Electrical Transport Mechanisms and Photovoltaic Characterisation of MgPc /p-Silicon Hybrid Organic–Inorganic Solar Cells

M.M. El-Nahass*, A.A. Atta, H.E.A. El-Sayed and E.F.M. El-Zaidia

Physics Department, Faculty of Education, Ain Shams University, Rorxy Square 11757, Cairo, Egypt

Abstract: Hybrid organic–inorganic solar cell was fabricated by thin film of nanocrystalline magnesium phthalocyanine, MgPc, on p-type Si substrates using the conventional thermal evaporation technique. The measured electrical parameters were used to determine the predominat conduction mechanisms of these heterojunctions in the temperature range 298 to 373 K. The dark forward current was found to be increased exponentially with the applied voltage. Where the dark forward current density-voltage characteristics indicated a thermionic emission conduction over the MgPc/p-Si interface at relatively low voltages followed by a space-charge-limited current (SCLC) controlled by a single dominating trap level of 0.34eV at relatively high voltages. On the other hand, the carrier generation-recombination process limits the reverse current. Also, electrical parameters were determined from the I–V characteristic. The capacitance–voltage characteristics indicated that the junction is of abrupt nature. Under illumination, the cell exhibits photovoltaic characteristics with an open-circuit voltage (V_{oc}) of 0.32 V, a short circuit current (I_{sc}) of 246μA, and a power conversion efficiency η of 2.71%. These parameters have been estimated at room temperature and under illumination of 6 mW/cm^2 white light.

1. INTRODUCTION

Metallophthalocyanines (MPcs) are well-studied macrocyclic compounds, which owing to their highly delocalised p-electron system exhibit, almost without exception, high thermal and chemical stability and wide range of intriguing physico-chemical properties, making the colorants useful for numerous applications [1,2]. The study of molecular semiconductors (MS), such as phthalocyanines (Pcs) has become in the last decade an active research and industrial field due to its interest for use in more advanced technological applications such as photovoltaic cells [3], laser printers [4], dyes, pigments, photocopying agents [5], gas sensors [6], optical data storage systems [7], and solar cells [8]. Perhaps one of the most interesting features, remaining a very active area of research, is the ability of MPc's to form complexes with electron donating molecules, which are additively bound to the central metal ion of MPc's. Heterojunction devices of p-MgPc/n-Si studied by Raid [9] in dark and under illumination showed that these junctions exhibit rectifying and strong photovoltaic characteristics with power conversion efficiency of 1.05%. Van *et al.* [10] concluded that the junction parameters, such as the rectification factor, RR, the saturation current density, Js, and the ideality factor, n, are strongly influenced by the dopant, the thickness, and the preparation temperature of the polypyrrol layer for metallophthalocyanine doped pyrrole/silicon heterojunction.

The objective of this investigation is to study the dark and illuminated current–voltage (I–V) characteristics and the capacitance–voltage (C–V) characteristics of MgPc/p-Si heterojunction at different temperatures. The results obtained from these measurements were analyzed to determine some heterojunction parameters and to suggest the dominant current transport mechanism.

2. EXPERIMENTAL PROCEDURE

The MgPc powder used in this study is obtained from Kodak, UK. The p-type Si wafer with (100) orientation and hole concentration of $10^{22} m^{-3}$ samples is obtained from Nippon Mining Co. In order to remove the native oxide on surface on p-Si, the substrate was etched by CP4 solution ($HF:HNO_3:CH_3COOH$) in ratio (1:6:1) for 10s, after etching, the Si wafers were washed with distilled water and then with ethyl alcohol. The p-Si substrates were coated from one side by MgPc thin film of thickness 102nm using thermal evaporation technique to fabricate MgPc/p-Si heterojunction cell. The front contact of this heterojunction was made with gold mesh electrode to be used as ohmic electrode. The back contact was made by depositing a relatively thick film of Al to the bottom of the p-Si substrate. Thus, an Au/MgPc/p-Si/Al cell was obtained. A schematic diagram of the heterojunction device is given in Fig. (**1**). The fabricated MgPc/p-Si cell was annealed in air at 383K for 1h to complete the junction formation. Annealing of heterojunction is the usual step for obtaining the best efficiency cells. This annealing might remove any channels, which could be raised during the fabrication. The dark capacitance–voltage (C–V) characteristics for the fabricated cell were measured at 1MHz and at room temperature, using a computerised CV-410 meter (Solid State Measurement, Inc., Pittsburgh). The current density– voltage (I–V) characteristics of the fabricated cell were achieved by measuring the current corresponding to a certain potential difference across the junction, using a conventional circuit. The voltage across the junction and current passing through it were measured simultaneously using high impedance electrometers (Keithley 617). The dark I–V characteristics were obtained in a complete dark chamber at room temperature or inside a dark furnace in case of measurements at higher temperatures. Illumination characteristics for the same samples under 6 mW/cm^2 white light source (halogen lamp) were measured. The intensity of the incident light was measured using a digital lux meter (BCHA, model 93408).

3. RESULTS AND DISCUSSION

3.1. Dark Current–Voltage Characteristics

To study the junction properties, current–voltage characteristics (I–V) have been measured. These measurements, usually provide a valuable source of information about the junction properties, such as the rectification ratio (RR), the diode quality factor (m), the series resistance (R_s) and the shunt (R_{sh}) resistance. Analysis of the I–

*Address correspondence to this author at the Physics Department, Faculty of Education, Ain Shams University, Rorxy Square 11757, Cairo, Egypt; E-mail: prof_nahhas@yahoo.com

1385-2728/10 $55.00+.00

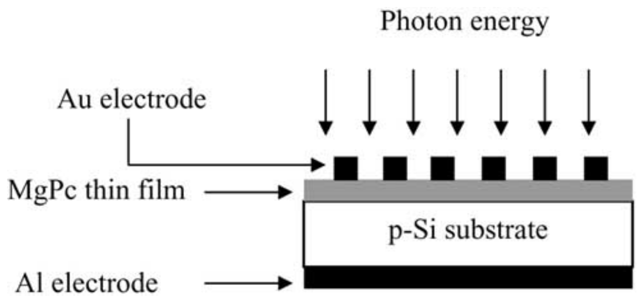

Fig. (1). Schematic diagram of Au/MgPc/p-Si/Al solar cell.

V characteristics is also extremely useful to identify the transport mechanisms controlling the conduction. The current–voltage characteristics of MgPc films with thickness 102 nm deposited onto p-Si at different temperatures ranging from 298 to 373 K is illustrated in Fig. (**2**). The device clearly exhibits the rectification behaviour in dark, which is enhanced by increasing the temperatures. The curves exhibited diode behaviour, with the forward direction to the positive potential on substrate. This behaviour can be understood by the formation of p-p$^+$ heterojunction, namely the barrier at the interface, limits forward and reverse carrier flow across the junction, where the built-in potential could be developed.

The ratio of the forward current to the reverse current at a certain applied voltage is defined as the rectification factor RR. It is evident that the junction exhibits strong rectifying characteristics showing diode-like behaviour of RR was estimated as $\approx 10^2$ for Au/MgPc/p-Si heterojunction at ±1 V. The series and shunt resistances (R_s and R_{sh}), which are important factors in improving cell performance and design, obtained at room temperature by the method stated in [11]. Their values can be calculated from the slope of the linear part of the forward and reverse I-V curve at room temperature, respectively. The obtained values of the series resistance (R_s) and the shunt resistance (R_{sh}) at room temperature were determined to be 376 Ω and 43×10^3 Ω, respectively.

The information about the conduction mechanisms can be obtained from current–voltage characteristics at different temperatures. Semi-logarithmic plots of the forward current–voltage for an Au/MgPc/p-Si heterojunction in the temperature range of 298–373 K are given in Fig. (**3**). Two distinct regions characterise these curves indicating different conduction mechanisms. As observed within the narrow low forward voltage (V≤0.25 V), the current increases exponentially. Such behaviour agrees with rectification characteristics, which are generally described by either the diffusion model, the emission model, or the recombination model [12]. Thus, the voltage dependence of the junction current can be expressed in the simplified form as

$$I = I_o \exp\left(\frac{eV}{mk_BT}\right) \quad (1)$$

Where I_o is the saturation current, which can be obtained by extrapolation of the linear ln(I)–V portion to the ln(I) axis at zero voltage and m is the diode quality factor. The parameters I_o and m can be readily determined from the curve (room temperature measurement) shown in Fig. (**3**) together with Eq. (1). The values of I_o and m are calculated as 1.63×10^{-7} A and 1.62±0.03, respectively. Deviation of m from unity may be attributed to either recombination of electrons and holes in the depletion region, and/or the increase of the diffusion current due to increasing the applied voltage [13]. The diode quality factor is almost found to be constant at different temperatures. This behaviour is in accordance with the thermionic emission mechanism. To confirm that the thermionic emission is the operating conduction mechanism, more analysis was carried out. According to the thermionic conduction, the saturation current is given by [14]

$$I_o \propto T^2 \exp\left(-\frac{e\phi_b}{k_BT}\right) \quad (2)$$

Where ϕ_b is the barrier height. The obtained straight line from the plot of logarithm of I_o/T^2 against $1/T$ supports the thermionic mechanism. Fig. (**4**) represents this plot, which clearly shows a linear behaviour. From the slope $(-e\phi_b/k_B)$ of the straight line the potential barrier height, ϕ_b, is determined as 0.48eV.

In the second region (higher voltage), other conduction mechanism seems to be predominant. It is observed that the current shows a power dependence of voltage with slope of log J–logV of about 2 as seen from plot in Fig. (**5**). This power dependence suggests that

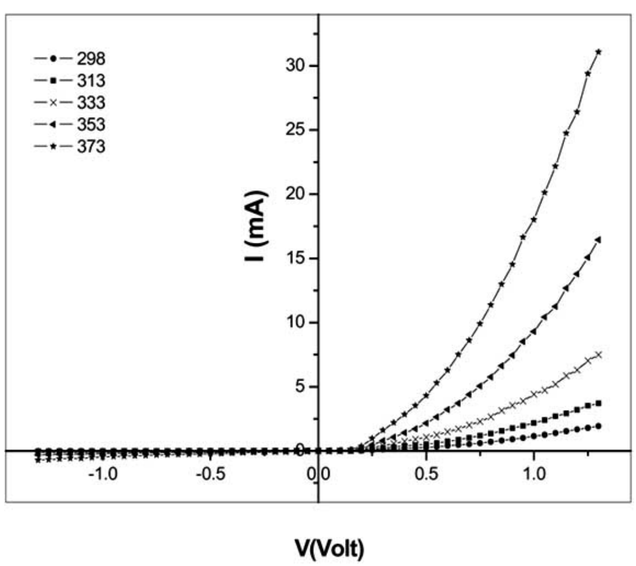

Fig. (2). I-V characteristics of MgPc/p-Si heterojunction at different temperatures in forward and reverse bias.

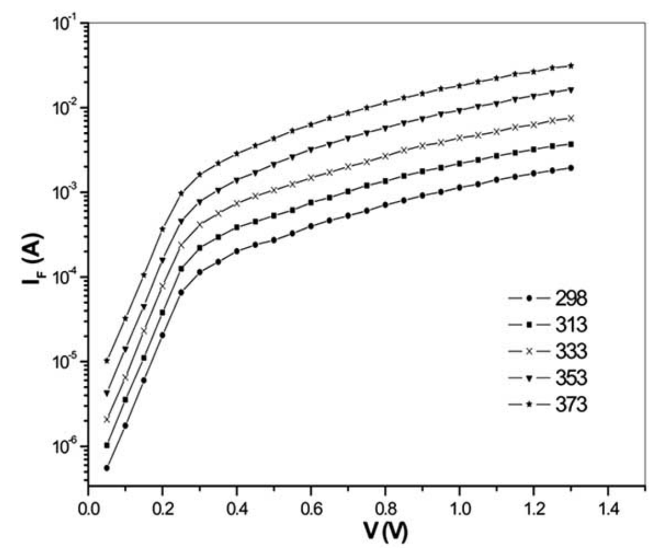

Fig. (3). Semilogarithmic plots of the forward bias of I-V characteristics at different temperature.

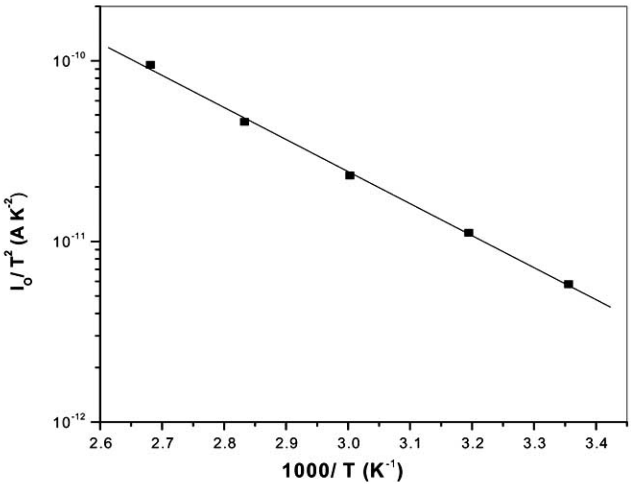

Fig. (4). Semilogarithmic plots of $\ln(I_o/T^2)$ versus 1/T for MgPc/p-Si heterojunction.

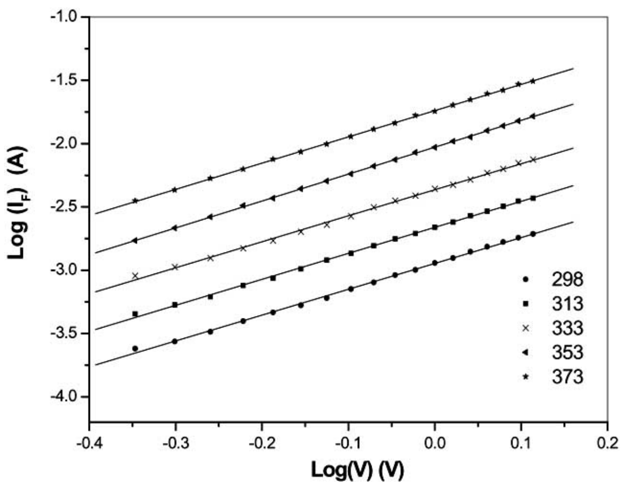

Fig. (5). Variation of log I with log V at higher forward voltage bias for MgPc/p-Si heterojunction.

the dark current is a space-charge-limited current (SCLC) dominated by a single trap level. According to Lampert theory, the relation for the current density in this case is given by [15]

$$I = (9/8)\varepsilon\mu\ \theta \frac{V^2}{d^3}, \tag{3}$$

Where d is the thickness of the MgPc film, ε_2 is the permittivity of MgPc, μ is the mobility of holes, and θ is the trapping factor, which is defined by the ratio of the free charge to trapped charge and given by

$$\theta = \frac{N_v}{N_{t(S)}} \exp\left(\frac{-E_t}{k_B T}\right) \tag{4}$$

Where k_B is Boltzmann's constant, N_v is the effective density of states in the valence band edge, and $N_{t(s)}$ is the total trap concentration at energy level E_t above the valence band edge.

The value of trap energy level E_t can be calculated by plotting ln I versus 1000/T as shown in Fig. (**6**) from the slope of the straight line E_t is determined as 0.34eVwere obtained assuming $N_v = 10^{21}$ $cm^{-3}$and using $\mu = 4.15\times 10^{-2} cm^2V^{-1} s^{-1}$, which is measured by us in different work under publication.

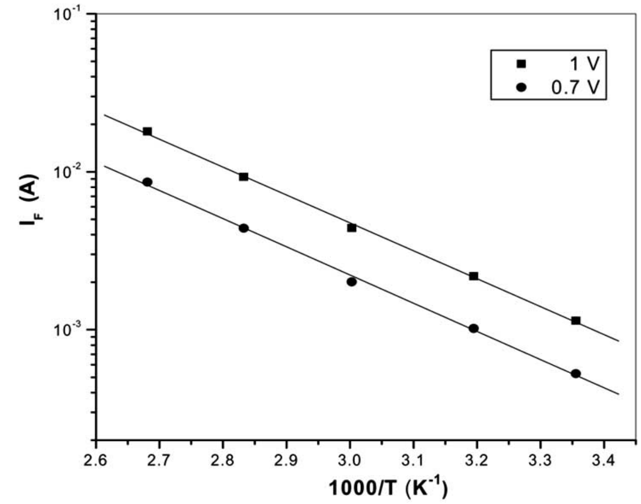

Fig. (6). Variation of log I_F with 1000/T in SCLC for MgPc/p-Si heterojunction.

On the other hand, the reverse current–voltage characteristics of MgPc/p-Si heterojunction at different temperatures ranging from 298 to 373 K are shown in Fig. (**7**). As usual for reverse direction of a rectifier, the current does not nearly depend on voltage. At relatively high voltage, the dependence of the current on voltage is stronger than predicted by pure thermionic emission or Schottky effect that leads to the assumption that nearly flat reverse I–V characteristics could be fit over a wide range of voltages assuming that generation and recombination of carriers in the Si substrate is the dominant source of the reverse current [4].

The reverse current due to carrier recombination is thermally activated according to the form [16]

$$I_R \propto \exp(-\Delta E / k_B T) \tag{5}$$

Where ΔE is the carrier activation energy. The dependence of the reverse current I_R on *1/T* is shown in Fig. (**8**). As it is shown, the activation energy is determined from the slope of the straight line, which has a value of 0.51 eV. The obtained activation energy is approximately equal to half the band gap of Si; which suggests that the main source of the reverse current is Si substrate and indicates that the reverse current should be limited by the carrier generation process.

3.2. Dark Capacitance–voltage Characteristics

The capacitance of the MgPc/p-Si cell was measured at a high frequency of 1MHz in dark and at room temperature as shown in Fig. (**8**). As observed from this figure, $1/C^2$–V variation is linear in the voltage range studied indicating that the junction is of abrupt nature. For abrupt junction, the junction capacitance as a function of reverse-bias potential is given by [17]

$$\frac{1}{C^2} = -\frac{2}{eN\varepsilon\varepsilon_o}(V_{bi} - V) \tag{6}$$

By plotting $1/C^2$ versus *V*, a straight line is obtained, the slope gives the free carrier concentration, *N*, of the semiconductor and the intercept at $1/C^2 = 0$ gives the built-in-voltage, V_{bi}.

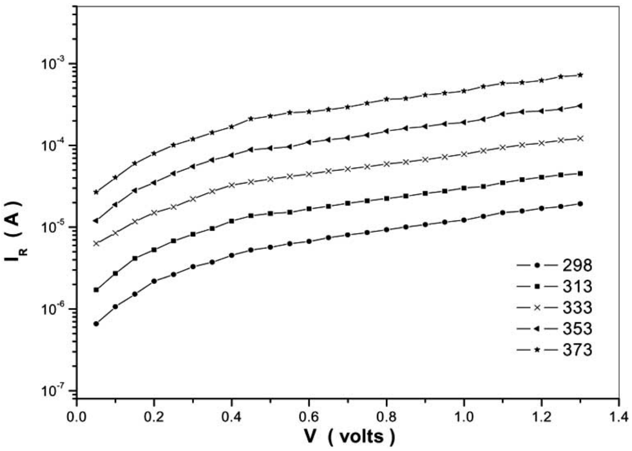

Fig. (7). Semi logarithmic plots of I_R against for MgPc/p-Si hetero junction.

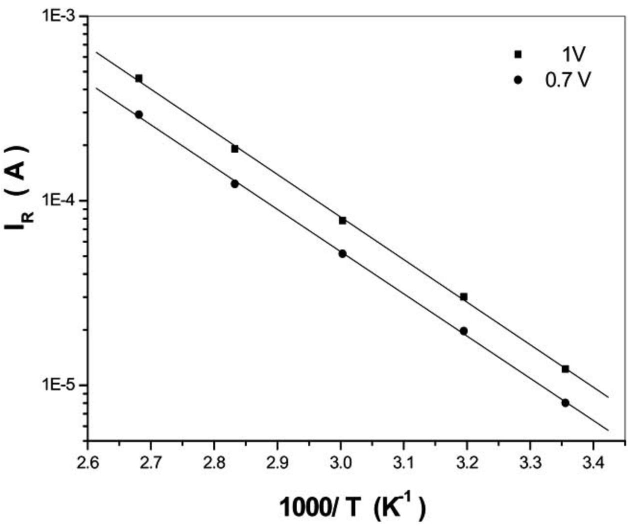

Fig. (8). Semilogarithmic plots of I_R versus 1/T for MgPc/p-Si heterojunction at different voltage.

The free carrier concentration, *N*, was found to be $\sim 2.69\times 10^{17} cm^{-3}$ and the built-in-voltage V_{bi} was estimated to be 0.32V. The value V_{bi} obtained from C-V measurements is in agreement with the value of the potential height, φ_b, that obtained from the I-V measurements.

The width of the depletion region width, W, is related to the junction capacitance at V = 0 V, C_o by the relation [9, 18]

$$W = \varepsilon\varepsilon_o A / C_o \quad (7)$$

The capacitance of the device, C_o, at zero bias was measured and found to be ~1.3 nF.

The maximum electric field is given by [19]

$$E_{max} = 2V_{bi}/W \quad (8)$$

The values of W and E_{max} are estimated to be 0.34 μm and 1.88 V/μm.

3.3. Photovoltaic Properties

The current–voltage characteristics of a MgPc/p-Si heterojunction solar cell in the dark and under white light illumination of 6 $mWcm^{-2}$ and active area of 0.25 cm^2 are shown in Fig. (**10**). It can be seen from this figure that the current value at a given voltage for MgPc/p-Si cell under illumination is higher than that in the dark.

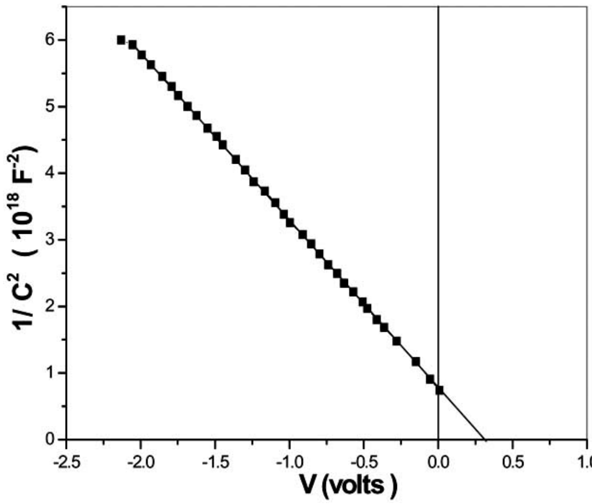

Fig. (9). C^2-V characteristics for MgPc/p-Si heterojunction.

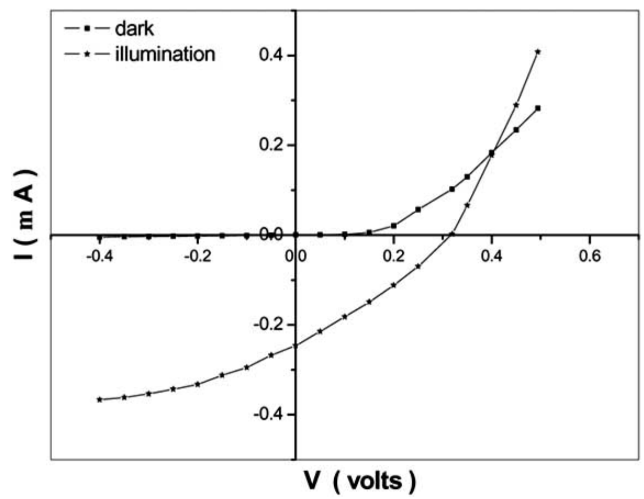

Fig. (10). Current-voltage characteristics under illumination for MgPc/p-Si heterojun*ction.*

This indicates that the light generates carrier-contributing photocurrent due to the production of electron–hole pairs as a result of the light absorption. It is well known that the absorption region of all phthalocyanines corresponds to the UV–VIS region [19]. It has been suggested that the light is absorbed at both MgPc and Si. The generation of photoelectrons, via both MgPc and Si exciton intermediate, is followed by electron transfer from p-Si into MgPc through the potential barrier at the interface. This is a result of a difference in electron affinities between the two semiconductors. It is note worthy that the photocurrent in the reverse direction is strongly enhanced by photo-illumination. This behaviour yields useful information on the electron–hole pairs, which were effectively generated in the junction by incident photons. Under the influence of the electric field at the junction, electrons were accelerated towards the MgPc, while the generated holes were swept towards the Si along the potential barrier at the interface. Different junctions were fabricated with different thicknesses of MgPc layers. This can be explained as the increasing of the thickness increases the series resistance of the junction. It can also be explained by considering that the thinner layer allows higher intensity of light to reach the Si substrate.

The incident light produced a short circuit current, $I_{sc,}$ and an open-circuit voltage, V_{oc}. The solar cell parameters are obtained from the following equations [20], where:

The experimental efficiency of the solar cell is given by

$$\eta = \frac{P_M}{P_{in}} = FF\frac{J_{sc}V_{oc}}{P_{in}} \times 100 \qquad (9)$$

Where P_{in} is illumination power impinging on the cell that was previously estimated by 6 mW/cm^2 and J_{sc} (= I_{sc} / A) is short circuit and FF is the filling factor given by

$$FF = V_M I_M / V_{oc} I_{sc} \qquad (10)$$

Where V_M and I_M are potential and current-densities at maximum power point, therefore, the maximum power obtained from the cell is given by

$$P_M = V_M I_M = FFV_{oc}I_{sc} \qquad (11)$$

The solar cell parameters of fabricated cells have been calculated and given as short circuit current (I_{sc}) of 246 μA, open circuit voltage (V_{oc}) of 0.32 V, fill factor (FF) of 0.31, and power conversion efficiency (η) of 2.71%.±0.03% . The value of the fill factor is lower in comparison to those of solar cells based on inorganic materials. The main cause of this effect is generally found to be the field dependent nature of the charge photogeneration process or high series resistance of the organic layer. However, the obtained value of η is in the order of the values, previously, reported for phthalocyanines heterojunction cells having Si as substrates [9].

4. CONCLUSIONS

The MgPc films were deposited onto p-Si <100> substrates by thermal evaporation technique. The dark current–voltage measurements suggest that the forward current transport in these junctions involve thermionic emission of the electrons from p-Si over the MgPc/Si barrier at low forward bias. Moreover, a space-charge-limited transport across the MgPc layer dominates due to the exponential distribution of traps above the valence band in the band gap of the MgPc layer at high forward bias. From the capacitance–voltage, measurements at high frequency (1 MHz) information can be obtained about the depletion layer extending in the Si side. These characteristics are interpreted by assuming the abrupt heterojunction model. Under illumination of ~6 mW/cm^2, the significantly high V_{oc}= 0.32V for the MgPc/p-Si junction, as compared to that (0.2 V) for the Au/p-Si cell, suggests that the excitons play an important role in the primary process of photo-carrier generation in MgPc. The obtained power conversion efficiency of the studied cell was 2.71±0.03%, which is comparatively high compared to those of other organic solar cells.

REFERENCES

[1] McKewon, N.B. *Phthalocyanine Materials: Synthesis, Structure and Function*. Cambridge University Press: Cambridge, **1998**.

[2] Leznoff, C.C.; Lever, A.B.P. *Phthalocyanines: Properties and Applications*, VCH Publishers: New York, **1996**, vol. 4.

[3] Gregory, P. *High-Technology Applications of Organic Colorants*. Plenum Press, New York, **1991**, pp. 759.

[4] Haisch, P.; Winter, G.; Hanack, M.; Lüer, L.; Egelhaaf, H.; Oelkrug, D. Soluble alkyl- and alkoxy-substituted titaniumoxo phthalocyanines: Synthesis and photoconductivity. *Adv. Mater.*, **1997**, *9*, 316.

[5] Mrwa, A.; Friedrich, M.; Hofmann, A. Response of lead phthalocyanine to high NO_2 concentration. *Sensors Actuators B*, **1995**, *24-25*, 596.

[6] Ao, R.; Kümmerl, L.; Haarer, D. Present limits of data storage using dye molecules in solid matrices. *Adv. Mater.*, **1995**, *7*, 495.

[7] Kerp, H.R.; van Faassen, E.E. Effects of oxygen on exciton transport in zinc phthalocyanine layers. *Chem. Phys. Lett.*, **2000**, *5*, 332.

[8] Lee, S.T.; Wang, Y.M.; Hou, X.Y.; Tang, C.W. Interfacial electronic structures in an organic light-emitting diode. *Appl. Phys. Lett.*, **1999**, *74*, 670.

[9] Riad, A.S. Dark and photoelectric conversion properties of p-MgPc/n-Si (Organic/Inorganic) heterojunction cells. *Thin Solid Films*, **2000**, *370*, 253.

[10] Van, C.N.; Kamloth, K.P. Electrical and NO_x gas sensing properties of metallophthalocyanine-doped polypyrrole/silicon heterojunctions. *Thin Solid Films*, **2001**, *392*, 113.

[11] Darwish, S.; El-Zawawi, I.K.; Riad, A.S. Photovoltaic properties of ZnSe/metal-free phthalocyanine heterojunctions deposited on substrates of InP single crystals. *Thin Solid Films*, **2005**, *485*, 182.

[12] Oueriagli, A.; Kassi H.; Hotchandani S.; Leblanc R.M. Analysis of dark current-voltage characteristics of Al/chlorophyll a/Ag sandwich cells. *J. Appl. Phys.*, **1992**, *71*, 5523.

[13] Rhoderick, E.H., Metal Semiconductor Contacts. Oxford University Press, Oxford, **1978**.

[14] Sze, M.S. Physics of Semiconductor Devices, second ed. Wiley Interscience, New York, **1981**.

[15] Lampert, M.A. Volume-controlled current injection in insulators. *Rep. Prog. Phys.*, **1964**, *27*, 329.

[16] Abdel-Malik, T.G.; Aly, A.A.; Abdeen, A.M.; El-Labany, H.M. Electric and photoelectric investigations of β-nickel phthalocyanine thin films. *Phys. Status Solidi (a)*, **1983**, *76*, 651.

[17] Soliman, H.S.; Farag, A.A.M.; Khosifan, N.M.; El-Nahass, M.M. Electrical transport mechanisms and photovoltaic characterization of cobalt phthalocyanine on silicon heterojunctions. *Thin Solid Films*, **2008**, *516*, 8681.

[18] Riad, A.S. Influence of dioxygen and annealing process on the transport properties of nickel phthalocyanine Schottky-barrier devices. *Physica B*, **1999**, *270*, 148.

[19] Davidson, A.T. The effect of the metal atom on the absorption spectra of phthalocyanine films. *J. Chem. Phys.*, **1982**, *77*, 168.

[20] Ashok, S.; Pande, K.P. Photovoltaic measurements. *Sol. Cells*, **1985**, *14*, 81.

Received: 06 May, 2009 Revised: 01 July, 2009 Accepted: 02 July, 2009