

PACS numbers: 68.55 – a, 73.61 – r

DETERMINATION OF THERMAL ACTIVATION ENERGY AND GRAIN SIZE OF IRON HEXADECACHLORO PHTHALOCYANINE THIN FILMS

Raji Koshy, C.S. Menon

School of Pure and Applied Physics, Mahatma Gandhi University,
Kottayam, Kerala, India, 686560
E-mail: rajirose23@yahoo.com

Electrical, structural and surface morphological properties of Iron hexadecachloro phthalocyanine thin films deposited onto glass substrates are studied as a function of post deposition annealing temperature in air. Organic semiconductors are extensively used in optical and electronic devices such as organic photovoltaic solar cells (OSC), thin film transistors (OTFT) and organic light emitting diodes (OLED). Metal phthalocyanines are one of the most promising candidates to be used in the fabrication of such devices. A No. of phthalocyanines have been extensively studied. But not much work have been carried out in $Cl_{16}FePc$ thin films. Basic characteristics of $Cl_{16}FePc$ are not reported in literature. Hexadecachloro phthalocyanines have attracted interest as possible n-type organic semiconductor with high electron mobility and good stability characteristics. In the present work we investigate the activation energy of the $Cl_{16}FePc$ thin films as a function of air annealing temperature. We also report the film structure and surface morphology by X-ray diffraction (XRD) and Scanning electron microscopy (SEM).

Keywords: IRON HEXADECACHLORO PHTHALOCYANINE, THIN FILMS, ELECTRICAL PROPERTIES, XRD, SEM.

*(Received 18 April 2011, in final form 24 May 2011,
published online 05 November 2011)*

1. INTRODUCTION

In recent years, organic semiconductors have attracted a great deal of attention due to their potential use in a wide range of technological applications. Due to their interesting physical properties combined with the low material cost make these organic compounds a strong candidate for the electronic and optoelectronic devices. Phthalocyanines are a class of organic dyes material that are weakly semiconducting. Phthalocyanines thin films are used in gas sensing devices [1], photovoltaic devices [2, 3], thin film transistors [4], organic light emitting diodes [5], and scattering diodes [6]. The light absorbing properties of the phthalocyanines in the visible and in the infrared regions are of significant importance because of the current interest in the conversion of solar to electrical energy [7]. For the fundamental understanding as well as for the device fabrication, the study of characteristics of the material is important. This can be carried out in different ways viz, electrical, optical and structural studies. It is observed that the electrical, optical and structural properties of Pcs are critically dependent on film morphology, which in turn is determined by ambient

parameters such as deposition rate, substrate temperature and post deposition annealing [8].

Relatively few studies have been made on the halogenated MPCs although there is evidence that they may exhibit properties suitable for gas sensing applications [9]. The family of phthalocyanine (Pc) represents one of the most promising candidates for ordered organic thin films, as these systems possess advantageous attributes such as chemical stability and excellent film growth, which result in optimized electronic properties [10].

Furthermore, they can be regarded as model systems for the entire class of low molecular weight, flat organic molecules. Some of the above referred applications are based on the semiconducting behavior of these materials in thin film form. Besides, their favorable characteristics such as thermal and chemical stability and insolubility in water, the ease and variety of film preparation make phthalocyanines, very attractive for investigation. The present work is focused on the electrical, structural and morphological characterization of Iron Hexadecachloro Phthalocyanine ($\text{Cl}_{16}\text{FePc}$) thin film.

In this paper we report the electrical, structural and surface morphological properties of as-deposited and heat treated $\text{Cl}_{16}\text{FePc}$ thin films.

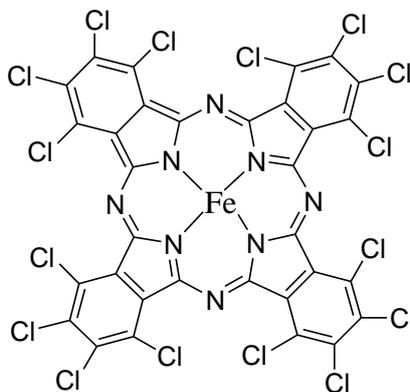


Fig. 1 – Molecular structure of $\text{Cl}_{16}\text{FePc}$ thin films

2. MATERIALS AND METHODS

$\text{Cl}_{16}\text{FePc}$ ($\text{C}_{32}\text{Cl}_{16}\text{N}_8\text{Fe}$) powder procured from Sigma-Aldrich Chemicals (USA), is purified by the train –sublimation technique using nitrogen as the carrier and is used as the source material for thermal evaporation. Thin films of suitable thickness are prepared by vacuum sublimation from a resistively heated molybdenum boat using a “Hind Hivac 12A4” coating system. Thin films are deposited onto thoroughly cleaned rectangular glass substrates of dimension $4\text{ cm} \times 1.2\text{ cm} \times 1.0\text{ mm}$ at room temperature at a pressure of 10^{-5} Torr. The thickness of the film is measured using a Dektac thickness profilometer and is cross checked with Tolansky’s multiple beam interference technique [11]. Film thickness is typically $350 \pm 5\text{ nm}$. The thin films annealed in air for 1 hour at 373 K, 423 K, and 473 K in a furnace with a temperature controller with recorder. Vacuum deposited silver, with an inter-electrode distance of 1 cm, is used for the contact electrodes. Electrical conductivity measurements are performed using a programmable Keithley electrometer

model No.617. To avoid any possible contamination, measurements are performed in vacuum at 10^{-3} Torr. Since phthalocyanines are photoconductive [12], the measurements are done in darkness. X-ray diffractograms of heat treated samples have been recorded using a Brucker AXS D8 model. Scanning electron micrograms of heat treated samples are taken by JOEL JSM scanning electron microscopy images.

3. RESULTS AND DISCUSSIONS

3.1 Electrical Studies

Electrical conductivity studies on $\text{Cl}_{16}\text{FePc}$ thin films are carried out to determine thermal activation energy and to study the effect of air annealing temperature on the activation energy. In inorganic semiconductors the semiconducting properties are brought about by thermal excitation, impurities, lattice defects and non stoichiometry. Holes in the valence band and electrons in the conduction band contribute to the electrical conductivity. The electrical conductivity σ can be expressed as

$$\sigma = A\exp(-E_1/k_B T) + B\exp(-E_2/k_B T) + C\exp(-E_3/k_B T) + \dots \quad (1)$$

Where σ is the conductivity at temperature T , E_1 , E_2 , E_3 are the thermal activation energies, k_B is the Boltzmann constant and A , B , C , etc. are the pre-exponential factors.

The electrical resistances of the samples are measured using a programmable Keithley electrometer. The electrical conductivity (σ) is calculated using the relation

$$\sigma = L/Rbd \quad (2)$$

Where L , b , d are the length, breadth and thickness of the film respectively. R is the resistance of the film. Arrhenius plots of $\ln\sigma$ vs $1000/T$ of $\text{Cl}_{16}\text{FePc}$ thin films are made to study the dependence of the conduction mechanism on annealing temperature 373 K, 423 K and 473 K. Here Figure (2a and 2b) shows the Arrhenius plots of $\ln\sigma$ vs $1000/T$ for the as deposited film and 473 K annealed film respectively.

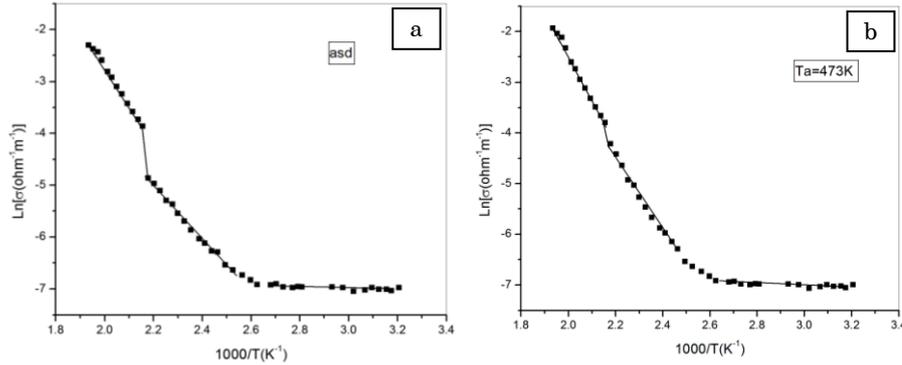


Fig. 2 – Plot of $\ln\sigma$ vs. $1000/T$ for the as-deposited film (a); plot of $\ln\sigma$ vs. $1000/T$ for the film annealed at 473 K

There are three linear regions for the samples deposited at room temperature, corresponding to three activation energies E_1 , E_2 and E_3 . Three activation energies for the films MnPc, InPcCl and H₂Pc have already been reported [13, 15]. The activation energy E_1 corresponding to the higher temperature region is associated with the resonant energy involved in a short lived excited state. E_2 and E_3 are associated with a short - lived charge transfer between impurity and complex. E_1 corresponds to an intrinsic generation process and E_2 and E_3 corresponds to the impurity conduction [16]. The activation energy is determined within an accuracy of ± 0.01 eV in all the measurements. There are many conduction mechanism suggested for amorphous and nearly polycrystalline materials. According to Davis and Mott [17], the formation of localized states has an important role in the conduction of charge carriers. The activation energies E_1 , E_2 and E_3 are collected in Table 1. The activation energy corresponding to the linear regions are estimated from the slope of the graph. We have given three activation energies for each sample and are given in Table 1.

Table 1 – Variations of activation energies with annealing temperatures

Annealing Temperature, K	Activation Energy ± 0.01 eV		
	E_1	E_2	E_3
As-deposited	0.65	0.50	0.02
373 K	0.67	0.51	0.02
423K	0.69	0.53	0.03
473K	0.71	0.55	0.04

In the extrinsic region, the charge carriers move by hopping along with ions and electrons [18]. Due to oxygen adsorption and restore the exponential distribution of traps is restored. As-deposited sample may contain different kinds of defects such as vacancies, grain boundaries and dislocations which can be partially annealed out by the heat treatments, resulting in a decrease in the density of defects [19].

The activation energy of Cl₁₆FePc thin films is found to increase with annealing temperature. The intrinsic activation energy E_1 for Cl₁₆FePc thin film for as-deposited film is obtained as 0.65 eV. This value rises up to 0.71 eV for film annealed at 473 K in air.

3.2 Structural Studies

Fig. 3 a, b show the X-ray diffractograms of the air annealed Cl₁₆FePc thin films of thickness 350 ± 5 nm at 373 K and 473 K respectively. Standard data's of Cl₁₆FePc powder are not available in literature. The studies are performed on the mean micro crystallite grain size L using Scherrer's formula

$$L = K\lambda/\eta\cos\theta$$

Where $\lambda = 1.5406$ Å is the X-ray wavelength, η the width of the strongest peak at half maximum intensity in radians, θ is the corresponding Bragg angle of the most intense peak. The Scherrer constant K has been assigned a value of 0.9 for phthalocyanines [20]. Variation of Grain Size with air annealing temperature is given in Table 2. Due to annealing the grain size decreases and grain boundary increases.

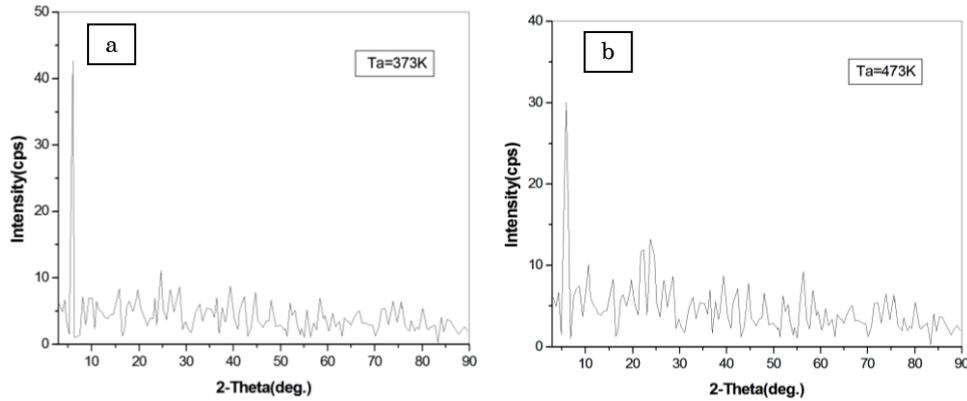


Fig. 3 – X-ray diffraction pattern of $Cl_{16}FePc$ at 373 K (a) and 473 K (b) air annealed thin films

Table 2 – Variation of grain size with air annealing temperature of $Cl_{16}FePc$ thin films

Annealing Temperature (K)	Grain Size(nm)
373K	18
423K	15
473K	13

3.3 Surface Morphological Studies

The SEM of air annealed $Cl_{16}FePc$ thin films at 373 K and 473 K are given in Figure 4 a, and b respectively.

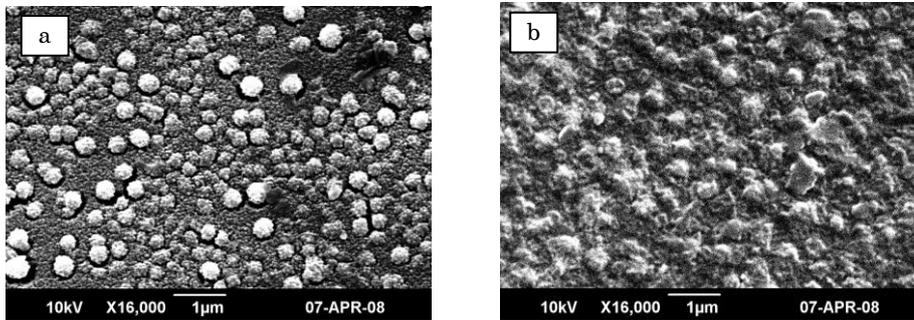


Fig. 4 – SEM images of air annealed $Cl_{16}FePc$ thin films at 373K (a) 473K(b)

Film deposited at 373K has well defined surface with large crystal grain structures. The fine grain crystallite on the 373 K films is transformed to a structure of nature with agglomerated form.

The microcrystalline grain boundaries of $Cl_{16}FePc$ thin films annealed in air increases with increase of temperature. These films are polycrystalline in nature. Surfaces of all the films are smooth and flat.

4. CONCLUSIONS

Iron Hexadecachloro phthalocynine thin films have been prepared on glass substrates by thermal evaporation technique. The basic electrical, structural and morphological properties of $\text{Cl}_{16}\text{FePc}$ thin films have been studied. Temperature dependence of electrical conductivity of the films is investigated. In the temperature dependence of electrical conductivity plots, more than one linear region is obtained. This confirms the existence of trap levels. The thermal activation energies increase with increase of air annealing temperatures. This can be due to better film ordering on annealing. The variation in the extrinsic activation energies due annealing can be attributed to the distribution of trapping states. The increase in activation energy is due to the reversible change in molecular interactions observed in chlorinated phthalocyanines, which are n-type semiconductors. The increase in activation energy is due to the decrease in interaction of molecular π -systems of the chlorinated phthalocyanine. This decrease in interaction leads to an increased barrier of charge transport in the film and hence the increase in activation energy. X-ray diffractograms and surface morphology of samples annealed at various temperatures are analyzed. Most of the films are found to be polycrystalline in nature. The microcrystalline grain boundaries are found to decrease with increase of annealing temperature and substrate temperature. The variation in grain size is small as is observed from the XRD patterns. Surfaces of all the films are smooth and flat. The SEM planar view adds supports to the XRD pattern.

REFERENCES

1. U. Geiersbach, A. Bergmann, K. Westerholt, *Thin Solid Films* **425**, 225 (2003).
2. M. Pteiffer, A. Beyer, T. Fritz, K. Leo, *Appl. Phys. Lett.* **73**, 3202 (1998).
3. J. Nelson, *Curr. Opin. Solid State Mater. Sci.* **6**, 87 (2002).
4. C.M. Joseph, C.S. Menon, *Mater. Lett.* **52**, 220 (2002).
5. D. Hohnholz, S. Steinbrecher, M. Hanack, *J. Mol. Struct.* **521**, 231 (2000).
6. K.R. Rajesh, C.S. Menon, *Semicond. Sci. Technol.* **20**, 464 (2005).
7. N. Kobayashi, *Coord. Chem. Rev.* **219**, 99 (2001).
8. R.A. Collins, A. Belgachi, *Mater. Lett.* **9**, 349 (1989).
9. S. Dogo, J.P. Germani, C. Maleysson, S. Pauly, *Thin Solid Films* **219**, 244 (1992).
10. S.R. Forrest, *Chem. Rev.* **97**, 1793 (1996).
11. L.I. Maissel, R. Glang, *Handbook of Thin Film Technology* (Mc-Graw Hill: New York: 1985).
12. T.G. Abdel-Malik, A.A. Aly, A.M. Abdeen, H.M. El-Labang, *phys. status solidi A* **76**, 651 (1983).
13. R. Rajesh, C.S. Menon, *Eur. Phys. J. B* **47**, 171 (2005).
14. S. Mammen, C.S. Menon, N.V. Unnikrishnan, *Mater. Sci. - Poland* **23**, 707 (2005).
15. K.N. Narayanan Unni, C.S. Menon, *J. Mater. Sci. Lett.* **20**, 1203 (2001).
16. S. Ambily, C.S. Menon, *Thin Solid Films* **347**, 284 (1999).
17. N.F. Mott, E.A. Davis, *Electronic Processes in Non-Crystalline Materials* (Oxford University Press: Oxford: 1979).
18. T.D. Anthopoulos, T.S. Shafai, *J. Appl. Phys.* **94**, 2426 (2003).
19. A.S. Md, S. Rahman, M.H. Islama, C.A. Hogarth, *Int. J. Electron.* **62**, 167 (1987).
20. A. Holmes-Siedle, L. Adams, *Hand Book of Radiation Effects* (Oxford University Press: Oxford, UK: 1994).