

Optical and Structural Studies of ZnPc Thin films

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Abstract

Stable and homogeneous Zinc phthalocyanine (ZnPc) thin films were prepared in a "Hind Hi Vac:" vacuum coating unit (Model No. 12 A4) using thermal evaporation technique. The thicknesses of the films are monitored by a single crystal thickness monitor and crosschecked by air wedge method and it is found to be 725nm. UV-Visible absorption spectra of as-deposited ZnPc thin films are recorded in the wavelength range 200-1000nm. Q band shows Davydov splitting. Transition is found to be direct and allowed. Optical absorption spectra of these films are analysed to get the energy band gaps. The energy band gap is found to be 2.848eV. X-ray diffractograms are recorded for as deposited ZnPc thin films. XRD pattern shows that the deposited film is amorphous.

Keywords: Zinc phthalocyanine, thin films, optical absorption spectra, structural studies, band gap.

1. Introduction

Zinc phthalocyanine (ZnPc) is one of the promising photosensitizers as it has a strong absorption cross-section in the spectral range of 650–900nm that guarantees maximum tissue penetration. ZnPc nanowires (NWs) directly grown from ZnPc powder by vaporization–condensation–recrystallization process show surprisingly increased water dispersibility without any functionalization. The ZnPc NW solution exhibits highly efficient dual PD and PT effects upon the irradiation of near infrared (808nm) laser [8]. Metal phthalocyanine is one of the promising organic compounds due to the possibility of applications in electro-optic devices, photo conducting agents, photo voltaic cell elements, nonlinear optics, electro catalysis, and other photo electronic devices. Many researchers have studied various metal substituted phthalocyanines [7-12]. In addition to traditional applications as dyes and pigments, peripherally substituted phthalocyanines are currently widely used as industrial catalytic systems, photosensitizers for photodynamic therapy of cancer, materials for electrophotography, ink-jet printing, semiconductors, chemical sensors, and electro chromic devices; functional polymers and liquid crystals; nanotechnology and non-linear optics. The majority of these applications take advantage of the unique optical (specifically low-energy Q-band) and redox properties of phthalocyanines which can be fine-tuned using appropriate peripheral substitutions. During the last 10 years, phthalocyanines have received increasing attention due to their potential applications in the area of organic light-emitting devices (OLED) [1,6], for flat-panel display applications [14]. Thermal evaporation under high vacuum is used in this work to prepare stable and homogeneous thin films Zinc phthalocyanine (ZnPc). In this paper, results of optical and structural studies of ZnPc thin films are discussed.

2. Materials and Methods

Commercially available ZnPc are used as source materials for the preparation of thin films. Pre-cleaned micro glass slides are used as substrates. Thin films of these materials are deposited on to the substrates in a "Hind Hi Vac:" vacuum coating unit (Model No. 12 A4) using thermal evaporation technique. We use the molybdenum boat in which the material is taken. The rate of evaporation is kept constant for 10 - 15 minute. Thin films of ZnPc are deposited by keeping the substrate at room temperature. The thicknesses of the films are monitored by a single crystal thickness monitor and crosschecked by air wedge method. UV-Visible absorption spectra of as-deposited ZnPc thin films are recorded using a 'JASCO UV VIS-650' spectrophotometer in the wavelength range 200-1000nm. Optical absorption spectra of these films are analysed to get the energy band gaps. X-ray diffractograms are recorded for as deposited ZnPc thin films. XPERT-PRO X-ray diffractometer is used to record the diffractograms.

3 Results and Discussion

3.1 Thickness measurement

In this experiment by measuring the separation between two consecutive dark fringes (equal to the width of the bright fringe) the thickness of the object forming an air wedge is determined. The experiment provides a method of finding the thickness of very thin films deposited on a glass plate.

Order	Microscopic reading(cm)	Width for 10 fringes(cm)	Mean (cm)	Fringe width(cm) (y)
M	4.063	1.351	1.05620	0.10562
M+2	4.520	1.053		
M+4	4.674	1.51		
M+6	4.999	0.896		
M+8	5.171	0.83		
M+10	5.414			
M+12	5.573			
M+14	5.825			
M+16	5.895			
M+18	6.001			

Tabular column for thickness measurement

Fringe width, $y=0.10562\text{cm}$.

Length of air wedge, $l=2.6\text{cm}$.

Wavelength of the sodium light used, $\lambda=589.3\text{nm}$.

Thickness of the thin film prepared, $t= \lambda l/2y=(589.3 \times 10^{-9} \times 2.6 \times 10^{-2})/(2 \times 0.10562 \times 10^{-2})=0.725 \times 10^{-6}\text{m}$.

3.2 Optical Properties

Optical properties of thin films have been studied extensively primarily because of their applications in various optical and electro-optical devices and it has been found that there is often a considerable deviation of optical parameters from that of a bulk material. Discrepancies in the optical behaviour of films have often been attributed to their physical state viz. crystalline or otherwise, inhomogeneity, compositional deviations, etc. The optical study of solid concerns not only with the physical phenomena such as refraction, reflection, transmission, absorption, polarization and interference of light, but also the electronic state. From reflection, transmission, and absorption process it is possible to evaluate the optical constants such as refractive index (n), absorption index or extinction coefficient (k), and absorption coefficient (α). Absorption studies provide a simple means for the evaluation of absorption edge, optical energy band gap, optical transitions which may be direct or indirect, allowed or forbidden and also of the nature of the solid material.

Interactions of the electromagnetic waves with the solid may cause several transitions in its band structure such as band to band, between sub-bands or impurity levels and a band, transitions of free carriers within a band and also resonance due to lattice vibrations. Hence a detailed study of the absorption band spectra is likely to provide a wealth of information about the electronic band structure of solids and also of films.

The UV-Visible absorption spectra of ZnPc thin film of thickness 725 nm is shown in figure 3.1.

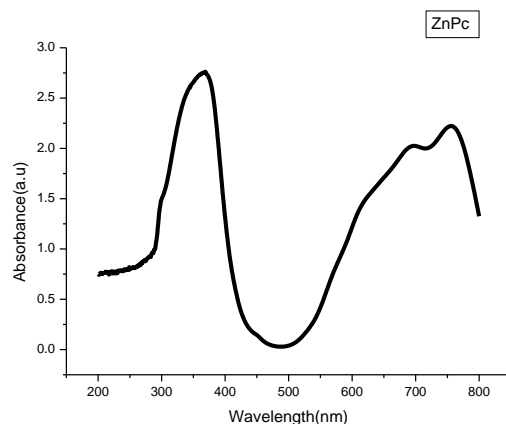


Fig3.1: The UV-Visible spectrum of ZnPc thin films of thickness 725nm.

All the samples possess a B-band near 360nm and Q-band with a splitting of Q_x and Q_y near 690nm and 760nm. The broadening of the absorption bands is caused by the aggregation of the molecules during film formation^[3]. The observation of more than one band in the Q due to the Davydov splitting^[5]. The UV-Visible spectrum observed for phthalocyanine originates from molecular orbitals within the aromatic $18-\pi$ electron system and from overlapping orbital on the central metal. The intense band in the B and Q region (Q_y) are due to the electronic transitions from $\pi-\pi^*$ transitions.

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

$$\alpha = \frac{2.303A}{d},$$

where, d is the film thickness and A is the absorbance

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

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

For more precise determination of α , it is necessary to perform corrections to the absorption due to reflection; also, n is the index which can have different values of $\frac{1}{2}$, $\frac{3}{2}$, 2, and 3^[4] or more depending on whether the transition is direct or indirect and allowed or

forbidden. In the direct and allowed cases the index $n = \frac{1}{2}$ whereas for the direct but forbidden cases it is $\frac{3}{2}$. But for the indirect and allowed cases $n = 2$ and for the indirect forbidden cases it will be 3 or more.

The dependence of absorption coefficient (α) on photon energy ($h\nu$) was plotted for different values of n . The best fit was obtained for $n = \frac{1}{2}$. This is the characteristic behaviour of allowed direct transitions. The band gap of Zn Pc thin film is found to be 2.848 eV.

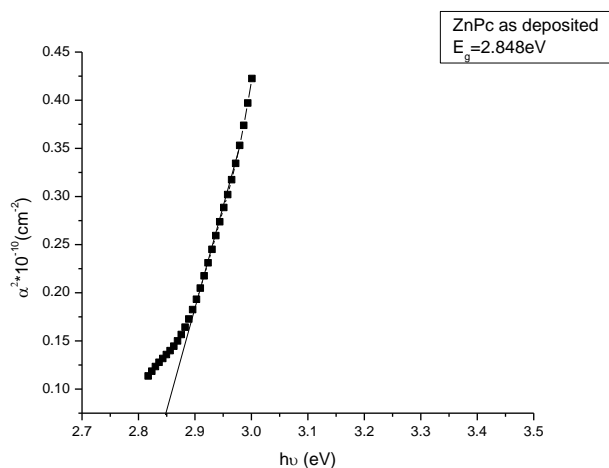


Figure 3.2: α^2 versus energy graph for ZnPc thin films of thickness 725 nm.

3.2 Structural Studies

The macro crystalline structure of thin film is found to have profound influence on the optical, electrical, mechanical and other thin film properties. The physical properties of thin films are known to differ widely from those of bulk material. This is evidently connected with the small size of the crystallites forming the film and in particular, with the large number of defects such as dislocations, vacancies, stacking faults, and grain boundaries etc. the method of film deposition and the electrical and thermal conditions of the substrate also influence the structure of the deposited film. The study of structure is particularly important when coupled with data concerning the film formation process and with physical-chemical properties of the film.

X-ray diffraction pattern of ZnPc thin film of thickness 725 nm is shown in figure 3.3. For the as deposited case, the film is found to amorphous due to the presence of hump in the pattern.

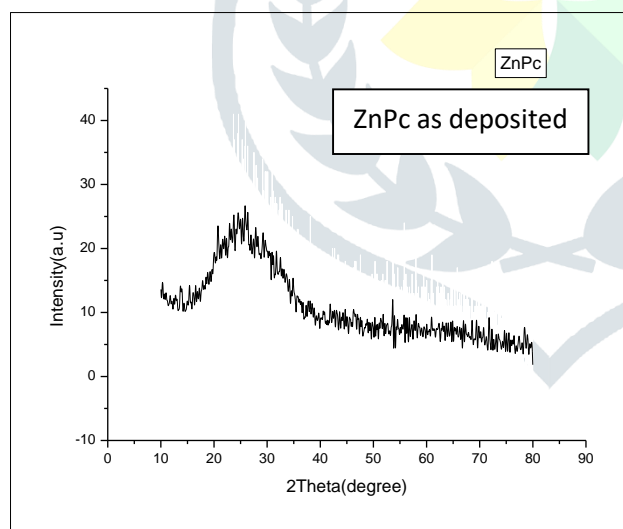


Figure 3.3: X-ray diffractograms of ZnPc thin films of thickness 725nm.

Conclusion

The thicknesses of the films are monitored by a single crystal thickness monitor and crosschecked by air wedge method and it is found to be 725nm. The optical studies include the analysis of absorption spectra and determination of fundamental energy gaps. The peculiar structure of phthalocyanines with conjugate double bonds and availability of molecular orbitals within the aromatic 18π electron system and overlapping orbitals of the central metal atom are responsible for the observed intense absorption peaks. The band

gap of the material is the difference between the energies of the valance band and conduction band. The absorption bands arise from $\pi - \pi^*$ transitions. The dependence of the absorption coefficient (α) on the photon energy ($h\nu$) was plotted for different values of n .

The best fit was obtained for $n = \frac{1}{2}$. Thus the photon energy dependence of the absorption coefficient in the fundamental absorption

region confirms the transition as direct and allowed band to band type. The charge transport is expected to be facilitated by $\pi - \pi$ overlap. Since the interactions of the molecules are Van der Waals type, the rearrangement of molecules at the crystal phase transition alters the energy gap between the valance band and conduction band. **The energy band gap is found to be 2.848eV.**

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