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Electrical and Optical Characterization of Thermally Evaporated Titanyl Phthalocyanine Thin Films

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The electrical and optical properties of thermally evaporated titanyl phthalocyanine-β modification (TiOPc) thin films have been investigated. Thin films of TiOPc are prepared by thermal evaporation method on to glass substrates in high vacuum. Temperature dependence of electrical conductivity of the films is also investigated. The dependence of activation energy on post deposition annealing in air and in vacuum are studied. Annealing in air and vacuum decreases the intrinsic activation energy of TiOPc thin films. The optical absorption spectra of TiOPc thin films in the range 300-900 nm are recorded. The absorption spectra obtained in UV-Vis region for the as deposited and annealed films show two absorption bands namely the Q-band and the soret band. The fundamental and onset energy gaps are estimated. It is observed that air annealing and vacuum annealing have no significant role in the optical band gap of TiOPc thin films.

Key Words: Titanyl phthalocyanine, Thin film, Thermal evaporation.

INTRODUCTION

Metal phthalocyanines (MPc's) are aromatic hydrocarbons exhibiting semiconducting properties, have gained considerable attention in recent years due to their immense applications, such as sensing elements in gas sensors[1,2], light emitting devices[3], solar cells[4,5], photoconducting devices[6], optical data storage and security printing. These materials are thermally and chemically stable and can be easily prepared in thin film form of high quality by thermal evaporation without dissociation.

In the present work, we study the electrical and optical properties of thermally evaporated TiOPc thin films. Electrical conductivity studies are done in the temperature range 300-500 K and the activation energies are estimated. The effect of annealing in air and in vacuum on the conduction mechanism and activation energy is studied. The optical absorption spectra are recorded in the wavelength range 300-900 nm. The fundamental and the onset energy gaps are estimated. The effect of air annealing and vacuum annealing on the optical absorption and the optical band gap are investigated.

EXPERIMENTAL

Thin films of TiOPc are prepared by thermal evaporation technique using a high vacuum coating unit (Hind Hivac 12A4). Spectroscopically pure TiOPc powder used in the study is procured from Sigma-Aldrich Inc. USA. Micro glass slides of dimensions 5 cm × 1.15 cm × 0.1 cm are cleaned using the standard cleaning procedure are used as substrates. The material is sublimed from a molybdenum boat of dimensions 2.9 cm × 1.2 cm × 0.5 cm, used as the resistive heating element. Evaporation of the material is carried out at a base pressure of 10^{-5} Torr. During evaporation the substrates are placed at a distance of 11 cm above the source and the deposition rate is controlled within a range of 10-12 nm/min. The thickness of the films is measured using Tolansky's multiple beam interference technique. Thin films deposited at room temperature are annealed at temperatures 323, 373, 423 and 473 K in air for 1 h using a furnace attached with a digital temperature controller cum recorder. Vacuum annealed samples are prepared by annealing the samples at the above temperatures for 1 h in vacuum at a base pressure of 10^{-3} Torr.

Electrical measurements are performed using a programmable Keithley electrometer (Model No. 617) in the constant current source mode. Evaporated silver electrodes are used for ohmic contacts. Each sample is mounted on the sample holder of the conductivity cell. Electrical contacts are made using copper strands of diameter 0.6 mm and are fixed to the specimen with a colloidal suspension of silver in alkadag. Electrical conductivity measurements have been performed in the temperature range 300 to 475 K. To avoid contamination the measurements are done in a subsidiary vacuum of 10^{-3} torr.

The absorption spectra of TiOPc thin films are recorded using the Shimadzu 160A UV-VIS-NIR Spectrophotometer in the wavelength range 300-900 nm. Absorption spectra of the films are analyzed to obtain the energy band gap.

RESULTS AND DISCUSSION

Electrical measurements are done to investigate the temperature dependence of conductivity and the effect of annealing on the activation energy. Conductivity in phthalocyanines is due to hopping of holes and charge transport *via* excited states. In such case, the conductivity is given by

$$\sigma = A\exp(-E_1/k_BT) + B\exp(-E_2/k_BT) + C\exp(-E_3/k_BT) + \ldots \quad (1)$$

where E_1 is the intrinsic energy gap and E_2, E_3 .... are the activation energy needed to excite the carriers from the corresponding trap levels to the conduction band. A, B, C, *etc.* are constants.

The electrical resistance of the samples are measured using the programmable Keithley electrometer in the temperature range 300 to 475K at intervals of 5 K and the corresponding electrical conductivity (σ) is calculated using the relation.

$$\sigma = \frac{L}{Rbd} \quad (2)$$

where L, b and d are the length, breadth and thickness of the film respectively. R is the resistance of the film.

The temperature dependence of conductivity shows Arrhenius type relationship[7]. The conductivity is strongly temperature dependent and the charge carrier transport mechanism is of free band type in the higher temperature region and of hopping type in the lower temperature region[8]. ln σ *vs.* 1000/T plots of TiOPc thin films of thickness 269 nm (as deposited and annealed in air for 1 h at temperatures 323, 373, 423 and 473 K) are given in Fig. 1. Fig. 2 shows the plots of ln σ *vs.* 1000/T for TiOPc thin films of thickness 269 nm (as deposited and annealed in vacuum for 1 h at temperatures 323, 373, 423 and 473 K). The plots give different linear regions and

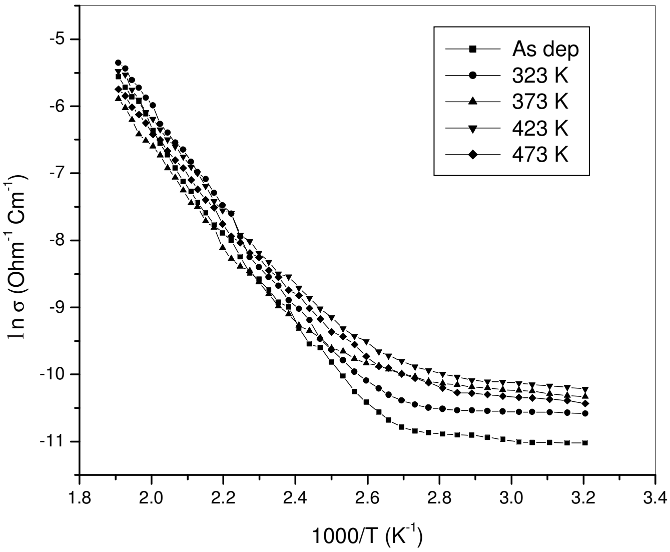


Fig. 1. Plot of ln σ *vs.* 1000/T for the as deposited and air annealed samples

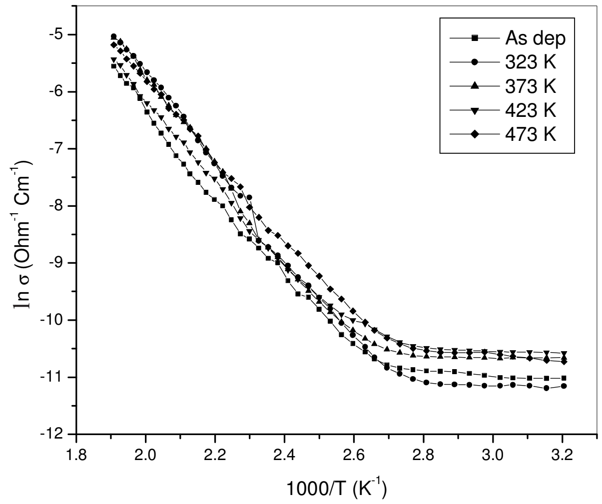


Fig. 2. Plot of ln σ *vs.* 1000/T for the as deposited and vacuum annealed samples

are attributed to different charge carrier transport mechanisms. The activation energy corresponding to the linear regions are estimated from the slope of the graph. We have obtained three activation energies for each sample and are given in Tables 1 and 2.

Activation energy in phthalocyanines may be interpreted as the energy difference between dominant energy levels[9] and the central metal ion in phthalocyanines strongly influences the activation energy as well as the mobility in phthalocyanines. It is observed that the activation energy corresponding to the intrinsic region E_I decreases with annealing temperature. The intrinsic activation energy E_I for TiOPc thin film annealed in air at 323 K is obtained as 0.64 eV. This value falls to 0.58 eV for film annealed at 473K in air. A similar behaviour of the intrinsic activation energy E_I is observed for TiOPc thin films annealed in vacuum. An intrinsic energy value of 0.68 eV is obtained for TiOPc film annealed in vacuum at 323 K; this value falls to 0.6 eV for film annealed in vacuum at 473 K. The number of trap levels is found to be independent of air and vacuum annealing. Gould[10], suggests that the change in transport mechanism and activation energy occurs as a result of change in mobility of charge carriers.

Though the optical behaviour of Pc's is well understood, the problems associated with the validity of application of band model in common with many organic semiconductors need improvement. Optical studies are done to determine the band gap and the effect of air and vacuum annealing on the band gap of TiOPc thin films. The optical absorption spectra in the range 300-900 nm are recorded using the Schimadzu 160A UV-VIS-NIR

TABLE-1
ACTIVATION ENERGY FOR TiOPc THIN FILM OF THICKNESS 269 nm AS DEPOSITED AND ANNEALED IN AIR AT DIFFERENT TEMPERATURES

Annealing temperature (K)	Activation energy (eV)		
	E_1	E_2	E_3
As deposited	0.73	0.52	0.04
323	0.64	0.52	0.02
373	0.63	0.43	0.05
423	0.62	0.40	0.06
473	0.58	0.44	0.04

TABLE-2
ACTIVATION ENERGY FOR TiOPc THIN FILM OF THICKNESS 269 nm AS DEPOSITED AND ANNEALED IN VACUUM AT DIFFERENT TEMPERATURES

Annealing temperature (K)	Activation energy (eV)		
	E_1	E_2	E_3
As deposited	0.73	0.52	0.04
323	0.68	0.55	0.03
373	0.65	0.54	0.02
423	0.63	0.46	0.04
473	0.60	0.51	0.04

spectrophotometer. The visible and near ultraviolet transitions in Pc molecule have generally been interpreted in terms of π-π^* excitation between bonding and antibonding molecular orbitals[11].

The absorption spectra of TiOPc thin films of thickness 245 nm (as deposited and annealed in air for 1 h at temperatures 323, 373, 423 and 473 K) are given in Fig. 3. Fig. 4 shows the absorption spectra of TiOPc thin films of thickness 245 nm (as deposited and annealed in vacuum for 1 h at temperatures 323, 373, 423 and 473 K). The absorption at 747 nm results from Q band and that at 354 nm results from B (soret) band. Both Q and B bands arise from π-π^* transitions[12,13]. The stability in the peak positions for the films annealed at different temperatures give an evidence of a stable structure of the films. To obtain information about direct or indirect interband transitions the fundamental absorption edge data is analyzed within the frame work of one electron theory of Bardeen *et al.*[14]. This theory has been employed to analyse the absorption edge of phathalocyanines[15]. The absorption ($\alpha \geq 10^4$ cm^{-1}) is related to direct band transitions[16].

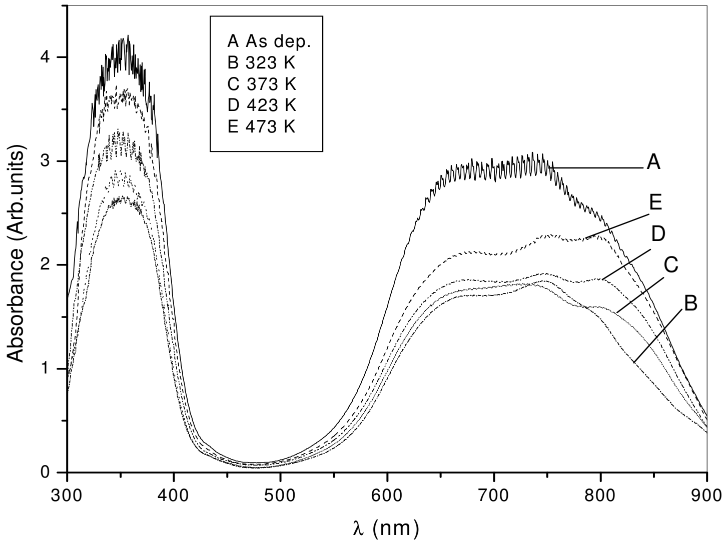


Fig. 3. Optical absorption spectra of as deposited and air annealed films

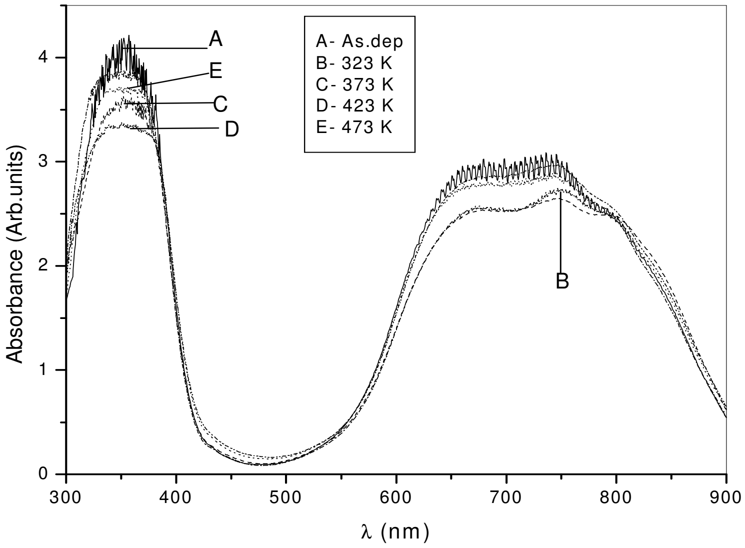


Fig. 4. Optical absorption spectra of as deposited and vacuum annealed films

For a film of thickness d; the absorption coefficient is given by

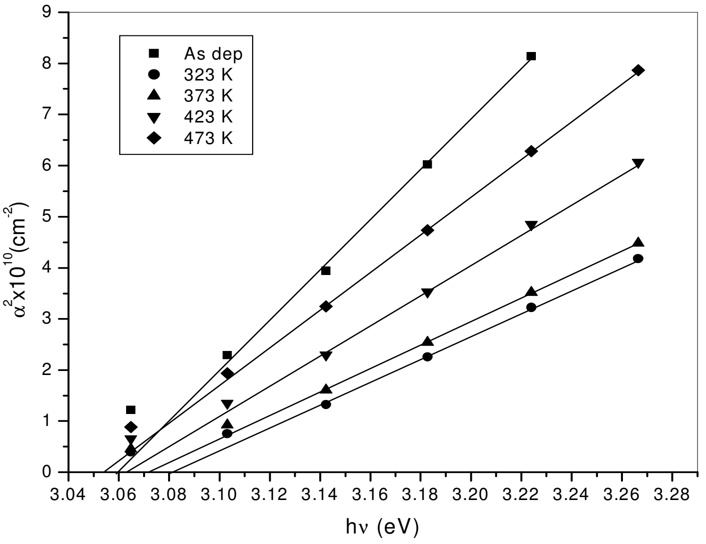
$$\alpha = \frac{2.303 \log A}{d} \tag{3}$$

where A is the absorbance.

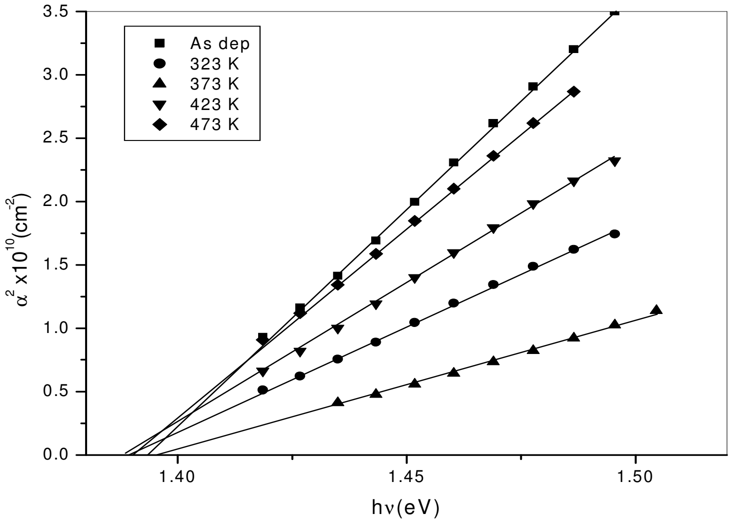
The absorption coefficient α is related to the band gap E_g and photon energy $h\nu$ by the relation

$$\alpha = \alpha_0 (h\nu - E_g)^n \tag{4}$$

where n = ½ for direct allowed transition and α_0 is a constant.

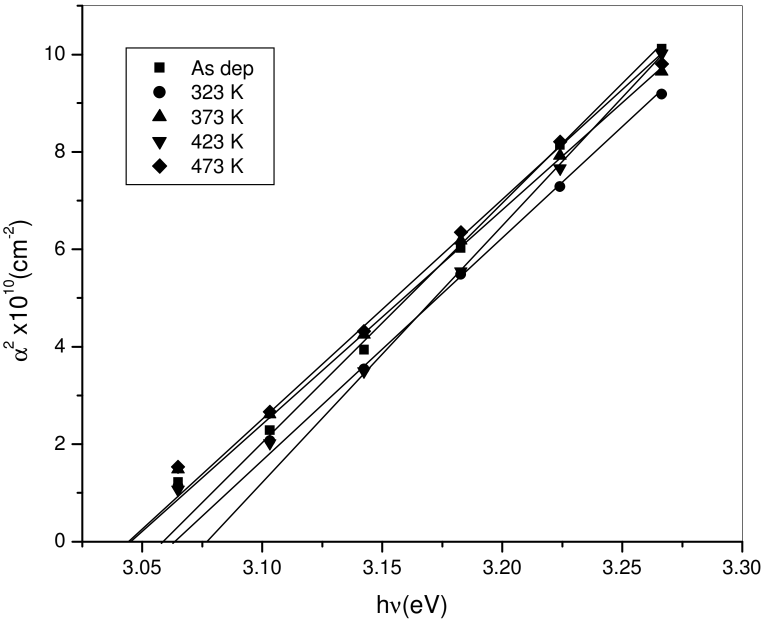


(a)

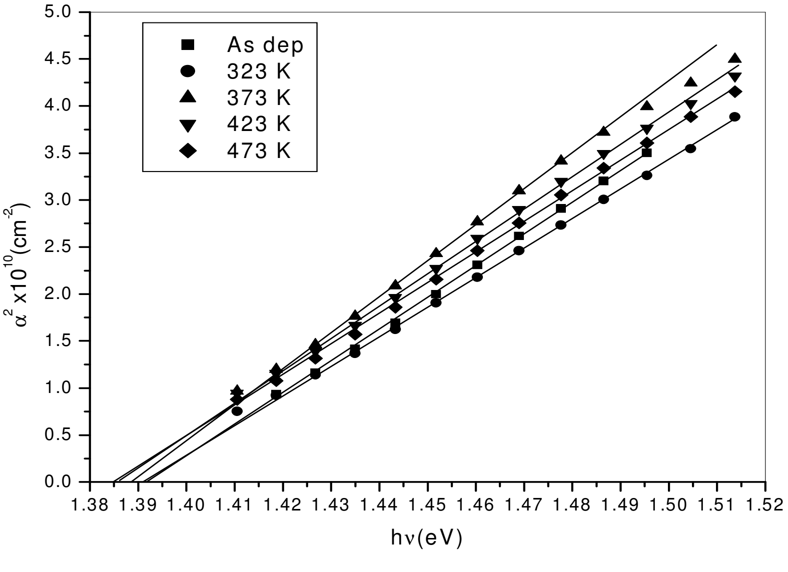


(b)

Fig. 5. Photon energy dependence of α^2 for as deposited and air annealed films



(a)



(b)

Fig. 6. Photon energy dependence of α^2 for as deposited and vacuum annealed films

The absorption coefficient α is calculated using eqn. 3. From the dependence of absorption coefficient on the photon energy, the band gap energy is determined by plotting α^2 as a function of photon energy. Extrapolation of these plots to $\alpha^2 = 0$ gives the optical band gap. The absorption at the lower energy side is related to singlet excitation and has been confirmed by many other phthalocyanines[17,18].

Fig. 5(a) and (b) show the plots of α^2 *versus* $h\nu$ for the as deposited and air annealed samples of TiOPc thin films of thickness 245 nm. α^2 *vs.* $h\nu$ plots for as deposited and vacuum annealed samples of TiOPc thin films of thickness 245 nm are given in Fig. 6(a) and (b).

The value of fundamental and onset energy gaps are determined in each case and are given in Tables 3 and 4.

TABLE-3
OPTICAL BAND GAP AND ONSET ENERGY GAP OF TiOPc THIN FILMS, AS DEPOSITED AND ANNEALED IN AIR AT DIFFERENT TEMPERATURES

Annealing temperature (K)	Optical band gap (eV)	Onset energy gap (eV)
As deposited	3.07	1.39
323 K	3.08	1.39
373 K	3.06	1.40
423 K	3.06	1.39
473 K	3.06	1.39

TABLE-4
OPTICAL BAND GAP AND ONSET ENERGY GAP OF TiOPc THIN FILMS, AS DEPOSITED AND ANNEALED IN VACUUM AT DIFFERENT TEMPERATURES

Annealing temperature (K)	Optical band gap (eV)	Onset energy gap (eV)
As deposited	3.07	1.39
323 K	3.07	1.38
373 K	3.06	1.39
423 K	3.06	1.39
473 K	3.05	1.39

The optical band gap of TiOPc thin films is found to be practically independent of annealing in air and annealing in vacuum.

Conclusion

Titanyl phthalocyanine (β-modification) thin films have been prepared on to glass substrates by thermal evaporation technique. Temperature dependence of electrical conductivity of the films is investigated. In the temperature dependence of electrical conductivity plots, more than one linear region is obtained. This confirms the existence trap levels. An extrinsic to intrinsic cross-over for the activation is identified. Annealing in air and vacuum decreases the intrinsic activation energy of TiOPc thin films. The number of trap levels is found to be independent of air and vacuum annealing. In conclusion the central metal ion influences the thermal activation energy of TiOPc thin films. The absorption spectra of TiOPc thin films show evidence for the existence of two absorption regions identified as the Q-band and the soret band. The peaks obtained in the visible and near infrared region are due to the π-π* transitions. The presence of peaks at high photon energy indicates that these transitions involve the *d*-electrons of the central metal ion. It is observed that air annealing and vacuum annealing have no significant role in the absorption spectra and optical band gap of TiOPc thin films. The fundamental and onset energy gaps are estimated to be 3.07 and 1.39eV, respectively.

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