Electrical transport mechanisms and photovoltaic characterization of cobalt phthalocyanine on silicon heterojunctions

H.S. Soliman\textsuperscript{a,b}, A.A.M. Farag\textsuperscript{a}, N.M. Khosifan\textsuperscript{b}, M.M. El-Nahass\textsuperscript{a,*}

\textsuperscript{a} Physics Department, Faculty of Education, Ain Shams University, Roxy, Cairo 11757, Egypt
\textsuperscript{b} Physics Department, Faculty of Education for Girls, King Abdel-Aziz University, Jeddah, Saudi Arabia

Received 16 March 2007; received in revised form 11 April 2008; accepted 23 April 2008

Available online 8 May 2008

Abstract

Heterojunction devices were fabricated by growing cobalt phthalocyanine, CoPc, films onto p-type Si using the conventional thermal evaporation technique. The dark current–voltage (\(I-V\)) measurements were performed in the temperature range 300 to 393 K. The measured electrical parameters were used to determine the conduction mechanisms of these heterojunctions. The forward current was found to be increased exponentially with the applied voltage in the region of \(V \leq 0.4\) V, which was dominated by the thermionic emission over the CoPc/p-Si interface. In the region 0.5 \(b\) V \(\leq 1\) V, the current transport was due to the space-charge-limited current controlled by an exponential trap distribution in the band gap of CoPc. A free carrier concentration of \(1.8 \times 10^{15}\) cm\(^{-3}\), built-in potential of 0.28 V and a maximum barrier field of 2.5 \(\times\) \(10^3\) V/cm were estimated from the dark capacitance–voltage measurements at 1 MHz. From the current–voltage characteristics under illumination and then photovoltaic properties of Au/CoPc/p-Si solar cell are evaluated.

© 2008 Elsevier B.V. All rights reserved.

Keywords: CoPc; Conduction mechanism; Photovoltaic; Organic solar cell

1. Introduction

In the last two decades, effort for finding suitable materials for electronic applications has attracted an increasing interest in the investigation of electrical and photoelectrical properties of organic compounds. Among these organic materials are the metal free (H\(_2\)Pc) and metal substituted phthalocyanines (MPcs) such as PbPc [1], FePc [2], MgPc [3], ZnPc [4] and CoPc [5]. These materials are generally p-type semiconductors and can easily sublimate resulting in pure thin films without decomposition [6]. They are used as gas sensors [7] for optical recording materials [8], rectifiers [9] and photovoltaic devices [10].

The effects of coating n-type Si electrodes with PcS films in aqueous redox solution have also been investigated [11]. The n-type Si electrodes coated with vacuum deposited CoPc or CuPc were stable, showing a slow decay of photocurrent and a high photovoltage, as compared to the Schottky Au/n-Si [12]. The results of the electrical properties of CuPc/p-Si obtained by Antohe et al. [13], were explained by a charge transport model in which, the charge transport is limited by thermionic emission at low current densities. The high stability and reproducibility of the electrical properties of CuPc/p-Si heterojunction observed by the same authors suggest that these materials have many useful applications.

The effect of dye coating with chloroaluminium phthalocyanine, AlPcCl/n-Si was examined by Yanagi et al. [14]. They found that the morphology and thickness of the deposited AlPcCl, which were controlled by changing substrate temperature of n-Si, have an important role in increasing the photovoltaic efficiency of the Au/AlPcCl/n-Si cells. The transverse current–voltage characteristics of CuPc/Si, PbTe/CuPc/Si junctions have been studied in the dark and under illumination by Lee and Kawai [15]. They found that the PbTe/CuPc/Si junctions exhibited a strong photovoltaic response with quantum efficiency of 15.4\% and power conversion efficiency of 0.035\%.

They concluded that the photocurrent is generated in CuPc layer and the carriers are separated by the steep incline of the potential near the CuPc/PbTe interface. CuPc/PbTe multilayer showed a large photoconduction effect in the in-plane
direction. Heterojunction devices of p-MgPc/n-Si studied by Raid [3] 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. [16] concluded that the junction parameters such as the rectification factor, RR, the saturation current density, \( J_s \) 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 p–n junction solar cells consisting of CuPc and perylene pigments were studied by Hu and Matsumura [17], showed stronger structure and thickness dependence. The devices with the structure of ITO/CuPc/PV/Ag show better properties than the devices with the structure of ITO/PV/CuPc/Au and in addition, the photo-absorbance near the p–n junction determines all the properties of the solar cells, which is the active centre of the devices. Darwish et al. [18] studied the photovoltaic properties of ZnSe/H2Pc heterojunctions deposited on substrates of InP single crystals. They found that the n-ZnSe/p-H2Pc/p-InP junctions gave stronger photovoltaic characteristics than those of p-H2Pc/p-InP and ZnSe/ p-InP junctions which may be due to the effective light absorbance of H2Pc layer and the effective charge separation at the H2Pc/ZnSe interface.

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 CoPc/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 details

The p-type Si single crystals were used as substrates. Chemical etching of p-Si was performed with HF:HNO\(_3\):CH\(_3\)COOH (1:6:1) composition for 30 s. After etching the silicon wafers were washed with distilled water and isopropyl alcohol then dried in nitrogen. Ohmic contact was obtained by deposition of indium electrode on one side of the p-Si specimen, while the other side was coated by CoPc films (with purity for powder as 99.7%, purchased from Kodak, UK). The deposition rate was constant through the deposition as 5 nm/min and the thickness of CoPc ranged from 30 to 60 nm. The structure of the obtained films grown on Si substrate was investigated by X-ray diffraction technique, shown in Fig. 1. A strong peak oriented along the (401) direction was observed confirming the monocry stalline structure of the Si substrate. The other small intensity peak around \( 2\theta \approx 6.87 \) belonging to the (100) reflecting plane of CoPc was also obtained, indicating that and the films are believed to have the same structure than CoPc films evaporated on glass as evidenced by XRD and IR studies [19]. The surface morphology was checked by scanning electron microscopy (Fig. 2) which gave evidence for the continuous prepared films on the p-Si substrates. From Fig. 2, the CoPc domains appear to be roughly round and definitely not to have any distinct crystalline habit planes. The other ohmic contact was made by evaporation of gold fingers onto the CoPc films. During evaporation, the vacuum was better than \( 10^{-4} \) Pa using a high-vacuum evaporation unit (Edwards 306 A). The film thickness was monitored by a quartz crystal thickness monitor (Edward, type FTM6). In this method, the film was deposited onto one electrode of a quartz crystal connected to an oscillator circuit. The frequency shift, in such a case, equals to that arising from the change of crystal mass. The thickness also measured by the multiple beams Fizeau fringes “Tolansky’s method”. In this method, a pre-cleaned glass slide masked with a sharp-edge mica sheet was placed on a rotating holder, during the deposition process of CoPc film. Then an opaque Al film is deposited onto the complete surface of the glass slide. There is now a step of the same height as that of corresponding thin CoPc film used as a lower component of an interferometer. The upper component of the interferometer consists of another optical flat coated with an Al layer of reflectivity 70%. The interferometer adjusted until straight-line fringes normal to the step are observed using a multiple beam interferometer (NIFE, JUNGER 68294). During deposition, the temperature of p-Si substrate was kept at 310 K. A schematic diagram of the device is shown in Fig. 3. The current flowing through the sample was determined using a stabilized power supply and a high-impedance Keithley 617 electrometer. The \( I–V \) characteristics were performed in dark over
the temperature range 300–393 K. The temperature was measured directly by means of chromel–alumel thermocouple connected to hand-held digital thermometer. Capacitance–voltage measurements were performed at 1 MHz, using a computerized capacitance–voltage system consisting of the 410 C–V meter interfaced via model 4108 C–V interface. The loaded I–V characteristics circuit used to determine the solar cell parameters under illumination. The incident power density of light illumination was ~80 mW/cm² provided by a tungsten lamp through a water filter. The intensity of incident light was measured using a digital lux-meter (BCHA, model 93408). The devices had an effective area of ~4 mm².

3. Results and discussions

3.1. Current–voltage characteristics

Fig. 4 shows the I–V characteristics of CoPc/p-Si heterojunctions under forward and reverse bias in the temperature range of 300–393 K. The observed exponential dependence of the forward current in the lower voltage range may be due to the formation of a depletion region between CoPc layer and Si single crystal substrate. 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 ≈10³ for Au/CoPc/p-Si heterojunction at ±1 V. The series and shunt resistances (Rₛ and Rₛ) which are important factors in improving cell performance and design obtained at room temperature by the method stated in [18], by using the relation between junction resistance, Rⱷ, and the applied voltage, V, shown in Fig. 5. As observed in Fig. 5, at sufficiently high forward bias the junction resistance approaches a constant value characterizing the series resistance Rₛ ≈ 2.46 kΩ. In addition, in Fig. 5, the junction resistance shows a constant value at sufficiently high reverse bias, which equals the diode shunt resistance Rₛ ≈ 1.7 MΩ.

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/CoPc/p-Si heterojunction in the temperature range of 300–393 K are given in Fig. 6. Two distinct regions characterize these curves indicating different conduction mechanisms. As observed in Fig. 6, within the narrow low forward voltage (V ≤ 0.4 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 [20]. The data of the narrow potential range (I ≤ 0.4 V) were fitted to the Schottky equation [21].

\[
I = I_s \exp \left( \frac{eV}{nkT} \right) - 1
\]

where n is the diode quality factor, k is the Boltzmann’s constant and Iₛ is the saturation current which can be obtained by extrapolating the ln I–V portion to the ln I axis at zero voltage. A reasonable good fit was obtained for the CoPc/p-Si heterojunction, whose parameters n and Iₛ are determined as 1.95±0.02 and ~1.98×10⁻⁹ A at room temperature, respectively. These parameters are direct indication for the electrical transport properties of the p–n junction and reflect the properties of the depletion layer [22]. The deviation of the diode quality factor n from unity may be attributed to the recombination of electrons and holes in the depletion region [16,23–25].

The saturation current, Iₛ, is given by

\[
I_s = A^* T^2 \exp \left( \frac{-\varphi}{kT} \right)
\]

where A is the effective area of the device, A* is the effective Richardson’s constant and \( \varphi \) the barrier height for the
predominant carriers. It is evident from the above equation that the relation of \( \ln \left( \frac{I_s}{T^2} \right) \) against the reciprocal temperature \( \frac{1}{T} \) gives a straight line with a slope equals \(-\frac{e\phi}{k}\), while the intercept with the vertical axis is \( \ln A^* \). Fig. 7 relating \( \ln \left( \frac{I_s}{T^2} \right) \) and \( \frac{1}{T} \) indicates a linear behaviour which confirms that the thermionic emission is the predominant conduction mechanism in the applied voltage range of \( V \leq 0.4 \) V and yields the values \( 0.5 \pm 0.03 \) eV and \( \sim 2.3 \times 10^7 \) Am\(^{-2}\) K\(^{-2}\) for \( \phi_b \) and \( A^* \), respectively.

According to Fig. 8, under relatively high forward voltages another mechanism is supposed to be operating above 0.4 V. As observed in Fig. 8, the current shows a power-law exponent of the form \( I \sim V^m \). The slope of the \( \ln I - \ln V \) relation, is about 3, showing that the forward biased current is space-charge-limited current (SCLC) controlled by exponentially trap distribution [26,27]. The equation for the \( I-V \) dependence for a p-type semiconductor with an exponential distribution of trapping levels is given by:

\[
I = eA^*N_V \left( \frac{e}{eP_\text{o}kT_i} \right) \frac{eV^2}{d^{2+1}}
\]

where \( N_V \) is the effective density of states in the valence band edge, \( P_\text{o} \) the trap density per unit energy range at the valence band edge, \( \mu \) the hole mobility and \( I = T_i/T \) where \( T \) is the room ambient temperature and \( T_i \) is the temperature parameter describing the exponential trapping distribution. From Fig. 8, the energy of the trap distribution, \( kT_i \), is found to be \( 0.05 \pm 0.001 \) eV at \( T = 300 \) K.

Fig. 9 shows the dependence of \( \ln I \) on inverse temperature \( \frac{1}{T} \) for Au/CoPc/p-Si heterojunction, at a constant voltage of 0.85 V. In this temperature range, the characteristics show linear segments. The total trapping concentration \( N_t \) is estimated from the measured slopes to be \( \sim 8 \times 10^{16} \) cm\(^{-3}\) which is in the same order of magnitude as that obtained before [27].

### 3.2. Capacitance–voltage characteristics

The dark capacitance–voltage characteristics of Au/CoPc/p-Si heterojunctions were measured at 1 MHz. This frequency is high enough to neglect the dielectric relaxation process in CoPc film [25] and get information on the depletion region extended in the p-Si side.

Fig. 10 shows the \( (C^{-2}-V) \) characteristics of the Au/CoPc/p-Si heterojunction at room temperature. The linearity of this dependence indicates that the junction is considered as an abrupt heterojunction. Thus, the capacitance is taken as [28]

\[
C^{-2} = \frac{2(V_b - V - kT/\psi)}{eN\psi^2}
\]

where \( V_b \) is the built-in voltage and \( N \) is the net carrier concentration. According to Eq. (4), the net carrier concentration and the built-in voltage are obtained from the slope and the intercept of the straight line of Fig. 10 as \( \sim 1.8 \times 10^{15} \) cm\(^{-3}\) and \( 0.28 \pm 0.02 \) V, respectively.
The maximum barrier field which exists at the interface of CoPc/Si is determined from the following equation \[24,29\]

\[ E_{\text{max}} = \frac{2V_b}{W} \]  

(5)

where \( W \) is the width of the depletion region \( \left( = \frac{\varepsilon_d}{n} \right) \) and \( C_0 \) is the capacitance at zero bias. The calculated value of \( E_{\text{max}} \) is \( \sim 2.5 \times 10^3 \) V/cm.

### 3.3. I–V characteristics under illumination

The photovoltaic properties of CoPc/n-Si heterojunction diode are determined by measuring the I–V characteristics using a load resistance and an illumination of power density of \( \sim 80 \) mW/cm\(^2\).

I–V characteristics of Au/CoPc/p-Si heterojunction are studied in the dark and under illumination. The dark current is found to be small at the negative bias and the behaviour can be understood by considering a p–n junction. The barrier at the interface limits the reverse carrier flow across the junction and the built-in potential could be developed. The photocurrent action spectra for the Au/CoPc/p-Si cells indicate photocurrent maxima at the Q-band absorption region as shown in Fig. 11. This spectrum suggests that the homogeneous CoPc layers contribute primarily to photo-carrier generation, create or/and consequently establish the p-Si electrode in this wavelength region. However, CoPc layers reduce the photocurrents by an order of magnitude because of their low conductivity. In addition, the incident light is absorbed by CoPc and produces excitons, which subsequently dissociate into electrons and holes due to the internal field created by Schottky barrier formed at the interface. The photocurrent action spectrum in the Q-band region is similar to the optical absorption spectrum of CoPc, indicating the generation of photoelectrons, via a CoPc exciton intermediate, followed by electron transfer from CoPc into p-Si through the potential barrier at the interface. This behaviour is believed to be due to the difference in the electron affinities between the two semiconductors. In addition, a relatively high photocurrent peak at about 0.6 \( \mu \)m is observed in Fig. 11 compared with the absorption spectrum, shown in Fig. 11. This may be due to a filtering effect of the light, which is absorbed by CoPc, for transverse photocurrents generated in the CoPc.
layers. Moreover, it is noteworthy that the photocurrent in the reverse direction is strongly enhanced by photo-illumination. This behaviour yields useful information about the excitons, which were effectively generated in the CoPc layer by the incident photons.

The low hole mobility, the disordered dissociation and charge dissociated recombination in organic materials lead to both lower efficiency and fill factor [17]. To estimate the efficiency of the cell, an illuminated cell was connected to a variable (from zero to infinity) load resistance. The current through the load resistor and the voltage across the junction were measured and plotted as shown in Fig. 12. It can be seen from this figure that the CoPc/Si junction shows the photovoltaic characteristics with $I_{sc}$ (short-circuit density) of $18.67 \pm 0.1$ mA/cm$^2$, $V_{oc}$ (open-circuit voltage) of $0.46 \pm 0.01$ volts, FF (fill factor) of $0.34 \pm 0.01$ and $\eta$ (power conversion efficiency) of $3.76 \pm 0.03\%$. It should be mentioned here that although the Au/p-Si Schottky cell shows a strong rectifying behaviour but its $V_{oc}$ value of $0.2$ V [28] is small with the compared $0.46$ V of the Au/CoPc/p-Si cell. This may be due to surface states barrier, which act as a recombination centres [25]. Such formation of surface states is repressed by inserting the CoPc layer between p-Si and Au, so that the barrier height is kept large to produce a higher $V_{oc}$. In addition, an effect of intervening layers has been recognized by Yanagi et al. [14] when the n-Si surface is covered with an insulating SiO$_2$ layer, i.e., constructed in the metal/insulator/semiconductor (MIS) cell. In general, CoPc is considered to be a p-type molecular semiconductor rather than an insulator. Therefore, the contact between CoPc and p-Si should produce an organic/inorganic heterojunction.

4. Conclusion

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 CoPcSi barrier at low forward bias. Moreover, a space-charge-limited transport across the CoPc layer dominates due to the exponential distribution of traps above the valence band in the band gap of the CoPc 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 $\sim 80$ mW/cm$^2$, the significantly high $V_{oc}$ ($0.46 \pm 0.01$ V) for the CoPc/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 CoPc. The obtained power conversion efficiency of $3.76 \pm 0.03\%$ is comparatively high compared to those of the presently available dye-sensitized solar cells.

References