Effect of Thermal Annealing on the Optical and Photoluminescence Properties of H_2PcOC_8 Thin Films

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2,3,9,10,16,17,23,24-Octakis(octyloxy)phthalocyanine (H_2PcOC_8), $C_{96}H_{146}N_8O_8$, is a plane organic molecule having numerous optical and electrical applications in organic electronics. This work investigates the influence of the annealing temperature on optical band gap, optical constants and photoluminescence spectrum of the H_2PcOC_8 films. The optical transition was found to be direct allowed. The band gap energy reduced on annealing from its as deposited value. As the annealing temperature increases, the intensity of the absorption peak also increases. Variation of optical parameters with annealing temperature was also investigated. The effect of thermal annealing on the films were studied by recording the photoluminescence spectra. The intensity of photoluminescence and the profile of the photoluminescence spectra were depend on the temperature of the post deposition annealing of the thin films. The morphology of the thin films is expected to influence the photoluminescence behaviour of the H_2PcOC_8 thin films.

Key Words: Octakis octyloxy phthalocyanine, Absorption spectra, Band gap energy, Optical parameters, Photoluminescence spectrum.

INTRODUCTION

New generation electronic and optoelectronic devices require thin films of new materials with specific properties. Such properties are discovered by the complex combination of many physical factors as well as the chemical nature of the starting material. Especially highly delocalized conjugated organic systems such as substituted as well as unsubstituted metal phthalocyanines (MPC's) represent the promising candidates in (opto) electronic applications, since appropriate substitutions of the phthalocyanine skeleton can result in different electronic and transport thin film properties¹⁻⁴. Also the electrical and optical properties of phthalocyanines are determined by a central metal ion and side groups⁵. Due to their high thermal and chemical stability, they have become an important material widely used in optical and electronic devices technology⁶⁻⁸. They are used, for instance, to fabricate light emitting diodes, field effect transistors and solar cells⁹. They find applications in the field of gas sensors^{10,11} and photodynamic therapy of cancer¹¹⁻¹³. Metal free and metal-containing phthalocyanine compounds with alkyl, alkoxy, thioalkoxy, ethyleneoxy chains have since been synthesized^{14,15}. Moreover, amongst the two possible peripheral octa-substitution patterns, ie; the lateral positions (2,3,9,10,16,17,23,24) and the radial ones (1,4,8,11,14,15,18,22,25)¹⁶, the former have been

commonly used one. In both cases columnar mesophases are formed and result from the stacking of the flat and rigid phthalocyanine cores into columns, which are themselves arranged into 2D lattice. The melting of the flexible side chains is responsible for the transition from the solid state to the liquid crystalline phase, while the aromatic cores retain some degree of the crystalline positional and orientational order. Incorporating substituents on to the phthalocyanine ring is also the most important method used to tune the physiochemical, electrochemical and spectroscopic properties of phthalocyanine derivatives. Prior to our studies, only a few data are available on octa substituted phthalocyanine having different functionalities¹⁷. The present work is an attempt to study the post deposition air annealing on the optical and photoluminescence properties of H_2PcOC_8 thin films.

EXPERIMENTAL

2,3,9,10,16,17,23,24-Octakis(octyloxy)phthalocyanine (H_2PcOC_8) powder imported from Aldrich chemicals(USA) is sublimed in vacuum using a Hind Hivac 12A coating unit at a base pressure of 10^{-5} Torr. The molecular structure of the material is given in Fig. 1. The microglass slides (75 mm $\times$ 25 mm $\times$ 1.3 mm) that are used as substrates are cleaned before coating, using liquid detergent, dilute nitric acid, distilled water, acetone and hot air. H_2PcOC_8 is held in a molybdenum

boat of dimension 2.9 cm × 1.2 cm × 0.5 cm and is heated and sublimed to substrates situated 12 cm above the source. The deposition rate is adjusted within the range 13–15 nm/min. the thickness of the film is directly measured as 250 ± 5 nm by thickness profilometer¹⁸. Further it is cross checked by Tolansky's multiple beam interference technique¹⁹. Films are annealed in air for 1 h at temperatures 323, 373, 423, 473 and 523 K. An UV-VIS Scanning Spectrophotometer, Model 240PC (Shimadzu Japan) is used to record the electronic absorption and emission spectra of the films at room temperature.

Fig. 1. Molecular structure of H₂PcOC₈

RESULTS AND DISCUSSION

UV-VIS absorption spectra: The absorption spectra of as deposited and annealed H₂PcOC₈ thin films of thickness 250 nm are shown in Fig. 2. The UV-VIS spectrum observed for phthalocyanines originates from molecular orbital within the aromatic 18 π -electron system and from overlapping orbital on the central metal atom^{19,20}. Similar to that of porphyrins, which are very important chromospheres in biological light harvesting system and photoreaction centres²⁰. A close examination of the absorption band in the visible region, known as Q band, appears in the region between 1.5 and 2.5 eV. The Q band consists of one shoulder at 1.99 eV which have been assigned to π - π^* transitions on the phthalocyanine macro cycle and one peak at 1.78 eV have been explained as exciton peak. It can also be noticed that the splitting characteristic (Davydov splitting), ΔQ , equals 0.21. In the UV spectral region at 3.74 eV, there is an intense band called Soret band (B-band). This is due to the electronic transition from π - π^* .

The effect of annealing on the absorption spectra is also shown in Fig. 2. As observed annealing process causes increase in the intensity of absorption bands. Table-1 represents the corresponding energies of the orbital transition (in eV) which are seen in the absorption spectra of the as deposited and annealed H₂PcOC₈ thin films.

The spectral distribution of the absorption coefficient (α) for the investigated as deposited and annealed films was calculated from UV-VIS absorption spectra by using the expression²¹

$$\alpha = \frac{2.303A}{d} \quad (1)$$

where d is the film thickness.

Fig. 2. Absorption spectra of H₂PcOC₈ thin films

TABLE-1
ENERGY OF ORBITAL TRANSITION OF H₂PcOC₈
THIN FILMS AND THE DAVYDOV SPLITTING

Orbital transition	Visible Q (eV)	ΔQ (eV)	Soret (B) (eV)	
As deposited	1.78	1.99	0.21	3.74
Annealed	1.78	2.00	0.22	3.74

The annealing process has no marked effect on the energy values for the different bands.

Determination of the energy gap: To obtain information about the direct and indirect interband transitions, the fundamental absorption edge data could be analyzed within the framework of one-electron theory²¹. This theory has been used to analyze the absorption edge data of molecular solids such as phthalocyanine derivatives²².

The variation in absorption coefficient (α) with photon energy for band to band transition is obtained as

$$\alpha = \alpha_0[(h\nu - E)]^n \quad (2)$$

where E is the energy gap and n determines the type of transition. The value of n can be 1/2 or 2 for allowed direct and allowed indirect optical transition or 3/2 and 3 in the case of forbidden direct and indirect optical transition, respectively. The dependence of the absorption coefficient (α) on photon energy ($h\nu$) was plotted for different values of n . The best fit was obtained for $n = 1/2$. This is the characteristic behaviour of allowed direct transitions. Fig. 3 shows the functional dependence of α^2 on $h\nu$ for the film as deposited and after annealing. The energy gap at the fundamental intense band was found to be 3.18 eV.

The values of energy gap and phonon energies for the film as deposited and after annealing are listed in Table-2.

TABLE-2
VALUES OF ENERGY GAP

	Fundamental gap (eV)	Onset energy (eV)
As deposited	3.18	1.52
Annealed	3.16	1.46

The band gap energy reduced on annealing from its as deposited values which might be due to the shift in the relative

Fig. 3. α^2 versus $h\nu$ graph of the H_2PcOC_8 thin films

positions of the valence band and conduction band due to temperature dependence of dilation of the lattice and/or electron lattice interaction. The change in band gap with temperature was quite linear and can be expressed as²³

$$E_g(T) = E_{g0} + \beta \quad (3)$$

E_{g0} being the absolute zero value of the band gap and β is the rate of change of band gap with temperature. The value obtained were $E_{g0} = 3.2587$ eV and $\beta = -2.6800 \times 10^{-4}$. The negative β value signifies the shifting of band gap towards lower energies with an increase in annealing temperature, this indicates that the temperature affects the band gap by changing interatomic distances. The reduction rate in the band gap could be attributed to shortening of inter atomic distances caused by the amplitude decrease of atomic oscillations around their equilibrium positions and/or due to electron-lattice interaction which is dominant at elevated temperatures²⁴. The decrease in energy band gap increases the width of the energy bands which induce to move the band edge of the conduction band downward and that of the valence band upward. A successful model to predict the correct low-temperature dependence of the absorption edge is the Urbach's rule²⁵. Further the temperature dependence of steepness parameter for the thin film was calculated from the slope of the band gap *versus* temperature curve (Fig. 4) *via* equation and is found to be

Fig. 4. Graph showing the linear dependence between annealing temperature and band gap energy

$$\frac{dE_g}{dT} = \frac{3K_B}{\alpha_0} \quad (4)$$

Determination of optical parameters: The fundamental optical parameters are determined from the transmittance and reflectance spectra of these thin films. The inequality $R + T < 1$ at shorter wavelength ($\lambda < 900$ nm) shows the existence of absorption. The reflectivity R of an absorbing medium of refractive index n and extinction coefficient k in air for normal incidence is given by

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (5)$$

The extinction coefficient k is given by

$$k = \frac{\alpha\lambda}{4\pi} \quad (6)$$

Thus by knowing α and k , n is calculated. The optical properties of the films are characterized by the complex refractive index ($N = n - ik$) and the complex dielectric constant ($\epsilon = \epsilon_1 - i\epsilon_2$). The real part ϵ_1 generally relates to dispersion, while the imaginary part ϵ_2 gives a measure of the dissipation rate of the wave in the medium²⁴.

The two parameters are related to n and k through the equation

$$\epsilon_1 = n^2 - k^2 \quad (7)$$

$$\epsilon_2 = 2nk \quad (8)$$

The values of k , n , ϵ_1 and ϵ_2 are calculated using these equations. The dependence of photon energy on n and k and ϵ_1 and ϵ_2 for the as deposited sample is plotted in Figs. 5 and 6, respectively.

Fig. 5. Variation of n and k with photon energy for the as deposited film

The refractive index n has a maximum value of 2.901 at 1.551 eV. The extinction coefficient k has a maximum value of 3.537 at 1.978 eV. The real part ϵ_1 shows a maximum value of 8.270 at 1.560 eV while the imaginary part ϵ_2 has a maximum value of 13.042 at 1.984 eV.

Photoluminescence studies: Fig. 7 shows photoluminescence (PL) spectra of annealed H_2PcOC_8 thin film as a function

Fig. 6. Variation of ϵ_1 and ϵ_2 with photon energy for the as deposited film

Fig. 7. Photoluminescence spectra of H_2PcOC_8 annealed thin film excited at 300 nm

of incident wavelength. Semiconducting thin films generally exhibit the threshold energy in the optical absorption measurement due to the size dependent band gap structure, which is affected by the absorption edge with decreasing grain size. The spectrum shows the emission peak under photoluminescence excitation wavelength at 300 nm with the range of 200–1000 nm. The strongest emission peak was centred at 468 nm. The observed peak was found to be broad full width half maximum indicates the nanocrystalline effect of the films.

Conclusion

H_2PcOC_8 thin films were prepared by vacuum deposition method. The prepared films were annealed at moderately high

temperatures to study its optical and photoluminescence properties. Absorption spectra show an increase in intensity with increase in the annealing temperature. The absorption spectra show characteristic Davydov splitting in the low energy side. Optical transition was found to be direct allowed. The band gap energy was reduced with annealing due to the temperature dependence of dilation of the lattice and/or electron lattice interaction. The emission peak from room temperature photoluminescence spectra is another significant of the quantum size effect of the films depending of annealing temperature.

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