufacturing gives suitable efficiency.

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