



## Electrical, optical and structural properties of tin phthalocyanine oxide thin films

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### Abstract

Vacuum sublimed thin films of tin phthalocyanine oxide were prepared at room temperature. Post evaporation annealing was done in air and vacuum at temperatures 348K, 398 K, 448 K and 498 K. Arrhenius plot yields thermal activation energy in the intrinsic region and impurity scattering region. It is found that the intrinsic activation energies for the air annealed and vacuum annealed films increase with annealing temperature. The variation in the electrical properties with thickness was also studied and activation energy was determined. The activation energy decreases as the thickness increases. Optical absorption spectra of films annealed at temperatures 348 K, 398 K, 448 K and 498 K were taken over a wavelength range of 200 to 900 nm and the optical energy band gap  $E_g$  and the onset energy gaps were calculated. The spectra consist of two strong Q and Soret bands at about 600-800 and 250-400 nm respectively, showing an enhanced broad optical window with lower linear absorption at about 500 nm. The Q-band shows its characteristic Davydov splitting. The results show no effect of the annealing on the optical properties of tin phthalocyanine oxide films. X-ray diffraction pattern was used to find the nano-crystalline grain size using Scherrer formula and a slight decrease in grain size with annealing temperature was observed.

**Keywords:** Phthalocyanine; thin film; activation energy; optical band gap.

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### 1. Introduction

Organic semiconductors are presently receiving a lot of attention because of their low-cost applications, easy processing, great possibilities in modification of electrical and optical properties and good compatibility with a variety of substrates. Among them, phthalocyanines are well-known materials that exhibit chemical and thermal stability, interesting non-linear optical behaviour and high conductivity (Shirota 2000). They exhibit p-type semiconductivity at all temperatures (Sadaoka *et al* 1989) and can easily be sublimed to get high purity thin films without decomposition. These compounds have been extensively used as main components in gas sensors (Newton *et al* 2000; Bouvet 2006), solar cells (Peumans *et al* 2000; Yang *et al* 2005) organic light emitting diodes (Fujii *et al* 1997; Kao *et al* 2006) and static induction transistors (Joseph and Menon 2002). Therefore, electrical, optical and structural properties of metal phthalocyanines have been extensively studied. The



development of thin film devices is based upon the fabrication of reproducible and thermally stable thin films. But the electrical, optical and structural properties of phthalocyanine thin films are dependent on various parameters such as evaporation rate, substrate temperature and post deposition annealing (Collins and Belgachi 1989 ; Collins *et al* 1990 ; Ambily and Menon 1999). Phthalocyanines usually present in thin films a certain crystalline form, or result to be amorphous depending mainly on the molecular self-stacking ability of the derivative and on the thin film fabrication procedure (TsuZuki 1996). The control of the film structure is of great importance in thin film technology as the photogeneration of charge carriers highly depends on the degree of molecular organization (Yamasaki *et al* 1997). Moreover, changes in film morphology can be induced through thermal annealing (Adams *et al* 1997). The electrical conductivity of phthalocyanine thin films changes due to the adsorption of gases such as oxygen. Hence the knowledge of the effect of air annealing and vacuum annealing on the electrical, optical and structural properties is necessary to understand the fundamental aspects of the materials. The interest about tin phthalocyanine oxide molecule is motivated by its peculiar non-planar shape and also by a relative lack of studies in the literature. The central metal atom of SnPc stands out of the macrocycle. This gives rise to directional anisotropy and selectivity in the adsorption geometry as well as in the intermolecular stacking. The origin of this distortion is the so-called 'inert pair effect'. The heavy post transition elements exhibit in some compounds a valence that is by two less than their group valence (eg. the divalent Pb and Sn atoms of group 4). This 'inert pair effect' manifests itself structurally by the distortion of the metal ion coordination environment (West 1984). The  $\text{Sn}^{2+}$  ion with electronic configuration (Kr)  $4d^{10} 5s^2$  presents a  $s^2$  lone pair which is stereochemically active in that these electrons are not in a spherically symmetric orbital but stick out to one side of the metal ion leading to various distorted coordination polyhedra. These films are found to absorb light on either side of blue-green region and can be used as photoconductor materials and colour filters. In the present work we study the electrical and optical properties of tin phthalocyanine oxide thin films. X-ray diffractograms of the films annealed at different temperatures are also taken to study the variation of grain size with annealing temperature. One particular aspect of the present work facilitates to improve the material characterization by determining the basic electrical and optical quantities and investigating their dependence on annealing temperature. Moreover, to the authors' knowledge there are no reports on the electrical and optical properties of tin phthalocyanine oxide thin films.

## 2. Experimental Details

Tin phthalocyanine oxide powder used in this study was procured from Aldrich Chemicals, USA. Thin films of tin phthalocyanine oxide were deposited onto thoroughly cleaned glass substrates at room temperature using a Hind Hivac 12 A4 coating unit at a base pressure of  $10^{-5}$  torr. The films were prepared by resistive heating of the powder from a molybdenum boat and the evaporation rate was kept constant. Several films of same thickness and different thicknesses were prepared in the same experimental condition simultaneously. This was achieved by arranging a series of substrates horizontally and keeping the



evaporating source to one side but well below the specimen plane. The reproducibility of the results was confirmed by making several such depositions under more or less the same deposition conditions. Thickness of the film was determined by Tolansky's multiple beam interference technique (Maissel and Glang 1983).

Tin phthalocyanine oxide thin films of thickness  $230 \pm 5$  nm were annealed in air for 1 hour at different temperatures in a furnace whose temperature could be controlled by a controller cum recorder. Another set of films was annealed in vacuum for 1 hour at 348 K, 398 K, 448 K and 498 K. UV- Visible absorption spectra were recorded using a Shimadzu 160 A UV-Visible spectro-photometer. The absorption edge was analyzed to get the optical band gap of tin phthalocyanine oxide. For electrical conductivity studies evaporated silver was used as the contact electrode. Thin copper strands were fixed by silver paste and the film was placed onto a hollow copper block in the conductivity cell that was heated. The temperature of the sample was measured using Chromel-Alumel thermocouple. The resistance was noted at regular intervals of 5 K using a programmable Keithley electrometer (Model No 617) in the temperature range 330-525K. The measurements were performed in vacuum at  $10^{-3}$  torr to remove the physically adsorbed gaseous layers on the surface of the film and also to avoid the adsorption of gases or reaction with them.

### 3. Results and discussion

#### 3.1 Electrical studies.

Electrical conductivity studies are done to determine the thermal activation energy and its variation with annealing temperature and thickness of the film. The electrical conductivity  $\sigma$  can be expressed as

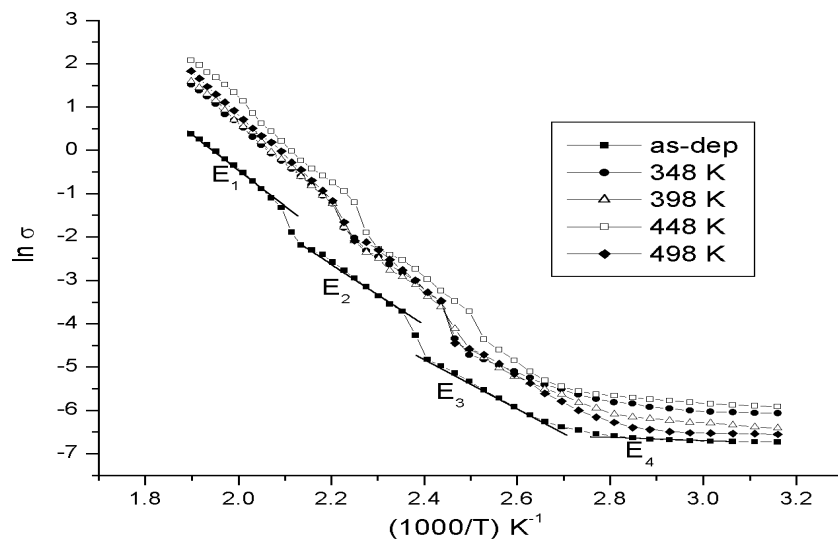
$$\sigma = \sigma_0 \exp(-E/k_B T) \quad (1)$$

where  $\sigma$  is the conductivity at temperature T, E is the thermal activation energy,  $k_B$  is the Boltzmann constant and  $\sigma_0$  is the pre-exponential factor. Graph of  $\ln \sigma$  versus  $(1000/T)$  for tin phthalocyanine oxide films annealed in air and vacuum at different temperatures are plotted and shown in figures 1 and 2. The plot of  $\ln \sigma$  versus  $(1000/T)$  is linear but the slope changes at different regions of temperature. This indicates a variation of activation energy due to the thermal excitation of impurities situated at different levels in the band gap. There are four linear regions for each graph in figure 1, which correspond to activation energies  $E_1$ ,  $E_2$ ,  $E_3$  and  $E_4$ . But for the films annealed in vacuum at 448 K and 498 K, only three regions are observed which means that vacuum annealing improves the quality of the film by releasing strains and removing some defects as well. The activation energies are determined within an accuracy of  $\pm 0.01$ eV in all measurements and collected in Table 1.

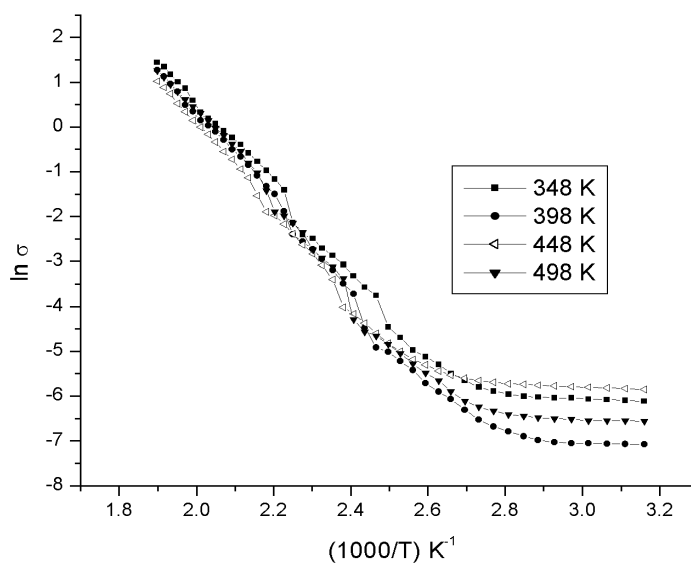


Tin phthalocyanine Oxide		Activation Energy (eV)			
		E <sub>1</sub>	E <sub>2</sub>	E <sub>3</sub>	E <sub>4</sub>
Film thickness (nm)	183	0.87	0.73	0.58	0.05
	245	0.83	0.71	0.62	0.09
	328	0.78	0.66	0.51	0.04
	460	0.74	0.66	0.55	0.05
Air annealing temperature (K)	as-deposited	0.77	0.65	0.50	0.09
	348	0.78	0.68	0.41	0.11
	398	0.81	0.68	0.47	0.09
	448	0.83	0.67	0.58	0.08
	498	0.84	0.74	0.54	0.06
Vacuum annealing temperature (K)	348	0.75	0.64	0.51	0.05
	398	0.78	0.73	0.56	0.08
	448	–	0.78	0.54	0.05
	498	–	0.79	0.56	0.06

Table 1. Variation of activation energy with film thickness and heat treatments.



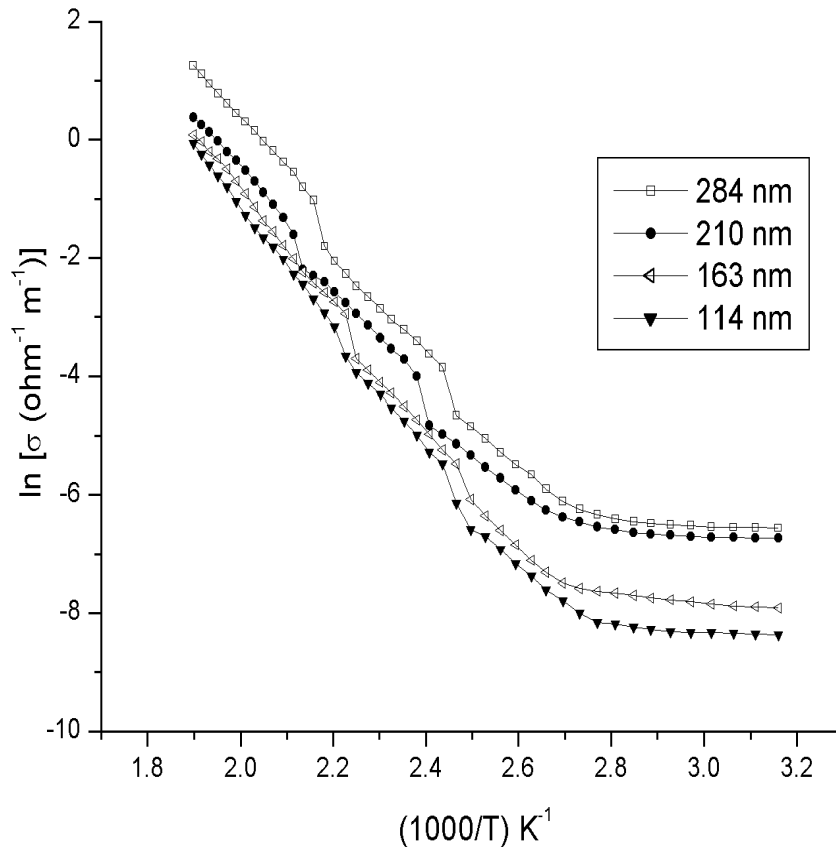
**Figure 1** Plot of  $\ln \sigma$  vs.  $1000/T$  for SnPcO thin films of thickness  $214 \pm 5$  nm annealed in air at different temperatures.



**Figure 2:** Plot of  $\alpha^2$  vs.  $h\nu$  for SnPcO thin films of thickness  $224 \pm 5$  nm annealed in vacuum at different temperatures.



The change in activation energy with temperature is more prominent in air-annealed films than in vacuum annealed films. Figure 3 gives the plot of  $\ln \sigma$  versus  $(1000/T)$  for SnPcO thin films with thicknesses 183,245,328 and 460 nm. It is observed that the activation energy



**Figure 3** Plot of  $\ln \sigma$  vs  $1000/T$  for SnPcO thin films of different thicknesses.

decreases with the increase of film thickness. It may be due to the presence of internal electric fields associated with the defects present in the films or it may be due to an increase of particle size. The change in the activation energy with temperature is interpreted as a change from extrinsic to intrinsic conduction by Nakada et al (Nakada *et al*/1964)]. It is seen that the activation energy increases as the annealing temperature increases. Sussman (Sussman 1967) has reported that the distribution of trapping sites is altered by annealing. Oxygen alters the distribution of trap levels during annealing. The adsorbed oxygen creates



carriers and acts as impurity in the extrinsic conduction region. Similar behaviour in activation energy has been reported for NiPc and MgPc thin films (Narayanan Unni and Menon 2000; Krishnakumar and Menon 2001)

### 3.2 Optical Studies

Optical studies are done to determine the energy band gap and the effect of annealing on the band gap of tin phthalocyanine oxide thin films since there is no report on the band gap study of these films. The principle of this technique is that photons with energies higher than the band gap energy will be absorbed and electrons are excited from the valence band to the conduction band with the absorption of energy equal to the band gap of the material. The rapid drop in the absorption coefficient on the high energy side of the absorption spectra leads to the band edge in semiconductors. The transition type is also important to be defined for the material characterization. The optical absorption spectra of SnPcO thin films annealed in air and vacuum at different temperatures over a wavelength range of 200-900 nm are taken and typical graphs are shown in figure 4. It can be seen that the plot is linear in the region of strong absorption near the fundamental absorption edge. Hence the absorption takes place through direct transition. The spectrum of phthalocyanine is believed to originate from orbitals within the aromatic  $18\pi$  electron system and from overlapping orbitals on the central metal atom (Ough *et al* 1993). In phthalocyanines the direct electronic transition from  $\pi$  to  $\pi^*$  orbitals in the energy range 300-450 nm results in an intense band called B-band (Soret band) which corresponds to the fundamental absorption from which the energy band gap is obtained (Collins 1993). The Q-band appeared in the 600-800 nm range gives onset energy. The fundamental absorption edge is analyzed within the one electron theory of Bardeen (Bardeen *et al* 1965) to obtain information about direct or indirect interband transitions. The absorption coefficient  $\alpha$  is calculated using the relation

$$\alpha = 2.303 A/t \quad (1)$$

where  $A$  is the absorbance of the film and  $t$  is its thickness. For direct allowed transition, the absorption coefficient  $\alpha$  is related to the photon energy  $h\nu$  by the relation

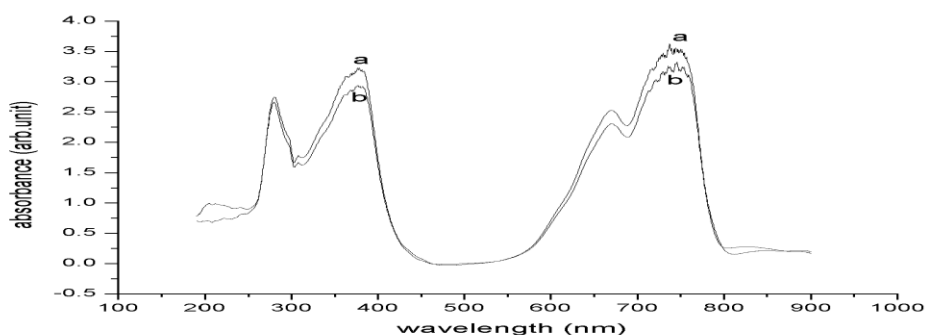
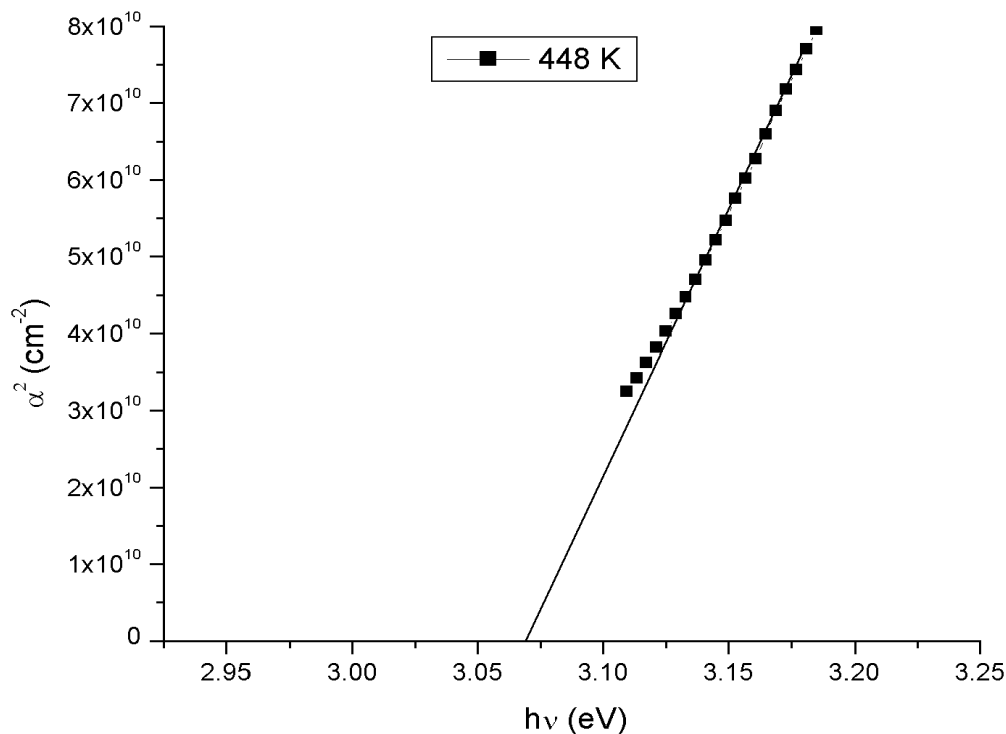


Figure 4: Optical absorption spectra of SnPcO thin films annealed in air and vacuum at 448 K



$$\alpha = \alpha_0 (h\nu - E_g)^{1/2} \quad (2)$$

where  $E_g$  is the optical band gap and  $\alpha_0$  a constant. A satisfactory straight line fit is obtained



**Figure 5:** Plot of  $\alpha^2$  vs.  $h\nu$  for SnPcO thin films annealed in air at 448 K.

for  $\alpha^2$  as a function of  $h\nu$ , showing the existence of a direct band gap. The value of absorption coefficient  $\alpha$  greater than  $10^4 \text{ cm}^{-1}$  obtained is also related to direct inter-band transitions. By plotting  $\alpha^2$  versus  $h\nu$  and extrapolating to zero absorption, the band gap  $E_g$  is obtained. Plot of  $\alpha^2$  versus  $h\nu$  for tin phthalocyanine oxide film annealed in air at 448 K is shown in figure 5. The values of fundamental and onset energy gaps are determined from the graph and are given in Table 2. In the near ultraviolet region, strong absorption occurs in the Soret band near 3.07 eV. Of interest here is that there is an absorption peak of variable intensity on the high energy side of the Soret band at 4.07 eV. In the visible region, we find two absorption peaks corresponding to 1.60 and 1.68 eV for SnPcO thin films. Here the low energy peak is the more intense of the doublet. For both air annealed and vacuum annealed films the optical band gap is not notably affected by annealing temperature.





Tin phthalocyanine Oxide	Soret band		Visible band		
		(eV)		(eV)	
Air annealing temperature K	348	4.05	3.06	1.68	1.59
	398	4.07	3.07	1.67	1.60
	448	4.07	3.07	1.69	1.60
	498	4.07	3.07	1.68	1.60
Vacuum annealing temperature (K)	348	4.00	3.07	1.67	1.60
	398	4.00	3.06	1.69	1.60
	448	4.02	3.06	1.68	1.59
	498	4.02	3.05	1.61	1.59

**Table: 2.** Energy gaps (in eV) seen in the absorption spectra of SnPcO thin films.

#### 4. Structural studies

The XRD spectra for as-deposited and air annealed tin phthalocyanine oxide thin films are shown in figure 6. For all annealed films, the most intense peak was found to be at  $2\theta \approx 5.338^\circ$ . The grain size  $L$  of the film was calculated using the Scherrer equation (El-Nahass *et al* 2005)

$$L = K\lambda / \beta \cos \theta$$

where  $\lambda$  is the wave length of the X-ray beam ( $\lambda = 0.15425$  nm of Cu  $K\alpha_1$ ),  $\beta$  is the value of the full width at half maximum (FWHM) of the most intense peak,  $\theta$  is the corresponding Bragg angle and  $K$  is Scherrer constant. The value of  $K$ , in general, depends on the crystallite shape and it is assigned a value of 0.9 for phthalocyanine films (Iwatsu *et al* 1990). The grain sizes corresponding to the annealed films are calculated and given in Table 3. It is seen that as the annealing temperature increases from 348 K to 498 K the grain size decreases from 23.47 nm to 22.35 nm. The decrease in the grain size, due to air annealing, is in agreement with the result previously obtained for iron phthalocyanine thin film (Krishnakumar and Menon 2001). The decrease in grain size at higher temperature may be due to recrystallization and partial resublimation.

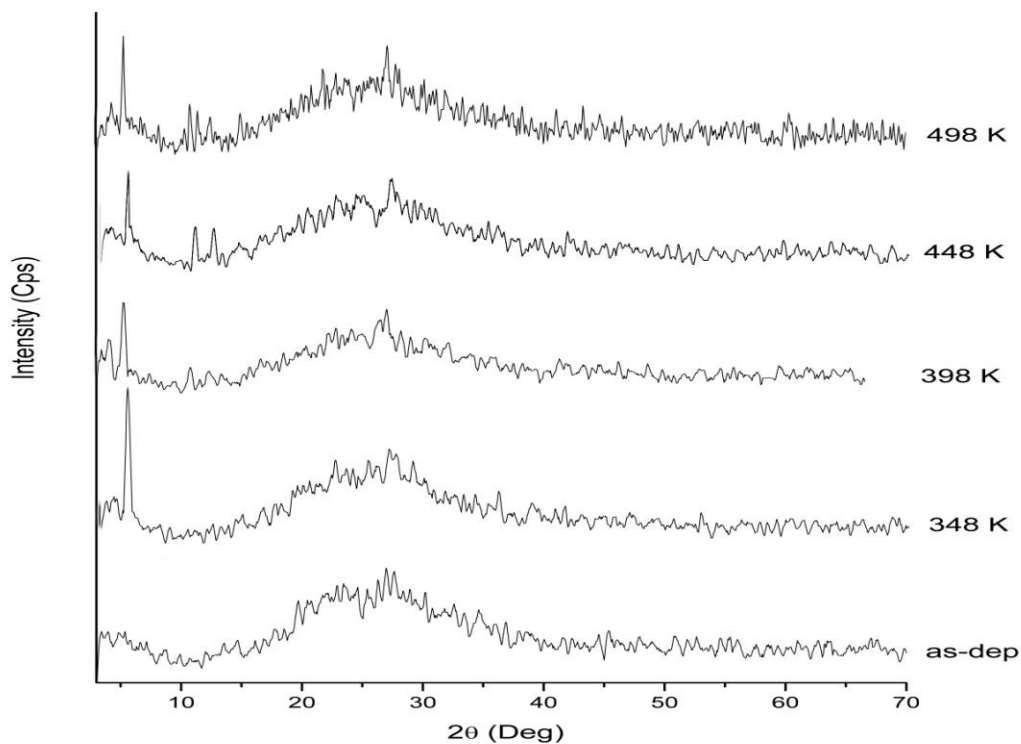


Figure 6: XRD of SnPcO thin films annealed in air at various temperatures.

Annealing temp. (K)	d (Å <sup>0</sup> )	2θ deg.	FWHM(b) x10 <sup>-3</sup> rad	Grain Size nm
348	16.542	5.338	6.088	23.47
398	16.604	5.318	5.949	23.33
448	16.681	5.396	6.001	23.12
498	16.733	5.227	6.210	22.35

Table 3: Observed interplanar distance (d), position of the most intense peak (2θ), FWHM (b) and grain size (L) for SnPcO thin films



## 5. Conclusion

The activation energies are calculated from the electrical conductivity studies. There are four activation energies, which are due to the intrinsic charge carriers ( $E_1$  and  $E_2$ ) and the impurity scatterings ( $E_3$  and  $E_4$ ). It is found that the intrinsic activation energy increases with annealing temperature. The variation in the activation energies of the as-deposited and annealed tin phthalocyanine oxide thin films can be attributed to the change in the distribution of trap levels and the removal of the trap levels during annealing of the film. An appropriate thermal annealing transforms vacuum deposited thin films from meta stable phases to stable phases. Heat treatment at 448 K in vacuum even for a short time favours a complete stabilization. Hence vacuum annealing is better than air annealing to produce stable films. As the film thickness increases activation energy decreases. Thus films having desired activation energy can be prepared by adjusting the thickness of the film during deposition. Absorption spectra of tin phthalocyanine oxide thin films consist of two strong Q and Soret bands at about 600-800 and 250-400nm respectively showing an enhanced broad optical window with lower linear absorption at about 500 nm. The Q-band shows its characteristic splitting-Davydov splitting of the main absorption peak in the metal phthalocyanine correlates with the relative tendencies of the metal to out-of-plane bonding. Tin phthalocyanine oxide absorbs light on either side of blue-green region and can be used as photoconductor materials and colour filters. The transition type is defined to be allowed direct transition and the optical band gap is not notably affected by annealing. The stability in the peak positions in the absorption spectra showed the stability of the structure of tin phthalocyanine oxide thin films. The fundamental study on phthalocyanine thin films offers the possibility of tailoring the electronic and chemical properties required for the fabrication of devices based on organic materials such as solar cells, field effect transistors, organic light emitting devices and sensors for molecular and bio-molecular recognition.

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