OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 1, No. 7, July 2007, p. 339 - 341

Effect of annealing on the electrical properties of gallium phthalocyanine chloride thin films

SUSAN MATHEW*, C. S. MENON, C. SUDARSANAKUMAR
School of Pure and Applied Physics, Mahatma Gandhi University, Kottayam 686 560, Kerala, India

Vacuum evaporated gallium phthalocyanine chloride thin films were prepared at room temperature. Post evaporation annealing was done in air at temperatures 348 K, 398 K, 448 K and 498 K. The electrical conductivities of these films were studied and thermal activation energies were calculated from the Arrhenius plots. A decrease in activation energy was observed with increasing annealing temperature.

(Received November 1, 2006; accepted July 10, 2007 in revised form July 9, 2007)

Keywords: Thin films, Annealing, Electrical properties, Activation energy

1. Introduction

Phthalocyanines are materials of special importance in the field of organic dyes and pigments. They exhibit high chemical and thermal stability and can easily be sublimed without decomposition to form high purity thin films by thermal evaporation technique. The electrical properties of phthalocyanine thin films have been studied extensively because of their applications in various electro-optical devices such as light emitting devices, photovoltaic cells, liquid crystal displays, optoelectronic devices and gas sensors [1-5]. They have a two dimensional 18 π electron conjugated system, in which more than 70 different metal and non-metal ions can be incorporated. A number of modifications can be made in the macrocycle either by introduction of different central ions or by substitution of functional groups at the peripheral sites of the ring. The halogenated phthalocyanines exhibit remarkable morphological and thermal stability over a larger temperature range compared to unhalogenated phthalocyanines [6]. The electrical properties of phthalocyanine thin films are dependent on various parameters such as evaporation rate, substrate temperature and post deposition annealing [7,8,9]. They exhibit p-type semiconductivity at all temperatures [10]. In the present study we report the effect of annealing on electrical properties of gallium phthalocyanine chloride thin films.

2. Experimental details

Gallium phthalocyanine chloride powder procured from Aldrich, USA was evaporated in vacuum using a Hind Hivac 12A4 coating unit onto well cleaned microglass slides held at a pressure of 10^{-5} Torr. The evaporation was carried out by resistive heating of the powder from a molybdenum boat and the evaporation rate was kept constant. Thickness of the film was determined by Tolansky's multiple beam interference technique [11].

GaPcCl thin films were annealed in air for 1 hour at 348 K, 398 K, 448 K and 498 K in a furnace whose temperature could be controlled by a controller cum recorder. Evaporated silver was used as the contact electrode for electrical conductivity studies. Thin copper strands were fixed by silver paste and the film was placed onto the hollow copper block of the conductivity cell that was heated. The electrical conductivity studies were done in the temperature range 300-525 K. The temperature was monitored by a Chromel-Alumel thermocouple. The resistance was noted at regular intervals of 5 K using a programmable Keithley electrometer (Model No 617). To avoid any possible contamination, measurements were performed in vacuum at 10^{-3} Torr.

3. Results and discussion

The electrical conductivity σ can be expressed as

$$\sigma = \sigma_0 \exp(-E/k_B T) \qquad (1)$$

where σ is the conductivity at temperature T, E is the thermal activation energy, k_B is the Boltzmann constant and σo is the pre-exponential factor. Graphs of ln σ Vs 1000/T for films annealed in air at different temperatures were plotted and shown in Figs. 1 and 2. The slope changes at different regions of temperature indicates a variation of activation energy due to the thermal excitation of impurities situated at different levels in the band gap and consequent jumping of electrons either to the conduction band or to the acceptor level. From the slopes of these graphs activation energies were evaluated and collected in Table 1. The activation energy was determined within an accuracy of ± 0.01 eV in all measurements. As shown by Belgachi and Collins [12], activation energy obtained may be interpreted as the difference between dominant energy levels. There are three linear regions for each graph, which correspond to three activation energies E_1, E_2 and E_3. The activation energies E_1, E_2 and E_3 were obtained at T > 430 K, between 390 to 430 K and between 360 to 390 K respectively. 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 the complex [13]. Three activation energies for thin films of NiPc, $Eu(Pc)_2$, H_2Pc and InPcCl have already been reported [14-17]. It is seen that the activation energy decreases as the annealing temperature increases.

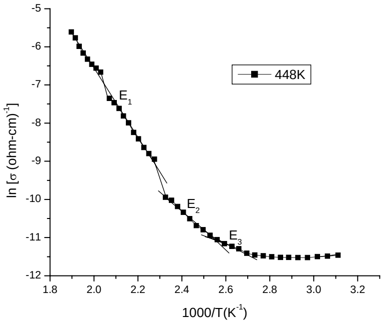

Fig. 1. Plot of lnσ vs 1000/T for GaPcCl thin film of thickness 483nm annealed in air at 448 K.

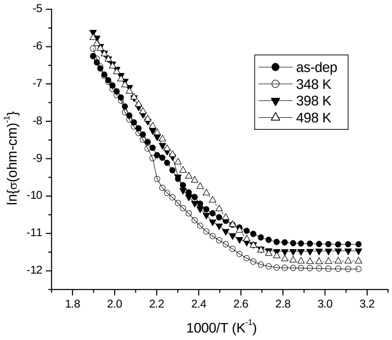

Fig. 2. Plot of lnσ vs 1000/T for GaPcCl thin films annealed in air at different temperatures.

Table 1. Activation Energy of Gallium phthalocyanine chloride thin films (of thickness 483 nm) annealed in air at different temperatures.

Annealing temperature K	Activation energy [eV]		
	E_1	E_2	E_3
As- deposited (Room temp.)	0.76	0.65	0.34
348	0.85	0.48	0.30
398	0.80	0.47	0.21
448	0.78	0.44	0.18
498	0.74	0.40	0.14

As suggested by Rahman et al [18], freshly prepared samples may contain different kinds of defects such as vacancies, grain boundaries and dislocations which can be partially annealed out by heat treatment resulting in a decrease in the density of defects. Ordinary air contains moisture as well as other contaminants that may form acceptor or donor levels in the film, contributing to the extrinsic carrier conductivity. The variation in the activation energies of the as-deposited and annealed thin films can be attributed to the change in the distribution of trap levels during annealing.

X-ray diffractograms of the films annealed at different temperatures were also taken to show that no degradation had taken place during annealing. The XRD spectra for as-deposited and air annealed GaPcCl films are shown in Fig. 3. For all the films the most intense peak was found to be at $2\theta \approx 27.307^0$. The intensity of this peak was found to increase with the annealing temperature. The increase in the main peak intensity with annealing temperature indicates a slight increase in the crystalline nature of the films. This can be attributed to better film ordering due to annealing.

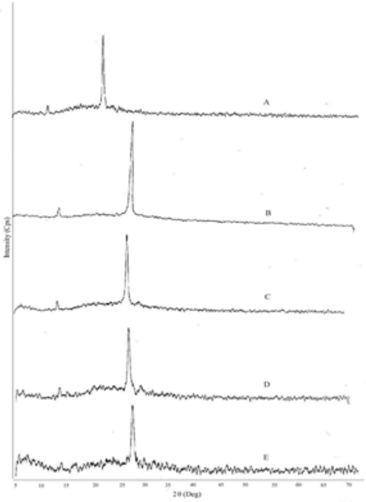

Fig. 3. XRD of GaPcCl thin films annealed in air at various temperatures: (A) 498 K (B) 448 K (C) 398 K (D) 348 K (E) as- deposited.

4. Conclusion

Gallium phthalocyanine chloride thin films were prepared by vacuum sublimation. The activation energies of the as-deposited and annealed samples were determined.

In the high temperature range intrinsic conductivity by holes are found to contribute to the conduction process whereas in the low temperature range impurities are found to play an active role. It is found that activation energy decreases with increase in annealing temperature. The variation in the intrinsic and extrinsic activation energy during annealing can be attributed to the change in the position of the Fermi level and the distribution of trap levels.

Acknowledgement

One of the authors (S.M.) would like to thank the University Grants Commission of India for providing a teacher fellowship under FIP scheme.

References

[1] K. Abe, H. Sato, T. Kimura, Y. Ohkatsu, T. Kusano, Macromol. Chem. **190**, 2693 (1989).

[2] C. W. Tong, Appl. Physics. Lett. **48**, 183 (1986).
[3] M. Brinkmann, J. C. Wittmann, C. Chaumont, J. Andre, Thin Solid Films. **29**, 192 (1997).
[4] C. L. Honeybourne, R. J. Ewin, J. Phys. Chem. Solids. **44**, 215 (1983).
[5] A. K. Ghosh, D. L. Morel, T. Fene, R. F. Shaw, C. A. Rowe Jr. J. Appl. Phy. **45**, 230 (1974).
[6] A. Napier, R. A. Collins, Phys. Stat. Sol (A). **144**, 91 (1994).
[7] R. A. Collins, A. Belghachi, Mater. Lett. **8,** 343 (1989).
[8] Y. Machida, Y. Saito, A. Taomoto, Jpn. J. Appl. Phys. **28,** 297 (1989).
[9] S. Ambily, C. S. Menon, Thin Solid Films **347**, 284 (1999).
[10] Y. Sadaoka, T. A. Jones, W. Gopel, J. Mater. Sci. Lett. **8**, 1095 (1989).
[11] L. I. Maissel, R. Glang, Handbook of Thin Film Technology, Mc Graw-Hill, New York (1983).
[12] A. Belghachi, R. A. Collins, J. Physics D: Appl. Phys **21**, 1647 (1988).
[13] S. Ambily, C. S. Menon, Thin Solid Films **347**, 284 (1999).
[14] K. N. Narayanan Unni, C. S.Menon, Mater. Let. **45**, 326 (2001).
[15] K. N. Narayanan Unni, C. S. Menon J. Mater. Sci. Let. **20**, 1203 (2001).
[16] K. N. Narayanan Unni, C. S. Menon, J. Mater. Sci. Let. **20**, 1207 (2001).
[17] S. Mammen, C. S. Menon, N. V. Unnikrishnan Mater. Sci. Poland **23**, 707 (2005).
[18] A. S. Md. Rahman, M. Islam, C. A. Hogarth, Int. J. Electron. **62**, 167 (1987).

---

[*] Corresponding author: soozan _mathew@yahoo.com