Study of dark electrical properties and photoelectric performance of organic/inorganic (ZnPc/p-Si) Solar cells

A A El Amin and M M Mahmoud*
Department of Physics, Faculty of Science, Aswan University, Egypt

*E-mail: mahasen.m.mahmoud@gmail.com

Abstract. A Zinc Phthalocyanine (ZnPc) film was deposited by thermal evaporation on a monocrystalline p-Si substrate to provide a p-ZnPc/p-Si organic/inorganic heterojunction. The electrical characteristics of the fabricated cell were examined by measuring the current density versus voltage (J-V). The fabricated cell was characterized by a contact barrier of 0.56 eV and a rectification ratio of 230 calculated at ± 1 V⁻¹. The dark J-V measurement suggested that the DC current density in this junction contains a thermionic conduction mechanism when the applied voltage is relatively low. At higher voltages another conduction is dominated called the space-charge limited conduction mechanism (SCLC) controlled by a single trapping level. The I-V measurement was performed with an illumination of 100 mWcm⁻² and the photoelectric conversion characteristics of the junction were also studied, achieving a power conversion efficiency of 2.7%. The other solar cell parameters such as the short-circuit current Isc, the open-circuit voltage Voc and the filling factor FF were evaluated and equaled to 2.5 A, 1.132 V and 0.477 at room temperature. The dependence of these parameters as a function of the temperature has also been studied in the temperature range from 300 to 400 K.

1. Introduction
The photovoltaic effect produced when a semiconductor/metal interface [1] exposed to sunlight or so called the process of solar energy conversation had been studied thoroughly over the years. Semiconductor materials like Si, GaAs and CdS [2] were used because of its stability in hostile environment and its sensitivity towards the spectrum of the sun. But these semiconductor materials are unable to detect visible light region due to their wide band gap, to overcome this problem photoactive dyes were incorporated on top of the semiconductor material surface as a light absorber; meaning to sensitize Si to the visible light region [3, 4]. Compounds such as phthalocyanines were studied to be light absorbers because of their high absorption coefficient in the solar spectrum, chemical stability, and their various synthesis techniques [5, 6]. Moreover, phthalocyanine compounds could be metal substituted phthalocyanines (MPcs) such as ZnPc, CoPc, and FePc or metal free (H₂Pc). These compounds have been utilized in solar cells, organic photoreceptors, sensors [7], light emitting diodes[8], the display devices in mobile phones[8], photosensitizers in laser printers[8], the active layer in Schottky diodes [9, 10] and in organic thin film transistors[11]. A heterojunction device made of organic material (Pc) and inorganic material (Si) was found to be highly stabilized as compared to the bare Si interface [12]. These heterojunction devices also presented rectification properties in the dark conduction in addition to the photoconversion efficiency ranging from 0.74 to 5.63 %, examples for these heterojunctions are ZnPc/Si [13, 14], H₂Pc/p-Si [15], CuPc/p-Si [16], MgPc/n-Si [17], CoPc/n-GaAs [18], NiPc/p-Si [19], CoPc/p-Si [20], TCVA/p-Si [21], FeTPPCl/p-Si [22], and DBM/p-Si [23].
In the present work, Zinc phthalocyanine (ZnPc) was used as organic material and silicon (Si) as inorganic material to compose the ZnPc/Si heterojunction. The J-V characteristics in the dark and under illumination of the ZnPc/Si heterojunction have been analyzed to determine the photovoltaic parameters and the various conduction mechanisms. Also, the optical energy gap was deduced.

2. Experimental techniques
Zinc phthalocyanine (ZnPc) powder as purchased from Sigma-Aldrich. The p-ZnPc/p-Si heterojunction was composed by using high vacuum coating unit (E306A, Edwards Co. England). The substrate temperature was kept at room temperature during deposition process. The film thickness and rate of deposition were controlled and monitored during deposition. Figure 1 shows a schematic diagram of the device, comprising a top ZnPc thin film and p-Si as a semiconductor absorber with back contact electrode (Al) and the chemical structure of Zinc phthalocyanine [24].

Keithley 2400 SourceMeter was used for the electrical J–V measurements. The p-type Si single crystal wafers with carrier concentration of \(10^{22} \text{m}^{-3}\). The back side of Si was coated by a thick layer of aluminum electrode.

Measurements of dark current–voltage characteristics within the temperature range 300–400 K were made in air. The cells were exposed to light coming from a light source (white light) to get an intensity of incident power of about 100 mW/cm². The optical measurements were done using double beam spectrophotometer (JASCO, V-670).

3. Results and discussions

3.1. The dark current density–voltage characteristics
Significant information about the properties of ZnPc/p-Si organic/inorganic heterojunction solar cell could be found by analyzing the current density–voltage characteristics (J–V) as a function of temperature. Also, this analysis is important in determining the transport mechanisms operating the conduction in this junction. Figure 2 shows the characteristic (J-V) curves for ZnPc/p-Si organic/inorganic heterojunction cell under the forward and reverse bias measured at different temperatures ranging from 300 to 400 K and in the voltage range \(-0.6\) to \(+4.25\) V. These curves are similar in behavior to the I-V diode characteristic curve. This similarity could be understood in terms of a p–n junction formed between ZnPc and p-Si, the barrier at this interface limits the forward and reverse carrier flow across the junction in which a built-in potential could be developed. These observations suggesting that the device exhibits a good rectifying performance with a rectification ratio of 230 calculated at a bias potential of \(\pm 1\) V. The rectification factor RR is the ratio of forward current to
reverse current at a certain applied voltage. Figure 2 also shows the current density was increasing as the temperature increased meaning that the diode had a negative resistance temperature coefficient or a positive coefficient of conductivity.

The semilogarithmic scale plots of the forward current density against the applied voltage at different temperatures illustrated in figure 3, is composed of two regions: region (I) at low voltage and region (II) at high voltage. The dark current moving through an ideal junction under forward bias could be represented by a single exponential diode equation as illustrated in[25].

However, for non-ideal diode such as the heterojunction studied here, the J-V curves maybe composed of two (or sometimes more) different regions associated with two varied conduction mechanisms. That behavior is more complex than to be simply represented by the single exponential expression, for that reason, the summation of these exponential expressions associated with their reverse saturation current density and ideality factors, would be best to accurately model these conduction mechanisms[26]. So, the forward current density for non-ideal junctions in low potential range is given by[27],

$$J = J_{s1} \left[ \exp \left( \frac{eV}{n_1 k_B T} \right) - 1 \right] + J_{s2} \left[ \exp \left( \frac{eV}{n_2 k_B T} \right) - 1 \right] + \frac{V - JR_s}{R_{sh}}$$

(1)

Where $J_s$ is the reverse-saturation current density, $e$ is the electronic charge, $V$ is the applied voltage, $n$ is the ideality factor of the diode, $T$ is the temperature and $k_B$ is the Boltzmann constant.

Also, the subscripts 1 and 2 indicating the possible presentence of two diode current. And $R_s$ is the series resistance and $R_{sh}$ is the shunt resistance.

The series resistance $R_s$ for ZnPc/p-Si heterojunction was estimated from temperature 300K to 400K, by plotting the diode junction resistance $R_j$ against the applied potential as viewed in figure 4 (a), where $R_j = \frac{\Delta V}{\Delta I}$[20, 28], that was determined from the current–voltage curves. At sufficiently high forward bias ($V \leq 1.75$ V), the junction resistance approaches a constant value $R_s$ that indicate the series resistance. The obtained values of the series resistances $R_s$ at temperatures of 300, 325, 350, 375 and 400 K are determined as $1.103 \times 10^4$, $7.395 \times 10^3$, $4.957 \times 10^3$, $3.323 \times 10^3$ and $2.227 \times 10^3 \Omega$, respectively. It can be observed from figure 4 (a) that as the temperature increases the series resistance decreases. These resistances are one the most playing factors in improving the solar cells performance and design. We used another way to measure $R_s$. To estimate the series resistance $R_s$, the I-V curve for example at room temperature would be analyzed as follows: at a certain current (I), the horizontal displacement between the observed curve in figure 4 and the extrapolated linear part, yields the voltage drop, $\Delta V = IR_s$, across the neutral region [18]. Then the resulted straight line after plotting the voltage
drop versus the current shown in the inset of figure 4 (b), gives a slope of 32.1 μΩ which is the value of $R_s$.

An equation that relate $I_s$ to the reciprocal of temperature and the activation energy is as follows [29],

$$I_s = I_{00} \exp \left( -\frac{E_a}{K_BT} \right)$$  \hspace{1cm} (2)

Where $I_{00}$ is a weak function of temperature and $E_a$ is the activation energy of the charge carriers.

The low voltage range ($V \leq 1.75$ V) illustrated in figure 5, shows a forward current density behavior that could be represented by a single exponential diode equation as follows,

$$J = J_s \left[ \exp \left( \frac{eV}{nK_BT} \right) - 1 \right]$$  \hspace{1cm} (3)

Both $J_s$ and $n$ would be found from the intercept and slope of figure 5 and written in table 1. The ideality factor listed in table 1 is constant with changing the temperature from 300 to 400, this result is a strong indication that the conduction mechanism is the thermionic emission one. With its saturation current density would be given as [30],

$$J_s = A^{**}T^2 \exp \left( -\frac{e\phi_b}{k_BT} \right)$$  \hspace{1cm} (4)

Where $A^{**}$ is the effective Richardson constant and $\phi_b$ is the barrier height.

![Figure 4](image)

**Figure 4.** (a) Junction resistance $R_j$ versus $V$ for Al/p-ZnPc/p-Si cell at the temperatures from 300 to 400 K. (b) The junction I-V characteristics of Al/p-ZnPc/p-Si heterojunction at 300 K. Inset is the voltage drop across the series resistance.

| $K$ | $J_s$       | $n$          |
|-----|-------------|--------------|
| 300 | 0.003962025 | 3.055125928  |
| 325 | 0.00591064  | 2.820116242  |
| 350 | 0.008817649 | 2.618679367  |
| 375 | 0.013154387 | 2.444100743  |
| 400 | 0.019624039 | 2.291344446  |

**Table 1.** The ideality factor listed ($T$, $J_s$, $n$) with changing the temperature from 300 to 400 K.
Drawing the logarithm of \( J_s / T^2 \) versus the reciprocal of \( T \) as shown in the inset of figure 5, result in straight line, which is a further confirmation of the presence of thermionic mechanism. Also, the intercept and the slope were used to calculate the potential barrier height \( \varphi_p \), and the effective Richardson constant \( A^* \), of values 2.48 J and 0.105 Am\(^{-2}\)K\(^{-2}\), respectively.

The downcurve curvature at relatively higher voltage (\( \geq 1.75 \)), observed in figure 5, indicate the presence of another conduction mechanism. In figure 6 of log \( J \) and log\( \sqrt{V} \) at different temperatures, shows that the increase in current form change from an exponential behavior to a behavior of power law relation. In this specific range (\( \geq 1.75 \)) which is formed because of the transport properties of organic material, could be interpreted in terms of the space-charge limited conduction mechanism (SCLC) controlled by a single trapping level[31]. Space charge is described as the existing net charge in a material dividing from the condition of charge neutrality.

The J–V relation showing a power law dependence on voltage of \( J \sim V^s \) which would be explained in terms of the single energy trap level since \( s \equiv 2 \)[32], is given by the equation[33, 34],

\[
f = \frac{9}{8} \varepsilon \varepsilon_0 \mu \frac{N_p V^2}{d^3} \exp \left( \frac{-E_t}{k_B T} \right)
\]  

Where \( \varepsilon \) and \( \varepsilon_0 \) are the relative permittivity of ZnPc and the permittivity of free space, which were taken to be equal to 3.95 [14] and 8.85 x 10\(^{-12}\) Fm\(^{-1}\) respectively, \( \mu \) is the mobility with a value of 7.6 x 10\(^{-9}\) m\(^2\)V\(^{-1}\)s\(^{-1}\) for ZnPc [14], \( d \) is the film thickness, \( N_p \) is the effective density of states in the valance band, and \( N_t \) is the total trap concentration at an energy level of \( E_t \) above the valence band edge.

**Figure 5.** ln\((J_s)\) versus 1/T for Al/p-ZnPc/p-Si/Al heterojunction, the inset is a plot of ln\((J_s/T^2)\) versus 1/T of Al/p-ZnPc/p-Si/Al heterojunction.

**Figure 6.** Variation of log \((J)\) with log \((V)\) at higher forward voltage bias for Al/p-ZnPc/p-Si/Al heterojunction

Estimation of further information from the previous equation, were obtained by plotting the logarithm of \( J \) against the reciprocal of \( T \) at the applied voltages of 1.75, 2, 2.25, 2.5, 2.75, 3, 3.25, 3.5, 3.75, 4 and 4.25 Volts in the SCLC region as viewed in figure 7.

Knowing the \( N_p \) for ZnPc to be equals 10\(^{27}\) m\(^{-3}\)[14, 35-37], leads to the calculation of \( E_t \) and \( N_t \) as:

From the slopes of these straight lines, the trap level \( E_t \) would be calculated and equals to the value of 1.14595 x 10\(^{-20}\).

In the other hand the total trapping concentrations \( N_t \) were evaluated from the intercepts and found equal to 3.08524 x 10\(^{11}\), 4.87763 x 10\(^{11}\) and 6.12589 x 10\(^{11}\)m\(^{-3}\) at the potential of 2.3 and 4 V respectively.
3.2. The illumination current–voltage characteristics

The current–voltage characteristics of Al/p-ZnPc/p-Si/Al heterojunction solar cell observed under the illumination of 100 mW cm$^{-2}$ is viewed in figure 8. In this figure the dark curve was included for comparison. The reverse current increased considerably with illumination as seen in figure 8, this observation is regarded to the production of charge carriers. Also, the short circuit current $I_{sc}$ and the open circuit voltage $V_{oc}$ were estimated to be equal to 2.5 mA and 1.132 V respectively.

Further solar cell parameter could be found from this figure such as $I_{M} = 1.5$ mA and $V_{M} = 0.9$ V, which are the current and the potential at maximum power point, consequently the maximum power could be calculated from

$$P_{M} = V_{M} I_{M}$$  \hspace{1cm} (6)

And found equal to 1.35 mAV.

Also, the filling factor evaluated to be equal to 0.477 from

$$FF = \frac{V_{M} I_{M}}{V_{oc} I_{sc}}$$  \hspace{1cm} (7)

Finally, the experimental efficiency of this organic/inorganic solar cell was given by

$$\eta \% = \frac{P_{M}}{P_{in}} = \frac{FF V_{oc} I_{sc}}{P_{in}} \times 100$$  \hspace{1cm} (8)

And found equal to 2.7 %. Where $P_{in}$ is the incident light intensity (100 mW/cm$^2$).

The parameters of the organic/inorganic p-ZnPc/p-Si heterojunction was compared to the ones of other heterojunctions in previous studies and listed in table 2.

| Organic/inorganic cell | $I_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | $FF$ | $\eta$ (%) | reference |
|------------------------|----------------------|-------------|------|------------|-----------|
| n-SnPcCl$_2$/p-Si      | 14.43                | 0.500       | 0.422| 3.05       | [30]      |
| MgPc/n-Si              | 3.760                | 0.35        | 0.4  | 1.05       | [17]      |
| CoPc/n-GaAs            | 3.5                  | 0.33        | 0.34 | 0.81       | [18]      |
| P-DCPF/n-Si            | 9.13                 | 0.297       | 0.329| 1.27       | [38]      |
| NiPc/Si                | $I_{sc} = 186 \mu$A  | 0.32        | 0.28 | 1.11       | [19]      |
| p-ZnPc/p-Si            | $I_{sc} = 2.5$ mA    | 1.132       | 0.477| 2.7        | This study|

Table 2. The parameters ($I_{sc}$, $V_{oc}$, FF, $\eta$) of the organic/inorganic p-ZnPc/p-Si heterojunction.
Table 2 shows values of η lower than that of p-ZnPc/p-Si, in the other hand there are values of η greater than p-ZnPc/p-Si. The lower efficiency of p-ZnPc/p-Si could be attributed to recombination losses in the bulk in addition to the one in the interface region. This result could be due to the series resistance of the junction and dissimilarity between organic thin film and p-Si substrate.

3.3. The optical characterization of p-ZnPc/p-Si

The molecules of the organic phthalocyanine show optical properties because of their structural ring. The zinc phthalocyanine nanoparticles thin films provide two types of electronic transitions; B-band (Soret band) and Q-band. The absorption coefficient of ZnPc thin film can be used to estimate the type of transition and the value of the optical energy gap $\eta$ according to well-known Tauc's relation [39].

$$ (a\nu h)^{1/r} = B(h\nu - \eta)^{r} $$  \hspace{1cm} (9)

where B is a constant and r is a constant which depends on the probability of transition; it takes the values $r = 1/2, 3/2, 2$ and $3$ for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions, respectively. The dependence of $(a\nu h)^{1/r}$ on photon energy ($h\nu$) was plotted for different values of r. The best fit was obtained for $r = 1/2$ and displayed in figure 9, which pointed out that the transitions are direct allowed transitions [40]. The direct optical band gap values can be determined by the extrapolated linear regression of the curves resulting from plotting of $(a\nu h)^{2}$ versus photon energy $(h\nu)$. From the presented graphs, the direct band gap of ZnPc were found to be 1.99 and 3.09 eV.

4. Conclusion

The organic/inorganic p-ZnPc/p-Si heterojunction was investigated after the deposition of the organic ZnPc on the inorganic (100) silicon wafer. The current density versus applied potential data were analyzed to find the junction electrical properties. At low forward applied voltages ($V \leq 1.75$ V), the J-V analysis indicate the presence of thermionic conduction mechanism. However, in the relatively high voltage region the space-charge limited conduction mechanism (SCLC) controlled by a single trapping level manifest itself as a different conduction mechanism. The current- voltage were examined under illumination as compared to the dark I-V data. From which significant solar cell parameters at room temperature were calculated to be equivalent to 1.132 V, 2.5 mA, 0.477 and 2.7% for the open circuit voltage, the short circuit current, the fill factor and the power conversion efficiency, respectively. Also studying the optical properties of ZnPc showed it had low energy gap of 1.99 and 3.09 eV.
References
[1] Chapin D M, Fuller C and Pearson G 1954 J. Appl. Phys. 25 676
[2] Yanagi H, Kataura H and Ueda Y 1994 J. Appl. Phys. 75 568
[3] Matsumura M, Matsudaire S, Tsubomura H, Takata M and Yanagida H 1980 Ind. Eng. Chem. Prod. Res. Dev. 19 415
[4] Memming R 1984 Prog. Surf. Sci. 17 7
[5] Moser F H and Thomas A L 1983 The Phthalocyanines (CRC Press)
[6] Simon J, Lehni J M, Andre J J and Rees C W 2012 Molecular Semiconductors: Photoelectrical Properties and Solar Cells (Springer Berlin Heidelberg)
[7] Kerpi H and Van Faassen E 2000 Chem. Phys. Lett. 332 5
[8] Simon J, Andre J J, Lehni J M and Rees C W 1985 Molecular Semiconductors: Photoelectrical Properties and Solar Cells (Springer)
[9] Roy M, Kumar M, Jasswal P and Sharma G 2004 Radiat. Meas. 38 205
[10] Samuel M, Monen C and Unnikrishnan N 2005 J. Phys.: Condens. Matter 18 135
[11] Puigdollers J, Voz C, Fonrodona M, Cheylan S, Stella M, Andreu J, Vetter M and Alcubilla R 2006 J. Non-Cryst. Solids 352 1778
[12] Nakato Y, Shioji M and Tsubomura H 1981 J. Phys. Chem. 85 1670
[13] Remaki B, Guillaud G and Mayes D 1998 Opt. Mater. 9 240
[14] El-Nahass M, Zeyada H, Aziz M and El-Ghamaz N 2005 Solid State Electron. 49 1314
[15] El-Nahass M, Farid A, Farag A and Ali H 2006 Vac. 81 8
[16] Antohe S, Tomozeiu N and Gogonea S 1991 Phys. Status Solidi A 125 397
[17] Riad S 2000 Thin Solid Films 370 253
[18] Darwish S 2003 Egypt. J. Sol. 26 55
[19] El-Nahass M, Abd-El-Rahman K, Farag A and Darwish A 2005 Org. Electron. 6 129
[20] El-Nahass M, Zeyada H, Abd-El-Rahman K and Darwish A 2007 Sol. Energy Mater. Sol. Cells 91 1120
[21] Soliman H, Farag A, Khosifan N and El-Nahass M 2008 Thin Solid Films 516 8678
[22] El-Nahass M, Metwally H, El-Sayed H and Hassanien A 2011 Synth. Met. 161 2253
[23] El-Nahass M, Kamel M, Atta A and Huthaly S 2013 Mater. Chem. Phys. 137 716
[24] National Center for Biotechnology Information [Internet], PubChem Database. CID=2735172.
[25] Rhoderick E H and Williams R H 1988 Metal-Semiconductor Contacts (Clarendon Press)
[26] Runavez J, Sánchez F G a and Ortiz-Conde A 1999 Solid-State Electron. 43 2129
[27] Sze S M 1981 Physics of Semiconductor Devices (John Wiley & Sons)
[28] Darwish S, Riad A and Soliman H 1996 Semicond. Sci. Technol. 11 96
[29] Das S and Morris G 1993 Sol. Energy Mater. Sol. Cells 28 305
[30] Darwish A, El-Shazly E, Atta A and El-Rahman K A 2016 J. Appl. Phys. 27 8786
[31] Pemans P, Yakimov A and Forrest S R 2003 J. Appl. Phys. 93 3693
[32] Ganesh V, Manthrammel M A, Shkir M, Yahia I, Zahran I, Yakuphanoglu F and AlFaify S 2018 Appl. Phys. A 124 424
[33] Gould R 1982 J. Appl. Phys. 53 3353
[34] Zeyada H, El-Nahass M and El-Shabaan M 2016 Synth. Met. 220 102
[35] Anthopoulos T and Shafai T 2001 Phys. Status Solidi A 186 89
[36] Riad A 1999 Physica B Condens Matter. 270 148
[37] Malik T A and Abdel-Latif R 1997 Thin Solid Films 305 336
[38] El-Nahass M, Zeyada H and Hendi A 2004 Eur. Phys. J. Appl. Phys. 25 85
[39] Pal U, Samanta D, Ghorai S and Chaudhuri A 1993 J. Appl. Phys. 74 6368
[40] Hamam K J and Alomari M I 2017 Appl. Nanosci. 7 261