

# Effect of Thickness on Activation Energy of Aluminium Phthalocyanine Hydroxide Thin Films

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**Abstract**-Thin films of aluminium phthalocyanine hydroxide are prepared onto glass substrates in high vacuum at room temperature by thermal evaporation technique. Electrical measurements are done using a programmable Keithley electrometer. Thermal activation energies are determined from the Arrhenius plot. There are different activation energies such as  $E_1$ ,  $E_2$  and  $E_3$  that can be differentiated at different temperature regions. It is found that the thermal activation energy  $E_1$  corresponding to the higher temperature region decreases with increase in thickness. X-ray diffraction pattern is used to find the nano-crystalline grain size using Scherrer formula. Scanning electron microscope (SEM) image is taken to study the surface morphology of the film.

**Keywords** – Phthalocyanine, Thin film, Activation Energy, Electrical Conductivity

## I. INTRODUCTION

Metallo-phthalocyanines are a class of organic compounds with particular electronic and structural characteristics which show semiconducting and nonlinear optical properties. These materials are generally p-type semiconductors [1] and have high thermal stability, strong colours and negligible vapour pressure at room temperature. The study of the electrical conductivity and the nonlinear optical properties of phthalocyanine thin films is of great interest for use in molecular electronics, non-linear optics, electrochromic devices, optical data storage, sensors, electro catalytic systems and static induction transistors[2-6].The major advantage of using organic semiconducting materials is their ability to modify their molecular structure, and hence ,their electrical and optical properties. Film properties of these organic semiconductors are dependent on the evaporation rate, substrate temperature and post deposition annealing [7,8]. Among the various metallophthalocyanine derivatives, aluminum phthalocyanine hydroxide (AlPcOH) is of great interest for its use as a toner in an electro-photographic developer. In this paper electrical conductivity, thermal activation energy and their dependence on temperature and thickness are investigated for aluminium phthalocyanine hydroxide thin films. The molecular structure of aluminium phthalocyanine hydroxide is shown in Figure 1.

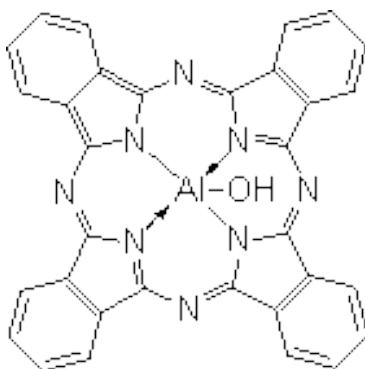


Figure 1 The molecular structure of aluminium phthalocyanine hydroxide

## II. EXPERIMENTAL DETAILS

Aluminium phthalocyanine hydroxide powder procured from Aldrich, USA is sublimed in vacuum using a Hind Hivac 12A4 coating unit onto well cleaned microglass slides held at a pressure of  $10^{-5}$  Torr. The evaporation is carried out by resistive heating of the powder from a molybdenum boat and the evaporation rate is kept constant as 10-12 nm/min. Thickness of the film is determined by Tolansky's multiple beam interference technique [9].

Aluminum phthalocyanine hydroxide thin films are annealed in air for 1 hour at 348 K. For electrical conductivity studies evaporated silver is used as the contact electrode. Thin copper strands are fixed by silver paste and the film is placed onto a hollow copper block in the conductivity cell. The temperature of the sample is measured using Chromel- Alumel thermocouple. The electrical conductivity studies are done in the temperature range 300-525K. The resistance is noted at regular intervals of 5K using a programmable Keithley electrometer (Model No 617). To avoid any possible contamination, measurements are performed in vacuum at  $10^{-3}$  Torr.

## III. RESULTS AND DISCUSSION

Semiconducting properties of phthalocyanines were first observed by Eley [10]. The electrical conductivity  $\sigma$  of a film of resistance R, length l, breadth b and thickness t is given by

$$\sigma = l/Rbt \quad (1)$$

The electrical conductivity can also be expressed as

$$\sigma = \sigma_0 \exp(-E/k_B T) \quad (2)$$

where  $\sigma$  is the conductivity at temperature T, E is the thermal activation energy,  $k_B$  is the Boltzmann constant and  $\sigma_0$  is the pre-exponential factor. Graphs of  $\ln \sigma$  vs  $1000/T$  for films of different thicknesses are plotted (Figure 1). From the slopes of these graphs activation energies are evaluated.

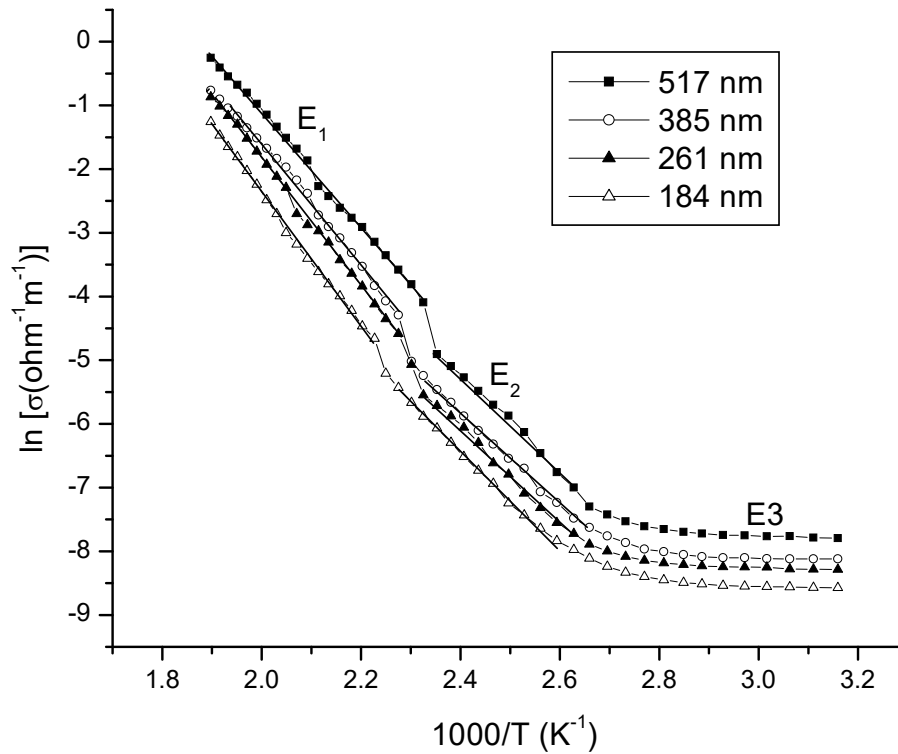


Figure 2 Plot of  $\ln \sigma$  versus  $1000/T$  for AlPcOH thin films of different thicknesses

The activation energy is determined within an accuracy of  $\pm 0.01$  eV in all measurements. As shown by Belgachi and Collins [11], activation energy obtained may be interpreted as the difference between dominant energy levels. In a film, due to the presence of various types of defects such as vacancies, grain boundaries and dislocations new energy states are created in the band gap region. These states will give rise to different activation energies such as  $E_1$ ,  $E_2$  and  $E_3$  which can be differentiated at different temperature regions. There are three linear regions for each graph, which correspond to three activation energies  $E_1$ ,  $E_2$ , and  $E_3$ . The activation energy  $E_1$  corresponding to the higher temperature region is associated with the resonant energy involved in a short lived excited state and  $E_2$  and  $E_3$  are associated with a short lived charge transfer between impurity and the complex [8]. Thus the change in the slope and hence the activation energy is interpreted as a change from extrinsic to intrinsic conduction. The activation energies are given in Table 1.

Thickness (nm)	Activation energy (eV) $\pm 0.01$ eV		
	$E_1$	$E_2$	$E_3$
184	0.90	0.68	0.05
261	0.86	0.67	0.05
385	0.81	0.65	0.05
517	0.77	0.65	0.05

Table 1 Variation of activation energy with thickness for AlPcOH thin films

It is seen that the conductivity increases with increasing temperature. The activation energy decreases as the thickness of the film increases. A similar behaviour has been reported for NiPc and InPcCl thin films [12,13]. Figure 3 shows X-ray diffraction pattern of aluminium phthalocyanine hydroxide thin film of thickness 261 nm. The microcrystalline grain size 'L' of the film is determined from the full width at half maximum (FWHM) of the X-ray peaks using the Scherrer formula [14]

$$L = \frac{B\lambda}{\eta_{\frac{1}{2}} \cos \theta} \quad (3)$$

where B is the Scherrer constant,  $\lambda=1.54$  Å,  $\eta_{\frac{1}{2}}$  is the FWHM in radians and  $\theta$  is the diffraction angle of the most intense peak. It is observed that the grain size increases as the thickness increases and a grain size of 34.93 nm is obtained for the thin film of thickness 261 nm. Scanning electron micrograph of aluminium phthalocyanine hydroxide film is shown in figure 4. From the SEM planar view, it is clear that the film is made of homogeneous small crystal grains.

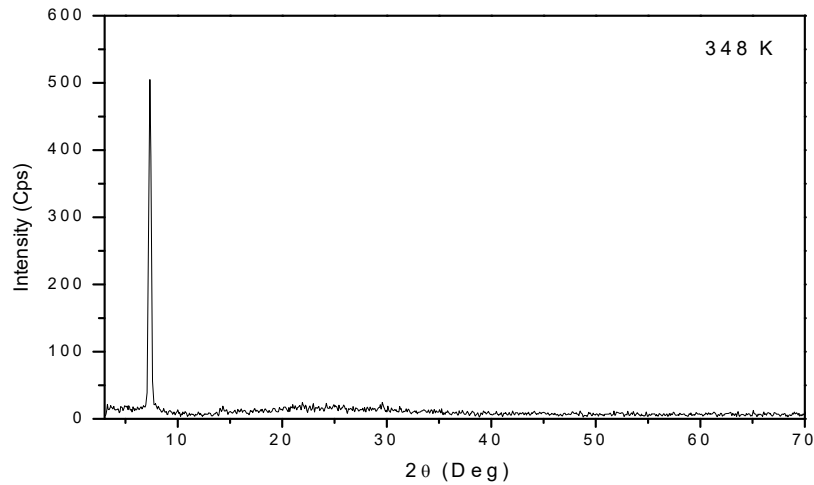


Figure 3 X-ray diffraction pattern of AlPcOH thin film of thickness 261nm.

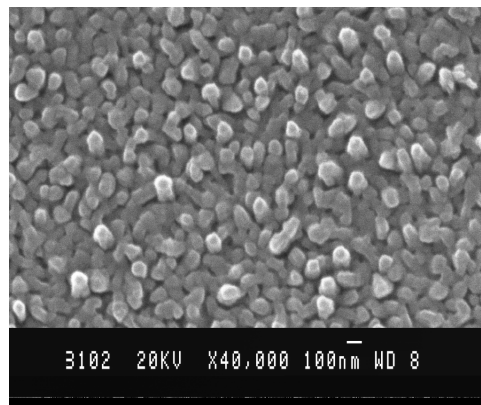


Figure 4 SEM image of AlPcOH thin film of thickness 261nm.

#### IV. CONCLUSION

Thermal activation energies of aluminium phthalocyanine hydroxide thin films of different thicknesses are investigated. The slope of the Arrhenius plot changes at different regions of temperature indicating a variation of activation energy due to the thermal excitation of defects or impurities situated at different levels in the band gap. The decrease in activation energy with an increase in the film thickness may be due to the presence of internal electric fields associated with the defects present in the films or it may be due to an increase of particle size. Film having desired activation energy can be made by adjusting the thickness during deposition.

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