CHARACTERIZATION OF TITANIUM PHTHALOCYANINE DICHLORIDE THIN FILMS AND ITS USE AS GAMMA RADIATION SENSOR

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ABSTRACT

The temperature at which the substrate is maintained during deposition is the most critical parameter determining the structure and properties of thin solid films. Halogenated metallo- phthalocyanine thin films are suitable for gas sensing applications. Titanium phthalocyanine dichloride (TiPcCl$_2$) thin films are prepared on pre-cleaned glass substrates kept at different temperatures ranging from 300K to 475K by vacuum sublimation technique. The effects of substrate temperature on the optical band gap have been studied by recording absorption spectrum. The dependence of substrate temperature on electrical conductivity of thin films is studied from the Arrhenius plots Ln Vs 1000/T. Structural studies are done by analyzing the X-ray diffractograms of thin films and different micro structural parameters such as lattice constant, grain size, lnternal strain and dislocation density are determined. It is found that optical band gap, thermal activation energy and structural parameters vary considerably with substrate temperature. . Thin films are irradiated with gamma radiation for different exposure times and different dosages. Effect of irradiation on optical and electrical properties of the samples are also studied.

KEYWORDS: Organic semiconductors, Substrate temperature, Optical properties, Electrical properties

1. Introduction

Organic semi conducting thin films have become increasingly important for applications in optical and electronic devices such as LED or FET [1-3].Industrial research field is focusing on the development of technologies for an economical deposition of the organic materials. Metal phthalocyanines (MPcs) with excellent thermal and chemical stability and strong absorption in the region of visible to NIR has become one of the main recording media for optical discs. MPcs are promising candidate for the active part of organic solar cells, and they exhibit a characteristic structural reorganization [4-6]. The phthalocyanines [Pc] are a class of planar aromatic organic compounds characterized by conjugated bonding and have attracted a great deal of attention for quite sometime because of their unique properties such as semi conductivity, photoconductivity, photochemical reactivity, thermal and chemical stability and their application in the field of color display technology and gas sensors [7,8]. Study has been done on the third order non-linearity in phthalocyanine related compounds and their derivatives [9,10]. The optical, electrical and structural properties of phthalocyanine thin films are determined by preparation parameters such as deposition rate, substrate temperature and post deposition annealing [11]. Although there is evidence that halogenated MPcs exhibit similar properties as that of MPcs, only very few studies have been reported so far. The halogenated Pc's exhibit remarkably larger temperature change compared to unhalogenated Pc's [12]. In the present work, we study the effect of substrate temperature on optical, electrical and structural properties of Titanium Phthalocyanine dichloride ($C_{32}H_{16}Cl_2N_8Ti$ - TiPcCl$_2$) thin films. The molecular structure of TiPcCl$_2$ is shown in figure 1. The structure of TiPcCl$_2$ powder is identified as triclinic [13].
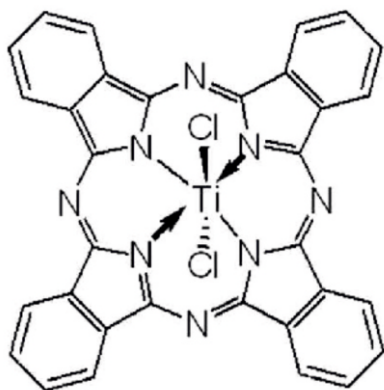

Fig. 1 Structure of TiPcCl$_2$ molecule

2. Experimental details

Spectroscopically pure TiPcCl$_2$ powder supplied by Sigma-Aldrich Company (USA) is used as the source material for the preparation of thin films. The purity of the material is counter-checked by the elementary CHN analysis. Thin films of varying thickness are prepared by vacuum sublimation from a resistively heated molybdenum boat using a Hind Hi-Vac coating unit. Films are deposited onto thoroughly cleaned rectangular glass substrate kept at temperatures 305K, 373K, 423K and 473K at a pressure of 10^{-5}torr. Substrates can be uniformly heated with a substrate heater. The temperature is monitored and controlled by an automated electronic temperature controller attached with a chromel-alumel thermocouple. The thickness of the films is measured by Tolansky's multiple beam interference technique [14].

UV-Visible absorption spectra of TiPcCl$_2$ thin films are recorded using a 'Shimadzu 160A' spectrophotometer in the wavelength range 300nm to 900nm. Ohmic contacts are made using evaporated silver electrodes for electrical conductivity measurements. A programmable Keithley electrometer (Model No. 617), in the constant current source mode is used for electrical measurements. The electrical conductivity of thin films is measured in the temperature range 323 – 538 K by keeping the samples in the film holder of the conductivity cell. Bruker (Model D8 Advance) X-ray diffractometer with Cu K radiation of wavelength $\gamma = 1.54059$ Å is used for the diffraction measurements.

3. Results and Discussions

The substrate temperature during deposition is perhaps the most critical parameter determining the structure and properties of thin solid films produced by the techniques of vacuum evaporation[15].

3.1 *Optical Studies*

Optical absorption spectra of films are analysed to get the optical energy band gaps. The absorption edge at the higher energy side is related to fundamental absorption and the absorption at the lower energy side is ascribed as excitonic absorption and is related to the formation of singlet excitons [16,17].

The absorption peak around 350 nm results from the B (Soret) band and the peak around 650 nm results from the Q-band. The Q-band that exists at the red end of the visible spectrum is connected with π (a_{1u}) to $\pi*(e_g)$ transition on the Pc macro cycle and B-band (Soret) in the UV region is due to the transition from π (a_{2u}) to $\pi*$ (e_g) transitions.

The absorption coefficient is related to the energy band gap Eg and the photon energy h by the equation

$$\alpha = \alpha_0 (h - Eg)^n \qquad (1)$$

where n is ½ for direct allowed transition and 2 for indirect allowed transition.

Figures 2 and 3 show typical absorption spectrum of TiPcCl₂ at substrate temperature 373 K and the corresponding α^2 versus h plot respectively.
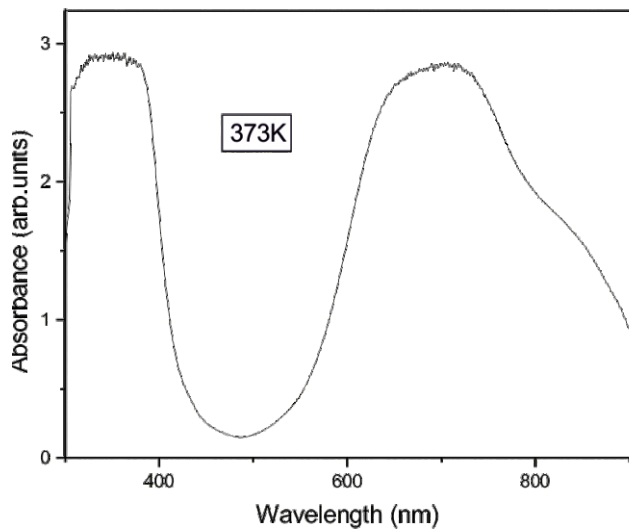

Fig. 2. Typical absorption spectrum of TiPcCl₂ thin films prepared at substrate temperature 373K
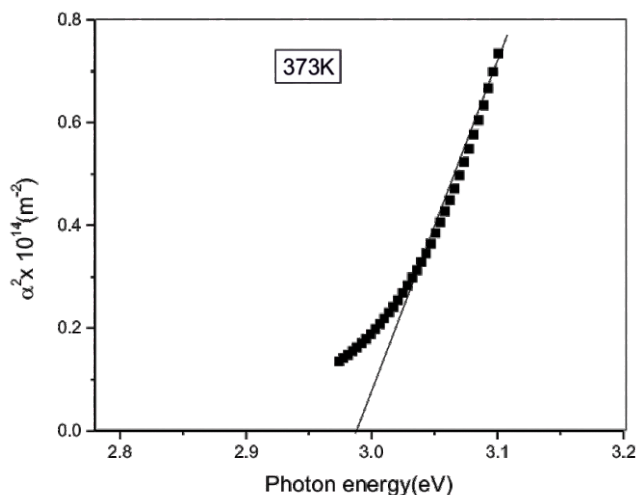

Fig. 3. Plot of ^{2} versus h for TiPcCl₂ thin films prepared at substrate temperature 373K

From the plot of ^{2} versus h the fundamental energy band gap and the excitonic energy gap are determined with an accuracy of ±0.01eV and the estimated values of energy gaps are entered in the Table 1. The optical band gap of TiPcCl₂ thin films decreases with the increase of substrate temperatures. This decrease in band gap is attributed to rearrangement of molecules at higher substrate temperatures

Table 1. Fundamental and excitonic energy gaps for TiPcCl₂ thin films deposited at various substrate temperatures.

Substrate Temperature (K)	Fundamental Energy gap (eV)	Excitonic Energy gap (eV)
305	3.13	1.64
373	2.99	1.47
423	2.95	1.37
473	2.00	1.30

3.2 *Electrical Studies*
The electrical conductivity is given by the relation

$$\sigma = \sigma_o \exp(-Ea/2k_BT) \qquad (2)$$

where σ_o a constant, Ea is the activation energy, k_B is the Boltzmann's constant and T is the absolute temperature. The activation energies are estimated from the slopes of the plot of Ln σ versus 1000/T. The delocalised π electrons is responsible for the conduction in phthalocyanines. At higher temperatures, band conduction is observed and at lower temperatures hopping conduction is observed [18]. Hopping conduction is related to the generation of additional carriers by the charge carriers hopping between the neighbours in the localized states near the Fermi level region [19].
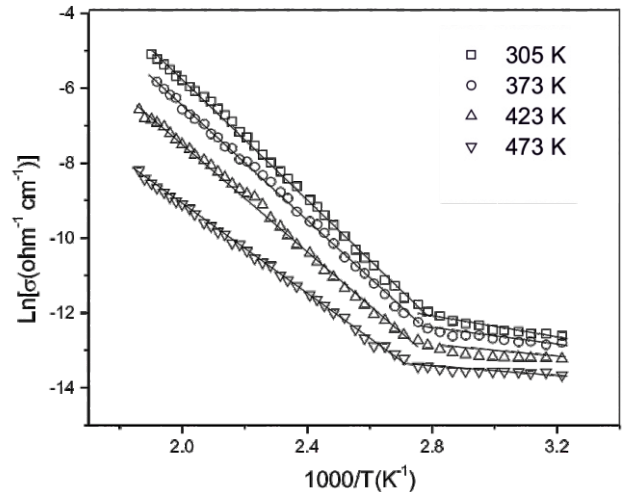

Fig. 4. Plot of Ln σ versus 1000/T or TiPcCl₂ thin films deposited at different substrate temperatures

Figure 4 shows the plot of Ln versus 1000/T for TiPcCl₂ thin films of thickness 550 nm deposited at substrate temperatures 305 K, 373 K, 423 K and 473 K. The graph shows two linear regions, indicating a change in conduction mechanism. The activation energy corresponding to these are estimated and collected in table 2. The intrinsic activation energy decreases with increase of substrate temperature. A sharp decrease is observed for an increase of substrate temperature from 423 K to 473 K. The decrease in activation energy with an increase of substrate temperature may be attributed to an increase in the size of the critical nucleus [20].

Table 2. Variation of activation energy for TiPcCl₂ thin films deposited at different substrate temperatures.

Substrate Temperature(K)	Activation energy (eV)	
	E₁	E₂
305	0.69	0.09
373	0.66	0.07
423	0.62	0.06
473	0.50	0.03

3.3 *Structural Studies*
The structural properties affect the performance of thin film as a functional material. XRD patterns are characteristic of the atomic arrangement in the given film.

The microcrystalline grain size D of the film is determined from the full width at half maximum L (FWHM) of the most intense peak in the XRD pattern using the Scherrer formula [21]

$$D = \frac{K\,\lambda}{L\,\cos\theta} \qquad (3)$$

where K is a constant equal to 0.9, =1.54059 Å and θ is the diffraction angle of the most intense peak.
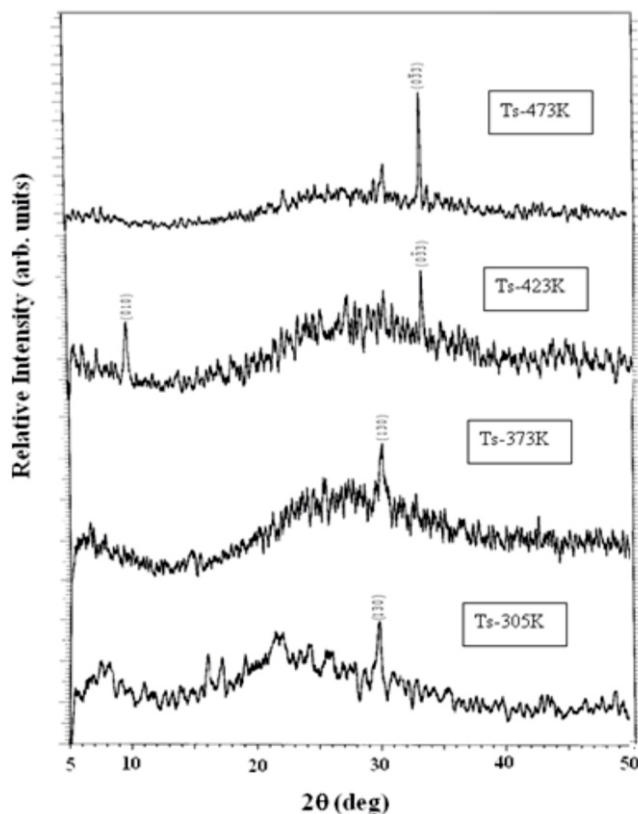
Fig. 4. X-ray diffraction pattern of TiPcCl₂ thin films prepared at different substrate temperatures.

Table 3 Variation of structural parameters with substrate Temperature for TiPcCl₂ thin films of thickness 330 nm.

Substrate Temperature (K)	Average Grain size(nm)	Average internal strain $\varepsilon \times 10^{-3}$	Dislocation density $\delta \times 10^{15}$ (m-2)
305	15.95	2.17	3.93
373	18.95	1.85	2.78
423	29.44	1.17	1.15
473	37.40	0.93	0.72

Dislocation density δ, is defined as the length of dislocation lines per unit volume of the crystal, which has been determined for thin films by making use of the values of average grain size D

$$\delta = \frac{n}{D^2} \qquad (4)$$

where n is a factor, which equals unity giving minimum dislocation density.

The micro strain ε developed in the thin film is calculated using the relation

$$\varepsilon = \frac{L Cos\theta}{4} \qquad (5)$$

Figure 4 shows the X-ray diffractogram of TiPcCl₂ thin films of thickness 330nm deposited at different substrate temperatures. The average grain size was found to increase from 15.95 nm to 37.40 nm with a decrease of internal strain from 2.17×10^{-3} to 0.93×10^{-3} with increase of substrate temperature from 305 K to 473 K for films of thickness about 330 nm. The average grain size, dislocation density and internal strain are calculated by measuring FWHM and entered in the Table 3. The film deposited at higher substrate temperature takes the preferential orientation along (0 3 3) the plane instead of (1 3 0) plane at lower temperature. The dislocation density has been observed to decrease with increase of substrate temperature. The number of grain boundaries gets reduced at higher substrate temperature. Intense peak is consistent with high degree of crystallization. The growth con-

ditions have strong influence on the properties of TiPcCl₂ thin films [22].

4. Conclusions

Optical and electrical conductivity studies of TiPcCl₂ thin films are done with respect to substrate temperature. Absorption spectra show the existence of two absorption region, which are identified as B-band and Q-band. Both the fundamental energy gap and onset energy gap shows variation with substrate temperature. Electrical conductivity by thermal activation process is found to involve different conduction mechanisms. In the high temperature region intrinsic conductivity by holes are found to contribute to the conduction process whereas in the lower temperature region impurities are found to play an active role. The conduction process is found to be controlled by different trap levels present in the forbidden energy gap. An increase of substrate temperature results in decrease of activation energy. Heat treatment led to significant changes in the film structures. Higher substrate temperature will offer higher mobility for the atoms condensing over the substrate for migration over its surface. So it improves the physical characteristics of the films.

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