



## EFFECT OF SUBSTRATE TEMPERATURE AND ANNEALING ON THE ELECTRICAL PROPERTIES OF LEAD PHTHALOCYANINE THIN FILMS

T. G. GOPINATHAN and C. S. MENON

School of Pure and Applied Physics, Mahatma Gandhi University,  
KOTTAYAM – 686560 (Kerala) INDIA

### ABSTRACT

Lead phthalocyanine (PbPc) thin films are prepared at different substrate temperatures on microglass slides of size 75 x 25 x 1.3 mm by thermal evaporation technique. at a base pressure of  $10^{-5}$  m.bar. Films of equal thickness coated at room temperature are annealed in air and in vacuum at different temperatures for one hour. The electrical conductivity observations are made in the temperature range 300 to 580 K. The thermal activation energies are calculated from the Arrhenius plots. It is observed that the thermal activation energy in the intrinsic region decreases with increase in substrate temperature and increases with increase in annealing temperature.

**Key words:** Lead phthalocyanine, Thin films, Thermal evaporation.

### INTRODUCTION

Phthalocyanines form a class of organic semiconductors. These are materials with a wide range of applications due to their stability against thermal and chemical decomposition and intense optical absorption in the visible region of the spectrum. They are used in gas sensors<sup>1</sup>, in electro topography and solar cells<sup>2,3</sup>, as dyes in textile and paint industries<sup>4</sup>, and in opto–electronic devices<sup>5</sup>. They are also used in electro–chromic display devices, photodynamic reagents and electro–catalysts for fuel cells<sup>6,7</sup>. Measurements have shown that freshly evaporated PbPc films absorb oxygen at room temperature over a period of several days<sup>8</sup> and distinct differences are observed in fresh, air exposed and subsequently annealed PbPc films<sup>9</sup>. The electrical behaviour of PbPc thin films in the triclinic phase, when exposed to both oxygen and dry air for various periods, are reported<sup>10</sup>. PbPc thin films can be effectively used to sense toxic NO<sub>2</sub> gas<sup>11</sup>.

Conduction in PbPc thin films with aluminium electrodes are already reported<sup>12</sup>. It has become apparent that the progress in the development of active materials for molecular

electronics, based on PbPc thin films require a more comprehensive knowledge of its material properties. In this paper, the electrical properties of PbPc thin films of thickness 2400 Å coated at different substrate temperatures and films subjected to post-deposition annealing in air and vacuum are studied. The thermal activation energies are calculated in each case.

## EXPERIMENTAL

PbPc in the powder form (99.99% pure) obtained from Aldrich is used as the source material. The samples are prepared in a "Hindi Hi Vac" vacuum coating unit (Model No. 12A4). Thermal evaporation technique is used for film preparation<sup>13</sup>. The films are coated on thoroughly cleaned glass substrates kept at different temperatures, at a base pressure of  $10^{-5}$  m.bar. The thickness of the films are controlled by a single crystal thickness monitor and are cross-checked by Tolansky's multiple beam interferometry method<sup>14</sup>. Samples are annealed in air for one hour in a specially designed furnace provided with a digital temperature controller cum recorder. Films of the same thickness are annealed in vacuum also. The electrical conductivity measurements of these samples are conducted by keeping them in a conductivity cell at a pressure of  $10^{-3}$  m.bar. The resistances of the films are measured using a Keithley programmable electrometer, Model No. 617 between an approximate temperature range of 300 to 580 K. Ohmic contacts are made with silver electrodes and silver paste.

## RESULTS AND DISCUSSION

The electrical conductivity is given by  $\sigma = L/Rbt$  where L is the length, R is the resistance, b is the breadth and t is the thickness of the film. The temperature dependence of conductivity is given by Arrhenius equation  $\sigma = \sigma_0 \exp(-E_T/kT)$  where  $\sigma_0$  is the pre-exponential factor,  $E_T$  is the thermal activation energy, k is Boltzmann constant and T is the absolute temperature.

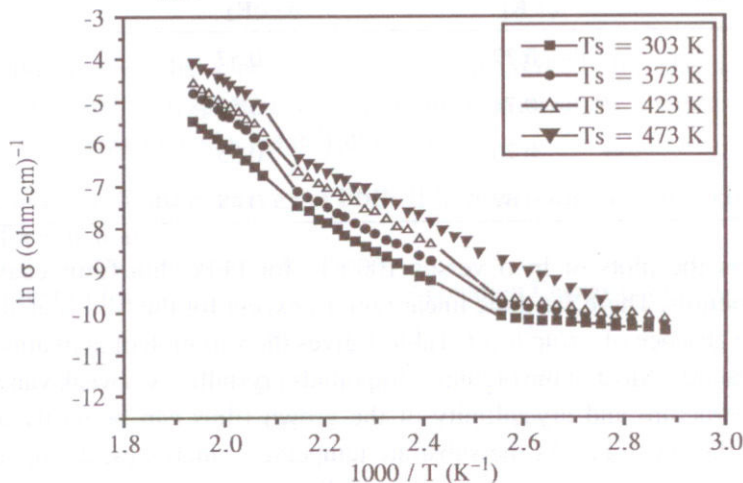


Fig. 1. Plots of  $\ln \sigma$  versus  $1000/T$  for PbPc thin films coated at different substrate temperatures

Plots of  $\ln \sigma$  versus  $1000/T$  show three linear portions and from their slopes, the thermal activation energies are calculated. The higher temperature region is called the intrinsic region with activation energies  $E_1$  and the two low temperature regions are known as the extrinsic region with activation energies  $E_2$  and  $E_3$ , respectively.

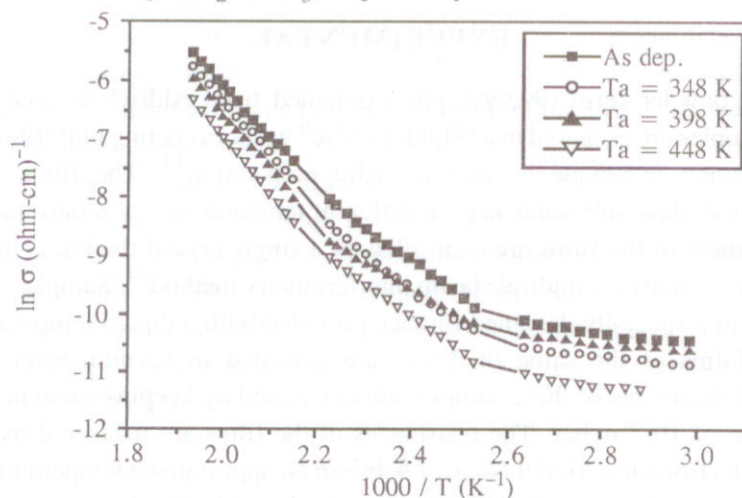


Fig. 2. Plots of  $\ln \sigma$  versus  $1000/T$  PbPc thin films annealed in air different temperatures for one hour

Table 1. Variation of activation energy of PbPc thin films coated at different substrate temperatures

Substrate Temperature (K)	Activation Energy (eV)		
	$E_1$	$E_2$	$E_3$
303	0.77	0.57	0.08
373	0.74	0.53	0.11
423	0.70	0.55	0.13
473	0.67	0.48	—

Fig. 1. shows the plots of  $\ln \sigma$  versus  $1000/T$  for PbPc thin films coated at different substrate temperatures. There are three linear regions except for the film coated at 473 K. This can be due to the absence of a trap level. Table 1 gives the variation of activation energies with substrate temperatures. Most of the organic compounds crystallize via weak van der Waals force and hence, the structure and crystallinity of the grown films can be easily affected by the interaction with the substrate. As the substrate temperature increases, the increase in surface energy causes an increase in grain size and crystallinity resulting in a lowering of activation energy.  $E_2$  and  $E_3$  change in a random manner, since these are due to impurity scattering.

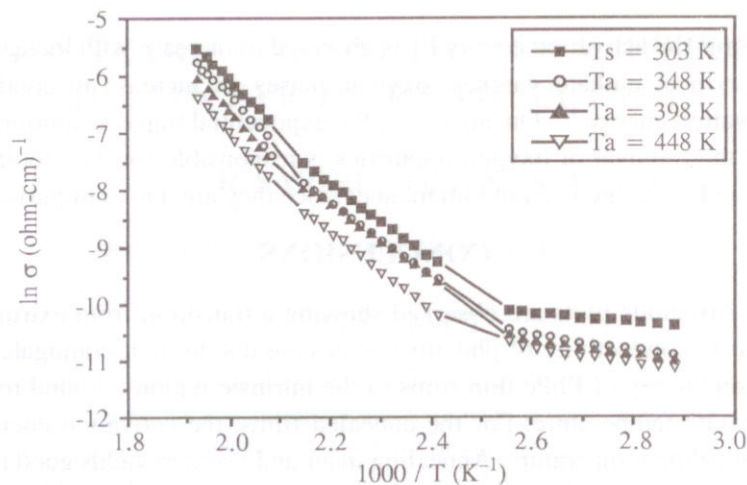


Fig. 3. Plots of  $\ln \sigma$  versus  $1000/T$  for PbPc thin films annealed in vacuum at different temperatures for one hour

Table 2. Variation of activation energy of PbPc thin films annealed in air at different temperatures for one hour

Annealing Temperature (K)	Activation Energy (eV)		
	E <sub>1</sub>	E <sub>2</sub>	E <sub>3</sub>
As deposited	0.77	0.57	0.08
348	0.79	0.51	0.07
398	0.82	0.40	0.06
448	0.86	0.49	0.09

Figure 2 and 3 give the plots of  $\ln \sigma$  versus  $1000/T$  for the air-annealed and vacuum-annealed samples, respectively. Variations in activation energies with annealing temperature in these cases are collected in Table 2 and 3.

Table 3. Variation of activation energy of PbPc thin films annealed in vacuum at different temperatures for one hour

Annealing Temperature (K)	Activation Energy (eV)		
	E <sub>1</sub>	E <sub>2</sub>	E <sub>3</sub>
As deposited	0.77	0.57	0.08
348	0.81	0.54	0.12
398	0.85	0.55	0.11
448	0.87	0.60	0.12

For these films, the activation energy  $E_1$  is observed to increase with increase in annealing temperature. For most phthalocyanines, oxygen causes an increase in conductivity and a decrease in activation energy<sup>15</sup>. On annealing, the exponential trap distribution is established, confirming that the removal of oxygen impurities is responsible for the modified behaviour. Here again  $E_2$  and  $E_3$  change in a random manner since they are due to impurity scattering.

### CONCLUSIONS

Three zone Arrhenius plots are observed showing a transition from extrinsic to intrinsic behaviour. Intrinsic conductivity of phthalocyanines are due to their conjugate structure. The thermal activation energy of PbPc thin films in the intrinsic region is found to decrease with increase in substrate temperature. For the annealed films, the activation energy is found to increase with annealing temperature. Annealing in air and vacuum yields good results.

### REFERENCES

1. A. Wilson and R. S. Collins, *Sens. Actuators*, **12**, 389 (1987).
2. K. Nebesny and G. E. Collins. P. A. Lee, *Chem. Mater.* **3**, 829 (1991).
3. C. W. Taug, *Appl. Phys. Lett.*, **48**, 183 (1986).
4. E. Orti, *S. Chem. Phys.*, **92**, 1228 (1990).
5. C. L. Honeybonme and R. J. Ewen, *J. Phys. Chem. Solids.*, **44**, 831 (1983).
6. F. M. Moser and A. L. Thomas, "The Phthalocyanines" Vol 1, CRC, Press Inc., Florida, USA.
7. C. C. Leznoff and A. B. P. Iever, "Phthalocyanines; Properties and Applications", VCH Publishers Inc., New York, (1993).
8. A. Belghachi and R. S. Collins, *J. Phys. D*, **23**, 223 (1990).
9. A. Ahmad and R. A. Collins, *J. Phys. D*, **24**, 1894 (1991).
10. A. Ahmad and R. A. Collins, *Thin Solid Films*, **217**, 25 (1992).
11. W. Jakubik, M. Urbanczyk and A. Opilski, *Ultrasonics*, **39**, 227 (2001).
12. R. D. Gould and T. S. Shafai, *Thin Solid Films*, **373**, 89 (2000).
13. Francis Garnier, *Chem. Physics*, **227**, 253 (1998).
14. K. L. Chopra, "Thin Film Phenomena", Mc Graw Hill, New York, (1985).
15. A. Ahmad and R. A. Collins, *Thin Solid Films*, **217**, 75 (1992).

Accepted : 23.1.2005