



INFLUENCE OF POST DEPOSITION ANNEALING ON THE OPTICAL AND STRUCTURAL PROPERTIES OF ZINC-TETRA-TERT-BUTYL PHTHALOCYANINE THIN FILMS

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ABSTRACT

Zinc-tera-tert-butylphthalocyanine (Zinc2, 9, 16, 23-tetra-tert-butyl-29H, 31H-phthalocyanine) (ZnTTBPC) is a new material in phthalocyanine family. Its molecular formula is C₄₈H₄₈N₈Zn. Phthalocyanines are organic semiconductors; ZnTTBPC in the powder form is used as the source material. Thin films of ZnTTBPC are deposited onto precleaned glass substrates kept at room temperature using a Hind Hivac vacuum coating unit. The thickness of the films is cross checked by Tolansky's multiple beam interference technique. Films of equal thickness prepared at room temperature are annealed in air by keeping them in a furnace fitted with a temperature-controller cum recorder for one hour. The UV-VIS-NIR spectra of these samples are recorded. The optical studies are carried out by analyzing the absorption and reflection spectra. Graphs are plotted α_2 against photon energy. From this band gap energy of ZnTTBPC thin films are calculated. The surface morphology of the films deposited on glass substrate of as deposited and annealed samples are studied using Scanning Electron Micrographs (SEM), which show that there is a change in surface morphology of the film due to annealing.

KEYWORDS :

1. Introduction

In the past three decades, phthalocyanine compounds have attracted much attention because they have enormous potential applications, such as, in photo voltaic and solar cell, gas sensors[1 - 5] and optical recording[6]. Pc molecules are thermally stable and may be sublimed without decomposition. These molecules have low sublimation temperature, so the preparation of Pc thin films by vacuum evaporation is feasible. Phthalocyanines are generally available in two morphological forms α and β [7, 8]. β form is monoclinic, whereas α form is reported to be tetragonal, orthorhombic or monoclinic. At room temperature, they are usually in the metastable phase.

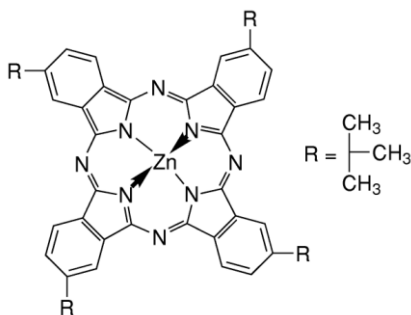


Figure 1. Molecular structure of zinc-tetra-tert-butyl phthalocyanine

The basic optical properties of semiconductors result from the electronic excitation in crystals when an electromagnetic wave is incident on them. The optical constants have been evaluated in order to correlate them to the electronic band structure. Under high intensity visible wavelength excitation in the region of 400-600 nm phthalocyanines behave as reverse saturable absorbers. Various workers have studied the basic properties of many of the metallo-phthalocyanines (MPcs) in detail [9 - 11]

The electrical, optical and structural properties of Pcs are critically depend on film morphology, which in turn determined by ambient parameters such as deposition rate, substrate temperature and post-deposition annealing [12]

The performance of the optical devices strongly depends on the wavelength dependence of the optical constants n and k of their layers and on their thickness. Knowledge of these parameters is necessary to understand the fundamental aspects of the materials.

In this paper, we report the optical and structural properties of ZnTTBPC thin films on a well cleaned glass substrate prepared by vacuum deposition method. Bulk ZnTTBPC in the powder form is purchased from Sigma-Aldrich Chemicals.

2. Experimental

Spectroscopically Pure ZnTTBPC powder (96%) is used as the source material for the present study. Films of thickness 250 nm were deposited by thermal evaporation at a base pressure of $\sim 10^{-5}$ Torr using a Hind-Hivac 12A4 coating unit. For deposition of films highly polished and thoroughly cleaned glass substrates are used. Evaporation of the material is carried out with a molybdenum boat of dimensions 2.91.2 0.5 cm used as the resistive heating element. During evaporation, substrates are placed at a distance of 11cm from the source and the deposition rate is kept at about ~ 0.5 nm/s. The thickness of the films is measured using the Tolansky's multiple beam interference technique. The UV-Visible-NIR spectra of the films were recorded using JASCO Corp., V-550 Spectrophotometer. SEM analysis is carried out by JEOL, JSM-6390 Scanning Electron Microscope [13]

3. Results and Discussions

3.1. Optical Studies

The UV-VIS spectrum observed for phthalocyanines originates from molecular orbital within the aromatic 18 p electron system and from overlapping orbital on the central metal atom [14]. The absorption band in the UV region which is known as the Soret (B) band $a_{2u} \rightarrow e_g$ (\rightarrow^*). The broad absorption band in the ultraviolet region is preceded by the ultraviolet absorption band edge of the phthalocyanine molecule. The other well known band of the phthalocyanine molecule, namely Q-band $a_{1u} \rightarrow e_g$ ($n \rightarrow^*$) appears in the region between 550 and 750 nm. Distinct characterized peaks in the visible region are generally interpreted in terms of $n \rightarrow^*$ transition [15] between bonding and anti-bonding molecular orbital. It can also be noticed that this band shows the characteristic splitting (Davydov Splitting) present in all phthalocyanine derivatives [16]. The low energy peak of the Q-band has been previously explained as a second $n \rightarrow^*$ transition.

The variation of the absorption coefficient (α) as a function of the photon energy ($h\nu$) for ZnTTBPC thin films of thickness 250nm at different annealing temperatures is shown in the figure 3. In the visible region there are two absorption peaks, which show absorption maxima at 1.79 and 2.00 eV in the Q-band for as deposited thin film. In the next band B (soret band) in UV region, the maximum absorption lies at 3.67 eV and the shoulder is seen near

4.14 eV on the high energy side of the Soret band

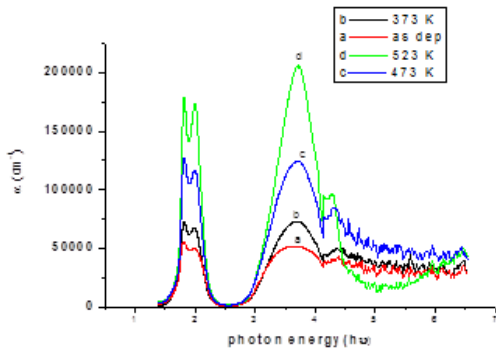


Figure 2. The absorption coefficient α Vs photon energy $h\nu$ for as deposited and annealed ZnTTBPC thin films

The high energy peak of the Q band has been assigned to the first $\pi-\pi^*$ transition of Pc macrocycle. The low energy peak of the Q band has been variously explained as a second $\pi-\pi^*$ transition and as a vibrational interval. The difference between Q_y and Q_x is defined as the Davydov splitting (ΔQ) which is at (0.18 eV) in the present spectrum. The annealing process has no marked effect on the energy values for the different bands.

The variation in absorption coefficient (α) with photon energy for band to band transitions is given by

$$\alpha = \alpha_0 (h\nu - E_g)^n \tag{1}$$

Where E is the energy gap and n determines the type of transition. The value of n can be $\frac{1}{2}$ or 2 for allowed direct and allowed indirect optical transition, $\frac{3}{2}$ and 3 in the case of forbidden direct and indirect optical transition, respectively. The dependence of the absorption coefficient (α^2) on photon energy ($h\nu$) was plotted for different values of n. The best fit was obtained for $n=1/2$. The ab

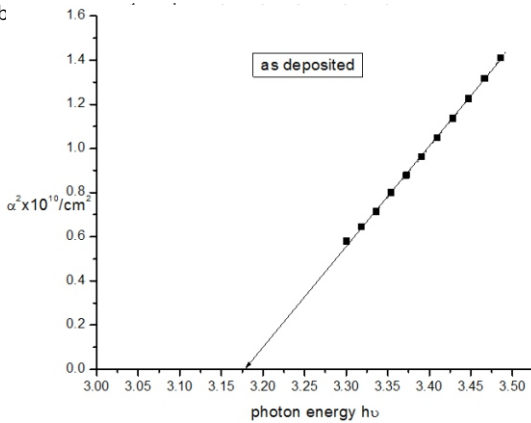


Figure 3. α^2 versus photon energy for ZnTTBPC as deposited thin film

Hence the square of the absorption coefficient versus photon energy for as deposited film can be plotted as shown in fig. 3. The intercepts on the energy axis of the respective graph give the direct allowed band gap for the sample. There is no significant variation of band gap energy due to annealing. The energy gap at the fundamental intense band was found to be 3.1 eV before and after annealing. This gap can be interpreted as a maximum in the refractive index, because the extinction at that photon energy is quite small [18]

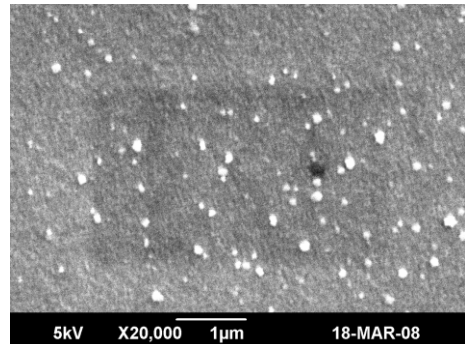
Table 1. Band gap energy E_g (eV) and trap levels of ZnTTBPC thin films with different annealing temperature (K)

Annealing temperature	Band gap energy (eV)	Trap levels (eV)
As deposited	3.1	1.7
323	3.2	1.7
373	3.2	1.6
423	3.1	1.8
473	3.2	1.8

3. SEM analysis.

SEM images of as deposited and annealed film at 573 K as shown in Fig.4. The as deposited film consists of small granular crystallites Fig.4 (a) and in an annealed film the clusters are formed Fig.4 (b). Thus annealed films are characterized by a looser structure and porosity, and crystallites become larger as the annealing temperature increases.

(a)



(b)

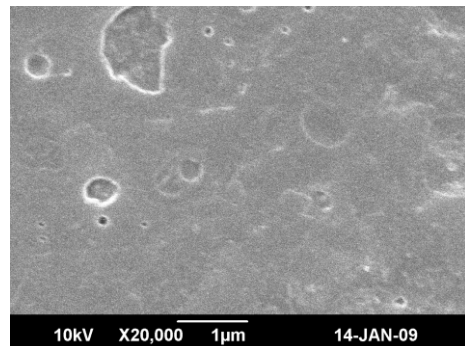


Figure 4. SEM images of the as deposited film (a) and annealed film (b)

4. Conclusion

The absorption band that appears in the region of 300-380nm is the Soret band and that in the 609-706nm is the Q-band. The Soret band is due to the $\pi-\pi^*$ transition. The phthalocyanines absorb light on either side of blue-green region and can be used as photo conductor materials and color filters. It has been found that the optical band gap is unaffected by annealing temperature. It shows that ZnTTBPC thin films before and after annealing provide evidence for the thermal stability of the deposited films.

References

- [1] Petty MC, 1995 Bio sensors and Bio Electronics 10 129
- [2] Cole A, McIlrou R J, Thorpe and Cook S C 1993 Sensors and Actuators 13 416
- [3] Azim M E, Araghi and Krier A 1997 Appl. Surf. Sci 119 260
- [4] Rella R, Serra A, Siciliano P and Tepore A 1996 Thin Solid Films 286 256
- [5] Sonmezoglu S, Tas R, Akm S and Can M 2012 Applied Physics Letters 101 253304
- [6] Leznoff C C, and Lever A B P 1993 VCH Publishers New York 3
- [7] Wu J S and Spence J C H 2003 Acta Cryst. A 59 495
- [8] Matsumoto S, Matsuhama K, and Mizuguchi J 1999 Acta Cryst. C 55 131
- [9] Ambily S, Menon C S 1999 Thin solid Films 347 284
- [10] Rajesh K R, Menon C S 2005 J. Non-Cryst. Solids 351 2414
- [11] Saleh A M, Abu-Hilai A O, Gould R D 2003 Curr. Appl. Phys 3 345
- [12] Collins R A, Belbachi A 1989 Mater. Lett. 9 349
- [13] Kumar G, Thomas J, George N, Radhakrishnan P 2000 Phys. Chem. Glass 41
- [14] Davidson A T, 1982 J. Chem. Phys. 77 168

- [15] Lee L K, Sabelli N H, LeBreton P R 1982 J. Phys. Chem. 86 3926
- [16] Chen Q, Gu D, Shu J, Tang X, Gan F 1994 Mater Sci Eng B 25 171
- [17] Abass A K, Krier A, Collins R A 1994 Phys. Stat. Sol. (a) 142 435
- [18] Collins R A, Krier A and Abass A K 1993 Thin Solid Films 229 113.