Research Paper Science

Comparative Study of Tin Phthalocyanine and Tin Phthalocyanine Dichloride Thin Films

Dr Regimol C Cherian | Department of Physics, Assumption College, Changanacherry, Kottayam-686101, Kerala

ABSTRACT

Organic semi conducting thin films are important for applications in optical and electronic device fabrications. Thin films of tin phthalocyanine and tin phthalocyanine dichloride are prepared by thermal evaporation technique. Optical absorption spectra of these films are recorded and analyzed to evaluate the optical energy band gap. Electrical characterization of thin films is done using the arrhenius plot. From the powder X-ray diffractograms, structure is identified and prominent peaks are indexed also.

KEYWORDS Organic Semiconductors, Optical band gap, Activation energy, Structural studies

INTRODUCTION

Organic semiconductors have many interesting characteristics compared to more traditional inorganic semiconductors like Silicon and Germanium. So these materials have attracted the researchers for the last few decades. Yet the future holds even greater promise for this technology with an entirely new generation ultra low-cost, light weight and even flexible electronic devices. Phthalocyanines are p-type organic semiconductors characterized by conjugate bonding. Phthalocyanines have many interesting properties and theses properties have been exploited in various applications such as photoreceptor devices in printers, photocopiers, infra red security devices, electro chromic devices, chemical sensors and phthalocyanine therapy of cancer

Many of the phthalocyanines form stable combination with metal and semi-metal atoms forming metallo-phthalocyanine [MPc]. When it combines with metal which prefer a higher co-ordination number either square based pyramidal or tetrahedral or octahedral structures occur. In such cases, the central metal atom is co-ordinated with one or two axial ligands such as chlorine. 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 .The object of this work is to compare the optical absorption, electrical conductivity and structural properties of tin phthalocyanine ($C_{32}H_{16}N_8Sn$(II)-SnPc) and tin phthalocyanine dichloride ($C_{32}H_{16}N_8Cl_2Sn$(IV) -$SnPcCl_2$) thin films. The chemical structure of SnPc and $SnPcCl_2$ are given in Figures 1 and 2 respectively.

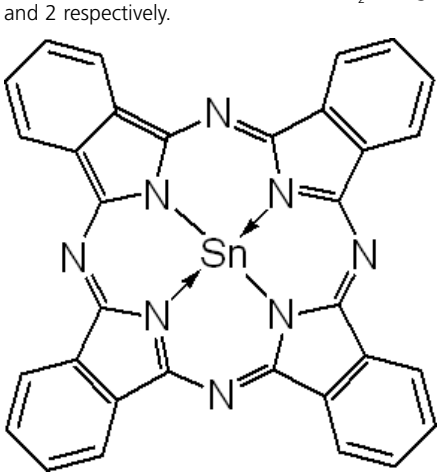

Fig. 1. Structure of SnPc molecule

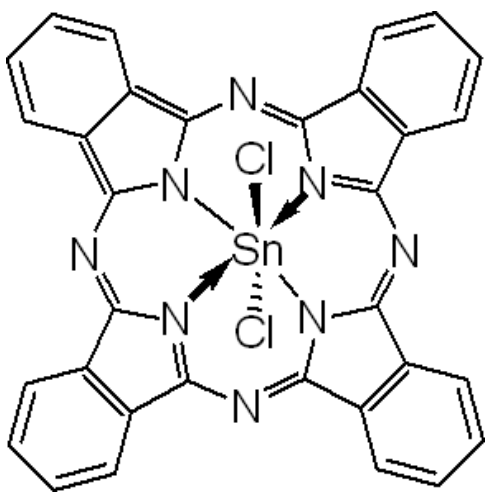

Fig. 2. Structure of $SnPcCl_2$ molecule

EXPERIMENTAL

Spectroscopically pure SnPc and $SnPcCl_2$ 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 room temperature at a pressure of 10^{-5} Torr. The thickness of the films is measured by Tolansky's multiple beam interference technique. UV-Visible absorption spectra of SnPc and $SnPcCl_2$ 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. Since Pcs are photosensitive, measurements are done in darkness. Structural characterizations of the samples are carried out by analysis of X-ray diffraction (XRD) pattern obtained using Bruker X-ray diffractometer with CuKα source.

RESULTS AND DISCUSSIONS

Optical absorption studies

The absorption spectrum has been closely connected with the

molecular structure of organic compounds. The conjugated π system containing 18 electrons in the macro cyclic ring leads to intense absorption bands in the UV-Visible region. 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

The absorption spectrum mainly consists two bands, B-band and Q-band. The Q-band that exists at the red end of the visible spectrum is connected with $\pi(a_{1u})$ to $\pi*(eg)$ transition on the Pc macro cycle and B-band (Soret) in the UV region is due to the transition from $\pi(a_{2u})$ to $\pi*(eg)$ transitions.

For a film of thickness t, the absorption coefficient α is given by

$$\alpha = 2.303A/t \quad (1)$$

The absorption coefficient α is related to the energy band gap Eg and the photon energy$h\nu$ by the relation $\alpha = \alpha_0 (h\nu - Eg)^n$ (2)

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

Figures 3 and 4 show typical absorption spectrum of SnPc and $SnPcCl_2$ at substrate temperature 305 K. Figures 5 and 6 shows the dependence of absorption coefficient α on photon energy hν SnPc and $SnPcCl_2$ thin films respectively.

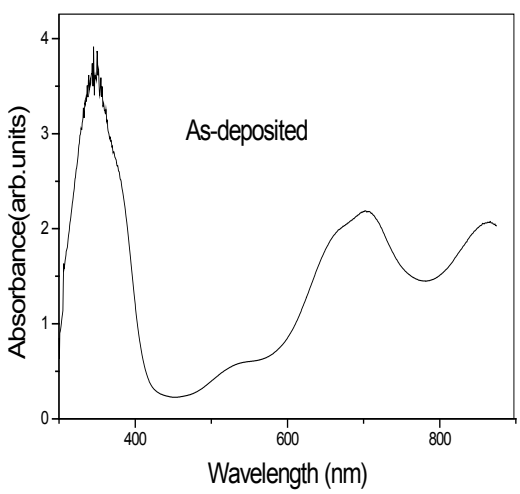

Fig.3 Absorption spectrum SnPc thin films

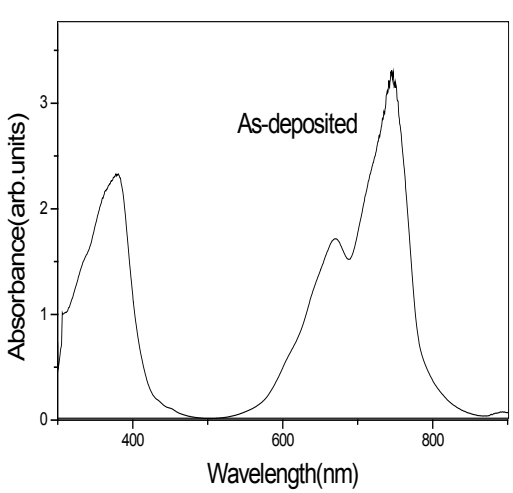

Fig.4 Absorption spectrum $SnPcCl_2$ thin films

In the case of SnPc thin films the absorption peak around 350 nm results from the B (Soret) band and the peak around 710 nm results from the Q-band. A satisfactory linear fit is obtained for α^2 versus hυ showing the existence of direct inter-band transitions between the energy levels. Absorption spectrum of $SnPcCl_2$ thin films also consists of two absorption bands, namely B band and Q band. It is evident that Q-band consists of a single peak at 375nm and Q-band consists of two peaks, one at 670nm and another strong peak at 745nm with an energy separation of 0.19eV. It consists of window region in the wavelength gap for $SnPcCl_2$ thin films. The indirect transition is attributed to deformation of range 430nm -500nm.

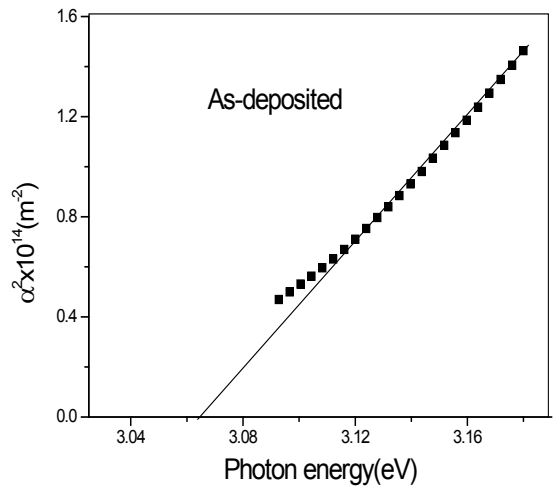

Fig.5. Dependence of α on photon energy for SnPc thin films

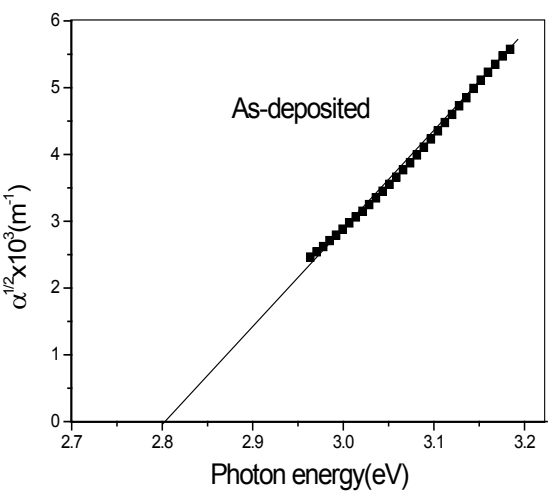

Fig.6. Dependence of α on photon energy for $SnPcCl_2$ thin films

A satisfactory linear fit is obtained for the plot of $\alpha^{1/2}$ versus hυ as in figure 6 indicating the presence of indirect band molecular structure due to the overlapping of neighbouring molecules. The estimated values of fundamental and excitonic energy gaps for both SnPc and $SnPcCl_2$ thin films are collected in Table1

Table 1. Fundamental and excitonic energy gaps for SnPc and $SnPcCl_2$ thin films

Thin films	Fundamental energy gap (eV)	Excitonic energy gap (eV)
SnPc	3.06	1.57
$SnPcCl_2$	2.80	1.54

Electrical studies

Various conduction mechanisms are observed in the case of phthalocyanine thin films. π-electrons in the Pcs are delocalised and are responsible for conduction. So there are localised electronic states associated with Pcs. In the case of Pc thin films, conductivity σ is given by $\sigma = A \exp(-E_1/k_BT) + B \exp (-E_2/k_BT) + ---$ (3)

where E_1 is the intrinsic activation energy and E_2 extrinsic activation energy

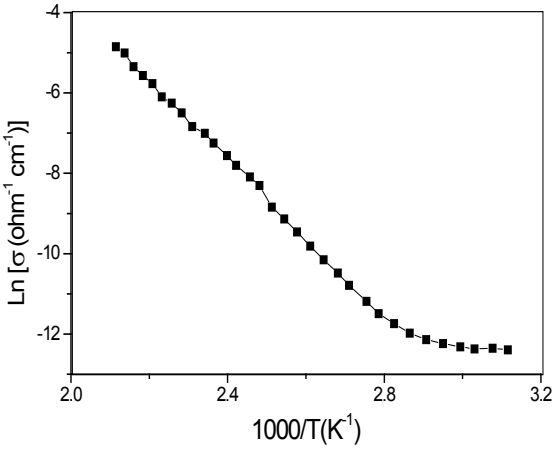

Fig.7. Plot of Ln σ versus 1000/T for SnPc thin films

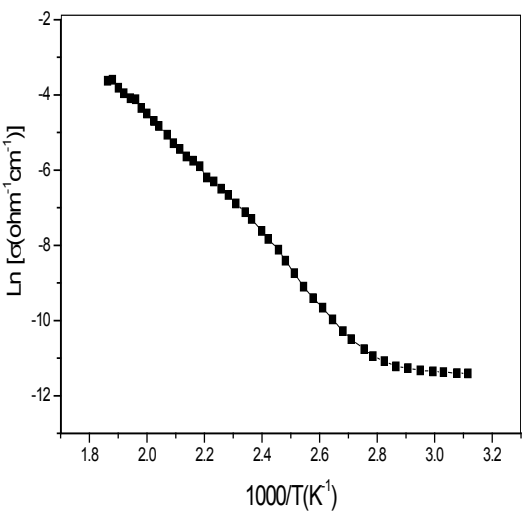

Fig.8. Plot of Ln σ versus 1000/T for $SnPcCl_2$ thin films

Figure 7 and 8 shows the dependence of Ln σ on temperature for SnPc thin films and $SnPcCl_2$ thin films. There are two linear parts with different slopes. The change in the slope corresponds to change in activation energy, which implies that different conduction mechanisms are involved in electrical conductivity.The activation energies are estimated from the slopes of the Arrhenius plot Ln σ versus 1000/T and are collected in Table 2.

Table 2. Activation energy of SnPc and $SnPcCl_2$ thin films

Thin films	Activation energy (eV)	
	E_1	E_2
SnPc	0.85	0.15
$SnPcCl_2$	0.76	0.10

Structural studies

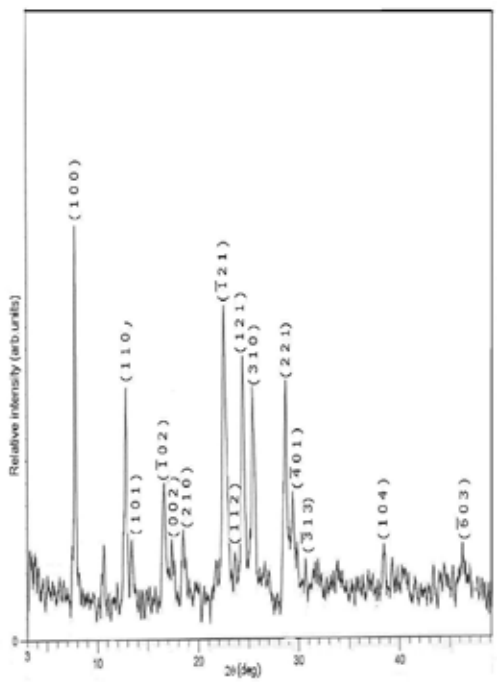

Fig.9. X-ray diffraction pattern of SnPc powder along with indexing of prominent peaks.

It is reported that the SnPc ($C_{32}H_{16}N_8Sn$(II)) molecules are partially overlapped and these parts are nearly planar while the non overlapping parts are bent. Figure 9 shows the X-ray diffractogram of SnPc powder with indexing of prominent peaks. The powder diffraction pattern is indexed giving monoclinic unit cell with a=12.13 Å, b=8.71Å, c=10.80 Å,α=90°, β=108.85° and γ=90°.

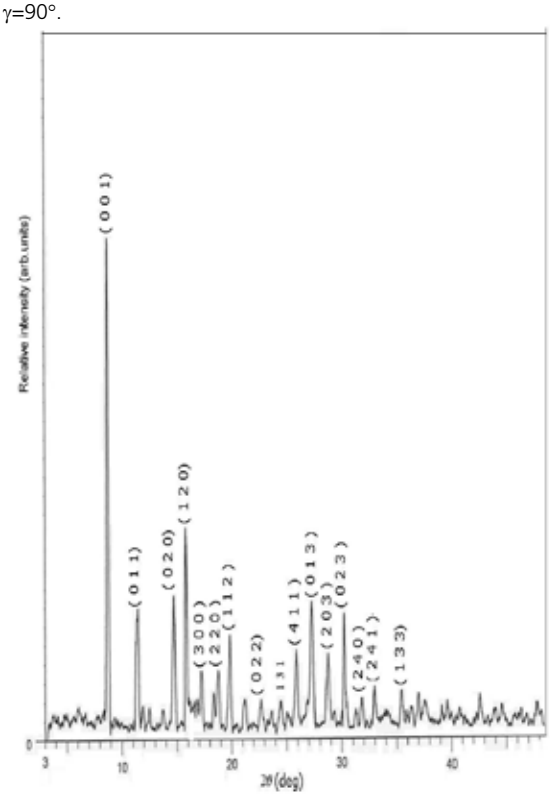

Fig.10 X-ray diffraction pattern of $SnPcCl_2$ powder along with indexing of prominent peaks.

Figure 10 shows the X-ray diffractogram of $SnPcCl_2$ powder. By indexing, the unit cell dimension of $SnPcCl_2$ has been determined. It is found that structure is orthorhombic with unit cell dimensions a=15.35 Å, b=12.06 Å, c=10.17 Å, $\alpha=\beta=\gamma=90°$. The molecules of $SnPcCl_2$ ($C_{32}H_{16}Cl_2N_8Sn(IV)$) have an exceptionally strong sinusoidal shape. It is thought that this sinusoidal deformation is only caused by the consideration of the overlapped Sn^{+IV} ion in the center of the macro cycle, which pushes two of the isoindoline nitrogen out of the plane. In a crystal, the two neighbouring molecules in a stack are overlapping with their benzene rings and that one hydrogen of these benzene rings is directed towards a chlorine atom of the neighbouring molecule with short distance of 2.75Å. This will assist the deformation of the molecular structure in the solid state.

CONCLUSION

Optical absorption studies shows that both SnPc and $SnPcCl_2$ thinfilm absorption spectra consists of two main peaks-B-band and Q-band. For SnPc thin films, optical transition is found to be direct type while for $SnPcCl_2$, it is of indirect type. The B-band is more sensitive to the central atom and Q-band to the axial ligands. The indirect optical transition may be due to the deformation of molecular structure due to the overlapping of neighbouring molecules. The conduction process is found to be controlled by different trap levels present in the forbidden energygap. The central metal atom of SnPc stands out of the macro cycle. This gives rise to directional anisotropy and selectivity in the absorption geometry as well as in the intermolecular stacking. The heavy post transition elements exhibit in some compounds a valance that is by two less than their group valence. This produces distortion of the metal ion coordination environment.

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