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OPTOELECTRIC PROPERTIES OF THERMALLY EVAPORATED ClAlClPc THIN FILMS

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Vacuum sublimed thin films of Chloro Aluminium Chloro phthalocyanine were prepared at room temperature onto glass substrates at a base pressure of 10^{-5} *Torr. Annealing was done in air and the effect of annealing temperature on the optical and electrical properties were studied. Optical absorption spectra of films annealed at temperatures,* 373 *K,* 423 *K,* 473 *K and as-deposited were taken over a wavelength range of* 200 *to* 900 *nm and the optical energy band gap* E_g *and the onset and excitonic energy gap were calculated. It is found that* E_g *slightly increases with increase in air annealing temperature and excitonic energy gap has practically unchanged. Arrhenius plot yields thermal activation energy in the intrinsic region and impurity scattering region. The variation in the electrical properties with air annealing temperature were also studied and activation energy was determined. Thermal activation energy is calculated from the Arrhenius plot in the intrinsic and extrinsic regions, it is found that it decreases with increase in the air annealing temperatures.*

Keywords*: CHLORO ALUMINIUM CHLORO PHTHALOCYANINE, THIN FILMS, PHTHALOCYANINE, OPTICAL PROPERTIES, ELECTRICAL PROPERTIES.*

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1. INTRODUCTION

Organic semiconductors are expected to play a vital role both in industry and research in the coming years [1]·Phthalocyanines (Pcs) have attracted much attention because of their interesting electrical and optical properties [2]. Metal – free (H_2Pc) as well as metal – substituted (MPc) phthalocyanines can be prepared. They are of great interest to researchers because of their versatility, architectural flexibility, low cost of preparation and wide applications in electronic industry as well as photonic technology.

Their stability against thermal and chemical decomposition [3] and intense absorption in the visible spectrum make them suitable as chemical sensors [4]. the dyes and colour filters [5]. They exhibit strong non-linear optical properties due to their spatially extended Pi-electron system [6] and find applications as active elements in photo conducting agents, photovoltaic cell elements, solar cells, light emitting diodes and static induction transistors [7]. The halogenated phthalocyanines exhibit remarkable morphological and thermal stability over a large temperature range compared to unhalogenated Pcs [8]. The band gap determination is practically useful to detect the impurity levels and defects when working with new compound semiconductors since radiative transitions in semiconductors involved localized defect levels. Electrons are excited from the valance band to conduction band with the absorption of energy equal to the band gap of the material. It is seen that the behavior of phthalocyanine thin films changes with various parameters such as evaporation rate, substrate temperature, and post deposition annealing [9]. Hence, the knowledge of the effect of air annealing on the electrical and optical properties is necessary to understand the fundamental aspects of the materials. The electrical and optical properties of several phthalocyanine thin films have been studied in recent years [10, 11] but relatively little work has been done on Chloro Aluminium Chloro phthalocyanine thin films.

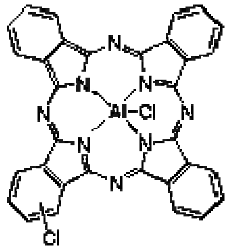

Fig. 1 - Molecular structure of ClAlClPc thin films

In the present paper, we report the optical and electrical properties of as deposited and heat-treated ClAlClPc thin films in air.

2. MATERIALS AND METHODS

Thin films of ClAlClPc are prepared by thermal evaporation technique using a high vacuum coating unit (Hind Hivac 12A4). Spectroscopically pure ClAlClPc powder used in the study is procured from Sigma-Aldrich Inc USA. Micro glass slides of dimensions 5 cm X 1.15 cm X 0.1 cm are cleaned using the standard cleaning procedure are used as substrates. The material is sublimed from a molybdenum boat of dimensions 2.9 cm × 1.2 cm × 0.5 cm, used as resistive heating element. Evaporation of the material is carried out at a base pressure of 10^{-5} Torr. During evaporation the substrates are placed at a distance of 11 cm above the source and the deposition rate is controlled within a range of 10-12 nm/min. The thickness of the film is measured using a Dektac thickness profilometer and is cross checked with a Tolansky's multiple beam interference technique. Thin films deposited at room temperature are annealed at temperatures 373 K, 423 K and 473 K in air for 1 hour using a furnace attached with a digital temperature controller cum recorder. The absorption spectra of ClAlClPc thin films are recorded using the Shimadzu 160 A UV-Vis-NIR Spectrophotometer in the wavelength range of 200-900 nm. Absorption spectra of the films are analyzed to obtain the energy band gap. Reflectivity measured by using a Jasco V-570 Spectrophotometer. Electrical measurements are performed using a Programmable Keithley electrometer (Model No.617) in the constant current source mode. Evaporated silver electrodes are used for ohmic contacts. Each sample is mounted on the sample holder of the conductivity cell. Electrical contacts are made using copper strands of diameter 0,6 mm and are fixed to the specimen with a colloidal suspension of silver in alkadag. To avoid contamination the measurements are done in a subsidiary vacuum of 10^{-3} Torr.

3. RESULTS AND DISCUSSIONS

3.1 Optical properties

The UV-NIR absorption spectra at 373 K, 423 K and 473 K and as deposited form are taken. Here Figure (2) shows the plot of absorbance versus wavelength of as-deposited ClAlClPc thin films having thickness 300 nm. The distinct characterized peaks in the visible region are generally been interpreted in terms of π - π^* excitation between bonding and antibonding molecular orbitals.

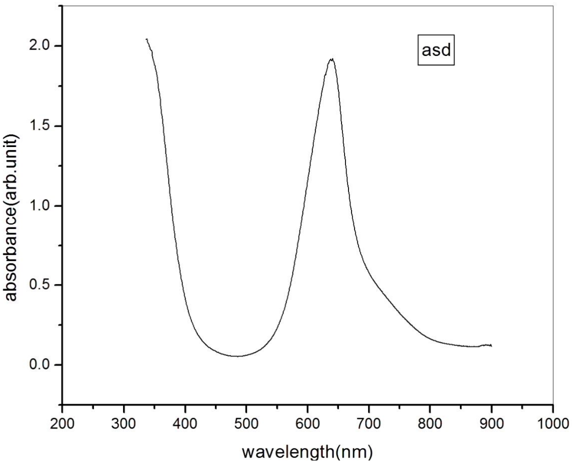

Fig. 2 *- Plot of absorbance versus wavelength for ClAlClPc thin films*

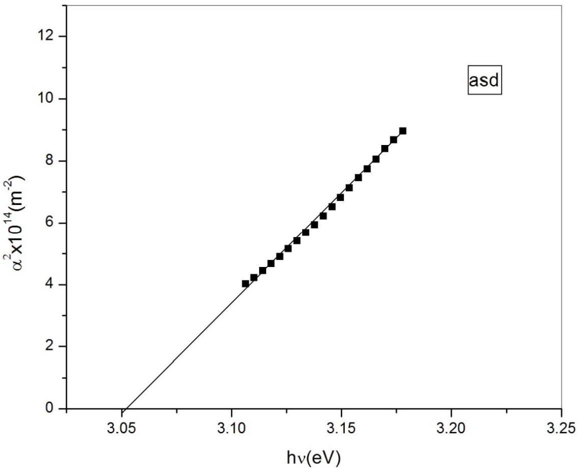

Fig. 3 *- Plot of α^2 versus photon energy hv for ClAlClPc thin films*

The absorption peaks at higher energy region and low region results from B (Sorret) band (325-425 nm) and Q-band (625-725 nm) respectively. Both Q and B bands arise from π to π^* transitions [12, 13]. To obtain information about direct or indirect interband transitions the fundamental absorption edge data is analyzed within the framework of one electron theory of Bardeen et al. [14]. This theory has been used to analyze the absorption edge data of molecular solids such as phthalocyanine [15]. The absorption ($\alpha \geq 10^{4}\ \mathrm{cm}^{-1}$) is related to direct band transitions [16]. The absorption coefficient α is related to the band gap E_g and photon energy $h\nu$ according to the relation [17],

$$\alpha = \alpha_0 \,(h\nu - E_g)^n \tag{1}$$

Figure 3 shows the plots of variation of α^2 with $h\nu$ for ClAlClPc thin film. A satisfactory fit is obtained for α^2 vs $h\nu$ indicating the presence of a direct band gap. A band gap of (3.06 ± 0.01 eV) is obtained. Similar calculations and graphs can be plotted corresponding to the Q-band of the samples and the trap levels also can be computed. The results of the fundamental energy band gap and trap levels are collected in Table 1.The absorption at lower energy side is related to singlet excitons and has been confirmed for many other phthalocyanines [18].

Table 1 *- Variation of Fundamental and excitonic band gap energies with annealing temperatures*

Annealing Temperature (K)	Fundamental Band gap (eV)	Excitonic Band gap (eV)
as deposited	3.05	1.83
373 K	3.06	1.84
423 K	3.07	1.83
473 K	3.09	1.84

The reflection spectra of as-deposited ClAlClPc thin films is given in Figure 4.

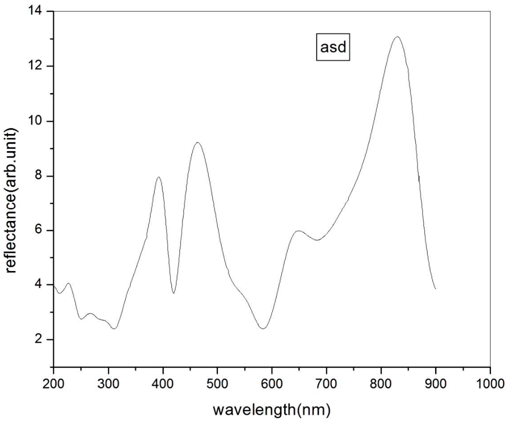

Fig. 4 *- Reflectance versus wavelength for as-deposited ClAlClPc thin film*

The extinction coefficient k is calculated using the equation.

$$k = \frac{\alpha\lambda}{4\pi} \tag{2}$$

Where α is the absorption coefficient and λ is the wavelength. The reflectivity of an absorbing medium of indices n and k in air for normal incidence is given by,

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \tag{3}$$

The optical properties of the medium are characterized by a complex refractive index ($N = n - ik$) and complex dielectric constants (ε_1 and ε_2). The real part generally relates to dispersion, while the imaginary part provides measure of the disspersive rate of the wave in the medium.

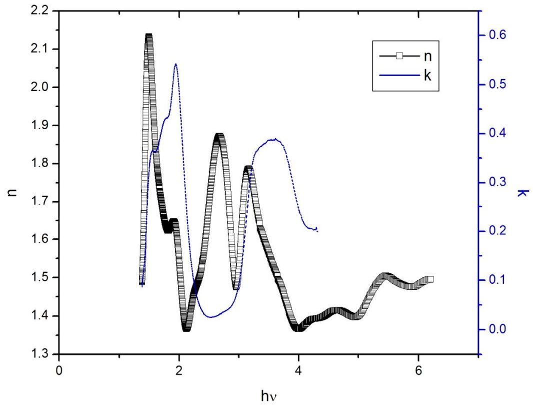

Fig. 5 *- Plot of refractive index n and extinction coefficient k versus photon energy for as deposited ClAlClPc thin film*

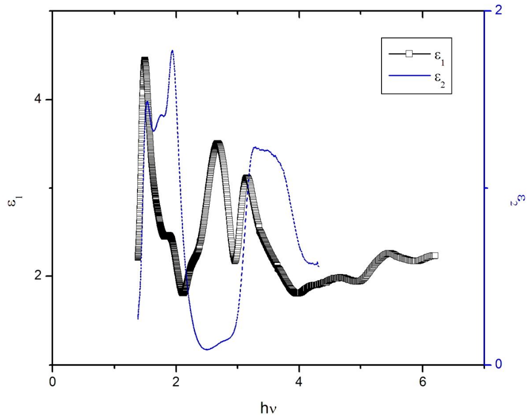

Fig. 6 *- Plot of real and imaginary parts of the dielectric constant versus photonenergy for as deposited ClAlClPc thin film*

The refractive index n has a maximum value of 2.13 at 1.478 eV for the ClAlClPc thin film. The extinction coefficient k has a maximum value of 0.534 at 1.942 eV.

In this way the dependence of the real and imaginary part of the dielectric constant (ε_1 and ε_2) and on photon energy and dependence of n and k on photon energy for ClAlClPc also are plotted. The real and the imaginary parts of the dielectric constants are calculated using equations 4&5 and the variations can be check.

$$\varepsilon_1 = n_2 - k_2,\ \varepsilon_2 = 2\,nk \tag{4, 5}$$

The real part ε_1 shows a maximum value of 4.486 at 1.478 eV, while imaginary part ε_2 has a maximum value of 1.770 at 1.942 eV.

3.2 Electrical propertites

Electrical measurements are done to investigate the temperature dependence of conductivity and the effect of annealing on the activation energy. Conductivity in phthalocyanines is due to hopping of holes and charge transport via excited states. In such case the conductivity is given by,

$$\sigma = A\exp(-E_1/k_BT) + B\exp(-E_2/k_BT) + C\exp(-E_3/k_BT) + \ldots\ldots\ldots \tag{6}$$

Where E_1 is the intrinsic energy gap and E_2, E_3 ... are the activation energy needed to excite the carriers from the corresponding trap levels to the conduction band. A, B, C etc are constants.

The electrical resistances of the samples are measured using the program-able Keithley electrometer. The electrical conductivity (σ) is calculated using the relation,

$$\sigma = L/Rbd \tag{7}$$

Where L, b, d are the length, breadth and thickness of the film respectively, R is the resistance of the film.

The temperature dependence of conductivity shows Arehenius type relationship [19]. The conductivity is strongly temperature dependent and the

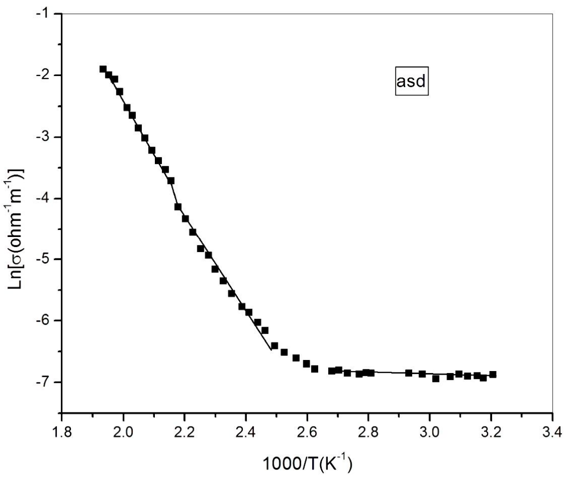

Fig. 7 – Plot of $\ln\sigma$ *vs.* $1000/T$ *for the as-deposited film*

charge carrier transport mechanism is of free band type in the higher temperature region and of hopping type in the lower temperature region (20). lnσ vs 1000/T plots of ClAlClPc thin films of thickness 300 nm as-deposited form and annealed in air for 1hour at temperature 473 K are given in Fig. (7 & 8). The plots give different linear regions and are attributed to different charge carrier transport mechanisms. The activation energy corresponding to the linear regions are estimated from the slope of the graph.

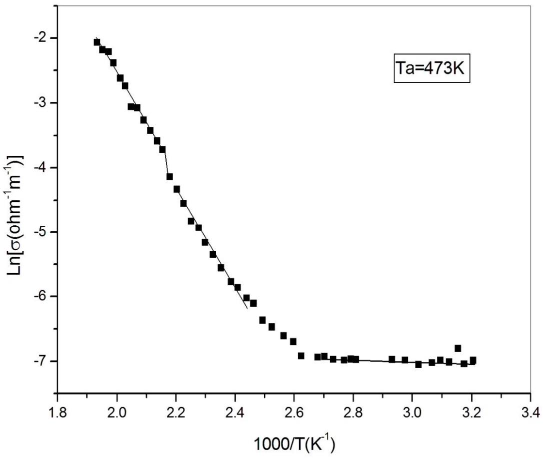

Fig. 8 *– Plot of ln*σ *vs.* 1000/T *for the film annealed at* 473 *K*

We have given three activation energies for each sample and are given in Table 2.

Table 2 *– Variations of activation energies with annealing temperatures*

Annealing Temperature (K)	Activation Energy (eV)		
	E_1	E_2	E_3
As deposited	0.72	0.61	0.06
373 K	0.70	0.60	0.05
423 K	0.67	0.57	0.05
473 K	0.64	0.55	0.04

Activation energy in phthalocyanines may be interpreted as the energy difference between dominant energy levels (21) and the central metal ion in phthalocyanines strongly influences the activation energy as well as the mobility in phthalocyanines. It is observed that the activation energy decreases with annealing temperature. The intrinsic activation energy E_1 for ClAlClPc thin film for as-deposited film is obtained as 0.72 eV. This value falls to 0.64 eV for film annealed at 473 K in air.

4. CONCLUSIONS

Chloro Aluminium Chloro phthalocynine thin films have been prepared on to glass substrates by thermal evaporation technique. The basic optical properties of ClAlClPc thin films have been studied. Two absorption peaks identified in the higher energy region 335 nm and low energy region 642 nm results from B (Soret) and Q-band respectively. A direct allowed transition at 3.06 eV is observed. Fundamental optical parameters have been determined from both absorption and reflection data. 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 decreases with increase of air annealing temperatures. The carrier conduction mechanism of the as deposited and films at different annealing temperatures is suggested to be of hopping by the charge carriers between localized states in the extrinsic region and a free band type conduction in the intrinsic region.

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