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Electrical and optical studies on thin films of indium phthalocyanine chloride

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Vacuum evaporated thin films of indium phthalocyanine chloride were prepared at room temperature. Post-evaporation annealing was done at 353, 403, 453, and 503 K. The electrical conductivities and optical absorption spectra of these films were studied. From the optical absorption spectra over a wavelength range of 200–900 nm, the optical energy band gap E_g was calculated. A decrease in E_g is observed with increasing annealing temperature. The thermal activation energy E_a is not notably affected by annealing. It is found that E_a varies with changing thickness of the film.

Key words: *phthalocyanine; activation energy; optical band gap; annealing*

1. Introduction

In the field of organic dyes and pigments, the materials considered to be most important are the phthalocyanines (Pcs). These materials are generally p-type semiconductors and have the advantage of being sufficiently stable towards chemical and thermal treatment. They can easily be vacuum deposited, resulting in high purity thin films without decomposition. Phthalocyanines are of interest in the fabrication of electronic molecular devices such as opto-electronic devices [1], gas sensors [2, 3], static induction transistors [4–6], and photoreceptor devices in laser beam printers and photocopiers [7]. Electrical, optical, and structural properties of phthalocyanine thin films are dependent on various parameters, such as evaporation rate, substrate temperature, and post-deposition annealing [8, 9]. Among various phthalocyanines, indium phthalocyanine chloride (InPcCl) has received considerably less attention. In the present study, we report on the electrical and optical properties of as-deposited and annealed InPcCl thin films.

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2. Experimental

Indium phthalocyanine chloride, procured from Aldrich Chemicals (USA), was purified by the train-sublimation technique using nitrogen gas as the carrier [10] and was used as the source material for thermal evaporation. Thin films of InPcCl were prepared on a glass substrate using a Hind Hivac 12A4 evaporation plant. Glass slides with dimensions of 7.5×2.5×1.3 mm^3 were used as substrates. Evaporation of the material was done at a base pressure of 10^{-5} Torr using a molybdenum boat. The deposition rate was controlled at 10–13 nm per minute. Surface samples 2 mm in breadth were used for the study. InPcCl thin films 230±5 nm thick were annealed in air for 1 h at 353, 403, 453, and 503 K in a furnace with a temperature controlled by a controller with recorder. Vacuum deposited silver, with an inter-electrode distance of 1 cm, was used for the contact electrodes. Electrical conductivity measurements were performed using a programmable Keithley electrometer model No. 617, in the temperature range of 303–548 K. To avoid any possible contamination, measurements were performed in vacuum at 10^{-3} Torr. Since phthalocyanines are photosensitive [11], the measurements were done in darkness. The thickness of the films was measured using Tolansky's multiple beam interference technique [12]. The absorption spectra of InPcCl thin films were recorded using a Shimadzu 160A spectrophotometer.

3. Results and discussion

3.1. Electrical conductivity studies

The electrical conductivity σ can be expressed as:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \tag{1}$$

where σ is the conductivity at temperature T, E_a is the thermal activation energy, k is the Boltzmann constant, and σ_0 is a pre-exponential factor. A plot of $\ln\sigma$ vs. $(1000/T)$ yields a straight line, whose slope can be used to determine the thermal activation energy of the film. Figure 1 gives the plot of $\ln \sigma$ vs. $(1000/T)$ for InPcCl thin films with thicknesses of 880, 595, 304, and 196 nm. There are three linear regions for each graph, corresponding to three activation energies, E_1, E_2, and E_3. Three activation energies for thin films of NiPc, $Eu(Pc)_2$, and H_2Pc have already been reported [13–15]. The thermal activation energy E_1 is associated with an intrinsic generation process, i.e. the resonant energy involved with a short-lived excited state. E_2 and E_3 are associated with impurity conduction, i.e. short-lived charge transfer forms between the impurity molecule and the host in which the supply of energy detaches the electron from the phthalocyanine complex [16].

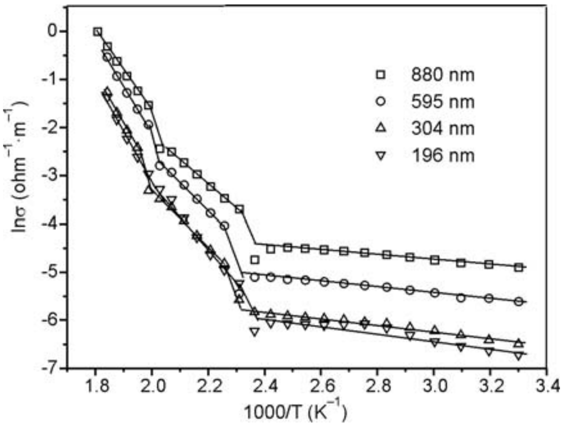

Fig. 1. Plot of lnσ vs. (1000/T) for InPcCl thin films of various thicknesses deposited at room temperature

In some cases, however, impurities can be traps as well. A change in the slope, and hence the activation energy, is interpreted as a change from extrinsic to intrinsic conduction [17], which adds support for the present result. The activation energies E_1, E_2, and E_3 are collected in Table 1. The calculated error in the determination of activation energy is ±0.01eV. It is seen that as thickness increases, the activation energy E_1 decreases. This lowering of activation energy is probably influenced by the structure of the film and therefore by the distribution of electronic tail states. A similar behaviour has been reported for Eu(Pc)$_2$ and H$_2$Pc thin films [14, 15].

Table1. Activation energy of InPcCl thin films of various thicknesses deposited at room temperature

Thickness	Activation energy (eV)		
	E_1	E_2	E_3
880 nm	0.73	0.44	0.05
595 nm	0.82	0.51	0.05
304 nm	0.92	0.49	0.06
196 nm	0.99	0.59	0.07

Figure 2 shows the plot of ln σ vs. (1000/T) for InPcCl thin films annealed at 353, 403, 453, and 503 K. For each sample there are three activation energies, E_1, E_2, and E_3. The three activation energies for InPcCl thin films annealed at 353, 403, 453, and 503 K are determined and collected in Table 2. It is seen 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 [13, 18, 19]. Variation in the

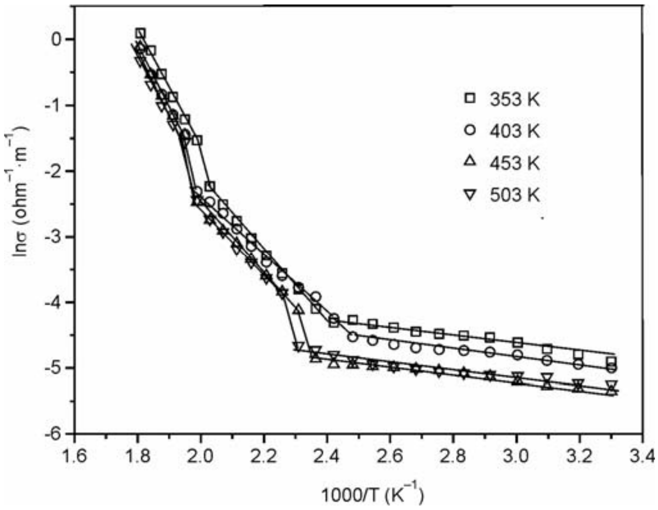

Fig. 2. Plot of $\ln\sigma$ vs. $(1000/T)$ for InPcCl thin films annealed in air at various temperatures

Table 2. Activation energy of InPcCl (of thickness 230±5 nm) thin films annealed at various temperatures

Annealing temperature	Activation energy (eV)		
	E_1	E_2	E_3
353 K	0.76	0.45	0.04
403 K	0.79	0.42	0.05
453 K	0.79	0.46	0.06
503 K	0.81	0.46	0.06

extrinsic activation energies of InPcCl thin films during annealing can be attributed to the distribution of trap levels [20].

3.2. Optical studies

The UV visible spectrum observed for phthalocyanines originates from the molecular orbitals within the aromatic 18π electron system and from overlapping orbitals on the central metal atom [21]. The direct electronic transition from π to π* orbitals in the 300–450 nm range results in an intense band called the Soret band (B-band). The absorption edge of this peak can be related to fundamental absorption from which the energy band gap is obtained [22]. The fundamental absorption edge is analysed within the one electron theory of Bardeen et al. [23], and the absorption coefficient α is calculated from the spectra shown in Fig. 3. The coefficient α is related to the photon energy $h\nu$ by the relation

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

for direct allowed transitions, E_g being the optical band gap and α_0 a constant.

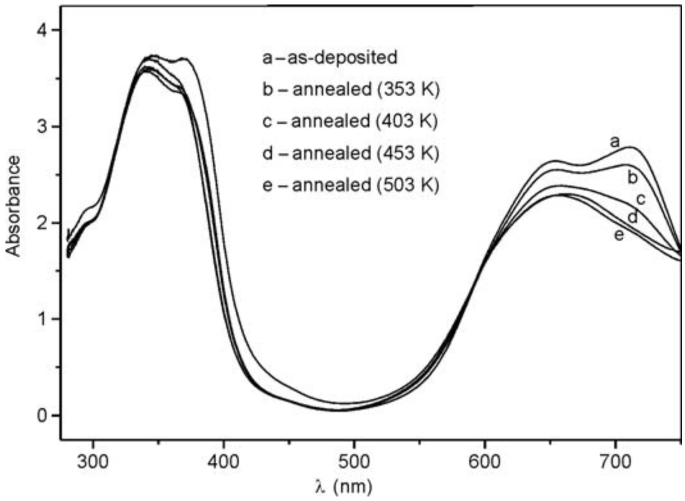

Fig. 3. Optical absorption spectra of InPcCl thin films: as-deposited and annealed in air at various temperatures

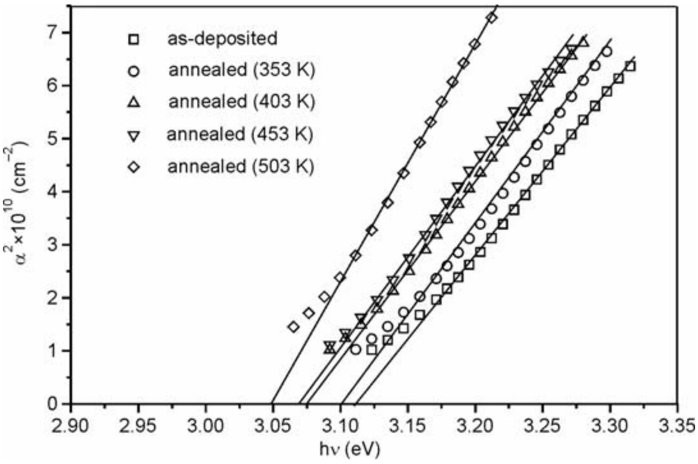

Fig. 4. Plot of α^2 vs. $h\nu$ for InPcCl thin films: as-deposited and annealed in air at different temperatures

Plots of α^2 vs. $h\nu$ near the absorption edge for as-deposited InPcCl thin films and films annealed in air at 353, 403, 453, and 503 K are shown in Fig. 4. A satisfactory straight line fit is obtained for α^2 as a function of $h\nu$, showing the existence of a direct gap. Extrapolation of the straight-line graphs to $\alpha^2 = 0$ gives the value of optical band gap. The band gaps obtained for InPcCl are given in Table 3. Any crystal phase

Table 3. Optical band gap of InPcCl as-deposited thin film and films annealed at different temperatures

Annealing temperature	Optical band gap E_g (eV)
353 K	3.10
403 K	3.08
453 K	3.07
503 K	3.05
As-deposited	3.11

change would affect the gap between the conduction band and valence bands in phthalocyanines, because the orbital overlap between parallel pairs of molecules will be affected [24]. The notable change in the optical band gap E_g for the film annealed at 503 K can be attributed to this.

4. Conclusions

The annealing of InPcCl thin film alters the activation energy for electrical conduction and the optical band gap. Also, by careful monitoring thickness during deposition, films having a desired activation energy can be made, which can help optimise properties of molecular electronic devices fabricated using InPcCl thin films.

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