Egypt. J. Sol., Vol. (26), No. (1), (2003)

Dark and Photovoltaic properties of p-CoPc/n-GaAs Heterojunction cells

S. Darwish

Department of Physics, Faculty of Science,
Minia University, Minia- Egypt

Organic / inorganic heterojunction cells of p-CoPc/ n- GaAs, fabricated by vacuum deposition of CoPc thin films onto GaAs single crystals, show a conversion efficiency as high as 0.81% and an open circuit voltage of 0.33V under illumination by light with a power density of 50 mWcm^{-2}. *These parameters have been estimated at room temperature. The estimated activation energy of the charge carriers was found to be 0.35 eV and the cell series resistance of 1k*Ω. *The above values have been evaluated from the measurements of the dark I-V characteristics. The linearity of the* C^{-2}-V *dependence indicates that the junction is perfectly abrupt. From such measurements the free-carrier concentration and the barrier width can be estimated. Their values were found to be 1.2 x 10*^{17} *cm*$^{-3}$ *and 32.4 nm, respectively.*

1. Introduction:

The study of semiconductor heterojunctions has been a topic of great interest due to their ubiquitous use in numerous optical and electronic devices [1]. Recently, investigations of a new class of heterojunctions, i.e. organic/inorganic semiconductor heterojunctions, have attracted some interest [2-5] due to both the unusual nature of these contacts as well as to the potential new devices can be applied. In particular, crystalline molecular semiconductors exhibit rectification when deposited onto inorganic semiconductor substrates. On the other hand, band-gap semiconductors such as Si, GaAs and CdS have successfully been applied in solar energy conversion because of the wide absorption band in the visible spectral region [2].

Phthalocyanine compounds, such as cobalt phthalocyanine, CoPc, have been potentially investigated because of their chemical stability, high absorption coefficient in solar spectrum, semiconducting properties and wide variety of synthetic modifications [6,7]. The n-Si electrodes coated with vacuum deposited

H_2Pc or CuPc were significantly stabilized as compared to the bare n-Si electrode [2,8]. Their photocurrent reaction spectra indicated that the excitation of n-Si only contributed to the photocurrents and the CuPc layer was not photoactive but attenuated the incident light.

The objective of this work is to study the current-voltage (I-V) properties in the dark and under illumination for P-CoPc / n-GaAs heterojunction cells. From the C-V measurements in the dark, one can better recognize the potential barrier region which is formed at the CoPc / GaAs interface.

2. Experimental Techniques:

Organic / inorganic heterojunction cells were fabricated using n-type GaAs (Te) single crystals wafer obtained from Wacker chemitronic Gmbt, prepared by the liquid encapsulating Czochralaski (LEC) technique along <100> orientation. The n-type GaAs as starting substrates were 400μm thick and electron concentration of 5×10^{17} cm^{-3}. The p-type CoPc powder obtained from Eastman Kodak Ltd., New York, was purified by the train sublimation technique using the method described previously [9]. The purified β-CoPc was examined spectroscopically. Before further treatment, the GaAs substrates were chemically etched in a freshly prepared solution of H_2SO_4: H_2O_2: $20H_2O$ for 45 sec. After etching the substrate were washed for 1min in pure alcohol and distilled water and then dried with nitrogen. After etching and cleaning, the ohmic electrodes were deposited on the bottom of the GaAs substrates by thermal evaporation of indium (In). The other side was coated by p -CoPc with thickness ranged between 55 and 75 nm. During the evaporation of p -CoPc, the temperature of the n-GaAs substrate was kept at 420 K and a vacuum better than 2×10^{-5} Pa. The structure of CoPc deposits on n-GaAs was examined by means of XRD and SEM. A very homogenous thin layer as well as large crystallites of 0.2 - 0.4 μm in size were obtained for CoPc deposited on n-GaAs maintained at 420 K. The crystallite size (C.S.) could be calculated using Scherrer's formula [10]:

$$\mathbf{C.S.} = \frac{\mathbf{K\lambda}}{\boldsymbol{\beta}\mathbf{cos}\boldsymbol{\theta}} \qquad \mathbf{(1)}$$

where β is the full width of the half maximum of the peak corrected for instrumental broadening, λ the wavelength of the X-ray and K the Scherrer's constant. The grain size is defined as the dimension of crystallite perpendicularly to the plane. Accordingly to this definition the constant is taken to be ≅ 1. The front ohmic contact was made by evaporation of gold (Au) onto the p-CoPc. The thickness of the semitransparent top Au electrode was about 20 nm giving a transmission of about 6%. The active area of the devices was ≅ 0.65 cm^2. A typical heterojuction cell is shown in Fig. (1). The current through the cells was determined using a conventional d.c. technique and a high impedance Keithley 610 C electrometer. The forward bias corresponds to the p-CoPc being positive. Optical exposure was performed with light from a tungsten halogen lamp, focused onto the semitransparent gold electrode from upper side of the devices. A water filter was used to eliminate the far infrared component from the light source. The incident power was 50 mWcm^{-2}. The incident light was measured using a thermopile (Laser Instrumentation Ltd., 71130) connected to a luxmeter (Pasco Scientific, model 9152 B). The temperature was measured directly by means of an NiCr/Ni-Al thermocouple connected to a Keithley 871 digital thermometer. The dark C-V characteristics were measured at a frequency of 10^5 Hz using a Tinsley 6471 LCR Data Bridge.

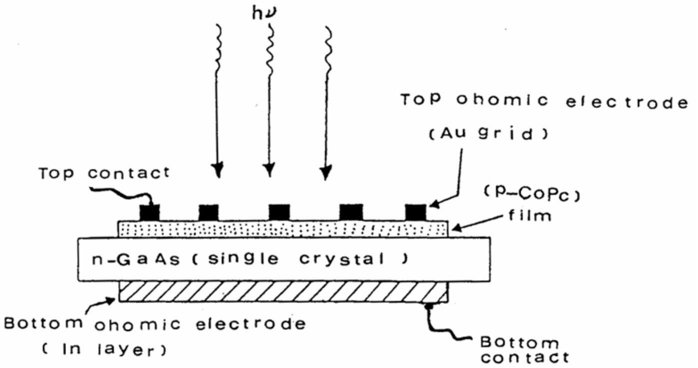

Fig. (1): Typical Schematic diagram of p-CoPc / n-GaAs heterojunction and electrodes connections

3. Results and Discussion :

In general , for non-ideal heterojunction, the forward current is given by [11] :

$$I = I_{01}[\exp (q(V-IR_s) / A_1kT)] + I_{02}[\exp (q(V-IR_s) / A_2kT)] + (V-IR_s) / R_{sh} \qquad (2)$$

where I_0 is the reverse-saturated current, A the diode quality factor, R_s the series resistance and R_{sh} the shunt resistance. The subscripts 1 and 2 refer to the two possible contributions to the diode current . In case of only one junction as p-CoPc/n-GaAs devices, eqn. (2) could be modified to the following equation [12] :

$$I = I_0 [\exp (q(V-IR_s) / AkT)] + (V-IR_s) / R_{sh} \qquad (3)$$

Fig.(2) illustrates the dark current-voltage (I-V) characteristic in the forward bias at room temperature. The semilogarithmic plot shown in the figure reveals that I increases exponentially at low voltages (V≤ 0.3V). The same behavior of the forward I-V plots at different temperatures ranged from 320 to 388 K was also obtained. For a given I, the horizontal displacement between the actual curve and the extrapolated linear part, shown in Fig.(2), gives the voltage drop, $\Delta V = IR_s$, across the neutral region. The plot of ΔV vs. I shown in Fig.(3) should give a straight line whose slope yields the value R_s of ≅ 1kΩ.

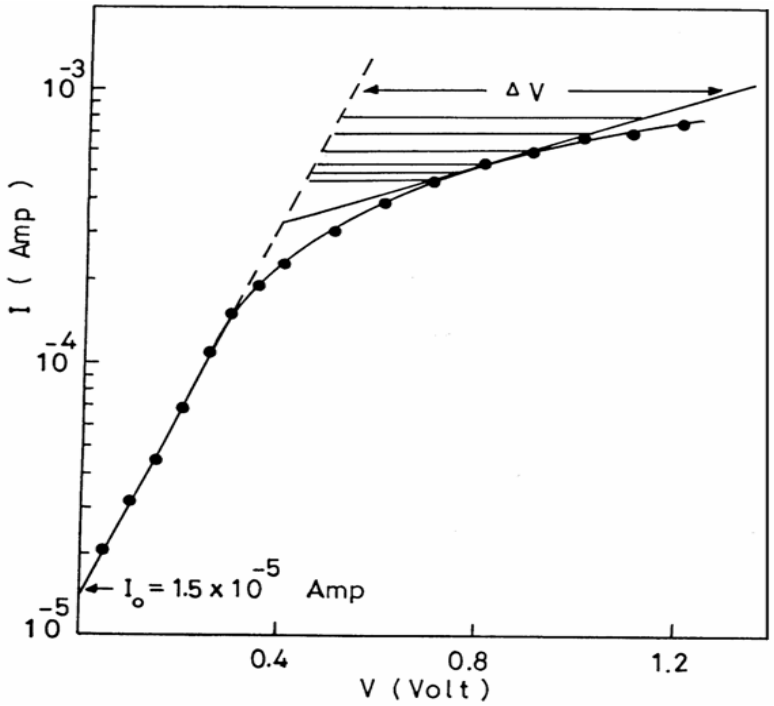

Fig. (2): Dark I-V plots at 298 K of p-CoPc/n-GaAs heterojunction in the forward bias.

The dependence of ln I_0 on 1/T shown in Fig. 4 was examined with the aid of the following eqn. [13]:

$$I_0 = I_{00} \exp(-\Delta E/kT) \quad (4)$$

where I_{00} is almost temperature independent and ΔE the activation energy of the charge carriers; its value was found to be (0.35 ± 0.02) eV.

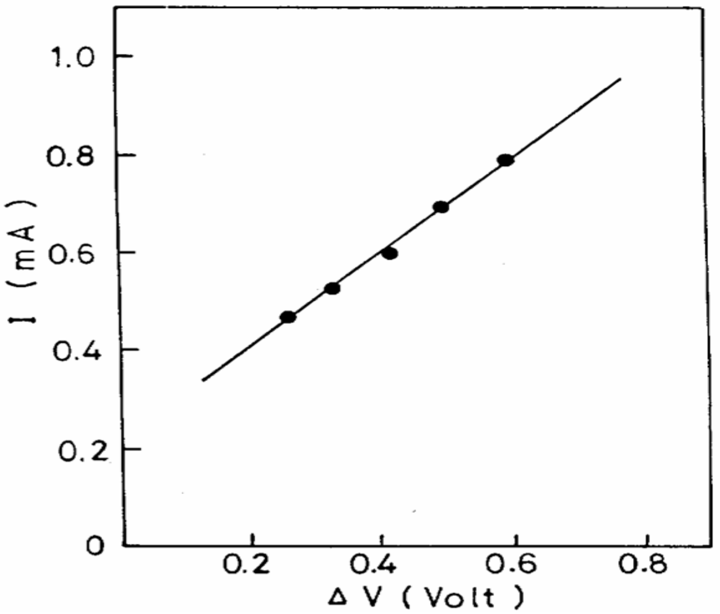

Fig. (3): The voltage drop across the series resistance as deduced from Fig.1.

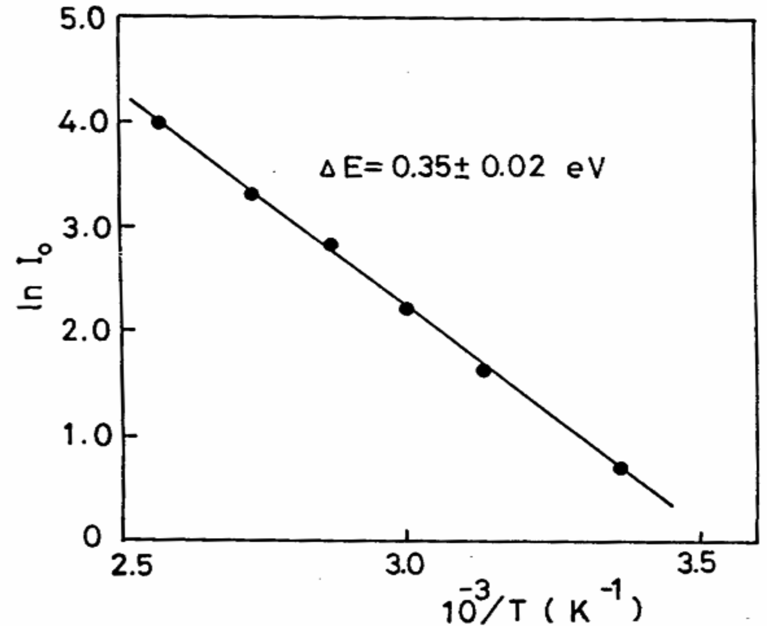

Fig. (4): Plot of ln I_0 vs. 1/T at 0.8 V.

Current density-voltage (J-V) characteristics of Au/CoPc/n-GaAs heterojunction device in the dark and at input power density of 50mW cm^{-2} are shown in Fig.(5). As shown in this figure, the dark current is small at the negative bias and the behavior can be understood by a p-n junction, namely the barrier at the interface limits the reverse carrier flow across the junction and the built-in potential could be developed. Dark I-V characteristic of Au/n-GaAs cell was also studied in comparison to that of the Au/p-CoPc/n-GaAs heterojunction. As shown in Fig.(6), the Au/n-GaAs device exhibits a well-rectified curve, in the dark, typically for metal/n-semiconductor Schottky junction, in which the forward bias corresponds to Au electrode being positive. Under illumination negative photocurrents arise with applying positive bias voltages, giving a short-circuit current density, J_{sc}, of 3.8 $mAcm^{-2}$, open-circuit voltage, V_{oc}, of 0.2 V, fill factor, FF, of 0.38 and conversion efficiency, η, of 0.58%. The values of J_{sc}, and η are comparatively high if an attenuation of the incident light through the Au top electrode (~ 6% transmittance) is taken into consideration.

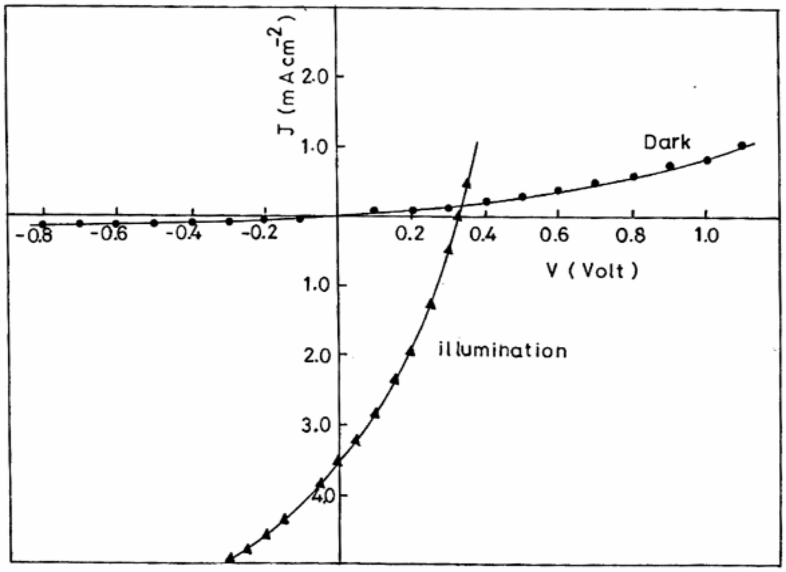

Fig. (5): Dark and photo J-V plots of p-CoPc/n-GaAs heterojunction cell. Effective area ≅ 0.65 cm^2. T = 298 K.

On the other hand, the CoPc/ GaAs junction shows the photovoltaic characteristic with J_{sc} of 3.5 $mAcm^{-2}$, V_{oc} of 0.33 V, FF of 0.34 and η of 0.81% with 70 nm thickness of CoPc films. It should be mentioned that although the Au/n-GaAs Schottky cell shows a strong rectifying behavior, its V_{oc} value (0.2 V) is rather small compared to that of the Au/CoPc/n-GaAs cell. This may be due to surface states formed at the Au/n-GaAs interface pin the Schottky barrier to a small height and act as a recombination center [14]. Such a formation of surface states is repressed by inserting the CoPc layers between n-GaAs and Au, so that the barrier height is kept large to produce higher photovoltaic efficiency than the Au/n-GaAs cell, thus producing an improved V_{oc} value. This high photovoltaic response, however, was attributed to an efficient charge- carrier separation from excitons that were generated on the uncoated n-GaAs surface and diffused to the edges of the CoPc deposit [2].

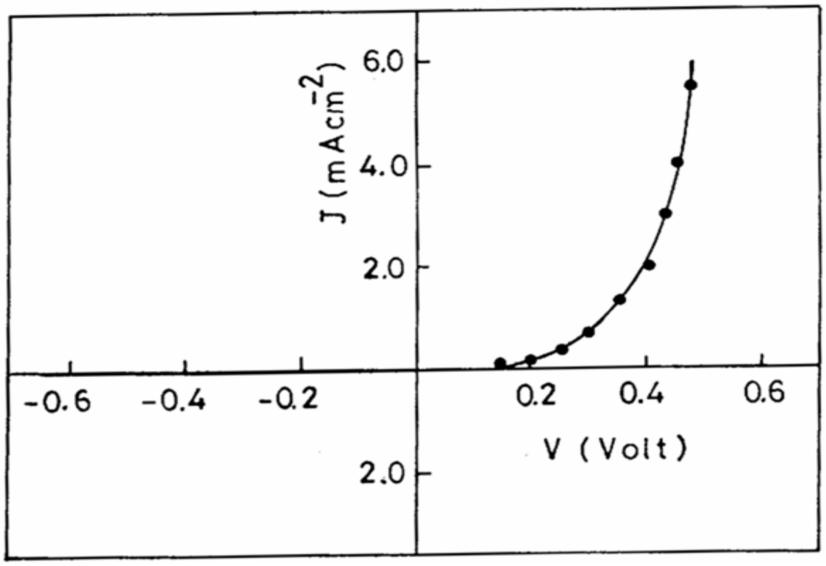

Fig. (6): Dark J-V characteristic of Au/n-GaAs Schottky junction cell.

The shunt resistance, R_{sh}, may be determined from the J-V curve under illumination shown in Fig. 5 and using the relation [11]:

$$\mathbf{R}_{\mathbf{sh}} = \left(\frac{\Delta\mathbf{V}}{\Delta\mathbf{I}}\right)_{\Delta V=0} \tag{5}$$

Its value was found to be ≅0.25 kΩ.

Dependence of the transverse photocurrent action spectra, normalized to the number of incident photons, on the wavelengths of illumination for p-CoPc/n-GaAs and Au/n-GaAs photovoltaic cells, together with an absorption spectra of CoPc films on glass substrate, is shown in Fig.(7). The CoPc film indicates a broad Q- band absorption at 600-800 nm (Fig.7c), which is due to a π - π* transition of the conjugating Pc macrocycle [15]. On the other hand, the

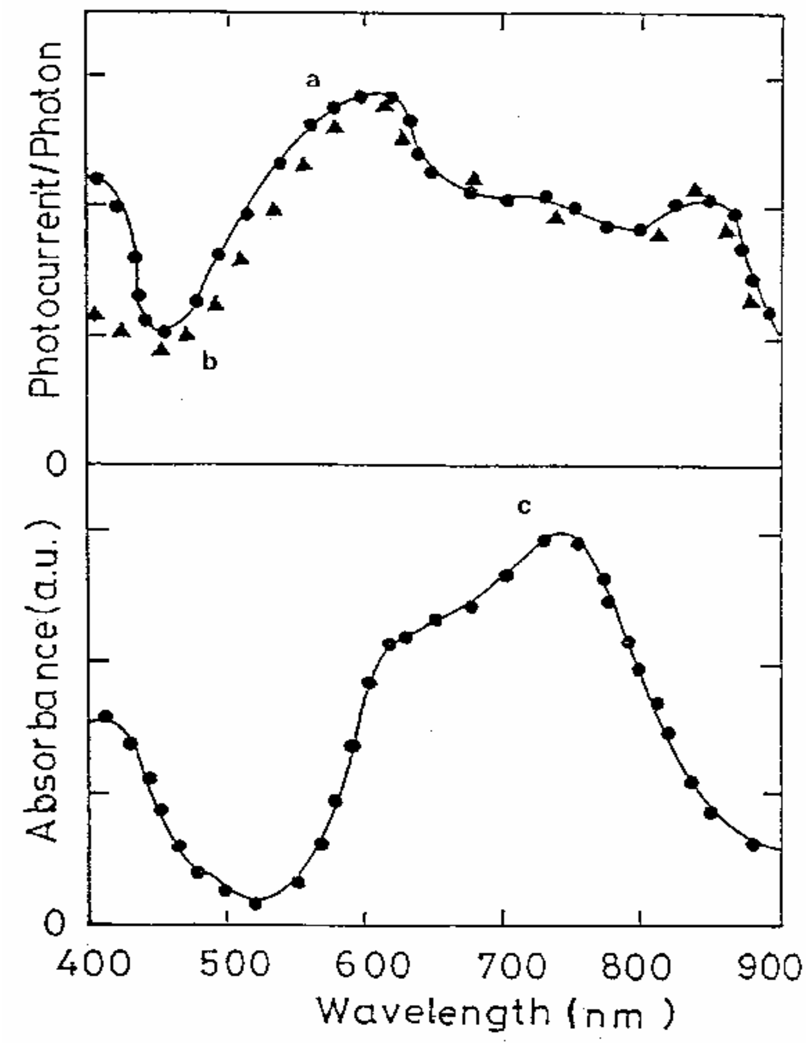

Fig. (7): Photocurrent action spectra for (a) p-CoPc/n-GaAs and (b) Au/n-GaAs photovoltaic cells. (c) absorption spectrum of CoPc films deposited on glass substrate.

Au/CoPc/n-GaAs cell with large crystallites of CoPc deposited on n-GaAs maintained at 420 K (Fig.7a) exhibits high photocurrent efficiency over the wavelength range, comparable to that for the Au/n-GaAs cell (Fig. 7b). Its action spectrum, showing a similar shape to that of the Au/n-GaAs cell, does not resemble the absorption spectrum of CoPc (Fig.7c), but rather matches the optical absorption of n-GaAs. This suggests that the charge-carrier separation occurs at the space-charge region formed near the CoPc/n-GaAs interface, so that only a small fraction of penetrated light beyond the CoPc absorber contributes to the generation of photocarriers. As mentioned above, the lower surface of n-GaAs forms the Schottky contact with Au, where space charges spread in the n-GaAs semiconductor region and the induced surface states restrict the barrier height. At the n-GaAs upper surface covered with the CoPc crystallites, on the other hand, a p/n heterojuction is formed by the CoPc/n-GaAs contact, and most of the space charges are distributed inside the CoPc. Therefore, most of the carriers are probably generated by photoexcitation at the n - GaAs surface. It is expected that excitons thus generated in the n - GaAs surface are diffused to the edges of CoPc deposit, and are efficiently separated into charge carriers by the steep potential barrier there [5,7].

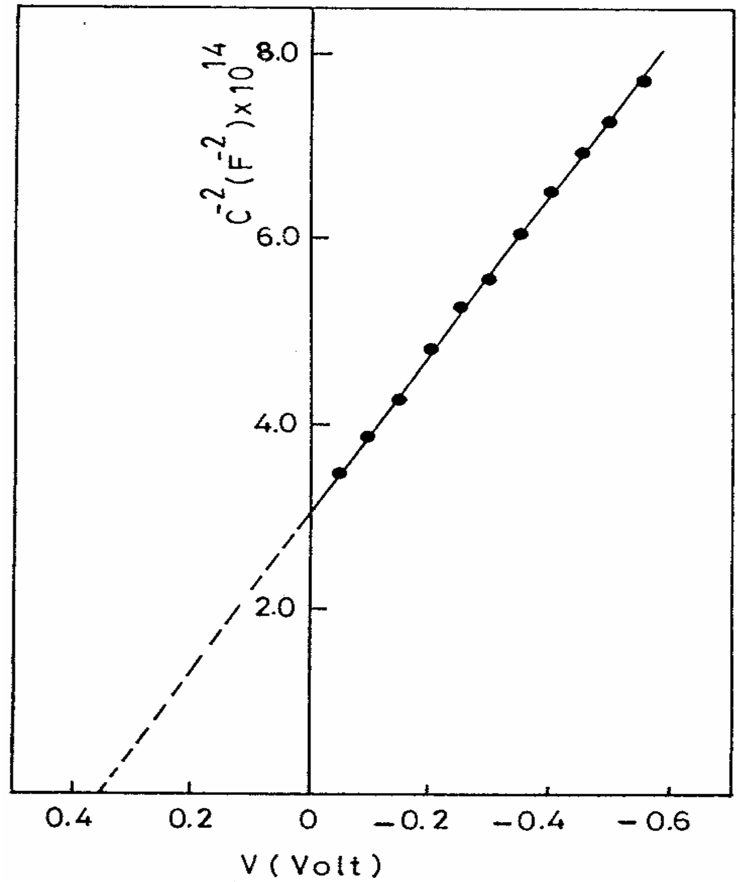

Fig. (8): Reverse-bias C^{-2} - V plot of p-CoPc/n-GaAs heterojunction measured in the dark.

Fig.(8) shows the dark C^{-2}-V characteristic of the p-CoPc/n-GaAs heterojunction cell measured in the reverse direction. As shown in this figure, it is clear that C^{-2} increases linearly with voltage. Consequently, the carrier concentration is homogenous and the linearity of the C^{-2}-V plot indicates that the junction is perfectly abrupt [16]. The free-carrier concentration, N, could be calculated from the slope shown in Fig.8 and using the relation [17]:

$$\frac{d(C^{-2})}{dV} = -\frac{2}{q\varepsilon\varepsilon_o NA^2} \tag{6}$$

where ε is the dielectric constant of CoPc, which equals 3.25 [18], assuming that the space charges are distributed in CoPc layer, and A is the effective area of the device. The derived value of N was found to be $\cong 1.2\times10^{17}$ cm^{-3} and the intercept of the line C^{-2} vs. V on the abscissa essentially gives the diffusion potential, V_b, which equals 0.35 eV. The capacitance of the device, C_0, at zero bias was measured and found to be ≅ 57.5 nF, which corresponds to a thickness ω of the depletion region ($\omega = \varepsilon\varepsilon_0 A/C_0$) of 32.4 nm.

It should be mentioned that with the Au electrode having a large work function (5.2 eV) , CoPc makes an ohmic contact as reported for various p-type MPcs [5]. When CoPc layer is deposited on GaAs, the space charges distribute within the measured layer width (ω = 32.4 nm) to produce the diffusion potential (V_b = 0.35 V), which is approximately consistent with the observed V_{oc} value (0.33 V).

4. Conclusions:

Heterojunction devices of p-CoPc/n-GaAs have been prepared by thermal evaporation of p-CoPc thin films onto n-GaAs <100> substrates. The structure of p-CoPc has been found to be polycrystalline. The junctions exhibit rectifying behavior as a p-n diode. The devices with large crystallites of CoPc deposited on n-GaAs maintained at 420 K have been exhibited high photocurrent efficiency over the wavelength range of the Q-band region. This is attributed to a space-charge layer generated inside the CoPc film, where the intervening CoPc layer prevents the n-GaAs surface from forming surface states because of noncontact with the Au top electrode. Information on the potential barrier thickness, diffusion potential and free-carrier concentration can be successfully obtained by studying the dark C-V characteristics.

References :

1. S.R. Forrest and F.F.So, *J. Appl. Phys.*, **64(1)**, 399 (1988).

2. H.Yanagi, H. Kataura and Y.Ueda, *J.Appl. Phys.*, **75(1)**, 568(1994).

3. J.Takada, H. Awaji, M. Koshioka and W. A. Nerin, *J. Appl. Phys.*, **75(8)**, 4055 (1994).

4. H.Lee and T. Kawai, *J. Appl. Phys.* **80(6)**, 3601 (1996).

5. A.S.Riad, *Thin Solid Films* **370**, 253 (2000).

6. F.H. Moser and A.L. Thomas, "*The phthalocyanines*", CRC, Boca Raton FL, (1983).

7. J. Simon and J.J Andre`, "*Molecular Semiconductors"*, Springer, Berlin, (1985).

8. Y. Nakato, M. Shioji and H. Tsu bomura, *J. Phys. Chem.,* **85**, 1670 (1981).

9. G.A. Cox and T.G. Abdel-Malik, *J. Phys.* **10C**, 63 (1977).

10. H.P.Klug, L.E.Alexander, ``*X-ray Diffraction Procedures for Polycrystalline and Amourphous Materials*``, Joun Wiley and Sons, Inc., New York (1974).

11. H.S.Soliman, M.M.El-Nahas, O. Jamjoum and KH. A.Mady, *J. Mat. Sci. Lett.*, **7**, 633 (1988).

12. S.M.Sze (1985), "*Semiconductor Devices, Physics and Technology*", New York : Wiley.

13. S.K. Das and G.C. Morris, *Solar Energy Materials and Solar cells*, **28**,305 (1993).

14. Y.Nakato, S.Nishiura, H. Oshika and H.Tsubomura, *Jpn. J. Appl. Phys*, **28**, L 261 (1989).

15. L. Edwards and M. Gouterman, *J. Mol. Spectrosc*, **33**, 292 (1970).

16. S.Darwish, H.S. Soliman and A.S.Riad, *Thin Solid Films*, **259**,248 (1995).

17. S.Darwish, A.S. Riad and H.S. Soliman, *Semicond. Sci. Technol*, **11**, 96 (1996).

18. T.G. Abdel-Malik and R.M.Abdel-Latif, *Thin Solid Films,* **286**, 277 (1996).