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Effect of annealing and γ irradiation on tin phthalocyanine thin films

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Metal phthalocyanines are important among organic dyes because of their chemical and thermal stability. Thin film samples of tin phthalocyanine (SnPc) have been prepared for examination by thermal evaporation technique. Some optical and electrical properties of the samples were studied as a function of annealing temperature and γ radiation doses. Optical transition is found to be of direct type and optical band gaps are determined by analyzing the absorption spectrum. The activation energy of the dark conductivity is found to be highly dependent on both annealing and γ radiation doses.

Key words: *phthalocyanine; thin film; optical band gap; activation energy*

1. Introduction

Phthalocyanines (Pcs) receive great interest nowadays due to their variety of applications such as gas sensors, organic thin film transistors, and various optoelectronic applications [1–4]. Metal phthalocyanines [MPc] are highly coloured, p-type organic semiconducting compounds which exhibit high chemical and thermal stability and thus can be sublimed without decomposition to form high quality thin films by the thermal evaporation technique. The stability of these films, however, at high temperature and high radiation environment is still a matter of research. Physical properties of Pcs are strongly influenced by the growth parameters and the post-deposition treatments such as annealing [5]. Irradiation of thin films with high energy radiations like γ rays, is expected to affect their physical properties. The study of irradiated samples enhances the efficiency improvement in its applicability in a radiation environment and is also important in obtaining basic information on vacancies, defects and their interaction with impurities [6, 7]. In this work, we have made a detailed in-

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vestigation on the effect of vacuum annealing and γ ray irradiation on the electrical and optical properties of vacuum deposited Tin Phthalocyanine (SnPc) thin films.

2. Experimental

Spectroscopically pure SnPc powder (Sigma-Aldrich Company, USA) was used as the source material for the preparation of thin films. The purity of the powder has been counter-checked by CHN analysis (C – 61.26%, H – 2.471%, N – 18%). Thin films of suitable thickness have been prepared by vacuum sublimation from a resistively heated molybdenum boat using a "Hind Hi-Vac" coating unit. The films were deposited onto thoroughly cleaned rectangular glass substrate at room temperature under the pressure of 10^{-5} Torr. The thickness of the films was crosschecked with the Tolansky multiple beam interference technique [8]. Thin films prepared at room temperature were annealed at various temperatures for one hour in a vacuum chamber. A programmable temperature controller (cam recorder) was used to control the temperature. UV-Visible absorption spectra in the wavelength range from 300 nm to 900 nm were recorded using a Shimadzu 160A UV-Vis spectrophotometer.

Electrical conductivity measurements were performed using a programmable Keithley electrometer (model No. 617). Electrical conductivity was studied in the temperature range 300–473 K under the pressure of 10^{-3} Torr to avoid possible contamination. The temperature was monitored using a chromel–alumel thermocouple. SnPc thin films were irradiated with ^{60}Co γ source. Radiation doses were controlled through the exposure time.

3. Results and discussion

3.1. Optical studies

The optical absorption spectra of as-deposited and γ irradiated SnPc thin films for various radiation doses are shown in Fig. 1. As the γ radiation dose increases, the absorbance decreases. The spectra originate from the orbital within the aromatic 18π electron system and from overlapping crystals on the central metal atom. The electronic $\pi \rightarrow \pi^*$ transition in the energy range 300–400 nm corresponds to an intense B band (Soret band) which gives the fundamental absorption edge, while the band in the energy range 700–800 nm (Q band) gives the onset energy [9, 10]. B band consists of a peak at 3.58 eV and Q band consists of two peaks at 1.43 eV and 1.76 eV. The interaction between molecules strongly influences the absorption spectrum leading to splitting of Q band into two distinct peaks. The fundamental absorption edge is analyzed within the framework of one electron theory of Bardeen et al. [11]. The absorption coefficient α is related to the energy band gap E_g and the photon energy $h\nu$:

$$\alpha = \alpha_0 \left(h\nu - E_g \right)^n \tag{1}$$

where n is 1/2, 3/2, 2 or 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions, respectively.

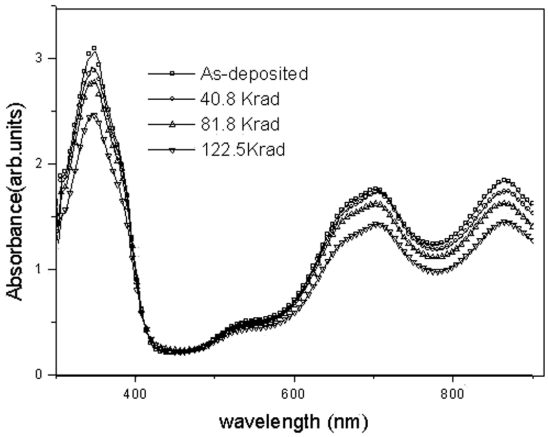

Fig. 1. Optical absorption spectrum of SnPc thin films irradiated with various doses of γ radiation

A satisfactory linear fit is obtained for α^2 vs. hν, indicating the presence of direct allowed transition for SnPc thin films. The intercept on the energy axis, as shown in Fig. 2, gives the band gap E_g of the material.

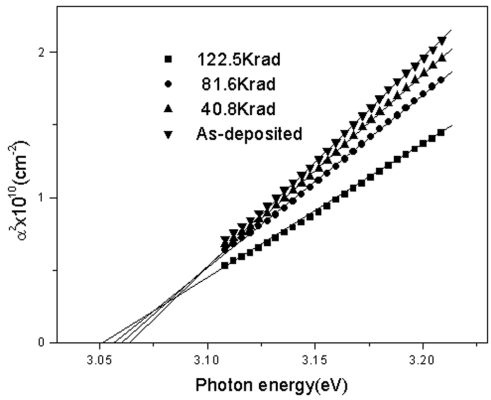

Fig. 2. Plot of α^2 versus $h\nu$ for as deposited and irradiated SnPc thin films with different dosage

The investigation of optical properties was also extended to samples annealed at various temperatures. The optical absorption spectra of annealed samples are shown in Fig. 3. Plots of α^2 vs. $h\nu$ for the as-deposited and annealed SnPc thin films are shown in Fig. 4.

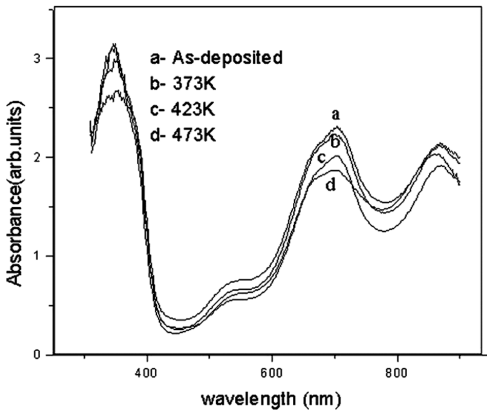

Fig. 3. Optical absorption spectra of SnPc thin films annealed under vacuum at various temperatures

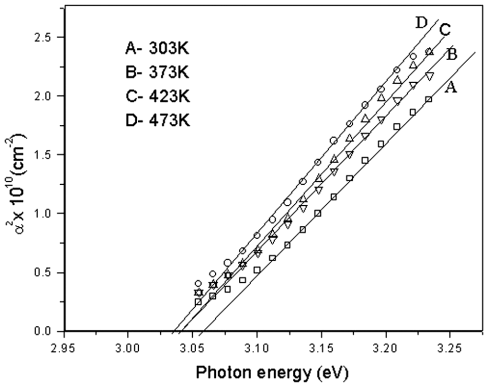

Fig. 4. Plots of α^2 versus $h\nu$ for vacuum annealed samples of SnPc

In the both cases, the fundamental and onset energy gaps amount to 3.06±0.01 eV and 1.55±0.01 eV, respectively. There is no appreciable variation in band gap and excitonic energy with annealing and γ irradiation. This shows that the optical band gaps of the material are stable upon high-energy irradiation and temperature.

3.2. Electrical studies

Electrical properties of organic semiconductor thin films strongly depend on the conditions of deposition and the post deposition treatments. For Pc thin films, the electrical conductivity σ fulfils the Arrhenius equation:

$$\sigma = \sigma_0 \exp\left(-E/k_B T\right) \tag{2}$$

where σ is the conductivity at the temperature T [K], E is the thermal activation energy, k_B is the Boltzmann constant and σ_0 is the pre-exponential factor. The Arrhenius plot ($\ln\sigma$ vs. $1000/T$) yields a straight line, with the slope corresponding to the value of thermal activation energy. In Figure 5, lnσ vs. 1000/T is plotted for SnPc thin films 400±5 nm thick before and after irradiation. According to Davis and Mott [12], in this type of material the conductivity exhibits different behaviour in various regions of the Arrhenius plot. There are two linear regions for each graph, which give two activation energies E_1 and E_2.

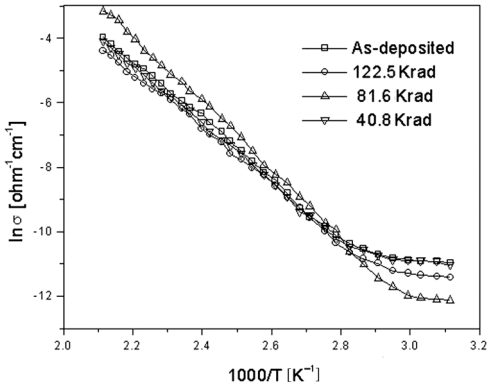

Fig. 5. Plot of $\ln\sigma$ vs. $1000/T$ for as deposited and irradiated SnPc thin films for various doses of radiation

The activation energy E_1 is related to the intrinsic generation process and E_2 to the impurity scattering [9]. The conduction mechanism at lower temperatures is explained in terms of hopping through a band of localized states and at higher temperatures – in terms of thermal excitation of carriers to the band edges. The change in the slope, and hence the change in activation energy, reflects a change from intrinsic conduction to the extrinsic one [13]. The activation energies determined for non-irradiated and irradiated samples are listed in Table 1.

Table 1. Variation of activation energy in the intrinsic and extrinsic region as a function of irradiation dosage

γ radiation dosage [Krad]	Activation energy [eV]	
	E_1	E_2
As deposited	0.65±0.01	0.06±0.01
40.8	0.76±0.01	0.16±0.01
81.6	0.90±0.01	0.20±0.01
122.5	0.75±0.01	0.17±0.01

The activation energy increases with exposure up to 81.6 Krad and then decreases. In the case of vacuum-annealed samples, the activation energy is found to increase with annealing temperature up to 423 K and then reduces as shown in Fig. 6. The activation energies of the samples annealed at various temperatures are given in Table 2. The reduction in activation energy at 473 K and for radiation dose of 122.5 Krad may be attributed to the instability of the material due to heavy vibrations of the atoms.

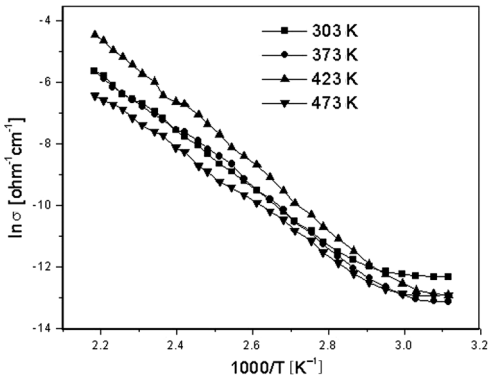

Fig. 6. Plot of $\ln\sigma$ versus $1000/T$ for SnPc thin film annealed under vacuum at various temperatures

Table. 2. Variation of activation energy in the intrinsic and extrinsic region as a function of annealing temperature

Temperature of annealing [K]	Activation energy [eV]	
	E_1	E_2
303	0.80±0.01	0.09±0.01
373	0.86±0.01	0.16±0.01
423	0.95±0.01	0.16±0.01
473	0.77±0.01	0.07±0.01

The charge carriers in Pc are thermally generated holes and the presence of traps plays a dominant role in the conduction of these materials [14, 15]. Presence of trap levels is attributed to defects generated by ambient nitrogen, hydrogen, and oxygen affecting electrical conductivity, mobility and trap density. Structural defects may also affect the conductivity. This, in turn, affects the position of the Fermi level [13]. During annealing in vacuum oxygen may be desorbed, which reduces the conductivity of the samples. On the other hand, irradiation of samples with high-energy radiation creates structural defects which act as trapping centres. This is indicated by the increase in activation energy and thus the reduction in the conductivity of SnPc thin films.

4. Conclusion

Thin films of SnPc have been prepared using vacuum deposition technique. Effect of post-deposition annealing and the effect of γ ray irradiation on the optical and electrical properties have been investigated. As the intensity of irradiation dose increases, the absorption intensity decreases. It is also found that the band gap remains constant but the conductivity is affected by irradiation and annealing. The activation energy varies with both annealing and irradiation.

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