Electrical Transport Properties of Thermally Evaporated Phthalocyanine (H_2Pc) Thin Films

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Thin films of H_2Pc of various thicknesses have been deposited onto glass substrates using thermal evaporation technique at room temperature. The dark electrical resistivity calculations were carried out at different temperatures in the range 298-473 K. Measurements of thermoelectric power confirm that H_2Pc thin films behave as a p-type semiconductor. The current density-voltage characteristics of H_2Pc at room temperature showed ohmic conduction mechanism at low voltages. At higher voltages the space-charge-limited conduction (SCLC) accompanied by an exponential trap distribution was dominated. The temperature dependence of current density allows determination of some essential parameters such as the hole mobility (μ_h), the total trap concentration (N_t), the characteristic temperature (T_t) and the trap density P (E).

1. Introduction:

Phthalocyanines (Pcs) form a large group of organic semiconductor compounds, which have been the main basis for the search of molecular semiconductors [1]. These materials are of interest, because of their high chemical and thermal stability [2]. Phthalocyanines are similar to the macrocyclic planar aromatic compounds, exhibiting semiconducting properties. The electrical properties of phthalocyanines have received the greatest attention [3], with most work focusing on metal-substituted phthalocyanines, such as nickel phthalocyanine, NiPc[4], copper phthalocyanine, CuPc[5], zinc phthalocyanine, ZnPc[6] and molybdenum phthalocyanine, MoPc [7].

Therefore, the aim of the present work is to investigate and analyze the electrical transport properties of thermally evaporated phthalocyanine (H_2Pc) thin films to determine some essential parameters and predict the electronic conduction properties.

2. Experimental Details:

Thin films of H_2Pc have been prepared by thermal evaporation technique with thickness ranging from 138 to 460 nm, deposited onto pre-cleaned glass substrates. The deposition temperature was kept at room temperature. A high vacuum coating unit (Edwards type E 306 A, England) was used. Thin films were deposited using a quartz crucible source heated by a tungsten coil in a vacuum of 10^{-4} Pa. The rate of deposition ~ 2.5 nm s^{-1} and film thickness were controlled using a quartz crystal thickness monitor (Model FTM4, Edwards Co., England). Moreover, the film thickness was checked interferometrically by Tolansky's technique [(8)]. The dark electrical resistance of H_2Pc thin films was measured by the two probe method in the temperature range from 298 to 473 K using high internal impedance electrometer (Keithely 617A) and the temperature was measured using chromel alumel thermocouple. The ohmic contacts were made by evaporating gold electrodes. In order to study the effect of annealing, some samples were heated at 623 K in the dark for one hour in a vacuum of 10^{-3} Pa.

For the thermoelectric power measurements, copper electrodes were deposited onto the two ends of the samples, because of the thermoelectric power of copper is small compared to H_2Pc films, which can be neglected. The Seebeck coefficient was measured within the temperature range 300-400 K.

For the Space-charge-limited current measurements, H_2Pc films were sandwiched between two gold electrodes.

3. Results and Discussion:

3.1. Dark electrical Resistivity Measurements

3.1.1. The Film Thickness Dependence

Figure 1a shows the dependence of the resisitivity, ρ, (for the as-deposited H_2Pc films) on film thickness, d, at different temperatures. As illustrated, the resisitivity decreases with increasing film thickness i.e. follows the known behaviour of organic and inorganic semiconductors [9, 10]. Figure 1b shows the dependence of the resistivity, ρ, (for annealed films at 623 K for one hour) on film thickness at different temperatures. As seen from the figure, the same behaviour for the as-deposited H_2Pc films is obtained for the annealed films at 623 K for one hour. So, the film thickness, d, has unremarkable effect on the resistivity.

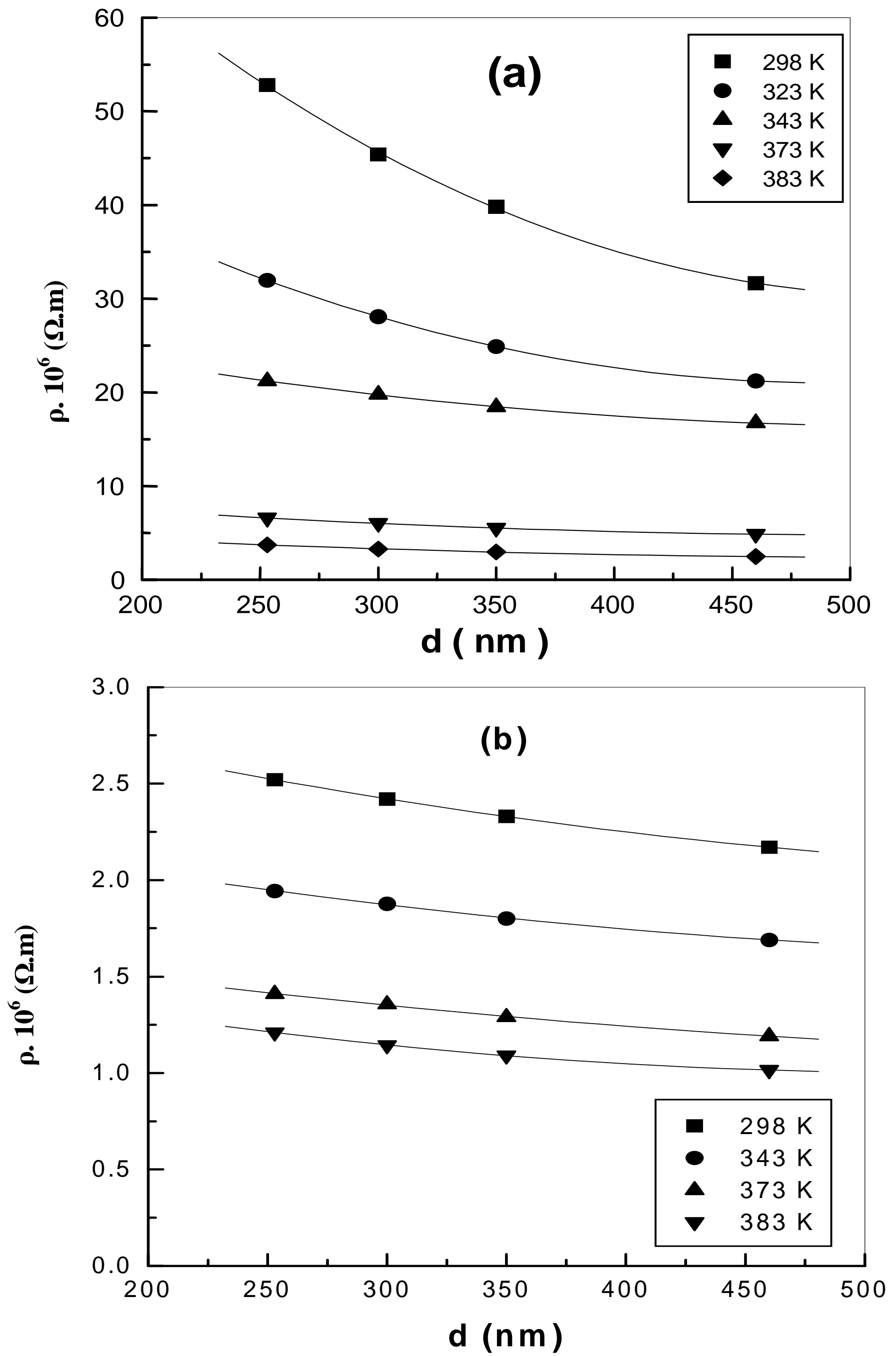

Fig. (1): The dependence of the dark electrical resistivity ,ρ, for H_2Pc thin films (a) as-deposited and (b) after annealing

3.1.2. The Temperature Dependence.

The electrical resisitivity of H_2Pc thin films were performed to determine the thermal activation energy. Measurements were carried out in the temperature range 298 to 473 K for films with different thickness ranging from 253 to 460 nm. The temperature dependence of the resistivity can be expressed by Arrhenius equation. [11]:

$$\rho = \rho_\circ \exp (\Delta E / k_B T) \tag{1}$$

where ΔE is the thermal activation energy and k_B is the Boltazmann′s constant. A plot of ln ρ against (1000 / T) yields a straight line whose slope can be used to determine the thermal activation energy of the film. Fig. (2a) shows the dependence of the dark electrical resisitivity of as-deposited H_2Pc films of different thickness on the temperature. As seen from the figure, there are two semiconductor distinct linear parts, which correspond to two activation energies ΔE_1 and ΔE_2. The activation energies ΔE_1 and ΔE_2 were obtained at T < 360 K, and T > 360 K, respectively. ΔE_1 corresponds to extrinsic region, and ΔE_2 corresponds to intrinsic region. The change in the slope and hence the activation energy is interpreted as a change from extrinsic to intrinsic conduction [12]. The value of the thermal activation energy ΔE_1 is nearly 0.156 ± 0.019 eV and ΔE_2 is nearly 0.766 ± 0.12 eV, which is in good agreement with those obtained by other workers [3-15]. The temperature dependence of the resistivity for annealed films is shown in Fig. (2b) .The values of activation energies ΔE_1 and ΔE_2 decreased after annealing to 0.057 ± 0.001 eV, and 0.196 ± 0.001eV, respectively. This may be referring to the change in the degree of crystallinity.

3.2. Thermoelectric power measurements

The variation of Seebeck coefficient, S, for H_2Pc thin films with temperature is shown in Fig. (3). It can be seen from the figure that the value of S is positive over the entire temperature range as observed for PbPc [16], CuPc [17] and FePc [12]. The positive value of Seebeck coefficient indicates p-type conduction.

For the organic materials [12], the concentration of holes was calculated as follows:

$$p_\circ = 2\left(\frac{2\pi m_h^* k_B T}{h^2}\right)^{3/2} e^{\frac{-\Delta E}{k_B T}} \tag{2}$$

where m_h* is the effective hole mass ≅ 1.06×10^{-29} Kg. [18]. ΔE is the thermal activation energy, which was obtained from temperature dependence of resistivity. The conductivity is equal to:

$$\sigma = |e| p_\circ (\mu_h + \mu_e) = |e| p_\circ \mu_h (1+c) \quad (3)$$

where μ_h is the hole mobility, μ_e is the electron mobility and c the mobility ratio i.e., μ_e / μ_h.

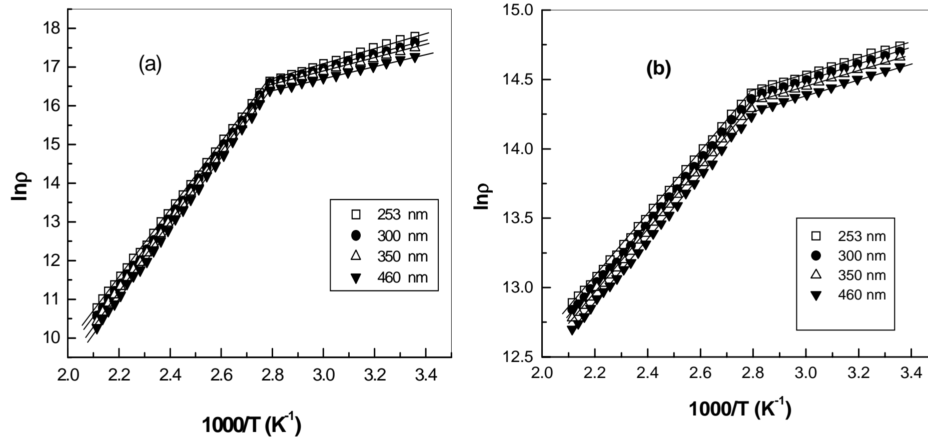

Fig. (2): Variation of the dark electrical resistivity,ρ, against 1000/T for H_2Pc thin films (a) as-deposited and (b) after annealing.

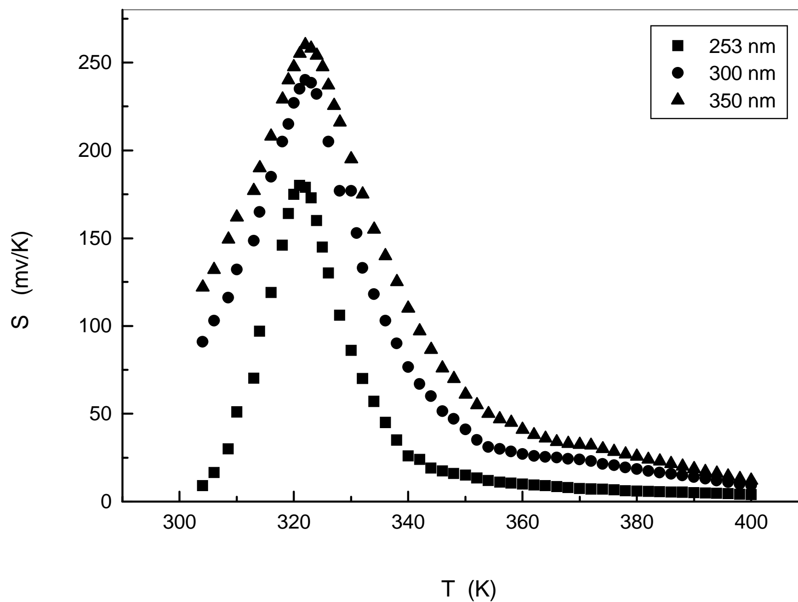

Fig. (3): Variation of seebeck coefficient, S, of H_2Pc thin films against temperature..

The Seebeck coefficient can be given as [12]:

$$S = \frac{-k_B}{|e|}\left(\frac{c-1}{c+1}\right)\left(\frac{\Delta E}{k_B T}+2\right) \tag{4}$$

It is possible to calculate p_o from eqn. (2). In addition, the value of c can be determined from the slope of the graph of S against 1/T in the intrinsic region as shown in Fig. (4), and then by substituting p_o and c in eqn. (3) the hole mobility is obtained. The mean values obtained for p_o, c and μ_h are 1.967×10^{17} m^{-3}, 0.663 and 8.54×10^{-6} $m^2V^{-1}s^{-1}$, respectively. A positive Seebeck coefficient can arise for an intrinsic semiconductor in which the mobility of the positive charge carriers is greater than that of the negative carriers.

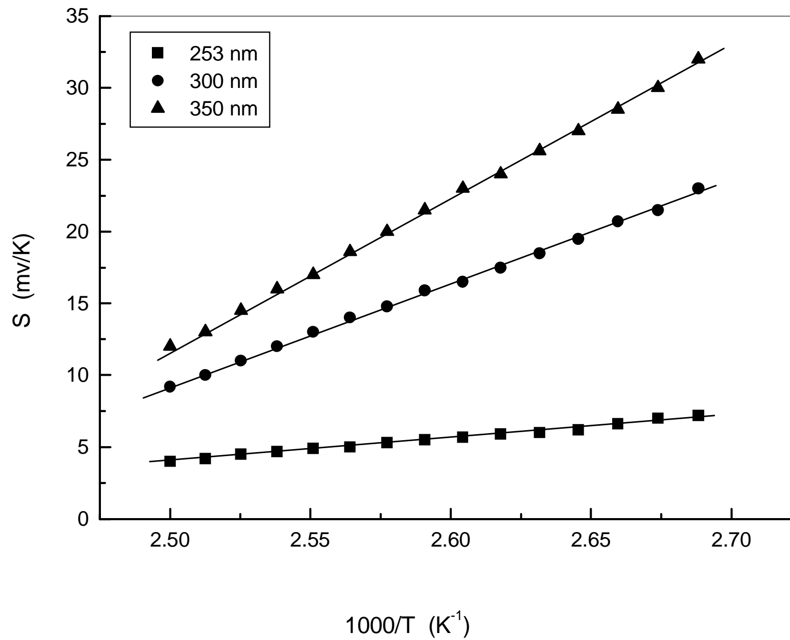

Fig. (4): Variation of Seebeck coefficient, S, of H_2Pc thin films against 1000/T.

3.3. Ohmic conduction and SCLC measurements

3. 3.1 Capacitance – voltage measurements

The capacitance – voltage measurements have been performed at room temperature for films, sandwiched between two ohmic contact electrodes, of varying thickness of H_2Pc ranging from 101 to 312 nm. Fig. (5) shows the variation of the capacitance, C, as a function of reciprocal film thickness, 1/d,

of the films. As it is clear from Fig.5, a linear relationship is obtained verifying the equation. [19]:

$$C=\varepsilon A/d \qquad (5)$$

where ε is the permittivity of H_2Pc and A is the effective sample area, which is equal to 1×10^{-6} m^2. The relationship between capacitance and the reciprocal film thickness is linear, with the slope of εA. The derived value of ε is 4.071×10^{-11} Fm^{-1}, which is in good agreement with available literature values: 3.19×10^{-11} Fm^{-1} [20, 21] and $2.12 - 4.5 \times10^{-11}$ Fm^{-1} [22, 23] for CuPc. The derived values of ε will be used in the analysis of the remaining reported measurements.

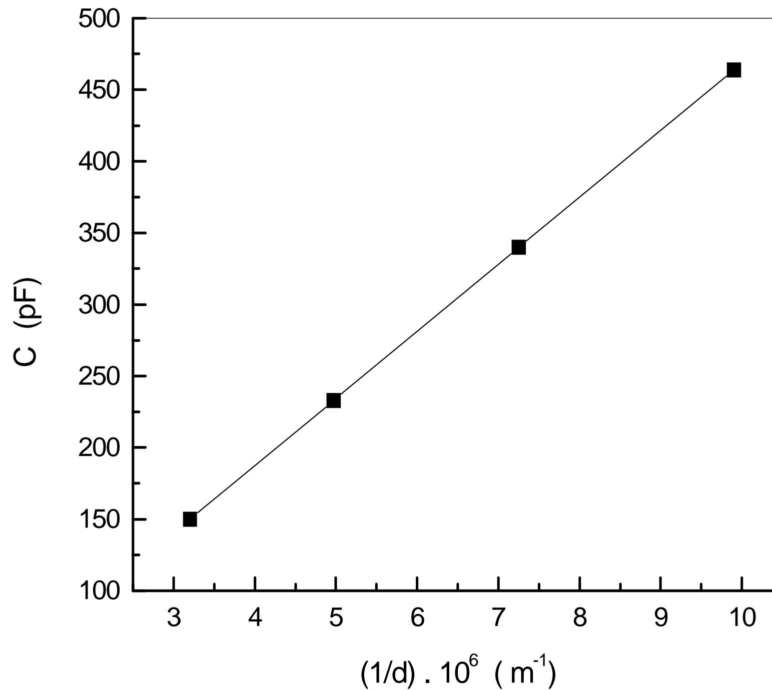

Fig. (5): Dependence of the capacitance, C, on the reciprocal of thickness, 1/d.

3.3.2 Current density – Voltage measurements

Figure (6) illustrates current density-voltage characteristics for H_2Pc in sandwich structure, of thickness ranging from 138-312 nm. As observed there are two distinct regions in this characteristic. At low voltages, the slopes of the log J versus log V plots are approximately equal to unity, while at higher voltages, above a well-defined transition voltage, V_T, the slopes are

approximately equal to 3.9. This value is in good agreement with that obtained by Amar et al. [24] for H_2Pc samples. At low voltages below V_T, the ohmic conduction is dominated and the dependence of J on V for a p-type material may be described by Ohm's law [25], given by:

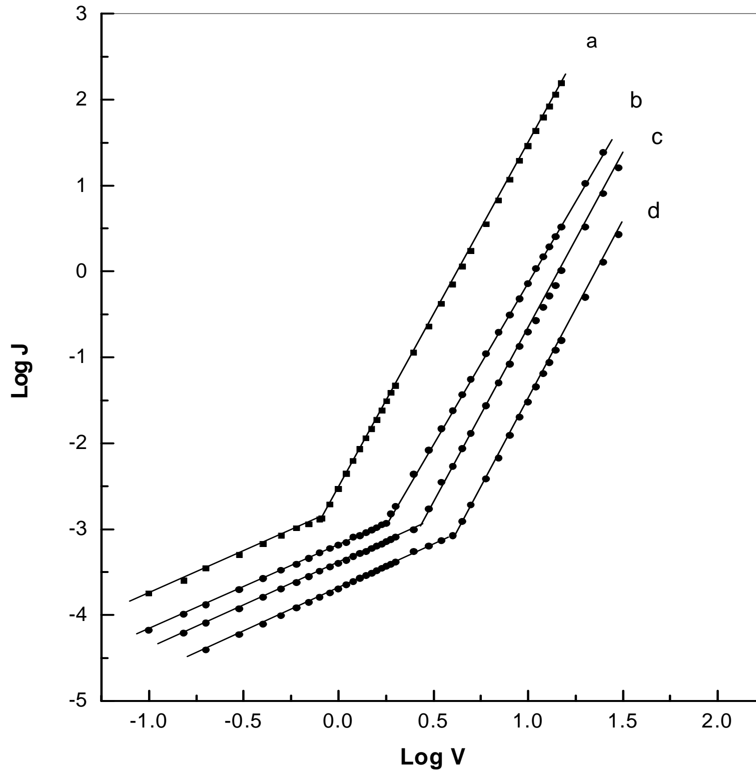

Fig. (6): Dependence of the current density, J, on the applied voltage, V, for samples of different thickness (a) 138, (b) 201, (c) 253 and (d) 312 nm.

$$J = p_o \, e \, \mu_h \, V/d \tag{6}$$

where J is the current density, p_o is the concentration of thermally generated holes in the valence band, e is the electronic charge, μ_h is the hole mobility, V is the applied voltage and d is the film thickness. At higher voltages the space-charge-limited conduction (SCLC) is dominated, with an approximate slope of 3.9. The J-V dependence in the SCLC region is given by [26]:

$$J = e\mu_h N_V \left(\frac{\varepsilon}{eP_o k_B T_t} \right)^l \frac{V^{l+1}}{d^{2l+1}} \tag{7}$$

where N^V is the effective density of states in the valence band, k_B is the Boltazmann′s constant, $P_\circ$ is the trap density per unit energy range at the valence band edge, ε is the permittivity and l is the ratio T_t / T, where T is the absolute temperature and T_t is temperature parameter characterizing trap distribution. For the cases where the exponent m > 2, the power law ($J \alpha V^m$) representing SCLC region appears to be dominated by an exponential distribution of trap levels in energy above the valance band edge according to the equation [24]:

$$P(E) = P_\circ \exp(-E / k_B T_t) \quad (8)$$

where P (E) is the trap density per unit energy range at an energy E above the valence band edge. From Fig.(6) the slope of 3.9 implies that $l = 2.9$ and thus the temperature parameter which characterises the trap distribution $T_t = 870$ K for a measurement temperature of 300 K. These values approach to those; slope of 4, $l = 3$ and $T_t = 900$ K derived for metal-free phthalocyanine [24].

The transition voltage, V_T, separating ohmic conduction and SCLC mechanism is given by [20]:

$$V_T = \left(\frac{p_\circ}{N_V}\right)^{1/l} \frac{d^2 e N_t}{\varepsilon} \quad (9)$$

The dependence of transition voltage on film thickness, d, is shown in Fig.(7). A linear relationship is obtained with a slope equal to 2, verifying eqn. (9). Figure 8 shows the thickness dependence of current density, J, for both ohmic current and SCLC regions at certain fixed values of voltages at room temperature. The ohmic dependence (slope of ≈ 1) exhibits good ohmic contacts. The slope of ≈ 6.71 in the SCLC region verifies the space-charge-limited conduction dominated by an exponential distribution of traps. From eqn. (7) the slope in this region should be ($2l + 1$) implying that $l \approx 2.86$, which is in excellent agreement with the values deduced from the J – V characteristics of Fig. (6).

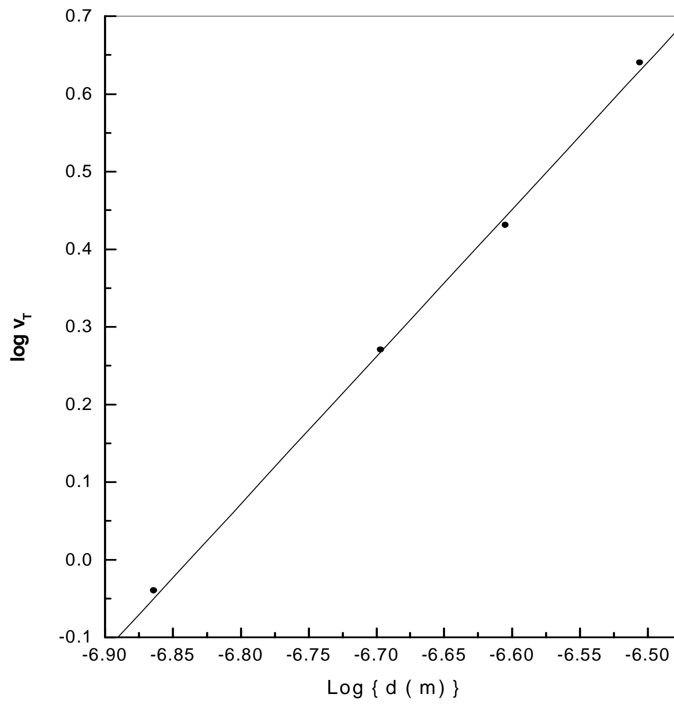

Fig. (7): Dependence of the transition voltage, V_T, on the film thickness.

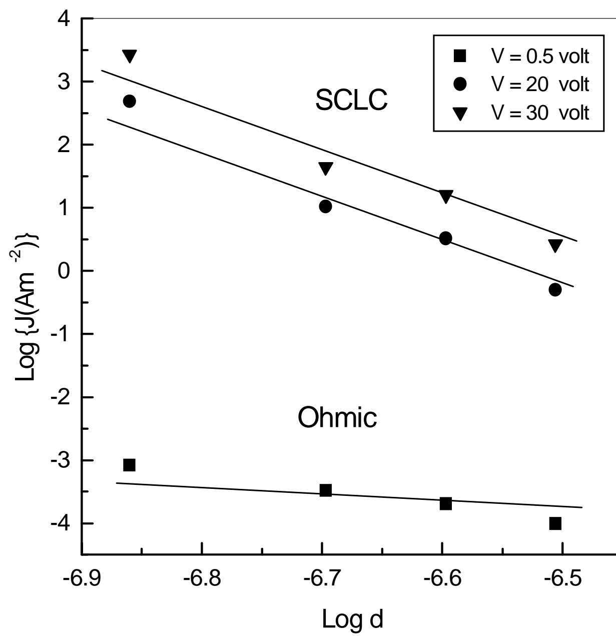

Fig. (8): Dependence of the current density, J, on the thickness, d, for various constant voltages in the ohmic and SCLC regions.

3.3.3. Temperature dependence

Figure (9) shows the dependence of log J on the reciprocal of temperature at different constant voltages for a sample of thickness 312 nm in the temperature range 300 to 400 K. Linear segments are obtained, which upon extrapolating in the direction of ordinate axis, it interacts at a common point whose coordinates [16] are given by:

$$\log J = \log\left(\frac{e^2\mu_h d N_v N_t}{\varepsilon}\right), \qquad \frac{1}{T} = -\frac{1}{T_t} \tag{10}$$

The slopes of these lines are given by

$$S = \frac{d(\log J)}{d(1/T)} = T_t \log\left(\frac{\varepsilon V}{ed^2 N_t}\right) \tag{11}$$

Moreover, the intercept with the log J axis is given by

$$\log J_\circ = \log(e\,\mu_h\, N_v V / d) \tag{12}$$

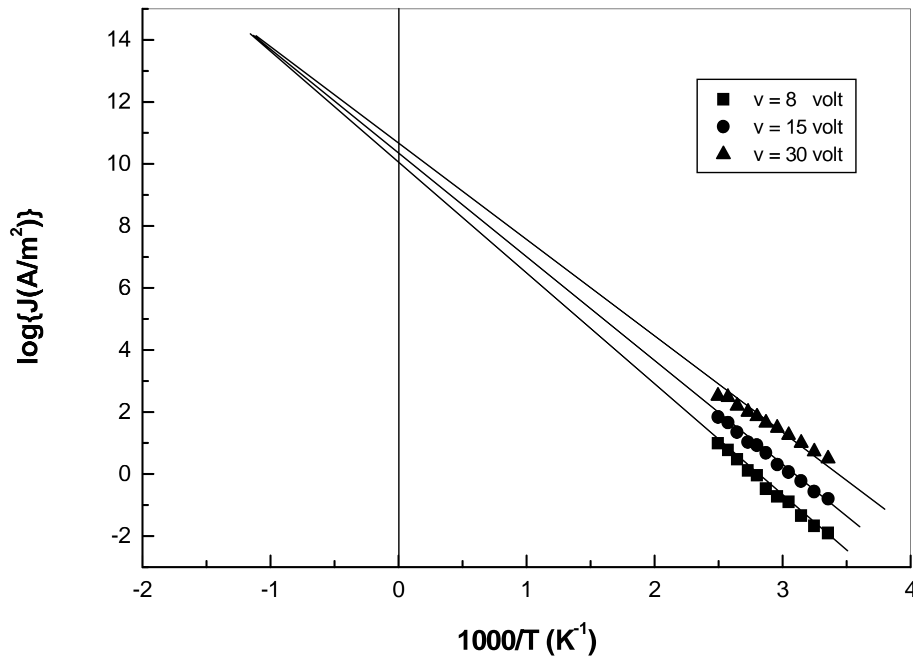

Fig. (9): Dependence of the current density, J, on the reciprocal temperature as a function of the applied voltage for a sample of H_2Pc of thickness 312 nm.

$J_\circ$ represents the current density at infinite temperature (1 / T = 0). The value of mobility μ_h can be obtained from eqn. (10) by substituting the value of $N_v = 10^{27}$ m^{-3} [18]. The measured value of T_t is ≈ 870 K, which is in good agreement with that obtained from the SCLC measurements. The value of trap concentration ($P_\circ$) per unit energy range at the valence band edge can be calculated from eqn. (7) by substituting the value of μ_h, N_v and the value of permittivity, ε, in it. The total trapping concentration N_t can be determined from the following equation. [27]:

$$N_t = P_\circ k_B T_t \tag{13}$$

The mean values of the obtained hole mobility, μ_h, the trap concentration per unit energy range at the valence band edge, $P_\circ$, the total trapping concentration, N_t and the hole concentration, $p_\circ$, are collected together with the published data in Table (1). The exponential trap distribution of eqn. (8) associated with SCLC is thus completely specified and is shown in Fig.(10).

Table (1): The calculated values of μ_h, $P_\circ$, N_t and $p_\circ$ for H_2Pc in comparison with that of the published Phthalocyanine derivatives.

Parameter / compound	**μ_h(m^2 $V^{-1}s^{-1}$)**	**$P_\circ$ ($J^{-1}m^{-3}$)**	**N_t (m^{-3})**	**$p_\circ$ (m^{-3})**
H_2Pc (our result)	1.63×10^{-6}	7.38×10^{45}	8.71×10^{25}	7.45×10^{15}
H_2Pc[28]	6.25×10^{-7}	1.29×10^{46}	1.6×10^{26}	8×10^{18}
CuPc[25]	5.1×10^{-7}	3.55×10^{43}	3.67×10^{23}	--------
NiPc[29]	1×10^{-7}	1.15×10^{42}	2.89×10^{22}	3.2×10^{15}
PbPc[16]	6.05×10^{-10}	2.79×10^{43}	2.97×10^{23}	1.6×10^{18}
FePc[12]	1×10^{-10}	2×10^{43}	2×10^{23}	1×10^{18}

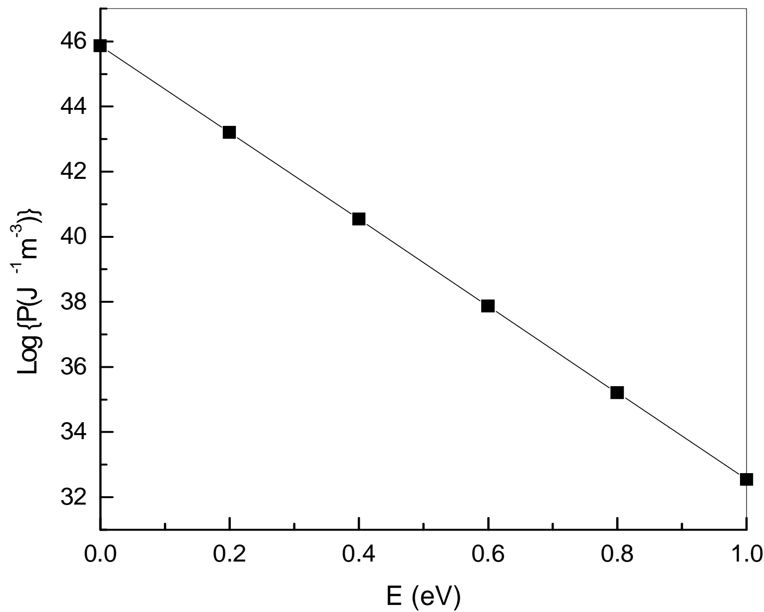

Fig. (10): The variation of P (E) as a function of energy.

4. Conclusions:

The main conclusion of the present work can be summarized as follows: The dark electrical resistivity, ρ, calculated for H_2Pc thin films decreases with increasing the film thickness. The two activation energies ΔE_1 and ΔE_2 determined below and above 360 K equal 0.156 ± 0.02 and 0.766 ± 0.12 eV, respectively. The change in activation energy is interpreted as a change from extrinsic to intrinsic conduction. The values of activation energy decrease by annealing process for H_2Pc thin films at 623 K for one hour. Seebeck coefficient measurements showed that H_2Pc thin films behave as p-type semiconductors, where the mobility of the positive charge carriers is greater than that of the negative charge carriers. The current transport mechanisms of Au-H_2Pc-Au system are ohmic conduction followed by space-charge-limited conduction with exponential distribution of traps levels at low and high voltage, respectively.

Acknowledgements

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