Research Article

Study the Effect of Annealing Temperature on the Structural, Morphology and Electrical Properties CoPc Thin Films

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Abstract

Cobalt Phthalocyanine (CoPc) thin films with different annealing temperatures (298,358,408,458)K have been prepared by thermal evaporation technique on glass substrate at RT under vacuum of 10^{-5} mbar Using Edwards 306 system with rate of deposition equal to 15 nm/minute. The structure and surface morphology of CoPc as powder and thin film of thickness (150 nm) were studied using X-ray diffraction and atomic force microscope (AFM), and showed that there are changes and enhance in the crystallinity and surface morphology due to change in the annealing temperatures. Analysis of X-rays diffraction patterns of CoPc in powder form showed that it had an β-polycrystalline phase with monoclinic system. Thermal evaporation of CoPc at different annealing temperatures led to α-crystalline films oriented preferentially to the (100) plane with different annealing temperatures. The mean crystallite size increased with annealing temperatures. This result was supported by AFM measurements, which exhibited a relatively larger grain size. The electrical properties of these films were studied with different annealing temperature, CoPc has two activations energy. Carrier's concentration and mobility was calculated. Hall measurements showed that all the films are p-type.

Keywords: Organic semiconductor, Cobalt Phthalocyanine, evaporation, X-ray diffraction, AFM , Electrical properties .

Introduction

Semiconductors are characterized by covalent bonding between atoms in the crystal. The basic property of semiconductors is its electrical conductivity, which depends on the mobility and concentration of charge carriers (A. M. Saleh *et al*, 2012; Honeybourne C L *et al*, 1983) . Numerous studies have been conducted in the last few years to the properties of conducting organic materials in view of their application as active semiconducting films in electronic devices Recently, many research groups from all over the world have focused on studying the various properties of phthalocyanine organic semiconductor thin films, bulk material or pellets. Metal-free and/or metal-substituted phthalocyanine systems are examples of such compounds. Phthalocyanines are aromatic and chemically stable compounds with semiconducting properties and also dense colors, which make them suitable for use as dyes and pigments in textile industries. In addition, many of these compounds have been technologically employed as gas sensors, solar cells, and opto-electronic devices (Wilson A *et al*, 1987; Van Ewyk R L *et al*, 1981). Phthalocyanine compounds such as NiPc, CoPc and CuPc have been intensively studied and then manufactured as gas sensing devices (Huo L, Cao L *et al*, 2001; Ho K C *et al*, 2001; Rellaa R *et al* 2002). These materials are generally p- type semiconductors; they can easily be sublimed resulting in high purity thin films without decomposition.

The electronic transports in phthalocyanines show ohmic conduction at low voltages and space charge limited conduction at high voltage (S.I. Shihub *et al*, 1995; R.D. Gould *et al*, 1993, S.I. Shihub *et al* 1993, S.I. Shihub and R.D. Gould, 1995). Discrete trap levels located in the conduction band is dominated either by an exponential trap distribution or by a uniform trap distribution (S. Ambily *et al*, 1999; Jason Locklin *et al*, 2006; H.S. Soliman *et al*, 2007). In the case of cobalt phthalocyanine (CoPc) thin films, the knowledge of the surface morphology and the preferred orientations of the crystallites are essential for their successful applications. In order to examine the molecular arrangement and crystallite orientation studies were performed on vacuum-deposited films of CoPc on crystalline substrates. The polymorphism of crystalline structure of CoPc layers plays an important role within the preferred orientation in CoPc layers. The preferred orientation is usually determined by sample preparation conditions such as type of crystallographic structures of the substrate surface used, substrate temperature, deposition rate, and quality of the substrate surface. Moreover, it was shown that organic single crystal devices show a markedly enhanced performance. Obviously, control of the growth of organic molecules on single crystal surfaces is needed for a further improvement in the device performance (A.K. Hassan *et al*, 1992; M.M. El-Nahass *et al*, 2003; Murali Gedda *et al*, 2014). In this study, the structural, morphology and some of the electrical properties of Co-phthalocyanine thin films are investigated and analyzed over a wide range of annealing temperature.

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Table 1: The lattices constants of CoPc powder

Parameter	present work	standard values	Error ratio %
a(A)	14.32	15	4.53
b(B)	4.03	4.77	1.5
c(C)	18.8	20.2	6.63
β(deg)	122.28	121.3	0.80

Table 2: The structural parameters of CoPc polycrystalline structural powder

hkl	2θ(exp) (deg)	2θ(sta)(deg)	I/I_O (Exp)	I/I_o (Stan)	d(exp) (A)	d(stan) (A)	Error ratio
(100)	7.294	7.066	69	95	12.109	12.500	3.12
($\bar{1}$02)	9.472	9.253	100	100	9.329	9.550	2.31
(002)	10.797	1o.599	6	16	8.187	8.340	1.83
($\bar{2}$02)	12.775	12.581	13	30	6.923	7.030	1.52
($\bar{1}$04)	18.422	18.239	19	45	4.812	4.860	0.56
(112)	24.030	23.901	12	40	3.700	3.720	0.53
($\bar{3}$11)	26.501	26.346	9	30	3.360	3.380	0.59
($\bar{1}$06)	28.319	28.217	6	16	3.148	3.160	0.63
($\bar{5}$02)	30.766	30.698	9	0	2.903	2.910	0.24

Experimental

Thin films of CoPc of thickness 150 nm, have been prepared onto pre-cleaned Corning slides at room temperature using a fine powder of phthalocyanine (purity _ 98%) (supplied by Fluka AG) were deposited by thermal evaporation technique at different annealing temperatures (298, 358, 408, 458) K using Edwards 306 system. Also the substrate is placed at a distance of 15cm from the molybdenum boat. Thickness of the film is measured by Fizeau fringes technique. X-ray diffractometer

(Philips X' pert), using Cu radiation operating at 40 kV and 30 mA, was used to investigate the structure.Surface morphological measurements for CoPc thin films with different annealing temperatures were done by SPM-AA3000 contact mode spectrometer, Angstrom Advanced Inc. Company, USA. Digital electrometer type Keithly 616 and electrical oven have been used for Electrical measurements. The Hall coefficient (R_H), carrier type and Hall mobility (μ_H) of films were measured by the circuit contain D.C power supply (0- 40) V and two digital electrometers (Keithley type 616 to measure the current and voltage

Result and Discussion

The structure of CoPc powder was determined which gives a polycrystalline structure, monoclinic phase. The spectrum of the CoPc powder has shown sharp peaks at reflection surfaces (100), (102), (202) and (104) and lower intensity for other peaks as shown in Fig .(1). The powder of CoPc identified as a mixture of α-form and β-form.

Table (1). The structural parameters for CoPc polycrystalline structural powder were investigated as shown in table (2). These results agree with (H.S. Soliman et al, 2007; Murali Gedda et al, 2014). The XRD pattern for CoPc thin films at different annealing temperatures were recorded and structure parameters were calculated as shown in Fig.(2) and the table (3). The patterns display strong reflections at (100) orientation, it is observe that the

reflection from other planes has disappeared at other films. The XRD pattern has shown a single crystal structure for temperatures (298,358,408,458)K, the intensity of (100) plane has increase for temp (358,408)K which means better arrangement and more crysttalinity.
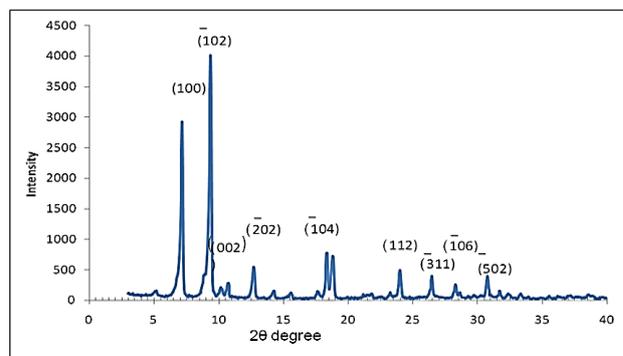
Fig.1: The XRD spectrum for CoPc Powder

This mean that the crystallization of the films is a function of annealing temperatures and decreased for (458)K because of phase changing. (S.I. Shihub et al 1993) observed that the CoPc thin film undergoes phase transformation on heating near 573K, and the direction of preferential orientation for CoPc films is (001) and the structure is tetragonal. They obtained a mixed phase of α and β forms up to an annealing temperature of 588K. Grain size studies confirm the transition temperature as 588K for CoPc. Prolonged heating at 513K produced a structural phase transition to β form, with preferential orientation in the (201) direction. (S. Ambily et al, 1999) have observed α to β phase transformation for CoPc thin films annealed in air at 573K. From the variations in relative peak magnitudes and exothermic/ endothermic behaviour they suggested that the α to β transition may not involve identical mechanisms in each case. Heating to higher temperatures resulted in an increase in crystallite size and increased sharpness. However, there was no

indication of any change in the crystal structure. It is apparent that the first peak is associated solely with the coalescence and growth of α –phase crystals. Where (S.I. Shihub *et al*, 1995) carried out step-by-step phase change measurements on CoPc thin films in which they found that at temperatures up to 473 K there was no evidence of a phase change. A similar observation was obtained in the structure study of *α*-phase of CoPc thin films deposited onto glass substrates held at room temperature (S.I. Shihub *et al* 1993; A.K. Hassan *et al*, 1992). It is observed that the structure is uniform grain formation with improved crystallinity of the film with increasing of annealing temperature. The mean crystallite size is estimated by using the Scherrer's expression,

$$D = 0.9\lambda \, / \, \beta\cos\theta \qquad (1)$$
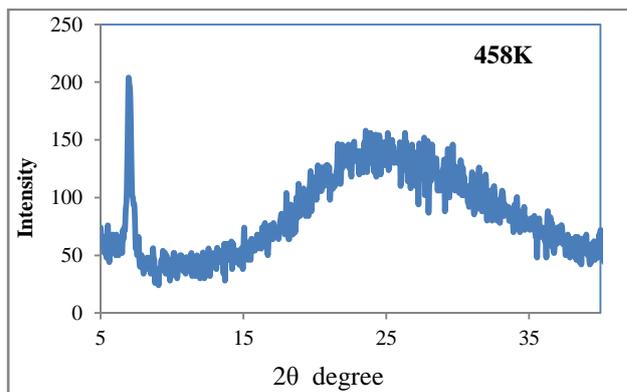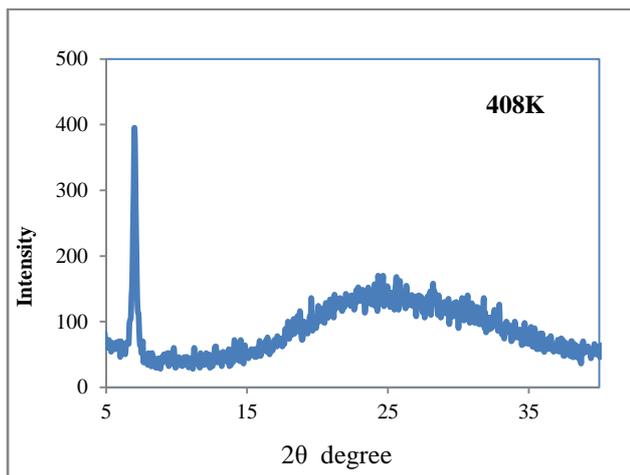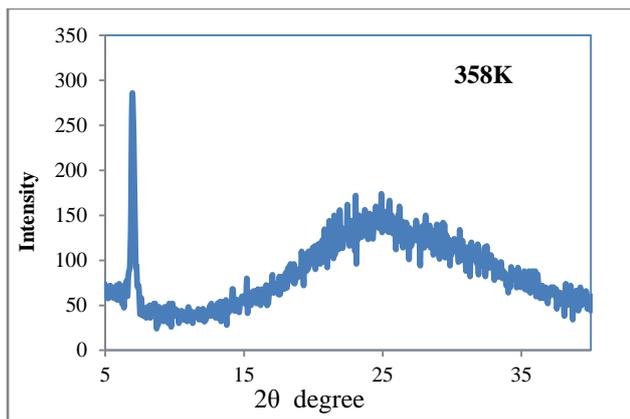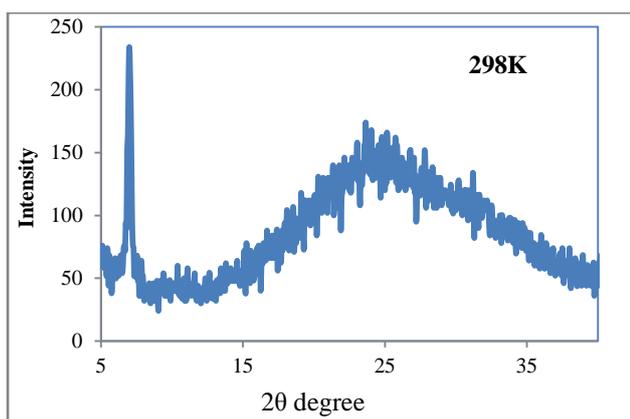
Fig.2: X_ray diffraction of the CoPc thin films at different annealing temperature (298,358,408,458)K

Where **D** is the particle size λ the wavelength for the XRD Source, β is the Full Wave at Half Maximum (FWHM), *θ* is the angel for X-Ray radiation, Table (3) shows the structure parameters of CoPc films, The full width at half maximum (FWHM) reduced with increasing temperatures and Grain size is increase for (T_a=358,408K) and decrease at (T_a=458K) because of phase changing indicates the formation of high quality films with annealing process., The crystallite size increased from 23.7 to 28.2 nm by annealing compared with 24 nm in (M.M. El-Nahass *et al*, 2003). Moreover, other authors (H.S. Soliman *et al*, 2007) have reported the values of the crystallite size in the order of 13.99 to 97.2 nm for various phthalocyanines. Similar observations for mean crystallite size were reported (H.S. Soliman *et al*, 2007; A.K. Hassan *et al*, 1992; Murali Gedda *et al*, 2014). Surface morphology of CoPc thin film is shown in Fig.(3) which prepared at different annealing temperatures (298,358,408,458)K. It shows that the morphology of the CoPc thin film has larger number of grain size, which indicates the crystalline nature of the film. It is obvious because the films were prepared at different annealing temperatures, and due to the heating, the grain growth will takes place which gives the crystallinity and good surface morphology (Rellaa R *et al* 2002). The diffusion of the atoms is described by the Arrhenius equation (Murali Gedda *et al*, 2014).

$$\text{Diffusion Coefficient } D = A \exp(-E/k_B T) \qquad (2)$$

Where *A* is Temperature independent constant; *E* is diffusion activation energy; *T* is substrate temperature and k_B is Boltzmann constant. Because of higher diffusion rate at higher temperatures leads to increase the diffusion of CoPc molecules throughout the surface and results uniform grain formation with improved crystallinity of the film (Murali Gedda *et al*, 2014).

These results are in good agreement with XRD characteristics. The crystal morphology and molecular orientation change with annealing temperatures. These structural characterizations confirm that the annealing temperature allows us to control the structural organization of cobalt phthalocyanine molecules in their solid state. 2_D AFM images and Granularity accumulation distribution chart of CoPc thin films at different annealing temperatures (298.358.408.458)K as shown in Fig.(4).

Table 3: X_ray diffraction of the CoPc thin films at different annealing temperature

T_a (K)	2θ(deg)	d(A)	FWHM	Grain size(nm)
298	7.129	12.389	0.327	**23.7**
358	7.104	12.432	0.312	**24.8**
408	7.139	12.370	0.274	**28.2**
458	7.141	12.367	0.532	**14.6**

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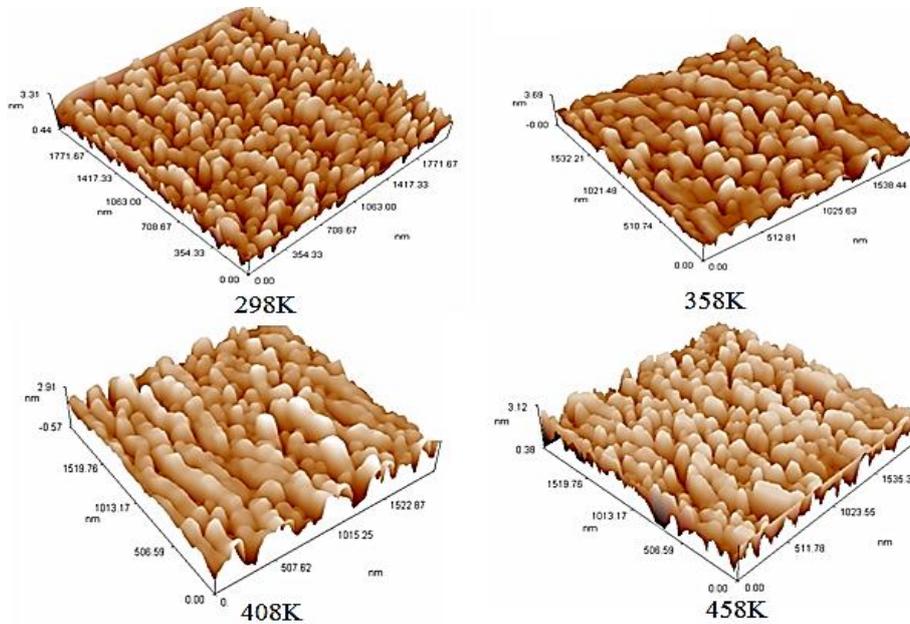
Fig.3: 3-D AFM images of CoPc thin films at different annealing temperatures
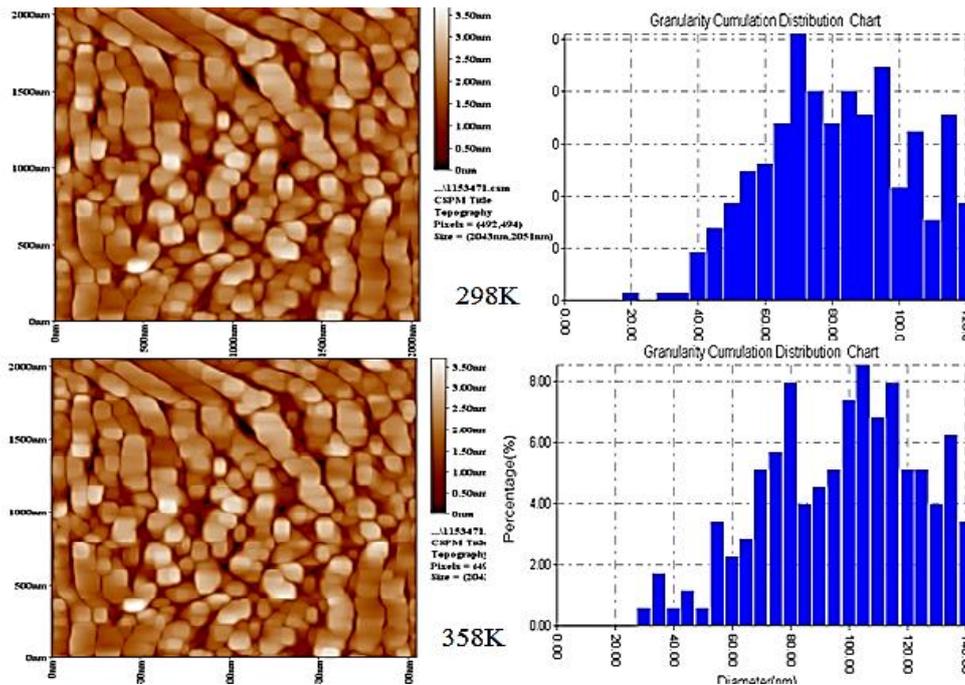
Table 4: Grain size and average roughness of CoPc thin films at different annealing temperature by AFM technique

T_a (K)	Grain size(nm)	Roughness Average (nm)
298	79.44	**0.434**
358	94.76	**0.471**
408	101.6	**0.406**
458	78.44	**0.453**
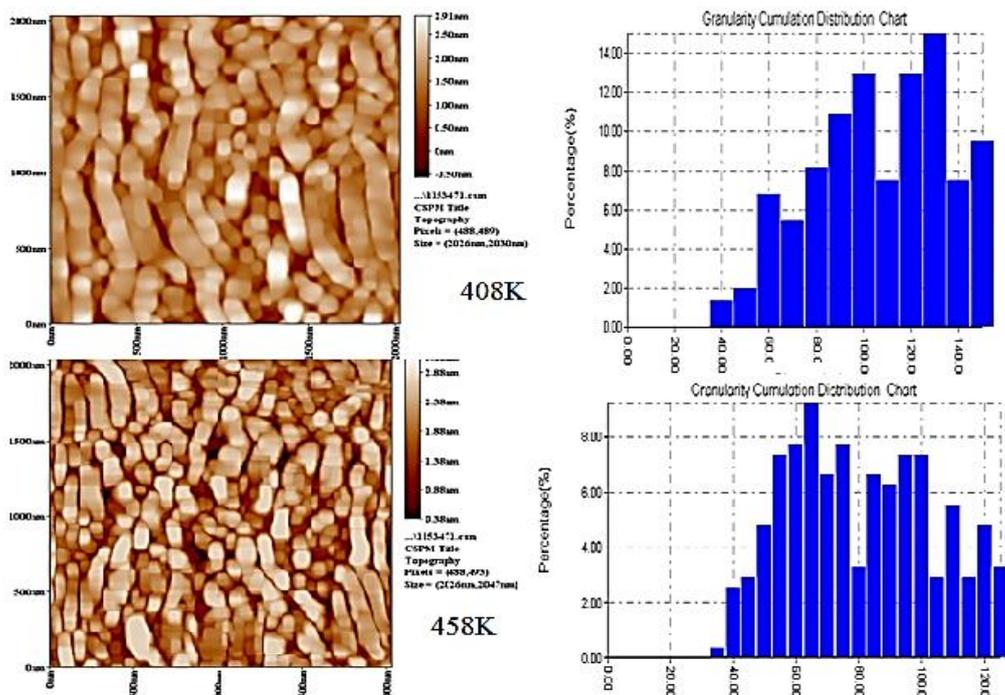
Fig.4: 2_D of AFM images and Granularity accumulation distribution chart of copc thin films at different annealing temperatures (298.358.408.458)K

Table 5: Variation of activations energies and room temperature conductivity for CoPc thin film at different annealing temperatures

T_a (K)	$\sigma *10^{-6}$ $(\Omega\ cm)^{-1}$	E_1 (eV)	Temp. Range(K)	E_2(eV)	Temp. Range(K)
298	3.53	0.493	403_473	0.026	303_393
358	3.6	0.625	423_473	0.032	303_413
408	3.64	0.651	423_473	0.027	303_413
458	3.65	0.653	413_473	0.022	303_403

Table 6: Values of Carrier Concentration and Carrier Mobility for CoPc Thin Films at different annealing temperatures

T_a (K)	Concentration$*10^{11}$ (cm^{-3})	Carrier Mobility $(cm^2/V.sec)$
298	2.28	123
358	2.60	118
408	3.908	92
458	7.464	57
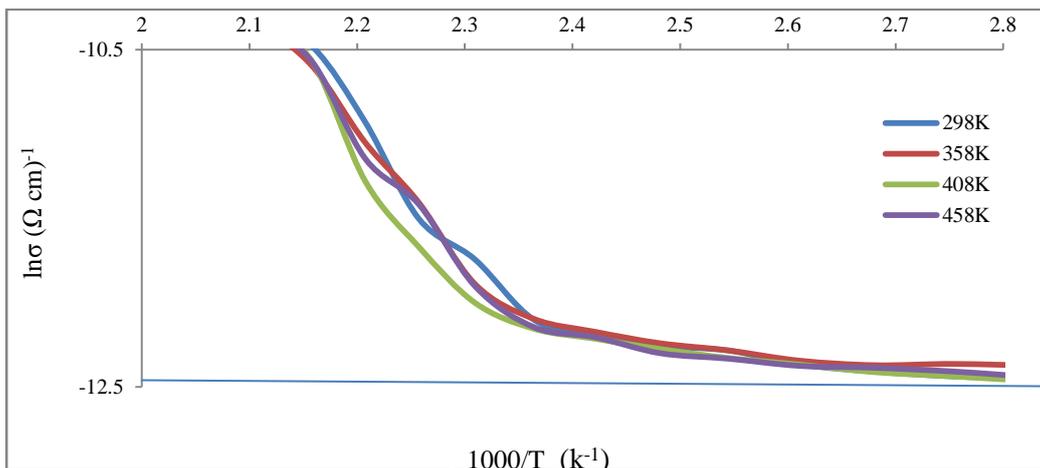
Fig.5: Lnσ as a function of $10^3/T$ for copc Thin films at different annealing temperatures

The Grain size and average roughness of the film at different annealing temperatures are shown in Table(4) that Grain size increases with increasing Ta and decrease at 458K. (Jason Locklin *et al*, 2006) studied the effect of morphology on organic thin film transistors provides a general introduction to organic field-effect transistors and their application as chemical sensors. Thin film transistor device performance is greatly affected by the molecular structure and morphology of the organic semiconductor layer. Surface topography and micro structural features control physical properties like the gas sensitivity, response-recovery speed, stability, reproducibility, and other sensing characteristics of thin films. It is found that the structural and topographical changes are also contributing the properties of Mps. The best results can be seen for the film at 408K. Table (4) shows the roughness increase with thickness increase, the highest roughness which means largest surface area, the best choice for solar cell making. and this is agreement with other researchers (Murali Gedda *et al*, 2014; Fakhra Aziz *et al*l, 2011; Benny Joseph *et al*l, 2008).

Electrical conductivity studies on CoPc thin films are used to determine thermal activation energy and study the effect of annealing temperature on the activation energy. The electrical conductivity σ can be expressed as by Arrhenius equation:

$$\sigma = \sigma_{o}\exp(-E_{a}/k_{B}T) \tag{3}$$

where σ is the conductivity at temperature T, E_{a} is the thermal activation energy, k_{B} is the Boltzmann constant, and σ_{o} is a pre-exponential factor. A plot of ln σ vs. (1000/T) yields a straight line, whose slope can be used to determine the thermal activation energy of the film. Fig.(5) gives the plot of ln σ vs. (1000/T) for CoPc thin films with different annealing temperatures (298.358.408.458)K. two linear regions for each graph, corresponding to two activation energies, E_{1}, E_{2} are obtained and given in table (5), two activation energies for thin films of CoPc, have already been reported (H.S. Soliman *et al*, 2007; K. R. Rajesh *et al*, 2005). The thermal activation energy E_{1} is associated with an intrinsic generation process. This corresponds to the process observed in inorganic semiconductors. It is based on the assumption of electron hole pair production via thermal transition from a valence band to the conduction band, and may occur in several organic solids. The assumption of an intrinsic excitation process explains the dependence of electrical conductivity of phthalocyanine compounds on the constitution of the molecules. This type of excitation provides the applicability of the electron gas model to the conduction process and the increase of conductivity with the number of π-electrons in the individual classes of compounds. The Pc owe its intrinsic conductivity to the partial charge transfer from phthalocyanine ring to the central ion. E_{2} is the activation energy needed to excite the carriers from the corresponding trap levels to the conduction band and are associated with the impurity conduction. The activation energies are found to decrease with the substrate temperatures Higher substrate temperature leads to an increase in the size of the critical nucleus and hence a decrease in the value of the activation

energy. Thus, we can see. in the low temperature region, where the carriers can not be excited into one of the allowed bands, the dominant conduction takes place through hopping conduction of the charge carriers in the localized states near the Fermi level. It is seen from Table (5) that the intrinsic activation energy E_{1} increases with increasing annealing temperature. This can be attributed to better film ordering due to annealing. A similar behaviour of activation energy has been observed for NiPc, MgPc, and CoPc thin films ((H.S. Soliman *et al*, 2007; (Murali Gedda *et al*, 2014; Benny Joseph *et al*l, 2008; K. R. Rajesh *et al*, 2005). Variation in the extrinsic activation energies of CoPc thin films during annealing can be attributed to the distribution of trap levels (S. Mammen *et al*, 2005). (S.I. Shihub *et al*, 1995; R.D. Gould *et al*, 1993) calculated the activation energy of cobalt phthalocyanine (CoPc) films as 0.54 eV, and it is agreement with our results. From Hall results, carrier concentration and Carrier mobility are shown in Table (6). It can be inferred from this Table that the carrier mobility decreased with the increase of the carrier concentration with increase of annealing temperatures for p-type thin film.

Conclusion

From the present work, we can conclude that the CoPc films with annealing temperatures (298,358,408,458) on glass substrate have been prepared successfully by vacuum evaporation technique.

The XRD tests of CoPc powder indicated that the structures are polycrystalline structure with a monoclinic phase, and the structures of thin films transform to single crystalline which influenced by annealing temperature. The intensity of peak of single crystal is increase with increasing of annealing temperature because of cryctallinity. The AFM topographic images founded that there are significant influence of annealing temperature on the surface morphology at CoPC films and the grain size is increase with increasing of annealing temperature. From the electrical properties measurements, The activation energy E_{1} corresponding to the high temperature region is identified as due to intrinsic carriers. This intrinsic activation energy arises from the intrinsic majority carriers, whereas that in the extrinsic regions depends on the extrinsic conduction due to impurity states. An extrinsic to intrinsic cross-over for the activation energy is found. Change in annealing temperature results in change in intrinsic activation energy. Hall effect measurements show that all the films are p-type. The Hall mobility decreases while carrier concentration increases with increasing of annealing temperatures, and conductivity is increase with increasing of annealing temperatures.

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