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Effect of annealing on vacuum evaporated zinc phthalocyanine thin films

Sridevi B R [1], Priya Hoskeri A [2] and Joseph C M [3]

1 (Department of Physics, K S Institute of Technology, India)

2 (Department of Physics, Dayananda Sagar College of Engineering, India)

3 (Department of Physics, Dayananda Sagar College of Engineering, India)

ABSTRACT

Thin films of Zinc Phthalocyanine [ZnPc] of different thicknesses were deposited onto glass substrates by thermal evaporation method. The variation of energy gap of these films was studied. It was found that the energy gap of these films decreases with increase in thickness. These films were later annealed at 393 K and variation of energy gap was calculated. Structural studies on ZnPc films annealed at different temperatures were carried out. XRD studies showed a maximum intensity peak at annealing temperature of 393 K indicating high crystalline nature of the film at this temperature.

Keywords— annealing, crystalline sizes, structural properties, thermal evaporation, zinc phthalocyanine,

1. INTRODUCTION

Phthalocyanines (Pcs) are a common class of organic compounds available in high purity due to the ease of crystallization and sublimation; extraordinary thermal and chemical stability [1]. The sublimation technique allows the deposition of these films with uniform and required thickness. Their ease of deposition, thermal stability and chemical stability against harsh chemical environment make them to be used in variety of electronic devices such as solar cells [2], photo detectors [3], transistors [4], electrochromic devises [5] etc. Phthalocyanines (Pcs) are two-dimensional aromatic molecules with an inner ring. The π-π orbital overlap and electrostatic interactions between adjacent Pc cores induce disc-like Pc molecules to self-assemble into one-dimensional columnar structures in condensed phases. Metallophthalocyanine (MPc) has a central metal atom and its optical and chemical properties depend on the variation of the metal atom and the position and nature of substitute atoms [6]. Among various MPcs, ZnPc has high absorption coefficient, high conversion efficiency in UV-Vis region, low optical band gap and high thermal stability. Hence they are extensively used in many opto-electronic devices. In most of the applications MPcs are used in the form of thin films. The thin films of MPcs

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can be obtained by spin coating, vacuum evaporation and Langmuir–Blodgett technique [7]. Hence it is necessary to understand the structural, optical properties of ZnPc films for device applications.

Senthilarasu et al. [8] have studied the variation of optical band gap with thickness of ZnPc film and were found to decrease with increase in film thickness. In the present study, the variation of optical band gap and structure as a function of annealing temperature carried out.

The most common polymorphs of Pc are 'α' and 'β' form which exist at low and high temperatures respectively. 'β' form is described as the most thermodynamically stable polymorph of Pc which is monoclinic [unit cell parameters *a* = 19.4 Å, *b* = 4.8 Å and *c* = 14.6 Å; β =120°], belongs to P21/a subgroups [9] with two Pc molecules per unit cell. Another metastable polymorph 'α' has a monoclinic lattice form [unit cell parameters *a* = 25.9 Å, *b* = 3.8 Å and *c* = 23.9 Å; α = 92°], belongs to *C2/c* group, with four molecules per unit cell. The main difference between 'α' and 'β' forms is the smaller (~27-30°) tilt angles for former and larger (45-49°) tilt angles [10] for later of the molecules relative to the b-axis of the crystal. A study done by Sathyamoorthy et al. [11] show the effect of substrate temperature on structural properties of ZnPc thin films diffraction peak appeared at 2θ = 6.86°, corresponding to the (200) lattice plane.

2. EXPERIMENTAL TECHNIQUE

2.1 Optical study of annealed ZnPc thin films

Organic molecules of phthalocyanines have unique molecular ring structure and their derivatives show exceptional optical characteristics. The chemical structure of ZnPc is as in the Fig. 1.Thin films of ZnPc [99.99% source powder purchased from Aldrich] were thermally deposited onto chemically cleaned glass substrates in a vacuum of around $2x10^{-6}$ Torr using a Hind hivac coating unit [Model no. 12A 4D].

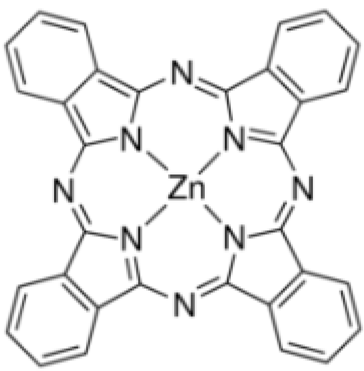

Figure 1: Zinc Phthalocyanine [ZnPc – $C_{32}H_{18}N_8Zn$]

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ZnPc powder was obtained from Sigma-Aldrich and was used without further purification. Thin films of ZnPc of varying thickness (350 nm, 200 nm and 100 nm) were deposited onto a pre cleaned glass substrates by vacuum evaporation technique using Hind hivac coating unit (Model no. 12A 4D). The rate of deposition was around 5 $Ås^{-1}$ and the average vacuum in the chamber was around 2×10^{-6} Torr. The thickness of thin films deposition rates were monitored while deposition using a quartz crystal thickness monitor. Then these thin films of ZnPc were vacuum annealed at 393 K for better crystallinity. Optical properties of deposited films were studied and variation of energy gap with thickness and for different annealing temperatures are reported in this work.

2.2 Structural studies

ZnPc thin films of thickness 200 nm were deposited onto glass substrates and these samples were annealed at different temperatures of 323 K, 373 K, 393 K and 423 K in a vacuum of 10^{-6} Torr. XRD studies of these annealed films were taken and variations of grain size with annealing temperatures are reported.

3. Results and discussions

3.1 Optical studies of ZnPc thin films

Organic molecules of Phthalocyanine have unique molecular ring structure and their derivatives show exceptional optical characteristics. The optical absorption spectrum was taken using uv- vis photometry and the variation of energy gap with the thickness of the sample was studied. Graph of absorbance versus wavelength of ZnPc thin films of different thicknesses is shown in Fig. 2. The absorbance of the films was maximum for the wavelengths 620 nm and 690 nm and is in agreement with the literature [12].

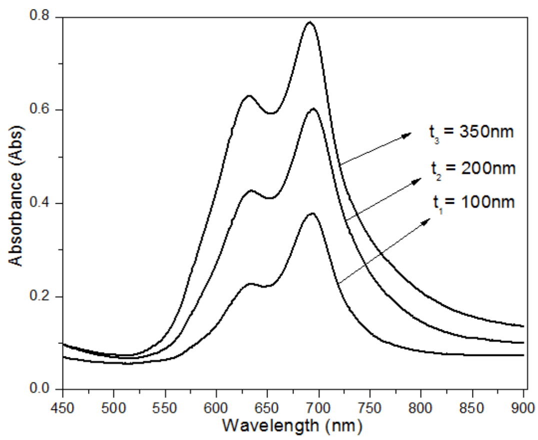

Figure 2: Graph of absorbance versus wavelength of ZnPc thin films of different thickness

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Absorption coefficient α is related to the photon energy hν by:

$$\alpha = \alpha_o (h\nu - E_g)^n \quad \text{---} (1)$$

where, E_g is the optical band gap. For allowed transitions, $(\alpha h\nu)^2$ was plotted against hν as shown in Fig. 3 for film of thickness 350 nm. The extrapolation of linear portion to α = 0 near the edge gave the band gap energy.

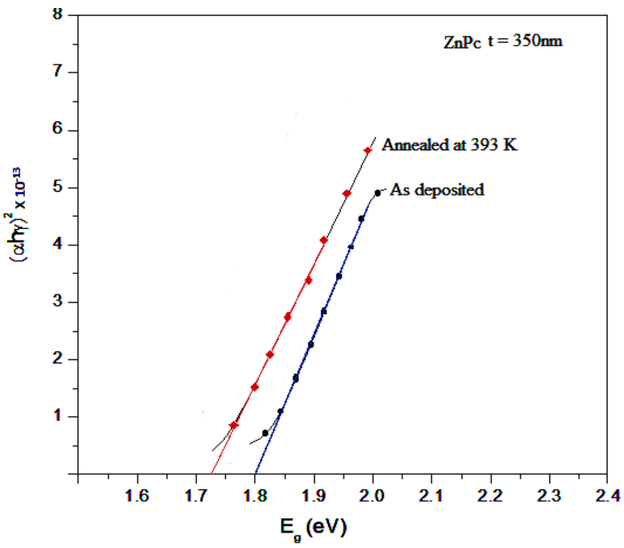

Figure 3: Plot of $(\alpha h\gamma)^2$ Vs E_g for RT deposited and annealed at 393 K ZnPc thin film [thickness = 350 nm]

Table 1: Energy gaps of ZnPc thin films deposited at room temperature and annealed at 393 K

Sample thickness [nm]	Energy gap [eV]	
	RT Deposited	Annealed at 393 K
100	1.85	1.78
250	1.82	1.76
350	1.80	1.72

From the optical studies, it was observed that the optical band gap decreases with the increase in the thickness of the film. It may be due to the presence of internal electric fields associated with the defects present in the films; or it may be due to the action of atmospheric oxygen on the surface of the film, which produces an acceptor level in the forbidden band or due to increase in particle size [13-15]. Further on annealing the films at 393 K, it was observed that the energy gap decreased which showed improved crystallanity and is attributed to the quantum confinement phenomenon due to the increase in grain size of the film [16]. The absorption peaks and the optical band gap values are in good agreement with literature survey [11].

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3.2 Structural studies of ZnPc thin films

ZnPc thin films of thickness 200 nm were deposited onto glass substrates and these samples were annealed at temperatures 323 K, 373 K, 393 K and 423 K in vacuum. Crystalline nature of the thin films was characterized by XRD using filtered CuK_{α} radiation [λ=1.54 Å]. X-ray diffraction spectra of ZnPc thin films at room temperature and annealed at different temperatures is shown in Fig.4.

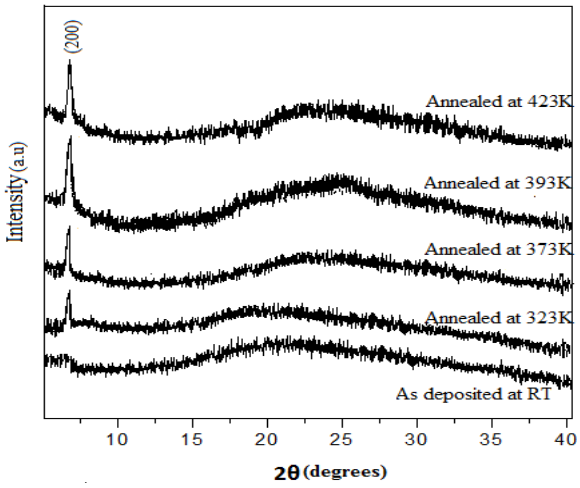

Figure 4: X-ray spectra of ZnPc thin films at room temperature and annealed at different temperatures

The intensity of XRD peak corresponding to room temperature was very weak showing amorphous nature of the film. For the annealed samples, the diffraction peak was observed at $2\theta = 6.78^{\circ}$ corresponding to (200) plane. This peak corresponds to monoclinic α phase with interplanar spacing of 1.29 nm. ZnPc film undergoes phase change from amorphous state to crystalline α phase with increase in annealing temperature. These results on ZnPc thin films are well in agreement with the literature [17]. The intensity of diffraction peaks of the film at different annealing temperatures are shown in Fig 4. Maximum intensity was obtained for the sample annealed at 393 K and the intensity decreased for higher temperatures (423 K).

Mean grain size (L) can be determined by using Scherrer's expression [12],

$$L = k_s\lambda / \beta \, \mathrm{Cos}\theta \text{ -------------------------- (2)}$$

where λ is the wavelength of X-ray CuK_{α} (1.54 Å), k_s is the Scherrer's constant, β is the width of the strong peak at half maximum intensity for the thin film, θ is the corresponding Bragg's angle. The lattice parameters of ZnPc thin films annealed at different temperatures were calculated and reported in table 2.

Table 2: Lattice parameters of ZnPc thin films annealed at different temperature

Temperature (K)	2θ (degrees)	FWHM	Grain size (D) (nm)
RT	Amorphous film		
323	6.78	0.60	13
373	6.78	0.49	16
393	6.78	0.20	41
423	6.78	0.35	23

From the table, it can be found that the grain size increases from 13 nm to 41 nm as the annealing temperature increases from 323 K to 393 K and further increase in annealing temperature to 423 K results in decrease in grain size. This decrease in the grain size is ascribed to re-crystallization and partial re-sublimation [18].

4. Conclusion

Thin films of ZnPc of different thicknesses were prepared by vacuum evaporation technique and vacuum annealed at 393 K and their optical studies were carried out. It was found that the optical band gap decreased due to annealing. Structural studies of the films at different annealing temperatures were carried out and the XRD patterns showed a major peak at 2θ = 6.78º corresponding to (200) plane with maximum intensity for an annealing temperature of 393 K indicating a high crystalline nature of the ZnPc film. The grain size was also calculated for various annealing temperatures and its value varied from 13 nm to 41 nm. In conclusion, the optical and structural properties of ZnPc thin films varied with different annealing temperatures.

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