

Effect of thickness on the absorption spectra of GaPcCl, SnPcO and AlPcOH thin films

SUSAN MATHEW*, C. S. MENON, C. SUDARSANAKUMAR

School of Pure and Applied Physics, Mahatma Gandhi University, Kottayam, 686 560, Kerala, India.

Vacuum sublimed thin films of gallium phthalocyanine chloride, tin phthalocyanine oxide and aluminium phthalocyanine hydroxide are prepared at room temperature. Optical absorption spectra of films of different thicknesses are taken over a wavelength range of 300 to 900 nm and the optical energy band gap E_g and the onset energy gaps are calculated. The absorption spectra consist of two well defined absorption bands of the phthalocyanine molecules, namely, the Soret (B) and the Q- bands at about 300-400 and 600-800 nm respectively, showing an enhanced broad optical window with lower linear absorption at about 500 nm. Tin phthalocyanine oxide has very different absorption spectra. The characteristic Davydov splitting of the Q-band in tin phthalocyanine oxide correlates with the relative tendencies of the metal to out-of-plane bonding. It is observed that the band gap decreases with the increase of film thickness.

(Received January 31, 2008; accepted June 4, 2008)

Keywords: Phthalocyanine, Thin film, Optical band gap

1. Introduction

Metallo-phthalocyanines are a class of organic compounds with particular electronic and structural characteristics which show semiconducting and nonlinear optical properties. These materials are generally p-type semiconductors [1] and have high thermal stability, strong colours and negligible vapour pressure at room temperature. The study of the electrical conductivity and the nonlinear optical properties of phthalocyanine thin films is of great interest for use in molecular electronics, non-linear optics, electrochromic devices, optical data storage, sensors, solar cells, light emitting diodes and static induction transistors [2-10]. The major advantage of using organic semiconducting materials is their ability to modify their molecular structure and hence, their electrical and optical properties. Optical properties of these organic semiconductors are influenced by various factors such as the evaporation rate, substrate temperature, film thickness and post deposition annealing [11]. Within the large family of phthalocyanine compounds, trivalent and tetravalent Pcs result to be of special interest. Gallium phthalocyanine chloride and aluminium phthalocyanine hydroxide belong to the group of trivalent metal phthalocyanines display interesting characteristics among pigments such as high photoactivity and charge generation efficiency in addition to a strong absorbance in the visible. Gallium phthalocyanine chloride exhibits emission efficiencies strong enough to be considered as potential new infrared emitters [12]. These films are found to have a large absorption coefficient and, therefore, they may have an industrial application as a medium for optical disc. Moreover, the halogenated phthalocyanines exhibit remarkable morphological and thermal stability over a larger temperature range compared to unhalogenated phthalocyanines [13]. The interest about SnPcO molecule

is motivated by its peculiar nonplanar shape and also by a relative lack of studies in the literature. The central metal atom of SnPc stands out of the macrocycle. This gives rise to directional anisotropy and selectivity in the absorption geometry as well as in the intermolecular stacking. The origin of this distortion is the so-called 'inert pair effect'. The heavy post transition elements exhibit in some compounds a valence that is by two less than their group valence (eg. the divalent Pb and Sn atoms of group 4). This 'inert pair effect' manifests itself structurally by the distortion of the metal ion coordination environment [14]. The Sn^{2+} ion presents a s^2 lone pair which is stereochemically active in that these electrons are not in a spherically symmetric orbital but stick out to one side of the metal ion leading to various distorted coordination polyhedra. These films are found to absorb light on either side of blue-green region and can be used as photoconductor materials and colour filters. Among the various metallo-phthalocyanine derivatives, aluminium phthalocyanine hydroxide is of great interest for its use as a toner in an electro-photographic developer.

The study of optical properties is one of the most direct methods to probe into the band structure of the organic semiconductors. This enables us to determine the fundamental and excitonic energy gaps. The optical properties of several phthalocyanine thin films have been studied in recent years [15,16], but relatively little work has been done on these films [17,18]. In the present work we study the effect of thickness on the optical properties of gallium phthalocyanine chloride ($\text{C}_{32}\text{H}_{16}\text{ClGaN}_8$), tin phthalocyanine oxide ($\text{C}_{32}\text{H}_{16}\text{N}_8\text{OSn}$) and aluminium phthalocyanine hydroxide ($\text{C}_{32}\text{H}_{17}\text{AlN}_8\text{O}$) thin films. The molecular structures of GaPcCl and SnPcO are shown in Figs. 1 and 2.

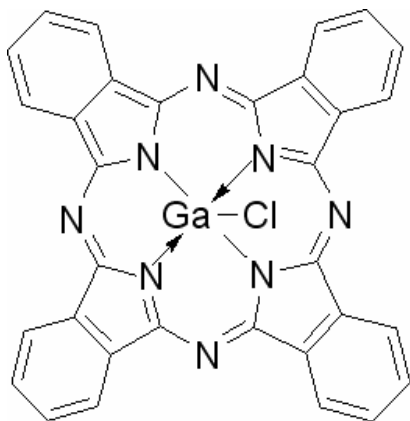


Fig. 1. Molecular structure of GaPcCl

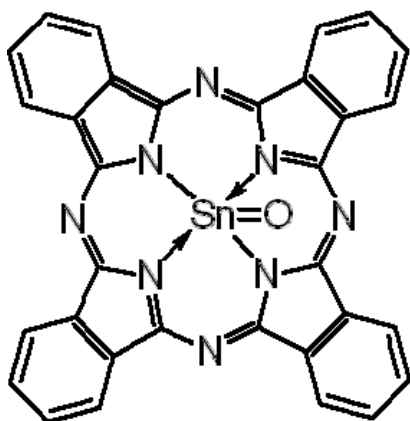


Fig. 2. Molecular structure of SnPcO.

2. Experimental details

Gallium phthalocyanine chloride, tin phthalocyanine oxide and aluminium phthalocyanine hydroxide were procured from Aldrich Chemicals, USA. Thin films were deposited onto thoroughly cleaned glass substrates at room temperature using a Hind Hivac 12 A4 coating unit at a base pressure of 10^{-5} torr. The films were prepared by resistive heating of the powder from a molybdenum boat and the evaporation rate was kept constant. Several films of same thickness and different thicknesses were prepared in the same experimental condition simultaneously. This was achieved by arranging a series of substrates horizontally and keeping the evaporating source to one side but well below the specimen plane. The reproducibility of the results was confirmed by making several such depositions under more or less the same deposition conditions. Thickness of the film was determined by Tolansky's multiple beam interference technique [19]. UV-Visible absorption spectra were recorded using a Shimadzu 160 A UV-Visible spectrophotometer. The absorption edge was analyzed to get the optical band gap.

3. Results and discussion

Optical studies are done to determine the energy band gap and the effect of thickness on the band gap of these films. The principle of this technique is that photons with energies higher than the band gap energy will be absorbed and electrons are excited from the valence band to the conduction band with the absorption of energy equal to the band gap of the material. The rapid drop in the absorption coefficient on the high energy side of the absorption spectra leads to the band edge in semiconductors. The transition type is also important to be defined for the material characterization. The optical absorption spectra of GaPcCl, SnPcO and AlPcOH films of different thicknesses are given in figures 3, 4 and 5 respectively. It can be seen that the plots are linear in the region of strong absorption near the fundamental absorption edge. Hence the absorption takes place through direct transition. The spectrum of phthalocyanine is believed to originate from orbitals within the aromatic 18π electron system and from overlapping orbitals on the central metal atom [20].

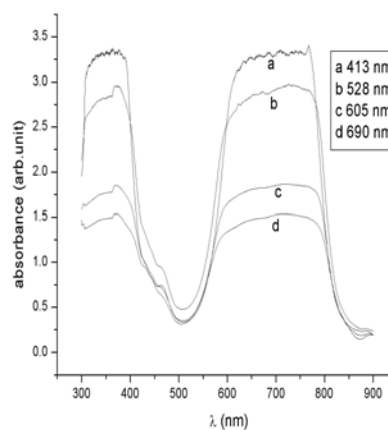


Fig. 3. Optical absorption spectra of GaPcCl thin films of different thicknesses.

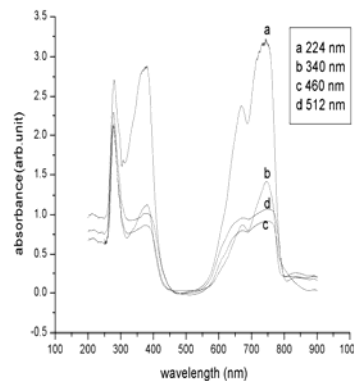


Fig. 4. Optical absorption spectra of SnPcO thin films of different thicknesses.

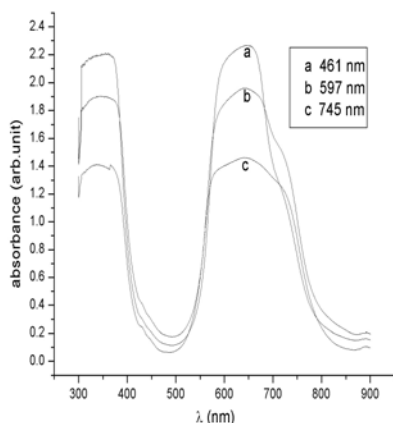


Fig. 5 Absorption spectra of AlPcOH thin films of different thicknesses.

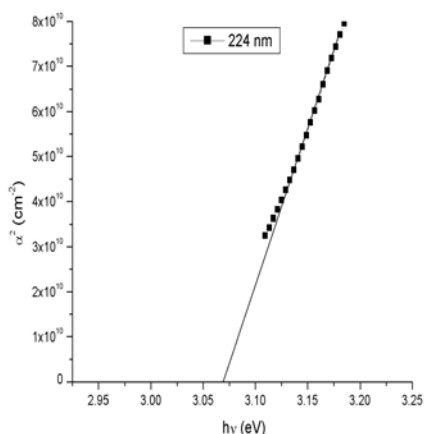


Fig.6. Plot of α^2 versus $h\nu$ for SnPcO

The conjugated ring system of the phthalocyanines comprises forty atoms. Each carbon atom in a conjugated system has three nearest neighbors with which it forms three equivalent sigma bonds made from the sp^2 hybridization of three valence atomic orbitals of the carbon atom: $2s$, $2p_x$ and $2p_y$. For such a hybridization state, the fourth orbital $2p_z$ lies perpendicular to the σ bond plane. It is the lateral overlap of these out of plane $2p_z$ atomic orbitals gives the π bonds. As p orbitals overlap is weaker than s orbitals overlap, the energy spacing between bonding and anti-bonding molecular orbitals is larger for π to π^* than for σ to σ^* . The π and π^* molecular orbitals are the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) respectively in terms of molecular physics. In phthalocyanines the direct electronic transition from π to π^* orbitals in the energy range 300-450 nm results in an intense band called B-band (Soret band) which corresponds to the fundamental absorption from which

the energy band gap is obtained [21]. The Q-band appeared in the 600-800 nm range gives onset energy. The fundamental absorption edge is analyzed within the one electron theory of Bardeen [22] to obtain information about direct or indirect interband transitions. The absorption coefficient α is calculated using the relation

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

where A is the absorbance of the film and t is its thickness. For direct allowed transition, the relation between absorption coefficient α and the incident photon energy $h\nu$ can be written as

$$\alpha = \alpha_0 (h\nu - E_g)^{1/2} \quad (2)$$

where E_g is the optical band gap and α_0 a constant. A satisfactory straight line fit is obtained for α^2 as a function of $h\nu$, showing the existence of a direct band gap. The value of absorption coefficient α greater than 10^4 cm^{-1} obtained is also related to direct inter-band transitions. By plotting α^2 versus $h\nu$ and extrapolating to zero absorption, the band gap E_g is obtained. α^2 versus $h\nu$ graphs are plotted for all the films and a typical graph is shown in Fig. 6.

The values of fundamental and onset energy gaps are determined from the graphs and are given in Table 1.

Table 1. Soret band gap and onset energy gap of the materials.

	Thickness (nm)	Soret band gap (eV)	Onset energy gap (eV)
GaPcCl	413	2.96	1.54
	528	2.91	1.53
	605	2.86	1.51
	690	2.80	1.50
SnPcO	224	4.00	1.67
		3.07	1.60
	340	4.02	1.61
		3.05	1.59
	460	4.04	1.57
		2.96	
	595	4.06	1.57
		2.94	
AlPcOH	295	3.22	1.63
		3.11	1.62
	597	3.06	1.61
		3.06	1.60

In the case of trivalent phthalocyanines such as GaPcCl and AlPcOH thin films two broad bands namely B-band with absorption peak in the 300-400 nm region and Q-band in the 580-780 nm region are observed. Here

Q-band is broader than B-band. The considerable inhomogeneous broadening obtained is attributed to the high concentration of defects in evaporated phthalocyanine thin films. It is seen from the figure that the width of the peak increases as the thickness of the film increases. On the other hand the absorption spectrum of tin phthalocyanine oxide thin film has only narrow peaks. In the near ultraviolet region, strong absorption occurs in the Soret band near 3.07 eV. Of interest here is that there is an absorption peak of variable intensity on the high energy side of the Soret band at 4.00 eV. In the visible region, we find two absorption peaks corresponding to 1.60 and 1.67 eV for SnPcO thin films. Here the low energy peak is the more intense of the doublet. This effect is found to depend on the thickness of the film. Referring to figure 4, we see that a thin film of SnPcO has a visible band consisting of a distinct maximum at 1.60eV and a shoulder at 1.67eV, whereas for a thick film the two features are of similar strength. A similar effect occurs in the Soret band also, where maximum absorption occurs at lower energies in thin films compared to thicker films. The optical band gap is shifted to lower energies as the thickness increases. This red shift of the B-band with increase in thickness is due to sintering of nano-crystallites into effectively larger crystallites. The decrease of optical band gap with the increase of thickness is likely to be attributed to an increase of particle size, a decrease of RMS strain or an increase of lattice constant.

5. Conclusion

Absorption spectra of phthalocyanine thin films consist of two strong Q and Soret bands at about 600-800 and 300-400nm respectively showing an enhanced broad optical window with lower linear absorption at about 500 nm. The emission wavelength of diode lasers used for optical recording and laser printing lies within the Q-band absorption region of GaPcCl and AlPcOH thin films. Hence these films can be used as optical recording media and photoreceptor for laser printing. In tin phthalocyanine oxide the Q-band shows its characteristic splitting. Davydov splitting of the main absorption peak in the metal phthalocyanine correlates with the relative tendencies of the metal to out-of-plane bonding. Tin phthalocyanine oxide absorbs light on either side of blue-green region and can be used as photoconductor materials and colour filters. The photon energy dependence of the absorption coefficient in the fundamental absorption region confirms the transition as direct band-to-band type in all the three materials. The stability in the peak positions in the absorption spectra showed the stability of the structure of phthalocyanine thin films. The optical band gap is shifted to lower energies as the thickness increases. The fundamental study on phthalocyanine thin films offers the

possibility of tailoring the electronic and chemical properties required for the fabrication of devices based on organic materials such as solar cells, field effect transistors, organic light emitting devices and sensors for molecular and bio-molecular recognition.

References

- [1] Y. Sadaoka, T. A. Jones, W. Gopel, *J. Mater. Sci. Lett.* **8**, 1095 (1989).
- [2] A.S.Riad, A.E.El-Samahy, S.M.Khalil, *Physica B*, **215**, 217 (1995).
- [3] H. Mockert, D. Schmeisser, W. Gopal, *Sensors and Actuators* **19**, 159 (1989).
- [4] Y. Qiu, Y. Gao, P. Wei, L. Wang, *Appl. Phys. Lett.* **80**, 2628 (2002).
- [5] J.Zhang, J.Wang,H.Wang, D.Yana, *Appl. Phys.Lett.* **84**,142 (2004)
- [6] P.Peumans, S.R.Forrest, *Appl. Phys.Lett* **79**, 126 (2001).
- [7] C. C. Leznoff, A. B. P. Lever, *Phthalocyanines: Properties and Applications*, Vol.3 (VCH, New York ,1993).
- [8] Fang, K. Kohama, H. Hoshi, Y. Maruyama, *Jpn. J. Appl. Phys.* **32**, L 1418- L 1420 (1993)
- [9] C.M.Joseph, C.S Menon, *Mater. Lett.* **52** ,220 (2002).
- [10] K.Kudo, M.Iizuka, S.Kuniyoshi, K.Tanaka, *Thin Solid Films*, **393**, 362(2001).
- [11] Y. Machida, Y.Saito, A.Taomato, *Jpn. J. Appl. Phys.* **28**, 297 (1989).
- [12] R.Aroca, T.Del Cano, J.A.De Saja, *Chem.Mater.***15**, 38 (2003).
- [13] A. Napier, R. A. Collins, *Phys. Stat. Sol (A)*, **144**, 91 (1994).
- [14] A. R. West *Basic Solid State Chemistry*, John Wiley and Sons Ltd (1984)
- [15] S. Senthilarasu, R. Sathyamoorthy, *Cryst.Res.Technol.***41**, 1136 (2006).
- [16] K.R.Rajesh, C.S.Menon,*Mater.Lett.* **51**, 266 (2001).
- [17] A.Ioannidis, J.P.Dodelet, *J.Phys.Chem. B* ,**101**, 901 (1997).
- [18] T.Del Cano, V.Parra, M.L.Rodriguez-Mendez, R..Aroca, J.A.De Saja *Appl.Surf.Sci.* **246**, 327 (2005).
- [19] L. I. Maissel, R. Glang, *Handbook of Thin Film Technology* (Mc Graw Hill, NewYork, 1983)
- [20] E. A. Ough, J. M. Stillman, *Can. J. Chem.* **71**, 1891 (1993)
- [21] R. A. Collins, A. Krier, A. K. Abass, *Thin Solid Films.*, **229**, 113 (1993).
- [22] J. Bardeen, F. J. Slatt, L. T. Hall, *Photoconductivity Conf.* 146 (Wiley, New York ,1965)

*Corresponding author: soozan_mathew@yahoo.com