



# Studies on the Optical Properties and Surface Morphology of Cobalt Phthalocyanine Thin Films

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Received 17 May 2007; Accepted 13 July 2007

**Abstract:** Thin films of Cobalt Phthalocyanine (CoPc) are fabricated at a base pressure of  $10^{-5}$  m.bar using Hind-Hivac thermal evaporation plant. The films are deposited on to glass substrates at various temperatures 318, 363, 408 and 458K. The optical absorption spectra of these thin films are measured. The present studies reveal that the optical band gap energies of CoPc thin films are almost same on substrate temperature variation. The structure and surface morphology of the films deposited on glass substrates of temperatures 303, 363 and 458K are studied using X-ray diffractograms and Scanning Electron Micrographs (SEM), which show that there is a change in the crystallinity and surface morphology due to change in the substrate temperatures. Full width at half maximum (FWHM) intensity of the diffraction peaks is also found reduced with increasing substrate temperatures. Scanning electron micrographs show that these crystals are needle like, which are interconnected at high substrate temperatures. The optical band gap energy is almost same on substrate temperature variation. Trap energy levels are also observed for these films.

**Keywords:** Cobalt Phthalocyanine, Thermal evaporation, Thin film, X-ray diffraction, Scanning electron micrograph.

## Introduction

In high-density optical data recording (ODR) media, organic dyes have attracted attention as novel materials due to their chemical stability, low heat conduction, and diversity of optical properties<sup>1,2</sup>. Phthalocyanine (Pc) is an organic semiconductor has excellent stability against heat, light, moisture and oxygen. Absorption spectra display the existence of strong absorption bands in the range of 400 and 800 nm caused by the  $\pi$ -  $\pi^*$  transitions of the conjugated macrocycle of  $18\pi$ -electrons. The physical properties are controlled by traps, which are associated with dislocations, imperfections, grain boundaries and surface topology of the material films<sup>3</sup>. Rapid drop in the absorption coefficient on the high-energy side of the absorption band leads to the band edge in semiconductors. In this paper the optical band gap of CoPc thin films deposited at various substrate temperatures are studied to investigate the changes in the optical properties.

X-ray diffraction (XRD) allows accurate determination of lattice 'd' spacing, lattice parameters and crystallite size and phase identification. The optical properties of these materials are dependent on the crystal phases and its structure<sup>4</sup>. The most common crystal phases occur in  $\alpha$  and  $\beta$ , that have two crystallite structures. The behavior of a gas sensor is significantly influenced by the crystal phase, crystal size and the degree of molecular stacking<sup>5</sup>. Sensor responses of Pcs are found that the sensitivity very much depended on the structure and morphology of the film. X-ray diffractograms recorded are analyzed to determine the structure and crystallinity of the films. Scanning electron microscopy (SEM) is one of the powerful tools for the investigation of surface topography, micro structural features *etc.* Scanning electron micrographs of CoPc thin films analyzed to study the surface morphology of the films.

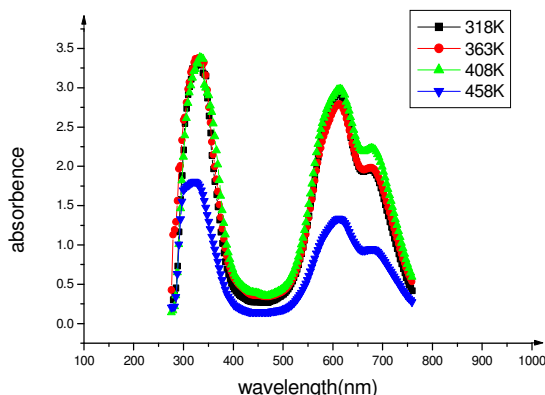
## Experimental

Powdered Cobalt Phthalocyanine from Aldrich Chemical Co, WI (USA) is used as source material. Physically and chemically cleaned glass substrates of dimensions 75mm x 25mm x 1.35mms are used for the thermal evaporation to avoid contaminants from the glass surface. Resistive heating of CoPc powder from molybdenum boat is carried at the rate 15 - 20nm per minute. The substrate is placed 20cm away from the molybdenum boat. Thin films of cobalt phthalocyanine of thickness 330nm are prepared at substrate temperatures, 318, 363, 408 and 458K, on to glass substrate kept in a base pressure of  $10^{-5}$  m.bar using Hind-Hivac thermal evaporation plant. Thickness of the film is measured by Tolansky's multiple beam interference technique<sup>6</sup>. Visible ultra-violet and near infrared absorption spectra of CoPc thin films are recorded using a Shimadzu 160A spectrophotometer. The optical band gaps and trap levels are investigated.

Thoroughly cleaned glass substrates of dimensions 20mm x 20mm x 1mms are used for film preparation for X-ray diffraction (XRD) studies. The thin films of 400nm thickness are deposited on to the substrates of temperatures 303, 363 and 458K using Hind-Hivac thermal evaporation plant and X-ray diffractograms are recorded using BRUKER D5005 diffractometer, which is using Cu K $\alpha$  radiation of wavelength 1.54059Å. A continuous scanning is employed to observe the preferred orientation of the deposited CoPc crystallites. The scanning speed is fixed at 2-degrees / minute. The diffractograms obtained are analyzed to determine the structure and crystallinity of the films. Pre-cleaned microscopic cover glass substrates of dimensions 16mmx 16mm x 0.1mm are used for CoPc film preparation for SEM analysis. The thin films of 400nm thickness on to the substrates deposited at substrate temperatures 303, 363 and 458K are used for scanning electron microscopy studies. The micrograms obtained by using scanning electron microscope LEO 435VP (U K). The micrograms obtained are analyzed for surface topology studies.

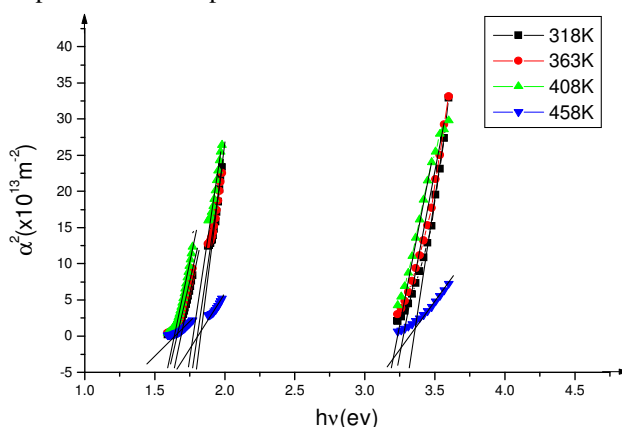
## Results and Discussion

The absorption spectra for Cobalt phthalocyanine thin films are given in the Fig 1. The tensile stress produced due to the constraint imposed by the substrate temperature, may affect the electronic structure and thereby result in new absorption spectra. The optical band gap for the as deposited thin film is found increased on crystallization<sup>7</sup>. Anderson *et al.*<sup>8</sup> have reported that the central metal atom of the phthalocyanines influences the optical absorption spectrum. Yamashita *et al.*<sup>9</sup> have observed that the Q band absorption shifts towards longer wavelengths when deposition temperatures are increased. The  $\alpha$ -phase of CoPc thin films (prepared at 303K) shows two absorption maxima at the Q band with wavelengths of 610nm and 678nm. The two maxima peaks are separated by 68nm as shown in Figure 1.



**Figure 1.** The absorption spectra for cobalt phthalocyanine thin films deposited at 318, 363, 408 and 458K temperatures.

The intensity of the higher energy peak is larger than that of the second peak. This behavior represents the typical features of the  $\alpha$ -phase of CoPc. As the substrate temperature increased to 458K, the higher energy peak was shifted slightly to higher wavelength side and the intensity is decreased gradually. For the increase in substrate temperature from 318K to 458K, the observed peaks located at 678nm remains there without shift but peak intensity is found decrease. This result is due to phase change activity<sup>10-12</sup>, and is in good agreement with the earlier observations of spectral change from  $\alpha$  to  $\beta$ -phase by heat-treatment at a temperature<sup>13, 14</sup> of approximately about 300°C. The absorbance spectrum shows sharp increase in absorption at wavelength near to the absorption edge of the threshold wavelength of the absorbance spectrum, the energy corresponds to this determines the band gap of the semiconductor material<sup>15</sup>. The absorption coefficient  $\alpha$  is related to the photon energy  $h\nu$  by  $\alpha = \alpha_0 (h\nu - E_g)^n$ . Where  $E_g$  is the optical band gap. The plot of  $\alpha^2$  vs.  $h\nu$  for CoPc thin films deposited at different substrate temperatures are shown given in the Fig 2. For allowed transition  $\alpha^2$  is plotted against  $E (h\nu)$  to yields a straight line for direct allowed transitions as shown in figure from which the extrapolation of linear portion to  $\alpha = 0$  near the absorption edge gives the band gap energy<sup>15</sup>. The variations in energy gap and trap levels with temperatures are tabulated in Table 1.



**Figure 2.** Plot of  $\alpha^2$  vs.  $h\nu$  for CoPc thin films deposited at substrate temperatures 318, 363, 408 and 458°K.

**Table 1.** The optical band gap energies of cobalt phthalocyanine thin films deposited at different substrate temperatures.

Substrate temperature	Trap level 1 eV	Trap level 2 eV	Energy gap $\pm 0.01$ , eV
318	1.66	1.84	3.25
363	1.65	1.81	3.23
408	1.66	1.78	3.22
458	1.66	1.82	3.23

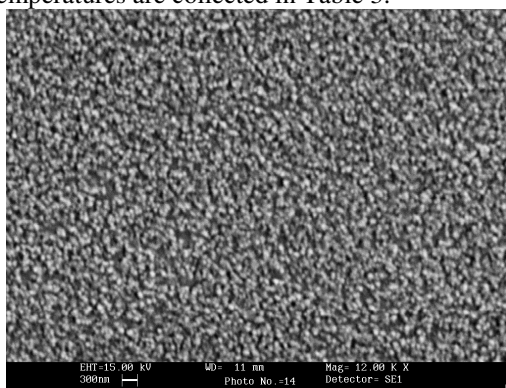
It is observed that the band gap energy is almost same on substrate temperature variation. The complete phase change was reported around  $300^{\circ}\text{C}$ <sup>10, 16</sup>. The film deposited at room temperature is identified to be of  $\alpha$ -form<sup>10, 16</sup>. Fustoss-Wegner<sup>17</sup> pointed out that for certain phthalocyanine the phase change occurs in two stages with a well-defined intermediate state. The band gap shows a change for the film deposited at 458K, which may be due to the phase transition from  $\alpha$  to  $\beta$ <sup>6</sup>. The phase separation could be responsible for the degradation of the optical properties<sup>4</sup>. No significant change is observed in the trap level-1 and trap level 2 with substrate temperature.

The  $\alpha$ - phase is metastable and obtained as a thin film deposited on a cold substrate in vacuum<sup>18</sup>. The  $\beta$  phase can be obtained in single crystal form or as a thin film formed by deposition of phthalocyanine on heated substrates<sup>18</sup>. The  $\beta$ -form is the thermodynamically stable one.  $\alpha$  -form is metastable and can be converted to  $\beta$ -form by temperature treatments with structures tetragonal and orthorhombic respectively<sup>19</sup>. The differences in the 'd' values are attributed to higher X-ray absorption, sample purity, particle size, preferred orientation and crystal texture. Intensities of the diffracted beams are determined by the positions of the atoms within the unit cell. The XRD pattern of as deposited film shows amorphous nature as reported by many investigators only a single peak is observed. Well-defined diffraction peak in the (001) direction gives the direction of the preferential orientation in the as deposited film (standard ASTM data). XRD pattern indicates all the samples are not of single phase<sup>20, 21</sup>. The preferential orientation is at an angle  $6.684^{\circ}$  with spacing between the planes,  $d = 1.32$  nm. The lattice parameters for the film deposited at 303K are  $a = b = 1.87\text{nm}$  and  $c = 1.32$  nm and hence the film prepared at room temperature is identified as tetragonal which is in agreement with Robinson and Klein<sup>19</sup>. The phase transition from  $\alpha$  to  $\beta$  is not complete at 458K. It can see that the intensity of the preferential peak increase with substrate temperature initially, and then reduces. The d-value is reduces initially and then increases and  $2\theta$  values are increases initially and then decreases with substrate temperature shows phase change activity. The difference between  $\alpha$  and  $\beta$ -phases are attributed to the tilt angle of b-axis of the unit cell<sup>10</sup>. The optical band gaps also support the above observations. Table-2 shows the full widths at half maximum (FWHM) intensity of preferential orientation, which shows that the FWHM are reduced with increasing substrate temperatures, which represents better lattice quality<sup>22</sup>.

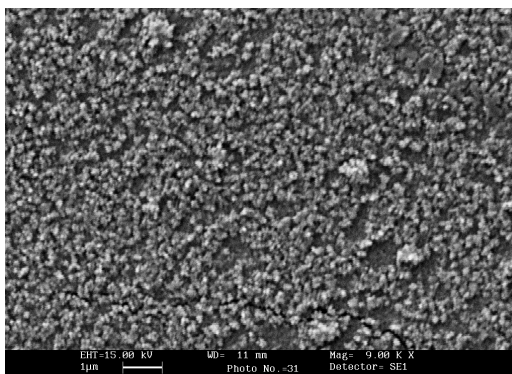
**Table 2.** Variation of FWHM of preferential orientation with substrate temperatures for the CoPc thin films.

Substrate temperature, K	FWHM, $^{\circ}\text{C}$
303	0.73
363	0.39
458	0.25

The scanning electron micrographs of thin films deposited at 303, 363 and 458K are shown in the fig-3, 4 and 5 respectively. The film growth is found perpendicular to the substrate surface. The film morphology is found changes for the elevated temperature of substrate. At low substrate temperature (303K) fine and smooth grain morphology were observed. The polycrystalline nature of thermally deposited  $\alpha$ -CoPc is confirmed by the electron micrographs. As substrate temperature increased to 363K, increase in grain size was found. As substrate temperature increased to 458K, the needle like grains were found which are interconnected, the growth of which are parallel to the substrate surface. Sizes of some grains are found to shrink at 458K. The reduction in grains can either be due to partial resublimation, recrystallisation or phase transformation from  $\alpha$  to  $\beta$ . The stacking axis of grains at 458K is parallel to the substrate surface as previous observations<sup>16</sup>. The grain size is measured from the micrographs. The average grain sizes of the CoPc thin films deposited at different substrate temperatures are collected in Table 3.

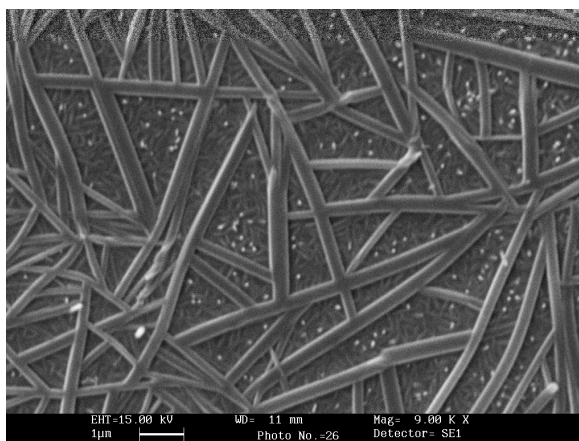


**Figure 3.** Scanning electron micrograph of thin film of CoPc on to the glass substrate deposited at 303K.



**Figure 4.** Scanning electron micrograph of CoPc thin film of on to the glass substrate deposited at 363K

Smoothest film produced at low substrate temperature was amorphous<sup>22</sup>. The crystal morphology and molecular orientation change depending on substrate temperature<sup>23</sup>. Dogo *et al.*<sup>24</sup> observed that crystallinity of CuPc thin films increases with substrate temperature. The average grain size increases as temperature increases. Gas sensitivity depends both on material parameters, such as the crystal phase of the material and on film parameters, such as the surface topography of the film<sup>23</sup>. The band gaps, trap levels and activation energies are influenced by the grain size<sup>25</sup>.



**Figure 5.** Scanning electron micrograph of thin film of CoPc on to the glass substrates deposited at 458K

**Table 3.** Variation of grain size with substrate temperatures for CoPc thin film

Substrate temperature, K	Grain length, nm	Grain breadth, nm
303	246	112
363	456	257
458	5670	279

The difference in grain size may be attributed by the difference in temperature. This is caused due to the nucleating behavior of the substance<sup>20</sup>.

## Conclusion

The optical properties of CoPc films are controlled by energy band gap and the trap levels present in the forbidden energy gap. Since the interactions of cobalt phthalocyanine molecules are of Vander Waals type, the rearrangements of molecule alter the energy band gap between valence band and conduction band. The band gap is found almost stable with variations in substrate temperatures. However a decrease in band gap is observed for film prepared at 458K. Diffraction peaks obtained for the films prepared at higher substrate temperatures are sharp and that is due to increased crystallinity. CoPc films prepared at room temperature are tetragonal. The difference in 'd' values shows phase changes activity with increase in substrate temperature. The SEM shows smooth grain morphology at 303K. Increase in grain size was found with increased substrate temperature. As substrate temperature increased to 458K, the needle like grains was found which are interconnected. The change in grain size, optical band gap and trap levels with substrate temperature shows that the properties of CoPc are controlled by its structure and morphology. The average grain sizes are found increase with increase in substrate temperatures.

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