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Effect of Substrate Temperature and Annealing on the Electrical and Optical Properties of Zinc Phthalocyanine Thin Films

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Zinc phthalocyanine thin films are prepared at different substrate temperatures at a base pressure of 10^{-5} m bar. Thin films are coated on glass substrates by thermal evaporation technique. Samples of equal thickness coated at room temperature are subjected to post-deposition annealing at different temperatures in air and vacuum for 1 h. The electrical conductivity studies are carried out by keeping the samples in a conductivity cell at a pressure of 10^{-3} mbar in the temperature range of 300–500 K. The electrical conductivity is plotted as a function of absolute temperature. The conduction mechanism is observed to be hopping. The thermal activation energy is calculated and is observed to vary with annealing temperature and substrate temperature. The optical absorption studies are done in the UV-Visible region. The optical band gap energies of the samples are calculated.

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

INTRODUCTION

Phthalocyanines are aromatic hydrocarbons coming under the class of organic semiconductors. They are highly stable against thermal and chemical decomposition and have an intense optical absorption in the visible region of the electromagnetic spectrum. So these materials have become very important candidates having a wide range of applications. They are used in gas sensors[1], in photovoltaic and solar cells[2, 3], as dyes in paint and textile industry[4], and in opto-electronic devices[5]. The electrical conductivity of ZnPc thin layers are influenced by gases like O_2, NO_2, H_2 and NH_3 which made it possible to be used in gas sensing devices[6, 7]. The effect of oxygen on the photovoltaic properties of organic solar cells consisting of zinc phthalocyanine (ZnPc) and a perylene pigment has been investigated by Kerp *et al.*[8] DC conduction processes and electrical parameters of ZnPc thin films have been studied by Saleh *et al.*[9] Zinc phthalocyanine is employed in medical application due to its selective binding to tumour-selective antibodies and it has

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been used in the synthesis of a novel compound applicable in photodynamic therapy of cancer[10, 11]. During the last few years, the interest of ZnPc in the thin film form has increased due to its potential application as a gas sensor. It is observed that the properties of ZnPc thin films depend on a number of parameters including the film morphology, which in turn is determined by the preparation parameters.

It has become apparent that the progress in the development of active materials for molecular electronics such as chemical sensors and thin-film transistors[12] based on ZnPc thin films require a more comprehensive knowledge of its material properties. In this paper, the electrical and optical properties of ZnPc thin films coated at different substrate temperatures and those of samples subjected to post-deposition annealing in air and vaccum at different constant temperatures are investigated and the thermal activation energies and optical band gap energies are calculated in each case.

EXPERIMENTAL

Zinc phthalocyanine in the powder form (99.99%) pure obtained from Aldrich is used as the source material. The samples are prepared in a "Hind Hi Vac" vacuum coating unit (Model No. 12A4). Thermal evaporation technique is used for film formation[13]. Thin films are formed on thoroughly clearned glass substrates keep at room temperature and also kept at different constant temperatures at a base pressure of 10^{-5} mbar. The thickness of the films is controlled by a single crystal thickness monitor and is cross checked by Tolansky's multiple beam interferometry method[14]. The samples of equal thickness coated at room temperature are annealed in air and vacuum for 1 h. For air-annealing, a specially designed furnace the temperature of which is controlled and recorded by a digital temperature controller cum recorder is used. The electrical conductivity measurements are made by keeping the samples in a conductivity cell in which a pressure of 10^{-3} mbar is maintained and using a Keithley programmable electrometer Model No. 617 between an approximate temperature range of 300–500 K. Ohmic contacts are made with silver electrodes and silver paste. The optical transmittance of these thin films in the UV-Visible region is recorded using Shimadzu 160A spectrophotometer.

RESULTS AND DISCUSSION

The temperature dependence of electrical conductivity is given by the Arrhenius equation, $\sigma = \sigma_0 \exp(-E_T/k_BT)$ where σ_0 is the pre-exponential factor, E_T is the thermal activation energy, k_B is Boltzmann constant and T is the absolute temperature. Such an exponential variation of electrical conductivity is known for semiconductors. Multiple donor levels exist within the forbidden energy gap and the deeper levels can be frozen out as the temperature is increased. Conductivity in phthalocyanines is due to both hopping of holes and charge transport *via* excited states. In such a case, the conductivity is given by

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

where E_1 is the activation energy in the intrinsic region and $E_2, E_3, \ldots$ are those corresponding to impurity scattering at comparatively low temperatures[15]. A, B, C are constants.

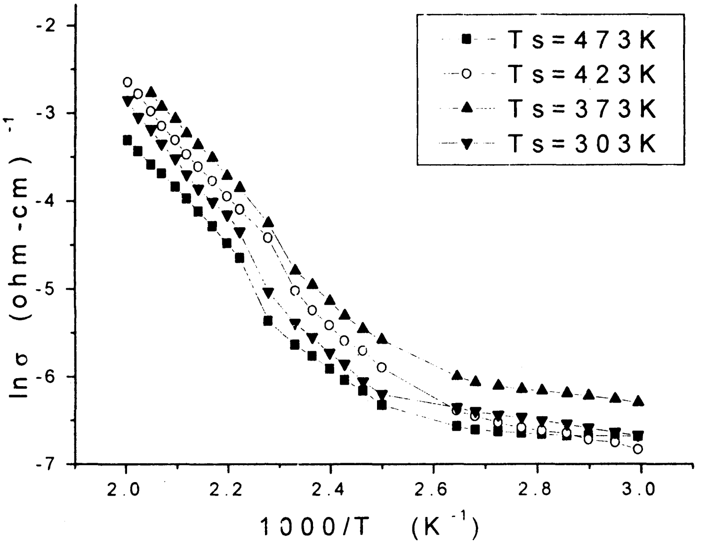

Fig. 1. Plots of ln σ *vs.* 1000/T for ZnPc thin films coated at different substrate temperatures

TABLE-1
VARIATION OF ACTIVATION ENERGY FOR ZnPc THIN FILMS COATED AT DIFFERENT SUBSTRATE TEMPERATURES

Substrate temperature (K)	Activation energy (eV)		
	E_1	E_2	E_3
303	0.58	0.45	0.08
373	0.56	0.41	0.07
423	0.54	0.43	0.09
473	0.52	0.37	0.03

The electrical conductivity of a thin film is given by $\sigma = L/Rbt$, where L is the length, R is the resistance, b is the breadth and t is the thickness of the film. A plot of ln σ *vs.* 1000/T shows three linear portions. From the slope of the straight-line parts the thermal activation energy is calculated. The higher temperature region is the intrinsic or the non-extrinsic region for which E_1 is the thermal activation energy. The other two low temperature regions are the extrinsic regions with activation energies E_2 and E_3. Plots of ln σ against 1000/ T are drawn for various cases and the corresponding activation energies are calculated. Such graphs for ZnPc thin films coated at different substrate temperatures are given in Fig. 1. The variation of the activation energies when the substrate temperature is increased is collected in Table-1.

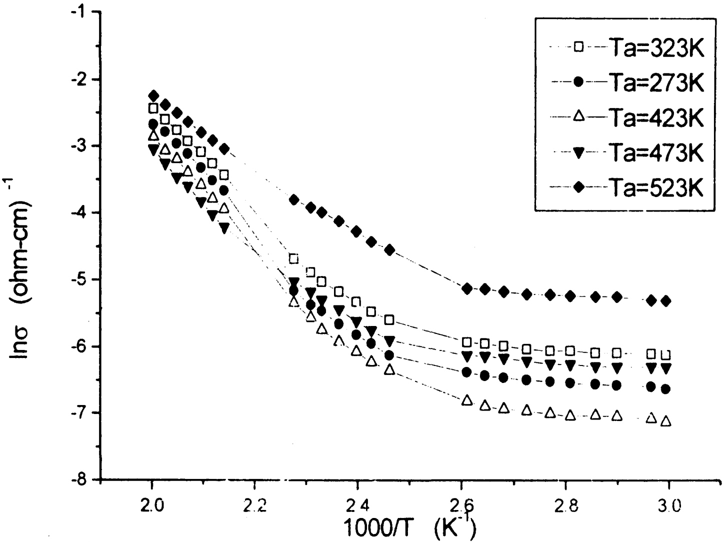

Fig. 2. Plots of ln σ *vs.* 1000/T for ZnPc thin films annealed in air at different temperatures for 1 h

TABLE-2
VARIATION OF ACTIVATION ENERGY FOR ZnPc THIN FILMS ANNEALED IN AIR AT DIFFERENT TEMPERATURES

Annealing temperature (K)	Activation energy (eV)		
	E_1	E_2	E_3
323	0.62	0.42	0.04
373	0.64	0.44	0.05
423	0.68	0.47	0.06
473	0.71	0.41	0.04
523	0.51	0.35	0.03

It is observed that the activation energy in the intrinsic region E_1 decreases with increase in substrate temperature. On increasing the substrate temperature the surface energy increases an the grain size of the film increases. The crystallinity also increases. Hence, a decrease in activation energy is expected. In the two extrinsic regions the activation energies E_2 and E_3 change in a random manner since the conductivity is due to impurity scattering. Plots of ln σ *vs.* 1000/T for ZnPc thin films annealed in air for 1 h are given in Fig. 2 and in Fig. 3 are given those for samples annealed in vacuum for 1 h. The corresponding variations in activation energies are given in Tables 2 and 3 respectively.

The thermal activation energy for the intrinsic region E_1 is found to increase with annealing temperature, both for air-annealed and vacuum-annealed samples. The steady state transport properties of carriers in organic semiconductors are dominated by the presence and energy distribution of carrier trapping sites. On annealing, some crystal defects may get rectified and a few trap levels may get removed which leads to an increase in activation energy. Also the removal of oxygen impurities on annealing can lead to a decrease in conductivity and a corresponding increase in thermal activation energy. The slightly higher activation energies of the samples annealed in vacuum suggest more degassing in vacuum. E_2 and E_3 change in a random manner.

TABLE-3
VARIATION OF ACTIVATION ENERGY FOR ZnPc THIN FILMS ANNEALED IN VACUUM AT DIFFERENT TEMPERATURES

Annealing temperature (K)	Activation energy (eV)		
	E_1	E_2	E_3
323	0.63	0.44	0.06
373	0.66	0.47	0.07
423	0.70	0.48	0.08
473	0.74	0.52	0.07
523	0.49	0.33	0.05

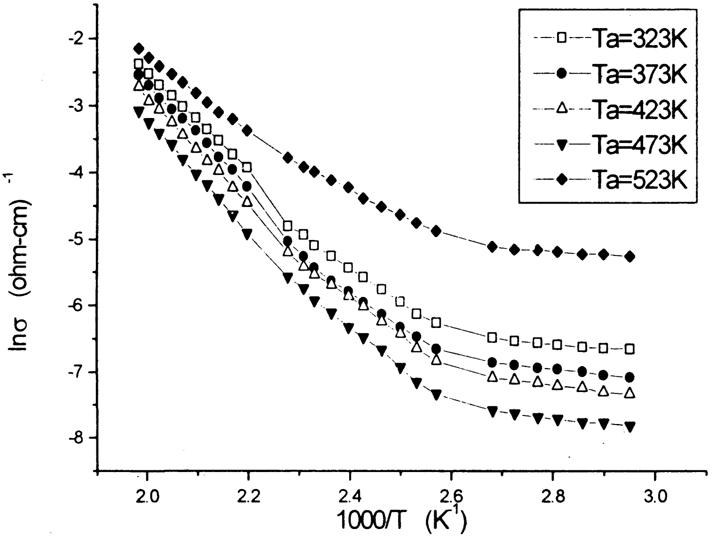

Fig. 3. Plots of ln σ *vs.* 1000/T for ZnPc thin films annealed in vacuum at different temperatures.

Plots of T% *vs.* λ for films coated at different substrate temperatures are given in Fig. 4 and those for the air-annealed samples are given in Fig. 5. Increase in substrate temperature makes the film less transparent.

The absorption coefficient α is related to the optical band gap energy E_g by the equation $\alpha = \alpha_0 (h\nu - E_g)^{1/2}$ where $\alpha = (2.303/t) \log (1/T)$. Here t is the thickness of the film and T is the transmittance. The optical band gap energy is found from the α^2 *vs.* hν graph. Fig. 6 shows such plots for samples coated at

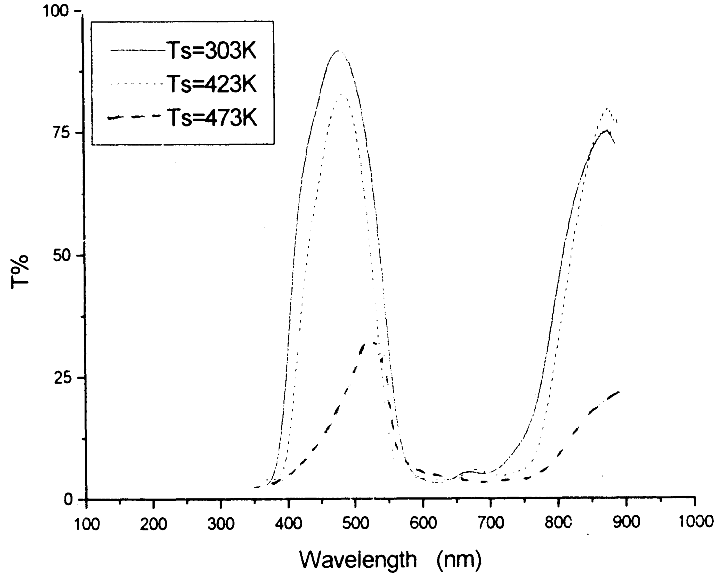

Fig. 4. Plots of ZnPc thin films coated at different substrate temperatures

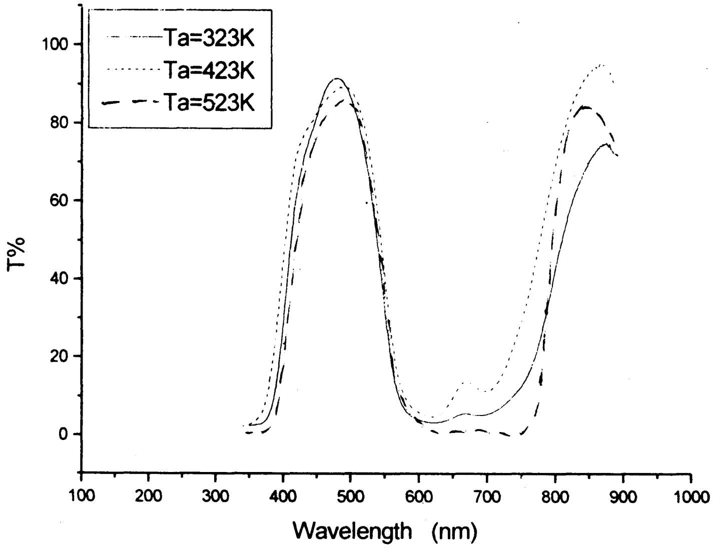

Fig. 5. Plots of T% *vs.* λ for ZnPc thin films annealed in air at different temperatures

different substrate temperatures. The observed values of the optical band gap energies and trap levels are given in Table-4. The optical band gap energies remain almost the same. The corresponding graphs and table for the air-annealed films are given in Fig. 7 and Table-5 respectively. The vacuum-annealed samples give almost the same results.

TABLE-4
VARIATION OF OPTICAL BAND GAP ENERGY AND TRAP LEVELS FOR ZnPc THIN FILMS COATED AT DIFFERENT SUBSTRATE TEMPERATURES

Substrate temperature (K)	Optical band gap energy (eV)	Trap levels (eV)
303	2.96	1.53
373	2.95	1.51
423	2.95	1.55
473	2.95	1.50

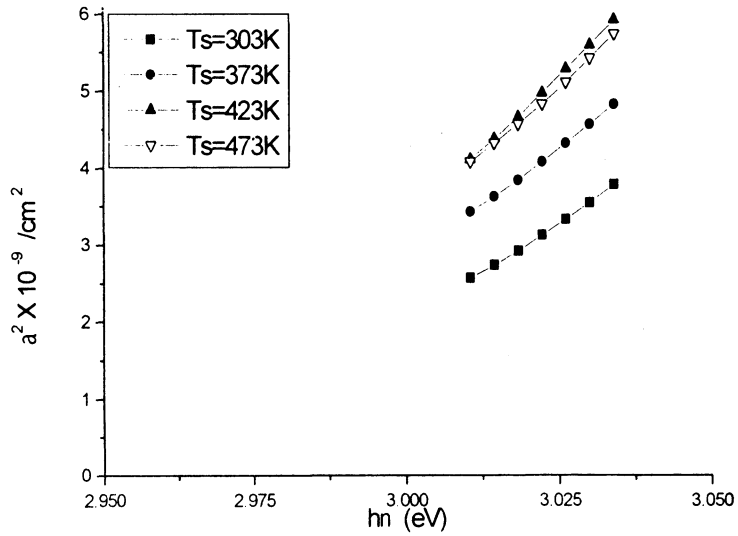

Fig. 6. Plots of α^2 *vs.* hv for ZnPc thin films coated at different substrate temperatures

No significant change in the optical band gap energy is observed due to an increase in the substrate temperature. Fig. 5 gives the plots of α^2 *vs.* hv for samples annealed in air at different temperatures and the respective optical band gap energies and trap levels are given in Table-4. The band gap energy remains the same except for the sample annealed at 523 K which shows an increase. This may be due to a phase change.

TABLE-5
VARIATION OF OPTICAL BAND GAP ENERGY AND TRAP LEVELS FOR ZnPc THIN FILMS ANNEALED IN AIR AT DIFFERENT TEMPERATURES

Annealing temperature (K)	Optical band gap energy (eV)	Trap levels (eV)
373	2.95	1.51
423	2.96	1.50
473	2.96	1.52
523	3.00	1.50

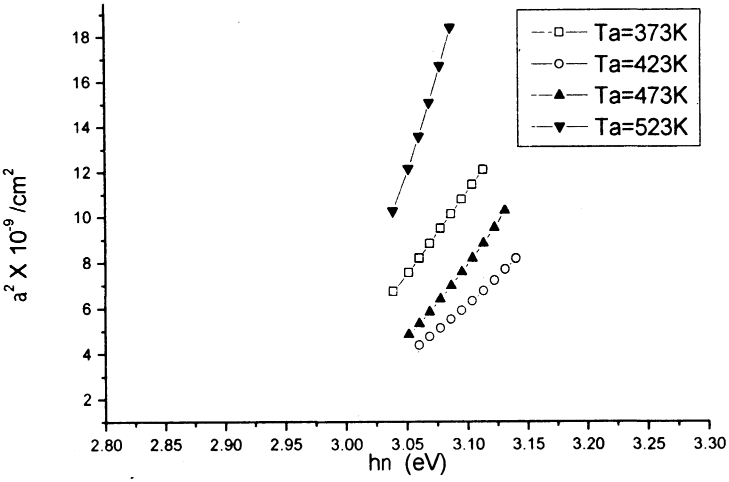

Fig. 7. Plots of α^2 *vs.* hν for ZnPc thin films annealed in air at different temperatures

Conclusion

The three-zone Arrhenius plot suggests a transition from extrinsic to intrinsic behaviour. The conjugation structure of phthalocyanine is the essential condition leading to non-extrinsic conductivity. The non-extrinsic activation energies of ZnPc thin films of thickness 2400 Å are found to decrease with increase in substrate temperature. The two extrinsic activation energies show random changes. For the air-annealed and vacuum-annealed samples the non-extrinsic thermal activation energy is found to increase in annealing temperature, which is due to the change in crystallinity and the oxygen impurities present in the sample. Both air-annealing and vacuum-annealing give good results.

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