Electrical properties study of Copper Phthalocyanine (CuPc) thin films

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(Abstract)

Thin film of copper phthalocyanine has been deposited onto glass substrates by using thermal evaporation technique at room temperature. The dark electrical resistivity (ρ) and thermoelectric power measurement were carried out at different temperatures in the range (293-503)K. The temperature dependence of current density allows the calculation of thermal activation energy that was (0.79)eV. Room temperature current-voltage characteristics measurement, using Hull effect allows the calculations of some essential parameters such as the electron mobility and concentration of electrons .

1. Introduction:

The phthalocyanines are a class of organic semiconductors which are chemically and thermally stable., and, thus, suitable for the preparation of thin films [1] . Phthalocyanines are widely used as charge generation materials in solid-state devices such as solar cells, electrophotography, security printing, gas detectors [2,3,4]. The mobile π electron of phthalocyanine can serve as current carries and provide the basis for semiconductor properties and to increase the current carries by substituting Cu metal by H_2. However, conductivity of these materials depends on the gaseous environment surrounding the material [5,6,7] . The electrical properties of phthalocyanines have been widely studied in the form of sandwich structures. The p-type semiconductivity is , thus, strongly modified by gaseous adsorption and is also dependent on impurities [8] and on film structure [9].

In the present work, thin films of copper phthalocyanine have been fabricated by thermal evaporation onto glass substrates. The electrical transport properties such as the dark electrical resistivity , conductivity, mobility, concentration of electrons and the thermoelectric power as well as thermal activation energy has been studied.

2. Experimental Details:

preparation of copper-phthalocyanine in the laboratory achieved by mixing (200gm)of phthalimide ($C_8H_5NO_2$)with (600ml) of concentrated ammonia solution (NH_3) in a one liter beaker and magnatic stir mechanically for(24 hours), the yield is (200gm)phthalamid ($C_8H_8N_2O_2$).

$$C_8H_5NO_2 + NH_3 \xrightarrow{Magnatic\ \ stir\ \ mechanically} C_8H_8N_2O_2$$

And in a one liter flat-bottom flask ,provided a reflux condenser, place (100gm) of phthalamid and (350ml) of acetic anhydride the yield is phthalonitril ($C_8H_4N_2$)

$$C_8H_8N_2O_2 + (CH_3CO_2)_2O_3 \xrightarrow{Reflux\ \ Condenser|\ \ heat} (C_8H_4N_2)$$

And when copper(Cu) is added to the yield we get CuPc ($C_{32}H_{16}N_8Cu$). {10}

$$4C_8H_4N_2 + Cu \xrightarrow{Oil\ \ path\ \ 220^\circ C} C_{32}H_{16}N_8Cu$$

Thin films of CuPc have been prepared by conventional thermal evaporation technique in university of Baghdad college of science department of physics , deposited onto pre-cleaned glass substrates kept at ambient conditions using a high vacuum coating unit (Edwards type E 306A). The evaporator was a quartz crucible source heated by tungsten coil in a vacuum of ($2*10^{-4}$ tor) during deposition. The deposition rate was controlled at (2 nm.s^{-1}).

To measure the electrical properties and other related properties of the CuPc , an ohmic contact for the prepared samples are produced by evaporating Aluminum electrodes of (200nm) thickness ,by means of thermal evaporation methods, we used various shapes of masks on the front side substrate onto CuPc to evaporate a suitable sample shape to suit the required measurement that is shown in Fig.(2). These masks have been cleaned carefully, then they were properly attached to the substrate and fixed at the substrate holder of the coating unit-Aluminum with a high purity (99.999), was used for the front side contacts,and we used an Al mask to create Al electrodes which were suitable for both electrical and detection measurements.

The dark electrical resistivity (ρ) of CuPc thin films was measured by the two probe method in a reasonable temperature range using high internal impedance electrometer (Keithly 616) and the temperature was measured using cromel-alumel thermocouple and contacts were made by evaporating high purity Al electrodes. Current – voltage measurements were made using a (Keithley616) programmable electrometer with internal power supply.

3. Result and discussion:

The dark electrical resistivity of CuPc thin film has been carried out in the temperature range (293-503)K. The temperature dependence of conductivity is expressed as follows {11}:

$$\sigma = \sigma_o \exp(\Delta E / K_B T) \text{ ---------(1)}$$

Where : ΔE= Thermal activation energy of free charge carriers.
K_B= Boltzman's constant.

To measure the electrical conductivity we measure the electrical resistivity of the deposition film was determined by by equation {12}:

$$\rho = \frac{RA}{l} \text{ -----------------(2)}$$

Where: R-Resistance of film=$142.3*10^{-9}$Ω at room temperature T= 273K
A- Area= width (w)* thickness (t)
$=0.3cm * 5*10^{-5}cm= 1.5*10^{-5}\ cm^2$
l –the distance between the probes on the line (l=0.2cm)

therefore, the electrical resistivity :

$$\rho = \frac{142.3*10^{9}\,\Omega*1.5*10^{-5}\,cm^2}{0.2cm} = 1.06725*10^{7}\,\Omega.cm$$

Later we can determine the conductivity by {13}:

$$\sigma = \frac{1}{\rho} = 9.3*10^{-8}\ \Omega^{-1}.cm^{-1} \text{ at } T=273K$$

A plot of lnσ against (1000/T) yield a straight line whose slope can be used to determine the thermal activation energy of the film Fig.(1), we 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□383K and T□383K, respectively. ΔE_1 corresponds to intrinsic region ,and ΔE_2 corresponds to extrinsic region . The change in the slope and hence the activation energy is interpreted as a change from extrinsic to intrinsic conduction {14}.

The value of thermal activation $\Delta E_1$and ΔE_2 are (0.79 eV) and (0.24 eV) respectively , which is in good agreement with other works {15}.

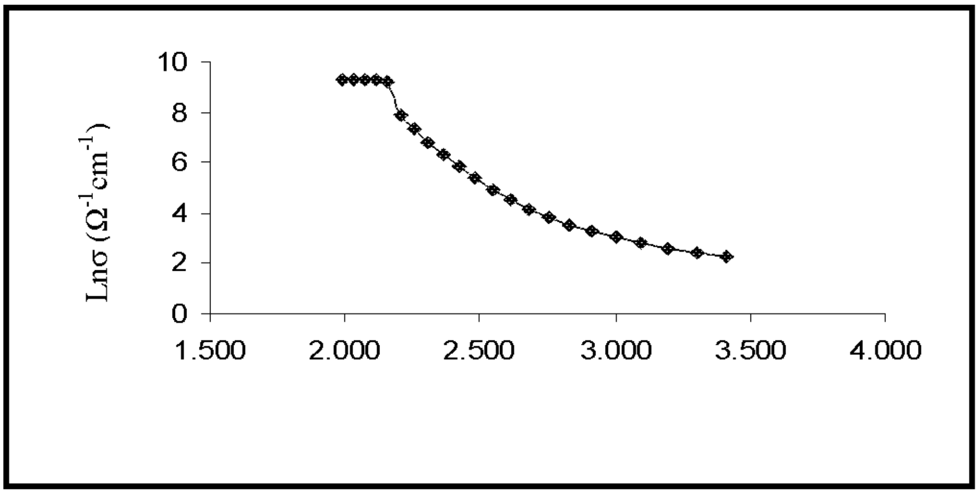


Fig. (1) : the variation of conductivity Lnσ against temperature 1000/T of CuPc thin films

the conductivity effected strongly with temperature variation observing that increase in conductivity with temperature increase

$$\ln\sigma = \ln\sigma_{\circ} - \frac{\Delta E}{KT} ------------(3)$$

Here we measured the changing in Lnσ with T change as shown in fig. (1) , from the gradient of this line we calculate the activation energies of the material. Using eq. (3):

$$\ln\sigma = -\Delta E * \frac{1000}{T} * \frac{1}{K_B * 1000}$$

$$\Delta E_a = -\frac{\ln\sigma}{1000/T} * 0.0862 = -slope * 0.0862$$

Slope (1) = -9.171 when T □383K

ΔE_1=0.79 eV

Slope(2) = -3.021 when T □ 383K

□E_2= 0.249 eV

In order to determine the electrical conductivity the method of Hall-effect is used. Four Aluminum stripes are deposited on the sample to act as electrodes using thermal evaporation in vacuum. An Aluminum mask is used to achieve the desired shape, size and position of the electrodes. After the completion of the deposition of the electrodes ,silver paste is used to solder connection wires. The circuit shown in Fig.(2) is used for the measurement.

A dc-magnetic field is applied perpendicular to the surface of the sample . Measurements of current and voltage is performed and the data is used to determine Hall-coefficient , electrical conductivity, carrier concentration and its type.

Hall effect was used to determine type of the carriers and charge concentration by putting the slides of CuPc under magnetic field (B=0.257Tesla) Fig. (2), by changing the supply voltage V(2-40)volt .

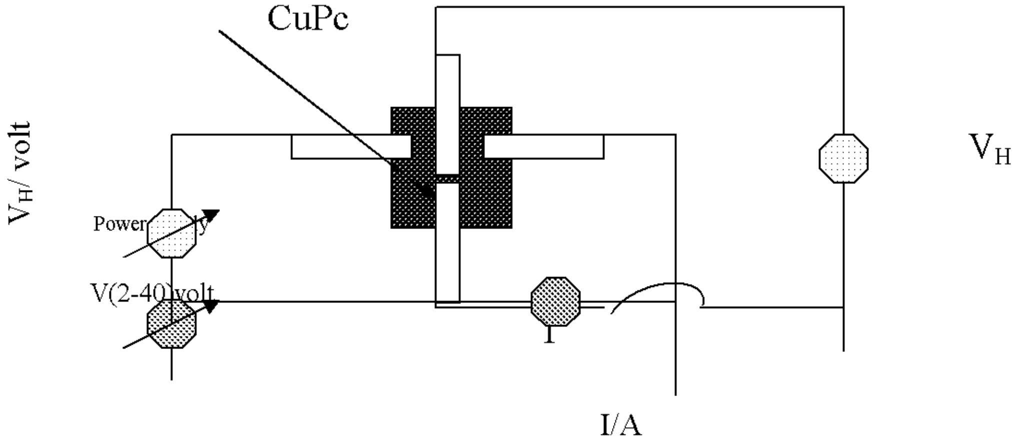
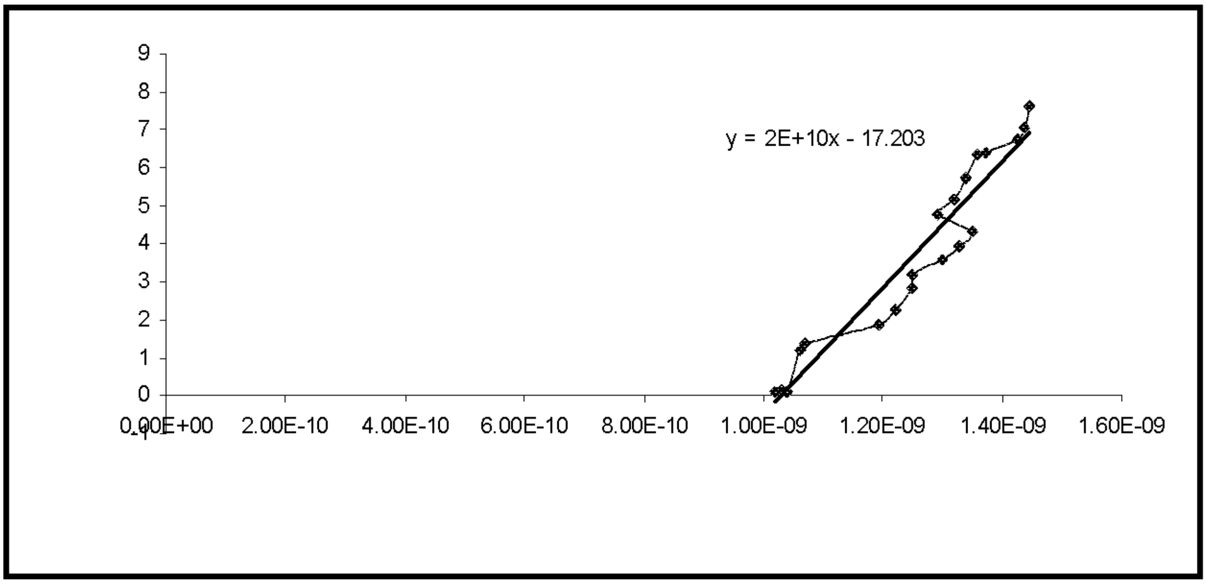


Fig. (2) Hall effect shown slides site CuPc under the magnetic field

*Fig.(3) the variation of V_H against current **I** and obtain slope.*



In Hall- effect experiment , the relation between the potential difference and the current which passes through the sample after applying a magnetic field as shown in Fig.(3) was plotted , and it was found that the relation between the current and Hall-voltage is liner, and from the slope of the line and the thickness of the sample(t= 500nm) and the value of the magnetic flux density (B= 0.257 T) , the calculated value of Hall coefficient is :

$$R_H = \frac{V_H}{I} * \frac{t}{B} -------------- (4)$$

Where : t- Thickness of slide = $5*10^{-7}$m.

R_H= slope* t/B = $2*10^{10} * 5*10^{-7} / 0.257 = 3.89*10^{4}\ m^3/C$

And from the geometry of he experiment and the slope of line it is concluded that the charge carriers are positive (p-type).
From Hall coefficient , the concentration of the carriers can be found :

$$R_H = \frac{1}{pq} \Rightarrow p = \frac{1}{R_H q} = 1.606*10^{14}\ m^{-3} ------- (5)$$

And from the measured value of the conductivity at room temperature,
σ - the conductivity at rome temperature = $9.3*10^{-6}\Omega^{-1}.m^{-1}$
On can obtain the value of mobility :

$$\mu_h = \sigma * |R_H| ---------- (6)$$

$\mu_h = 9.3*10^{-6}\Omega^{-1}.m^{-1} * 3.89*10^{4}\ m^3/C = 0.\ 3617\ m^2.V^{-1}.sec^{-1}$

4- **Conclusions:**

The main conclusion of the present work can be summarized as follows:

- The nonlinear relation between Lnσ and 1000/T due to the polycrystalline in the molecules of copper phthalocynine (CuPc).
- The two activation energies ΔE_1 and ΔE_2 determined below and above (382K) equal ΔE_1= 0.79 eV and ΔE_2 = 0.24 eV respectively . the change in activation energy is interpreted as a change from extrinsic to intrinsic conduction.
- The straight line relation between voltage (V_H) and current(I) under Hall effect experimental means that the CuPc is p-type.

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دراسة الخواص الكهربائية لغشاء فثالوسيانين- نحاس

الخلاصة

حضرت أغشية فثالوسيانين –نحاس وذلك ترسيب مادة CuPc على قواعد زجاجية باستخدام طريقة التبخير الحراري في درجة حرارة الغرفة ، وتم قياس المقاومية الكهربائية (ρ) ولمدى مختلف من درجات الحرارة K(273-503) . وباعتماد درجة الحرارة على كثافة التيار تم حساب طاقة التنشيط للمادة CuPc وكانت (0.79eV).

وتم دراسة الخواص الكهربائية للنموذج المصنع من خلال قياس تيار-جهد في حالة الظلام بأجراء تجربة هول لمعرفة نوع التوصيلية الكهربائية للحاملات وحساب تركيزها وكذلك حساب التحركية للحاملات.