Asian Journal of Chemistry Vol. 20, No. 1 (2008), 245-253

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

BENNY JOSEPH* and C.S. MENON
School of Pure and Applied Physics, Mahatma Gandhi University
Kottayam-686 650, India
E-mail: sjvben@yahoo.com

Vacuum sublimed thin films of copper phthalocyanine (CuPc) at a base pressure of 10^{-5} m.bar are fabricated using a 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 studied and found that the optical band gap energies of CuPc thin films are highly dependent on the substrate temperatures. The structure and surface morphology of the films deposited on glass substrates of temperatures 303, 363 and 458 K are studied using X-ray diffractograms and scanning electron micrographs, which shows that there is a change in the crystallinity and surface morphology due to change in the substrate temperature. Full width at half maximum (FWHM) intensity of the diffraction peaks is also found reduced with increasing substrate temperatures. The structure and lattice constants are determined. The optical band gap is found increased and then reduced with flake shaped large grains with increase in substrate temperatures. Additional trap levels are also found in films prepared at high substrate temperatures.

Key Words: Copper 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[1,2]. Phthalocyanine is an organic semiconductor widely used for sensor applications and has excellent stability against heat, light, moisture and oxygen[3]. The electronic spectra arise through the transitions from one molecular orbital to another[4]. Yoshida *et al.*[5] have suggested the effect of hybridization between intramolecular excitations and charge transfer plays a significant role in the absorption spectra of MPc crystals. Anderson *et al.*[6] have reported that the central metal atom of the phthalocyanines influences the optical absorption spectrum. The physical properties are controlled by traps, which are associated with dislocations, imperfections, grain boundaries and surface topology of the material[7]. It has been reported that the growth conditions have a strong influence on the properties of phthalocyanine thin films. In this paper the optical band gap of copper phthalocyanine thin films deposited at various substrate temperatures are investigated to study the changes in the optical properties.

The technique of X-ray diffraction (XRD) allows accurate determination of lattice d spacing, lattice parameters and crystallite size and phase identification[8,9]. The behaviour of a gas sensor is significantly influenced by the crystal phase, crystal size and the degree of molecular stacking[10]. X-ray diffractograms are recorded for the CuPc thin films coated at different substrate temperatures and are analyzed to determine the structure of the films. It is known that the optical properties are depended on grain size, crystallinity, stoichiometry and surface roughness of the film. Scanning electron microscopy (SEM) is one of the powerful tools for the investigation of surface topography and micro structural features. Scanning electron micrographs of CuPc thin films coated at different substrate temperatures are analyzed to study morphology of the films.

EXPERIMENTAL

Powdered copper phthalocyanine from Aldrich Chemical Co, WI (USA) is used as source material. Glass substrates are cleaned physically and chemically to avoid contaminants from the glass surface. Pre-cleaned glass substrates of dimensions 75 mm × 25 mm × 1.35 mm are used for the evaporation. Resistive heating of CuPc powder from molybdenum boat is carried at the rate of 20 nm/min. Thin films of copper phthalocyanines of thickness 400 nm are prepared on glass substrates of temperatures 318, 363, 408 and 458K kept in a base pressure of 10^{-5} m.bar using a Hind-Hivac thermal evaporation plant. Thickness of the film is measured by Tolansky's multiple beam interference technique[11]. Visible ultra-violet and near infrared absorption spectra of CuPc thin films are recorded using a Shimadzu 160A spectrophotometer. The optical band gaps of these films are investigated.

Thoroughly cleaned glass substrates of dimensions 20 mm × 20 mm × 1 mm are used for film preparation for X-ray diffraction (XRD) studies. The thin films of 400 nm thickness are deposited on to the substrates. X-ray diffractograms are recorded for the CuPc thin films coated at substrate temperatures 303, 363 and 458K using Bruker D5005 X-ray diffractometer, which is using Cu Kα radiation of wavelength 1.54059 Å. The scanning speed is fixed at 2-degrees/min. Full width at half maximum (FWHM) intensity of the diffraction peaks is studied. Pre-cleaned microscopic cover glass substrates of dimensions 16 × 16 × 0.1 mm are used for film preparation for SEM analysis. The thin films of 400 nm thickness are deposited on to the substrates at temperatures 303, 363 and 458 K are used for SEM studies. The micrographs obtained by scanning electron microscope LEO 435VP (UK) are analyzed for surface morphology.

RESULTS AND DISCUSSION

The absorption spectra for copper phthalocyanine thin films deposited at 318, 363, 408 and 458 K temperatures are given in the Fig. 1. The tensile stress produced due to the constraint imposed by substrate temperature affect the electronic structure and thereby result in new absorption spectra. It is observed that the Q-band shifts by 12, 7 and 12 nm towards longer wavelength for the variation of substrate temperature from 318 to 363, 363 to 408 and 408 to 458 K, respectively which is in agreement with Yamashita[12] and Xia[13]. It is also observed that the intensity of absorption maxima observed are increased with increasing temperature is due to phase change activity from α to β, which is in agreement with Jungyoon *et al.*[14], Djurisic *et al.*[15] and Xia *et al.*[13]. The high-energy side of the absorption spectrum shows a sharp absorption edge. The absorption coefficient α is related to the photon energy hν by $\alpha = \alpha_0 (h\nu - Eg)^n$. Where Eg is the optical band gap. The plot of α^2 *vs.* hν for CuPc thin films deposited at substrate temperatures 318, 363, 408 and 458 K is given in Fig. 2. The extrapolation of linear portion to $\alpha^2 = 0$ near the absorption edge gives the band gap energy. The energy gap and trap levels for different temperatures are shown in Table-1.

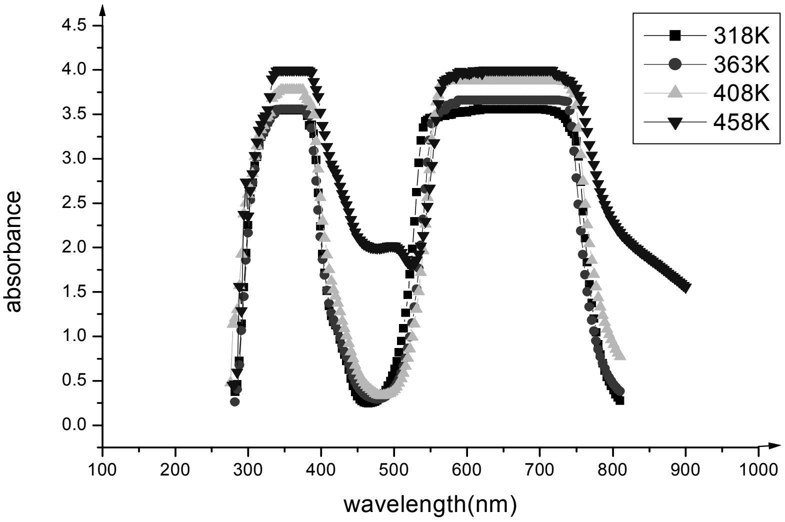

Fig. 1. Absorption spectra of copper phthalocyanine thin films deposited at 318, 363, 408 and 458 K substrate temperatures

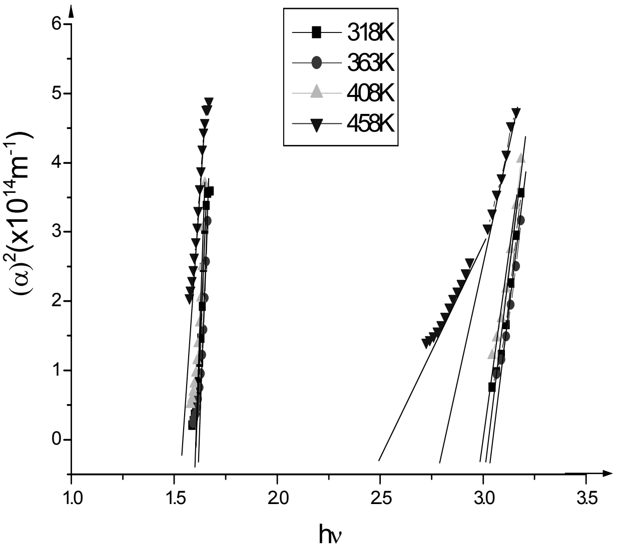

Fig. 2. Plot of α^2 *vs.* hν of copper phthalocyanine thin films deposited at 318, 363, 408 and 458 K substrate temperatures

TABLE-1
BAND GAP ENERGIES OF COPPER PHTHALOCYANINE THIN FILMS DEPOSITED AT DIFFERENT SUBSTRATE TEMPERATURES

Substrate temperature	Trap level 1 (eV)	Trap level 2 (eV)	Energy gap (eV)
318	1.60	-	3.032
363	1.62	-	3.046
408	1.60	-	3.000
458	1.54	2.53	2.810

It is observed that the band gap energy increases initially on substrate temperature and then decreases at 458 K. The optical band gap for the as deposited thin film is found increased on crystallization[16]. An increase of the band gap energy can be expected when the chain length lowers[17]. The sharp decrease of band gap at 458 K is due to phase change activity and complete phase change was reported around 300 °C[14,18,19]. Collins and Mohammed[20] and Fustoss-Wegner[21] have pointed out that for certain phthalocyanines the phase change occurs in two stages with a well-defined intermediate state. The phase separation could be responsible for the de-gradation of optical properties[22]. Campbell and Collins[23] have shown that the band gap of PbPc is narrowing by forming trap levels above the valence band. The trap level slightly increases as the temperature increases and then decreases with temperature 458 K[16]. An additional trap level is also found at substrate temperature 458 K. The band gap shows a drastic change for the film deposited at 473 K for H_2Pc and is attributed to the phase transition from α to β[11].

The most common polymorphic crystal phases occur in phthalocyanines are α and β, that have two crystallite structures. The α-phase is metastable and obtained either as a polycrystalline powder or as a thin film deposited on a cold substrate in vacuum[24]. Phase separation could be responsible for the degradation of the optical properties[22]. The α-form can be converted to β-form by temperature treatments. The CuPc film deposited at room temperature is identified to be of α-form and has tetragonal structure[25]. The differences in the d values are attributed to higher X-ray absorption, sample purity, particle size, preferred orientation and crystal texture[26]. The diffractograms have been analyzed using the American Society for Testing Materials (ASTM) data and the lattice constants are calculated. X-ray diffraction pattern of CuPc thin films prepared at substrate temperatures 303, 363 and 458 K. The XRD pattern of as deposited film shows amorphous nature as reported by many investigators. The structure of CuPc thin films at room temperature is adjudged to be tetragonal with six molecules per unit cell, which is in agreement with Robinson and Klein[25]. Well-defined diffraction peak by (001) gives the direction of the preferential orientation. The distance between planes 'd' is related to the (hkl) of the plane by the relation $1/d^2 = (h^2+ k^2)/a^2 + l^2/c^2$. The lattice parameters obtained as a = b = 1.5920 nm, c = 1.2776 nm and $\alpha = \beta = \gamma = 90°$. The crystal structure assumes a similar configuration reported by Debe and Kam[27] and Komiyama *et al.*[28]. The increased intensities of the preferential peaks with substrate temperature show the increased crystallinity of the film. The phase transition from α to β is not complete at 458 K. The increase in 'd' and decrease in 2θ value with increase in substrate temperature show a phase change activity. The difference between α- and β-phases are attributed to the tilt angle of b-axis of the unit cell[14]. The β-phase can be obtained in single crystal form or as a thin film formed by deposition of phthalocyanine on heated substrates[29]. Table-2 shows the full widths at half maximum (FWHM) intensity of preferential orientation, which shows the FWHM are reduced with increasing substrate temperatures, which represents better lattice quality[30]. The increased crystallinity is attributed to the destruction of pseudomorphic layers present in the film upon high substrate temperature. The CuPc thin film shows a poor degree of crystallinity for the as-deposited film like EuPc[11].

The scanning electron micrographs of thin films deposited at 303, 363 and 458 K substrate temperatures are shown in the Figs. 3, 4 and 5, respectively. The film morphology changes for the elevated temperatures of the

TABLE-2
VARIATION OF FWHM OF PREFERENTIAL ORIENTATION WITH SUBSTRATE TEMPERATURES FOR THE CuPc THIN FILMS

Substrate temperature (K)	FWHM (°)
303	0.40
363	0.27
458	0.13

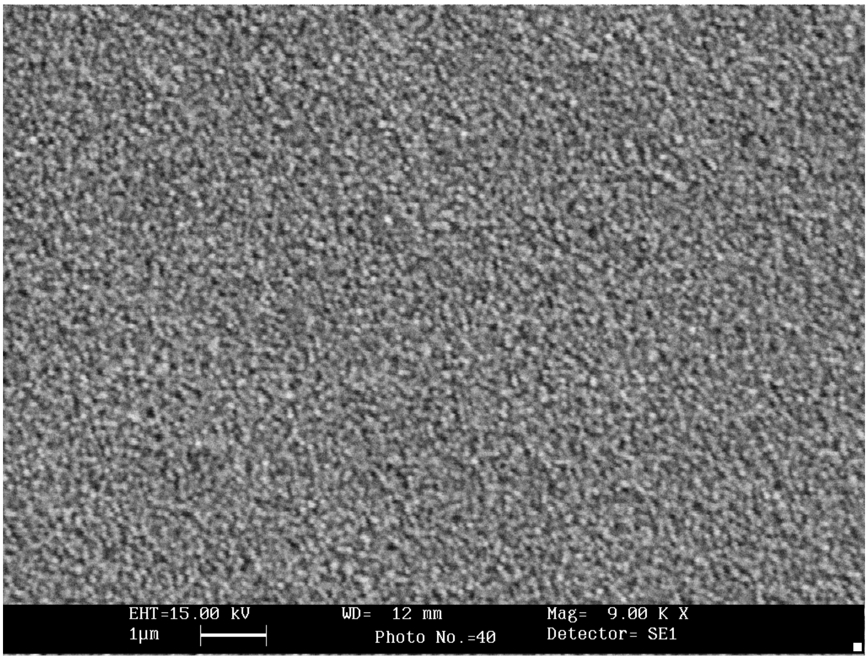

Fig. 3. Scanning electron micrograph of copper phthalocyanine thin film deposited at 303 K substrate temperature

substrate. At low substrate temperature (303 K) fine and smooth grain morphology is observed as in work of Jungyoon *et al.*[14]. The polycrystalline nature of thermally deposited α-CuPc is confirmed by these electron micrographs. As substrate temperature increased to 363 K the size of the grains are found increased. As the substrate temperature increased to 458 K flake shaped grains with increased size are found in agreement with other observations[31]. The grain sizes at different substrate temperatures are measured. The average grain sizes of the CuPc thin films deposited at different substrate temperatures are collected in Table-3.

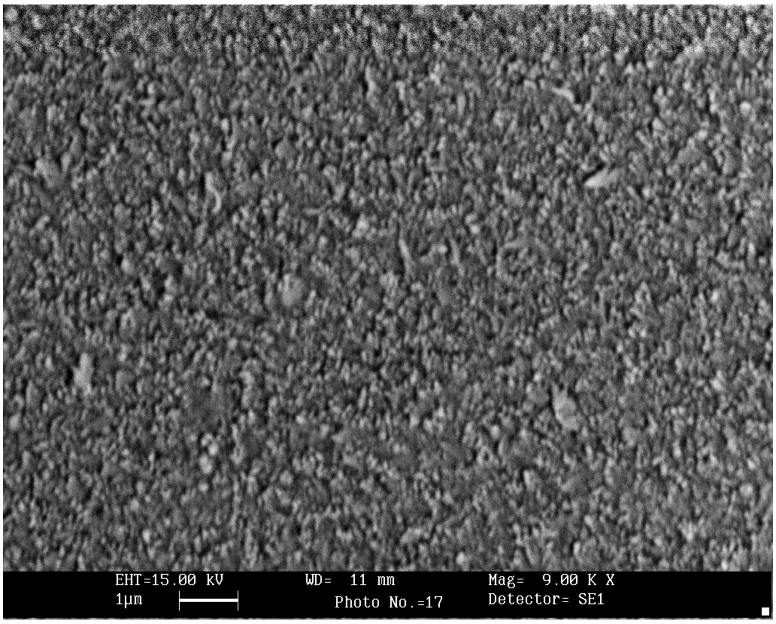

Fig. 4. Scanning electron micrograph of copper phthalocyanine thin film deposited at 363 K substrate temperature

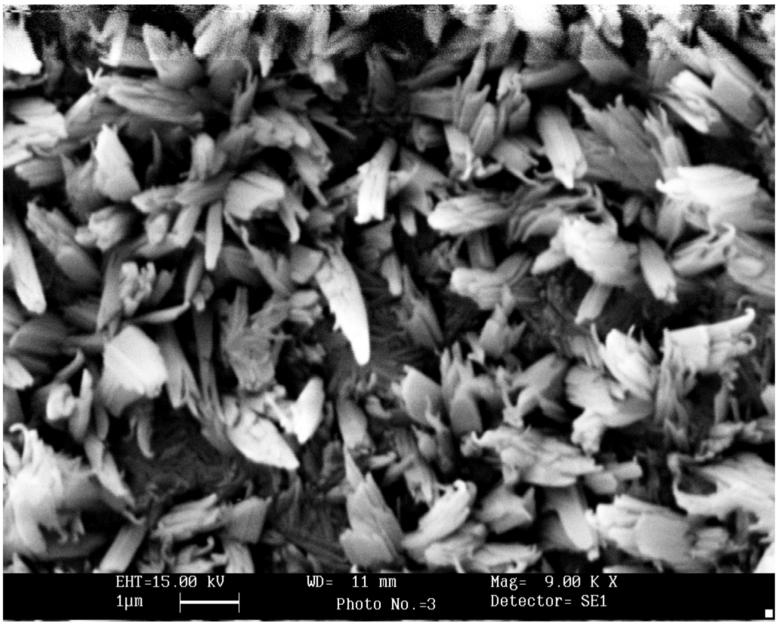

Fig. 5. Scanning electron micrograph of copper phthalocyanine thin film deposited at 458 K substrate temperature

TABLE-3
VARIATION OF GRAIN SIZE WITH SUBSTRATE TEMPERATURES FOR CuPc THIN FILM

Sub temp (K)	Grain length (nm)	Grain breadth (nm)
303	250.0	90.0
363	500.0	200.0
458	1700.0	540.0

The film deposited at 458 K has the maximum value of grain size. The micrograph shows some fused or shrinked (thread like formation) grains at temperature 458 K and which enhanced surface roughness. Fusing of grains at high temperatures has been observed earlier[16]. The grain size increases slightly at small increase in temperature and then shows a sudden increase at 458 K. Sizes of some grains are found to shrink due to phase change activity at 458 K. The reduction in grain size can either be due to partial resublimation, recrystallization or phase transformation from α to β. The microphotographs also show some preferential orientations in grains at high temperature due to difference in coefficient of thermal expansion between substrate and the film. Grain boundaries act as barriers for the cross transport of charge carriers and the barrier character of the grain boundary is pronounced in the low temperature regime[8].

The difference in grain size may be attributed by the difference in temperature. This is caused due to the nucleating behaviour of the substance[8].

Conclusion

Thin films of CuPc are prepared by thermal evaporation at different substrate temperatures and its optical, structural and morphological properties are studied. The optical properties of CuPc films are controlled by band gap and trap levels present in the forbidden energy gap, which are found dependent on substrate temperatures. Since the interactions of copper phthalocyanine molecules are of vander Waals type, the re-arrangements of molecule alter the energy band gap between valence band and conduction band. Re-arrangements of molecule are taking place with different substrate temperatures. Diffraction peaks obtained for the films prepared at different substrate temperatures are sharp which is due to increased crystallinity, which is also clear from the FWHM values. Lattice constants are calculated and the CuPc films prepared at room temperature is conformed tetragonal in structure. A sharp change in band gap is observed for film prepared at 458 K shows phase change activity. Grain sizes are investigated from SEM studies, which is found increased with substrate temperature. Large flake shaped grains are observed at 458 K. The present study shows the optical parameters of CuPc thin films are strongly influenced by surface morphology and the crystal structure of the film.

REFERENCES

1. P.J. Kivits, M.R.J. de Bont and J. Van der Veen, *Appl. Phys. A*, **36**, 101 (1981).
2. A.N. Burgess, *J. Appl. Phys.*, **61**, 74 (1987).
3. Y. Sadaoka, T.A. Jones and W. Gopel, *Sens. Actuators B,* **1**, 148 (1990).
4. S. Basu, *Indian J. Phys.*, **28**, 511 (1954).
5. H. Yoshida, Y. Tokura and T. Koda, *Chem. Phys.*, **109**, 375 (1986).
6. J.S. Anderson, E.F. Bradbrook, A.H. Cook and R.P. Linstead, *J. Chem. Soc.*, Part II, 1151 (1938).
7. J.D. Wright, *Prog. Surf. Sci.*, **31**, 1 (1989).
8. S.K. Rout, S. Panigrahi and J. Bera, *J. Bull. Mater.*, **28**, 275 (2005).
9. X.J. Hu, R.B. Li, H.S. Shen, Y.B. Dai and X.C. He, *Carbon*, **42**, 1501 (2004).
10. Y. Sadaoka, Y. Sakai, I. Aso, N. Yamazoe and T. Seiyama, *Denki Kagaku*, **48**, 486 (1980).
11. K.N. Narayanan Unni, Ph.D. Thesis, p. 121 Unpublished.
12. A. Yamashita, T. Maruno and T. Hayami, *J. Phys. Chem.*, **97**, 4567 (1993).
13. H. Xia and M. Nogami, *Opt. Mater.*, **15**, 93 (2000).
14. E. Jungyoon, S. Kim, E.L. Lee, D. Cha and B. Friedman, *Appl. Surf. Sci.*, **205**, 274 (2003).
15. A.B. Djurisic, C.Y. Kwong, T.W. Lau, W.L. Guo, E.H. Li, Z.T. Liu, H.S. Kwok, L.S.M. Lam and W.K. Chan, *Opt. Commun.*, **205**, 155 (2002).
16. G. Agarwal, G.B. Reddy, *J. Mater. Sci., Mater. Electr.*, **16**, 21 (2005).
17. F. Garnier, *Chem. Phys.*, **227**, 253 (1998).
18. Yuh-Lang Lee, Wen-Ching Tsai and Jer-Ru Maa, *Appl. Surf. Sci.*, **173**, 352 (2001).
19. S.I. Shihub and R.D. Gould, *Thin Solid Film*, **290**, 390 (1996).
20. R.A. Collins and K.A. Mohammed, *Thermochim. Acta*, **109**, 397 (1987).
21. M. Fustoss-Wegner, *Thermochim. Acta*, **23**, 93 (1978).
22. M. Herrera, D. Gonzalez, M. Hopkinson and P. Navaretti, *J. Semicond. Sci. Technol.*, **19**, 813 (2004).
23. D. Campbell and R.A. Collins, *Thin Solid Films*, **261**, 311 (1995).
24. F.K. Schoch Jr., J. Greggi Jr. and T.A. Temofonte, *J. Vac. Sci. Technol.*, **6A**, 155 (1988).
25. M.T. Robinson and G.E. Klein, *Am. Chem. Soc.*, **74**, 6294 (1952).
26. A.K. Hassan and R.D. Gould, *Phys. Stat. Solid*, **91**, 132 (1992).
27. M.K. Debe and K.K. Kam, *Thin Solid Films*, **186**, 298 (1990).
28. M. Komiyama, Y. Sakakibara and H. Hirai, *Thin Solid Films*, **151**, LI09 (1987).
29. A. Twarowski, *J. Chem. Phys.*, **77**, 5840 (1982).
30. P. Raji, C. Sanjeeviraja and K. Ramachandran, *Bull. Matter. Sci.*, **28**, 233 (2005).
31. A. Goswami, Thin Film Fundamentals, New Age International (P) Limited, New Delhi, p. 72, (1996).

(*Received*: 22 September 2006; *Accepted*: 5 September 2007) AJC-5814