

Determination Of The Optical Constants In Thin Films Of Tetrakis Phthalocyanine

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Abstract: Vacuum evaporated thin films Tetrakis phthalocyanine thin films were prepared at room temperature onto glass substrates at a base pressure of 10^{-5} Torr. Annealing was done in air and the effect of annealing temperature on optical properties were studied. Optical absorption spectra of films annealed at temperatures 323 K, 373 K, 423K, 473K and 523 K were taken over a wavelength range of 300 to 900 nm and the optical energy band gap E_g and the onset energy gap were calculated. Refractive index n , extinction coefficient k and the real and imaginary parts of the optical dielectric constant ϵ_1 and ϵ_2 were also evaluated and were plotted against the photon energy.

Keywords: Thin film, Annealing, Refractive index, Optical band gap, optical dielectrics

I. INTRODUCTION

In the past two decades organic thin film technology and its device applications have attracted the interest of researchers and industry due to their interesting optoelectronic properties [1]. Because of their attractive processing characteristics and demonstrated performance, organic semiconductors could compliment or even replace silicon-based technology for existing or emerging thin film transistor applications requiring large area coverage, structural flexibility and low temperature processing. Their application in new flexible and transparent devices [2,3] and their tuning possibilities lead to an increase of the academic activity in this field. They are promising materials for development of various modern and future technologies in solid-state devices such as field-effect transistors, light emitting diodes, optical recording, organic solar cells and sensors [4-11]. Electronic charge transport in organic molecules does not require perfect single crystals. A regular arrangement of atoms, ions or molecules over a distance of only a few lattice spacing of the structural units is necessary for the electronic charge transport and is usually a sufficient condition for electrical conductivity of the organic system. Knowledge of the molecular structure and semiconducting characteristics of the organic compounds, allows the design of new materials that have pre-defined and

controlled characteristics. The molecular structure of Tetrakis Phthalocyanine is shown in Fig. 1.

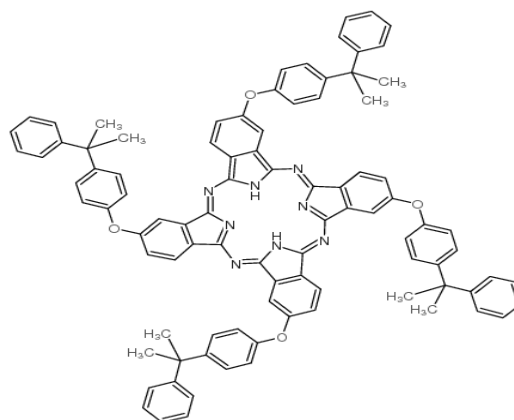


Figure 1: The molecular structure of Tetrakis Phthalocyanine

II. EXPERIMENTAL DETAILS

Tetrakis Phthalocyanine powder procured from Aldrich, USA was evaporated in vacuum using a Hind Hivac 12A coating unit onto well cleaned micro glass slides held at a

pressure of 10^{-5} torr. Thin films were prepared by resistive heating of the powder from a molybdenum boat and the evaporation rate was kept constant as 10^{-12} nm/min. Several films of same thickness were prepared in the same experimental condition simultaneously. The reproducibility of the result was confirmed by making several such depositions under the same deposition conditions. Thickness of the film was determined by Tolansky's multiple beam interference technique [12]. Tetrakis Phthalocyanine thin films of thickness 335 ± 5 nm were annealed in air for 1 hour at temperatures 348 K, 398 K and 448 K in a furnace whose temperature could be controlled by a controller cum recorder. UV-Visible absorption spectra and Reflectance spectra were recorded using a Carry 5000 UV-Visible spectro-photometer. The absorption edge was analyzed to get the optical band gap of Tetrakis phthalocyanine.

III. RESULTS AND DISCUSSION

A. OPTICAL STUDIES

The optical absorption spectrum of the film annealed in air at 523 K over a wavelength range of 300-900 nm is shown in Fig. 2.

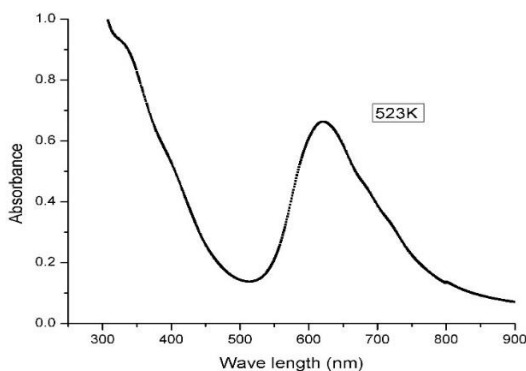


Figure 2: The optical absorption spectrum of the film annealed in air at 448 K

In the case of Tetrakis Phthalocyanine thin films the two well-defined absorption bands of the phthalocyanine molecules namely B band and Q band were observed. The spectrum of phthalocyanine is believed to originate from orbitals within the aromatic 44π electron system and from overlapping orbitals on the central metal atom [13]. 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 [14]. The Q-band appeared in the 600-800 nm range gives onset energy [15]. The fundamental absorption edge was analyzed within the one electron theory of Bardeen [16] to obtain information about direct or indirect inter band transitions. The absorption coefficient α was calculated using the relation

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

where A is the absorbance of the film and t is its thickness. For direct allowed transition, the absorption coefficient α is related to the photon energy $h\nu$ by the relation

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

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. Plot of α^2 versus $h\nu$ for the film annealed at 523 K is shown in Fig.3. The values of fundamental and onset energy gaps are determined from the graph and are given in Table 1. The results showed no effect of the annealing temperature on the optical properties and hence the stability of the structure of Tetrakis thin. The reflectance spectrum of Tetrakis phthalocyanine thin film is given in Fig. 4

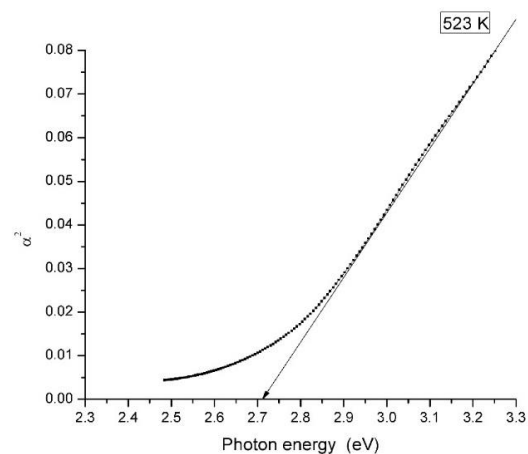


Figure 3: Plot of α^2 versus $h\nu$ for the film annealed at 523 K

Annealing Temperature (K)	Fundamental Band Gap E_g (eV)	Exitonic Bandgap (eV)
As Deposited	2.84	1.85
323K	2.83	1.85
373K	2.81	1.84
423K	2.78	1.82
473K	2.75	1.80
523K	2.72	1.78

Table 1: Optical band gap, onset energy gap and grain size of Tetrakis Phthalocyanine thin films annealed at different temperatures

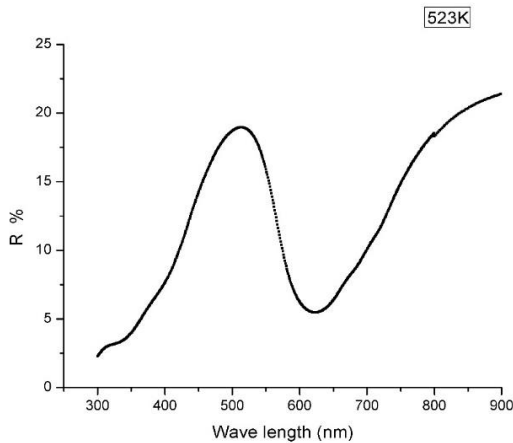


Figure 4: The reflectance spectrum of Tetrakis Phthalocyanine thin film

The main feature of the reflection spectrum is the sharp rise in reflectivity at ~ 500 nm. The optical properties of any material are characterized by two parameters the extinction coefficient k and the refractive index n . The extinction coefficient is calculated using Eq. (3) and n , using Eq. (4).

$$k = \frac{\alpha\lambda}{4\pi} \quad (3)$$

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (4)$$

Fig. 5 shows the variation of refractive index n and extinction coefficient k with photon energy for Tetrakis Phthalocyanine thin film. For Tetrakis Phthalocyanine thin film of thickness 500 nm the maximum value of refractive index is 2.54 at 2.42 eV. Similar result is reported by Senthilarasu *et al.* [17] for zinc phthalocyanine thin films. The refractive index and the extinction coefficient are used for the calculation of the real and imaginary parts of the dielectric constant. The real and imaginary parts of the dielectric constant ϵ_1 and ϵ_2 are calculated using the expressions [18]

$$\epsilon_1 = n^2 - k^2 \quad (5)$$

$$\epsilon_2 = 2nk \quad (6)$$

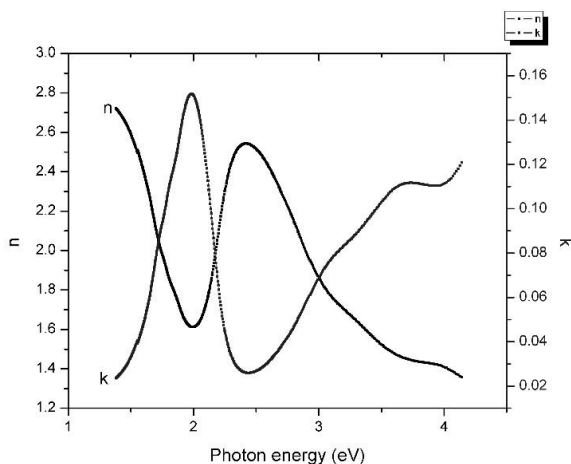


Figure 5: Variation of n and k with photon energy for Tetrakis Phthalocyanine thin film

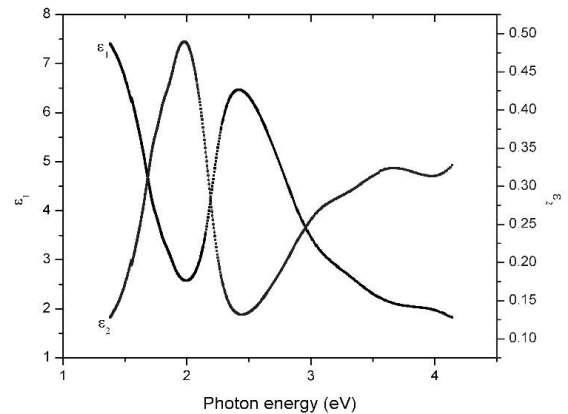


Figure 6: Variation of ϵ_1 and ϵ_2 with photon energy for Tetrakis Phthalocyanine thin film

Fig. 6 shows the variation of ϵ_1 and ϵ_2 with photon energy for Tetrakis Phthalocyanine thin film. The real part ϵ_1 is related to dispersion, while the imaginary part ϵ_2 provides a measure of the dissipation rate of the wave in the material. The real part ϵ_1 showed maximum value at 2.42 eV for Tetrakis Phthalocyanine thin film. A similar behavior has been observed for chloroaluminium phthalocyanine thin films [19].

IV. CONCLUSIONS

The absorption spectra of Tetrakis thin films show two absorption bands which we have identified as the fundamental absorption at high energies (B-band) and the exciton absorption at low energies (Q- band). However, it is noticed that the band gap does not show much variation with various annealing temperatures. This is because the crystallite size is not small enough to show a distinct variation of the band gap. Refractive index n , extinction coefficient k and the real and imaginary parts of the optical dielectric constant ϵ_1 and ϵ_2 were also evaluated and were plotted against the photon energy.

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