

## Comparison of Photoconduction Property of Pbpc and Cupc Thin Films

S. Sivamalar<sup>1</sup>, J. Shanthy<sup>2</sup>, Pon Kalugasalam<sup>1</sup>

<sup>1</sup>Department of Physics, Tamilnadu College of Engineering, India

<sup>2</sup>Department of Physics, Avinashilingam University, India

---

**Abstract:-** A thin film of Lead Phthalocyanine (PbPc) and Copper Phthalocyanine (CuPc) on glass substrates were prepared by Vacuum deposition method for a study of photoconduction properties. The thicknesses of the films were 150 nm, 300 nm and 450 nm on glass substrate. The higher thickness 450 nm films were annealed in air at 323 K and 373 K. The Current-Voltage characteristics were measured under dark and illumination conditions at the temperature of 30°C using a double beam spectrometer. For illuminating, light of 100 W halogen lamps was used and focused on the sample. The light intensity varied from 0 to 1 mW/cm<sup>2</sup> and applied voltage from -30 V to 30 V. The conductivity of PbPc and CuPc on the glass substrates was studied. The electrical property of PbPc and CuPc were caused by the orientation of the molecular planes in the films, which was due to their one dimensional conductivity nature of Pb ions.

**Keywords:-** Phthalocyanine, one dimensional conductivity, photoconduction and molecular orientation.

---

### I. INTRODUCTION

The search for materials suitable for low cost, versatile electronic devices has stimulated interest in organic thin film transistors[OTFTs] and sensors has led in recent years to an extensive investigation of a range of metal substituted phthalocyanines [1,2]. Application of OTFTs as chemical sensors has shown promise in the development of electronic noses and in nerve agent detection [3-5]. A key issue regarding the widespread production of OTFTs is the long term stability and device integrity in ambient operating conditions [6,7]. Among the small molecule based OTFTs, pentacene OTFTs have received significant attention regarding instability to ambient components such as oxygen and humidity [8-12]. Several mechanisms have been proposed to explain this instability in pentacene OTFTs, including water adsorption in grain boundaries [10,11] and oxygen generated impurities[13].

Phthalocyanines have potential applications in optical logic display devices, electrophotography, security printing, gas detectors [14], solar cells [15, 16], sensitizers and colour filters [17]. These materials are generally p-type semiconductors and have the advantage of being sufficiently stable towards chemicals and heat. They can be easily sublimed, resulting in high purity thin films without decomposition. The physicochemical properties can be altered by changing the metal ion. Film properties of this prototype organic semiconductor are dependent on the evaporation rate, substrate temperature and post-evaporation annealing [17, 18]. Photovoltaic devices made from organic pigments have reached power conversion efficiency of a few percent [19, 20] that is much lower than those of their inorganic combinations.

In fabricating organic devices with PbPc, it is necessary to control the orientation of the molecular plane in Pc films [21-24]. The electrical properties of Pc, Copper Pc and PbPc films were investigated by in situ field effect measurement [25]. Metal-Pc films which consist of amorphous and/or polycrystalline states have been used generally as carrier transport layers in organic devices. It is important to investigate the opto electronic properties of Pc films which depend on the orientation of the molecular plane [26-29].

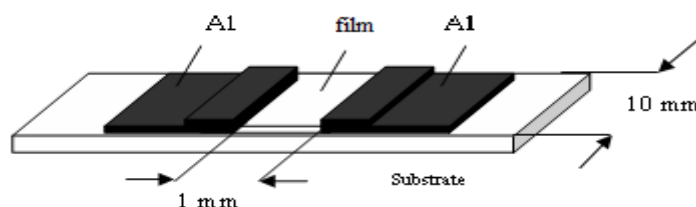
In this paper, we will report on the photoconduction properties of PbPc and CuPc thin films prepared by evaporation and deposition technique. The current-voltage characteristics under dark and illumination conditions were studied. We discuss the origin of the conductivity from the view point of the molecular orientation of the PbPc and CuPc thin films.

### II. EXPERIMENT

The powder of PbPc (80% dye, Sigma Aldrich company, Bangalore, India) is kept in a molybdenum boat (100 A current rating) heated with high current controlled by a transformer. The transformer is capable of supplying 150 amps at 20 volts which is used to provide the accessory current for heating the molybdenum source. It is used for the evaporation process. Prior to evaporation, the evaporant material is carefully degassed

at lower temperature for about 45 minutes with the closed shutter. Thin films of PbPc are deposited at room temperature on pre-cleaned glass substrates under the pressure of  $10^{-6}$  Torr using a (12 A 4D Hind Hivac, India) coating unit. The rate of evaporation is properly controlled and maintained constant during all the evaporations. Rotary drive is employed to maintain uniformity in film thickness. The thicknesses of the films are 150 nm, 300 nm and 450 nm. The thickness of the films is measured by Quartz crystal monitor. This procedure is used for preparing PbPc and CuPc thin film on pre-cleaned glass substrate. The adhesion of the films to the substrate seems to be extremely good. The samples prepared in a similar environment were used for studying their various properties.

Al-PbPc-Al sandwich structures were sequentially evaporated at a pressure of  $1.3 \times 10^3$  Pa onto the substrates at room temperature, to give an active sample area of  $1.0 \times 10^{-5}$  m<sup>2</sup>. Al electrodes with 1mm gap and 10 mm width were deposited onto PbPc and CuPc films shown in Figure 1. Al electrodes were evaporated from a tungsten filament and is deposited at a rate of 1nm/s, while the thin film was evaporated from a tantalum boat and deposited at a rate of 0.5 nm/s.



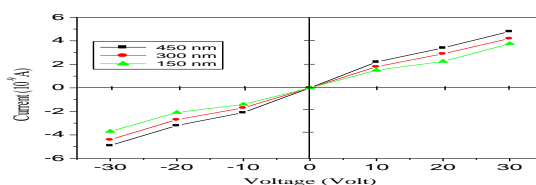
**Figure 1** Cell configuration of films with Al electrode

The absorption spectra of the PbPc films were measured at room temperature using a double-beam spectrometer. Under dark and illumination condition, the Current-Voltage characteristics (I-V curve) were measured. For illumination, 100W halogen lamp was used and focused onto the sample. The light intensity was varied from 0 to 1 mW/cm<sup>2</sup>. The applied voltage was varied from -30 to 30 V. The photocurrent spectra under the applied voltage of 30 V were measured using monochromatic light produced by the combination of a 25 cm single spectrometer and a 100 W halogen lamp with resolution of 1.0 nm in all the optical measurement.

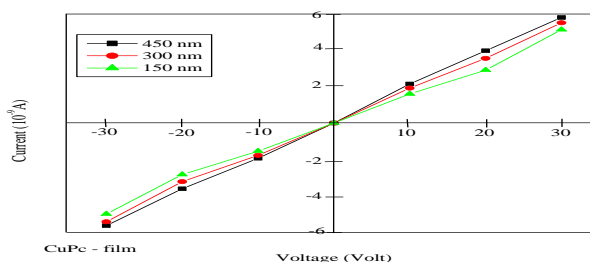
### III. RESULTS AND DISCUSSION

#### 3.1 Effect of Thickness

The electrical properties of the deposited PbPc and CuPc films of different thicknesses were investigated under both dark and illumination conditions. The applied voltage was changed from -30 to 30 V. In both forward and reverse bias region, the current is directly proportional to the applied voltage. The variation of current with voltage of PbPc and CuPc films of 150 nm, 300 nm and 450 nm thicknesses are shown in Figure 2 & 3. The spectrum reveals that the current increases with increase in the thickness of the film [30]. As the thickness is increased, the number of injected carriers also increases, so that space charge accumulates limiting the current.



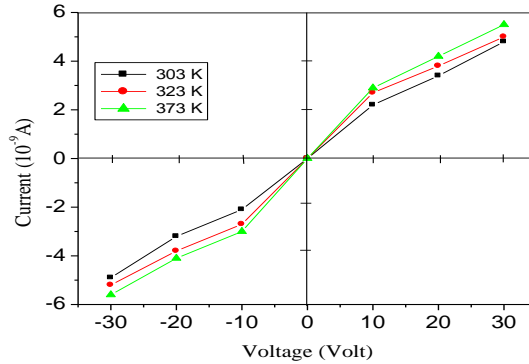
**Figure 2** Photocurrent for PbPc film on glass substrate with intensity of 1 mW/cm<sup>2</sup> for various thicknesses



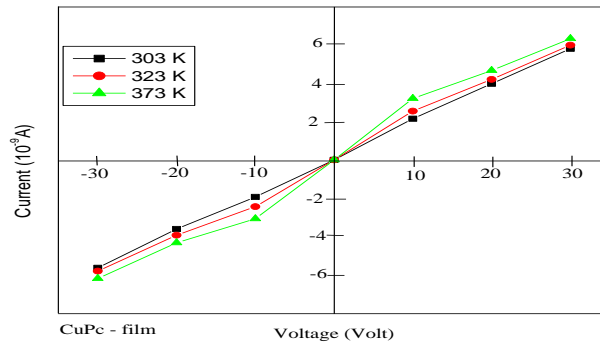
**Figure 3** Photocurrent for CuPc film on glass substrate with intensity of 1 mW/cm<sup>2</sup> for various thicknesses

### 3.2 Effect of Temperature

The electrical properties of the deposited PbPc and CuPc films of 303 K, 323 K and 373 K annealed temperature of thickness 450 nm were investigated under both dark and illumination conditions. The applied voltage was changed from -30 to 30 V. In both forward and reverse bias region, the current is directly proportional to the applied voltage. The variation of current with voltage of PbPc and CuPc films of 303 K, 323 K and 373 K annealed temperature of thickness 450 nm are shown in Figure 4 and 5. The spectrum reveals that the current increases with increase in the annealing temperature of the film. As the temperature is increased, the number of injected carriers also increases, so that space charge accumulates limiting the current.



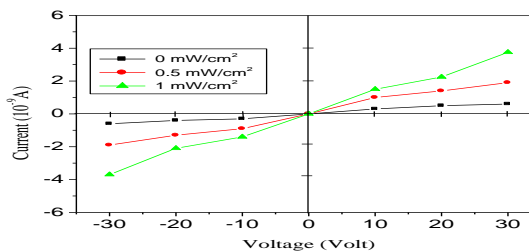
**Figure 4** Photocurrent for PbPc film on glass substrate with intensity of  $1 \text{ mW/cm}^2$  for various annealed temperature of 450 nm thickness



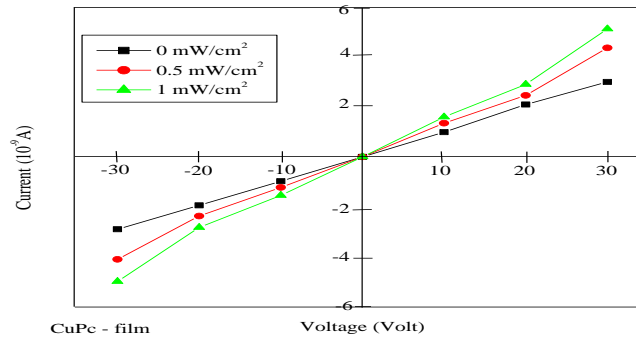
**Figure 5** Photocurrent for CuPc film on glass substrate with intensity of  $1 \text{ mW/cm}^2$  for various annealed temperature of 450 nm thickness

### 3.2 Effect of Intensity

The electrical properties of the deposited PbPc and CuPc film of thickness 150 nm was investigated under variation of light intensity. The applied voltage was changed from -30 to 30 V. In both forward and reverse bias region, the current is directly proportional to the applied voltage. The variation of current with voltage of PbPc and CuPc films of dark,  $0.5 \text{ mW/cm}^2$  and  $1 \text{ mW/cm}^2$  light intensities were shown in Figure 6 and 7. The spectrum reveals that the current increases with increase in the annealing temperature of the film. As the intensity of light was increased, the number of injected carriers also increases, so that space charge accumulates limiting the current.



**Figure 6** Photocurrent for PbPc film of 150 nm on glass substrate with intensity of a)  $1 \text{ mW/cm}^2$ , b)  $0.5 \text{ mW/cm}^2$  and c)  $0.0 \text{ mW/cm}^2$



**Figure 7** Photocurrent for CuPc film of 150 nm on glass substrate with intensity of a) 1 mW/cm<sup>2</sup>, b) 0.5 mW/cm<sup>2</sup> and c) 0.0 mW/cm<sup>2</sup>

In semiconductor, both electrons and holes are charge carriers and they will take part in conduction. In general, the conductivity of a semiconductor depends on the carrier density and the mobility. Conductivity  $\sigma$ , under the illumination condition is expressed by the sum of the dark conductivity  $\sigma_d$  and the photoconductivity  $\sigma_p$ , as [31].

$$\begin{aligned}\sigma &= \sigma_d + \sigma_p \\ &= n\mu + n^*\mu \\ &= (n + n^*)\mu\end{aligned}$$

where

$$n^* = \eta\tau\phi = \eta\tau\alpha I$$

$n$  and  $n^*$  are the intrinsic and photo generated carrier densities,

$\mu$  – the mobility

$\eta$  – the generation efficiency of the photo carrier

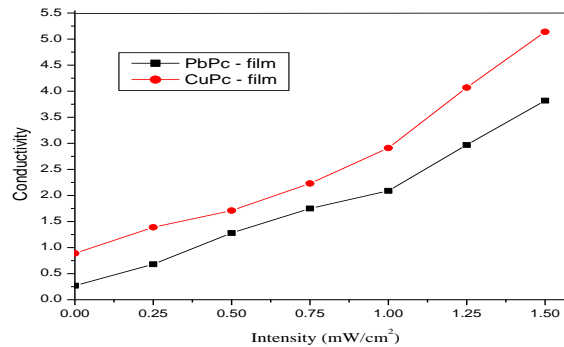
$\tau$  – the free lifetime of the photocarrier

$\phi$  – the photon flux density of the film

$\alpha$  – the optical density of the film

$I$  – the light intensity.

The above equation indicates that the conductivity is linearly proportional to the light intensity. As the light intensity is increased, the conductivities of the films increase linearly as shown in Figure 8. This result is satisfactorily explained by the above equation.



**Figure 8** Conductivity of films with light intensity

In dark conductivity, the photoconductivity is affected by the generation efficiency of the photo carrier and the carrier lifetime. The intrinsic carrier densities of both films are same. We consider that the large difference in the mobility originates from the one dimensional conduction associated with the orientation of the molecular plane. The dynamical properties of the excitons in the VOPc and PbPc film with a shuttle-cock shaped molecular structure have been investigated using a pump-probe transient absorption method [32]. The annihilation of the excitons due to collisions under an intense excitation is explained by a model of one-dimensional diffusion limited annihilation. The one-dimensional diffusion nature enables us to analogize that photo carriers can easily conduct perpendicular to the molecular plane via Pb ions [33, 34].

#### IV. CONCLUSION

The electrical properties of PbPc and CuPc thin film sandwich structures having Al-Al electrodes have been investigated, the samples showed field lowering behaviour for both polarities. In Al/PbPc/Al sample, forward bias is defined as the situation when the top electrode is biased positively. The orientation of molecular planes in the PbPc films on the glass substrates surface. The current-voltage characteristics are measured under dark and illumination condition. The conductivity of CuPc on the glass substrate was larger than PbPc on glass substrate. The conducting property of PbPc and CuPc was caused by the orientation of the molecular planes in the film, which is due to their one dimensional conductivity nature of Pb and Cu ions. The annihilation of the excitons due to collisions under an intense excitation is explained by a model of one-dimensional diffusion limited annihilation.

#### REFERENCES

- [1]. C. D. Dimitrakopoulos and P. R. L. Malenfant, *Adv. Mater.* (Weinheim, Ger.) 14, 99(2002).
- [2]. G. Horowitz, *Adv. Mater.* (Weinheim, Ger.) 10, 365 (1998).
- [3]. R. D. Yang, J. Park, C. N. Colesniuc, I. K. Schuller, W. C. Trogler, and A.C. Kummel, "Ultralow drift in organic thin-film transistor chemical sensors by pulsed gating" *J. Appl. Phys.* 102, 034515, (2007).
- [4]. F. Liao, C. Chen, and V. Subramanian, "Organic TFTs as gas sensors for electronic nose applications", *Sensors and Actuators B-Chemical*. Vol. 107, pp. 849-855, (2005).
- [5]. J. B. Chang, V. Liu, V. Subramanian, K. Sivula, C. Luscombe, A. Murphy, J. Liu, and J. M. J. Frechet. "Printable polythiophene gas sensor array for low-cost electronic noses" *Journal of Applied Physics*, 100(1):014506, (2006).
- [6]. R. Ben Chaabane, A. Ltaief, L. Kaabi, H. Ben Ouada, N. Jaffrezic-"Renault, and J. Davenas, Influence of ambient atmosphere on the electrical properties of organic thin film transistors" *Mater. Sci. Eng., C* 26, 514, (2006).
- [7]. G. Guillaud, J. Simon, and J. P. Germain, *Metallophthalocyanines: "Gas sensors, resistors and field effect transistors"* *Coord. Chem. Rev.* 178-180, 1433 -1484, (1998).
- [8]. S. Cipolloni, L. Mariucci, A. Valletta, D. Simeone, F. De Angelis and G. Fortunato "Aging effects in high performance Pentacene Thin Film Transistors." *Thin Solid Films*, vol. 515 , pp. 7546-7550 (2007).
- [9]. D. Knipp, T. Muck, A. Benor, and V. Wagner, "Environmental stability and electronic transport of pentacene thin film transistors" *J. Non-Cryst. Solids* 352, 1774 (2006).
- [10]. Y. Qiu, Y. Hu, G. Dong, L. Wang, J. Xie, and Y. Ma, "H<sub>2</sub>O effect on the stability of organic thin-film field-effect transistors" *Appl. Phys. Lett.* 83,1644 (2003).
- [11]. Z.-T. Zhu, J. T. Mason, R. Dieckmann, and G. G. Malliaras, "Humidity sensors based on pentacene thin-film transistors" *Appl. Phys. Lett.* **81**, 4643 (2002).
- [12]. C. R. Kagan, A. Afzali, and T. O. Graham, "Operational and environmental stability of pentacene thin-film transistors" *Appl. Phys. Lett.* 86, 193505 (2005).
- [13]. Y. Natsume, "Characterization of solution-processed pentacene thin film transistors" *Phys. Status Solidi A* 205, 2958-2965 (2008).
- [14]. Mrwa A., Friedrich M., Hofmann A. and Zahn D.R.T. (1995) 'Response of PbPc to high NO<sub>2</sub> concentration', *Sensors and Actuators B*, Vol. 24-25, pp. 596-599, (1995).
- [15]. M. Pope, C.E. Swenberg, *Electronic Process in Organic Crystals*, Clarendon Press, Oxford, (1992).
- [16]. Tang C.W. and Van Slyke S.A. 'Organic electroluminescent diodes', *Appl. Phys. Lett.*, Vol. 51, p. 913 (1987).
- [17]. Collin R.A. and Belgachi A. 'Electrical and optical studies on thin films of indium phthalocyanine chloride', *Mater. Lett.*, Vol. 9, pp. 340-349, (1989).
- [18]. Machida Y., Saito Y., Taomoto A., Nichogi K., Waragi K. and Asakawa S. 'Electrical Switching in Evaporated PbPc Films', *Jpn. J. Appl. Phys.* Vol. 28, pp 297-298, (1989).
- [19]. B.A. Gregg, 'Excitonic Solar Cells' *J. Phys. Chem. B* 107, 4688 (2003).
- [20]. Peumans P. and Forrest S.R. 'Very-high-efficiency double-heterostructure copper phthalocyanine/C<sub>60</sub> photovoltaic cells', *Appl. Phys. Lett.*, Vol. 79, p. 126(2001).
- [21]. Hoshi H., Fang S. and Maruyama Y. 'X-ray emission spectra and structural models of BCN materials', *J.Appl.Phys.*, Vol. 73, p. 311, (1993).
- [22]. Miyamoto A., Nichogi K., Taomoto A., Nambu T. and Murakami M. 'Structural control of evaporated PbPc films', *Thin Solid Films*, Vol. 256, pp 64-67, (1995).
- [23]. Yanagi H., Mikami T., Tada H., Terui T. and Mashiko S. 'Site-specific physisorption and chemical reaction of subphthalocyanine molecules on silicon (111)-(7×7)', *J.Appl. Phys*, Vol. 81, p. 7306, (1997).

- [24]. Ottaviano L., Lozzi L., Phani A.R., Ciattoni A., Santucci S. and Di Nardo S. 'Thermally induced phase transition in crystalline PbPc films investigated by XRD and atomic force microscopy', *Appl.Surf. Sci.*, Vol. 136, pp. 81-86, (1998).
- [25]. Kazuhiro kudo, Tsutomu Sumimoto, Kouji Hiraga, Shigekazu Kuniyoshi and Kuniaki Tanaka 'Evaluation of electrical properties of evaporated thin films of metal free copper and PbPc by In-Situ field effect measurements', *J. Appl. Phys., Jpn.*, Vol. 36, pp. 6994- 6998, (1997).
- [26]. Yasunaga H., Kojima K., Yohda A. and Takeya K. 'Effect of Oxygen on Electrical Properties of Lead Phthalocyanine' *J.Phys.Soc., Jpn.*, Vol. 37, p. 1024, (1974).
- [27]. Colins R.A., Krier A. and Abbas A.K. 'Optical properties of PbPc(PbPc)thin films', *Thin Solid Films*, Vol. 229, pp. 113-118, (1993).
- [28]. Campbell D. and Collins R.A. 'Spectral response of monoclinic and triclinic PbPc to nitrogen dioxide' *Thin Solid Films*, Vol. 261, pp. 311-316, (1995).
- [29]. Yanagi H., Imamuma M. and Ashida M. 'Optoelectronic Properties of Orientation-controlled Lead' *J. Appl. Phys.*, Vol.75, p. 2061, (1997).
- [30]. Wright J.D. 'A typical response of a CuPc', *Prog.Surf.Sci.*, Vol. 31, p. 1, (1989).
- [31]. R.H.Bube, *Photoconductivity of solids*, John Wiley & sons, Newyork, 1960.
- [32]. Gulbinas V., Chachisvilis M. Valkunas L. and Sundstrom V. 'Excited state dynamics of phthalocyanine films', *J. Ame. Chem. Soc.*, pp. 10-16, (1995).
- [33]. Ukei K., Takamoto K. and Kanda E. 'One-dimensional quantum transport in Lead Phthalocyanine' *Phys. Lett. A*, Vol. 45, p. 345, (1973).
- [34]. Ukei K. 'Electroconductive properties of a one-dimensional. conductor PbPc', *J. Phys. Soc. Jpn.*, Vol. 40, p. 140, (1976).