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Optical, electrical and structural characterization of gallium phthalocyanine chloride thin films

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Vacuum sublimed thin films of gallium phthalocyanine chloride were prepared at room temperature onto glass substrates at a base pressure of 10^{-5} Torr. Annealing was done in air and vacuum and the effect of annealing temperature on the electrical, optical and structural properties were studied. Arrhenius plot yields thermal activation energy in the intrinsic region and impurity scattering region. The variation in the electrical properties with thickness was also studied and activation energy was determined. The activation energy E_1 corresponds to intrinsic region decreases as the thickness increases. Optical absorption spectra of films annealed at temperatures 348 K, 398 K, 448 K and 498 K were taken over a wavelength range of 300 to 900 nm and the optical energy band gap E_g and the onset energy gap were calculated. It is found that E_g decreases with annealing temperature. The novel finding in the present work is that the Soret band shows a red shift with the increase of annealing temperature. X-ray diffraction pattern was used to find the nano-crystalline grain size using Scherrer formula and an increase in grain size with annealing temperature was observed.

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1. Introduction

Phthalocyanines are organic compounds exhibiting p-type semiconductivity [1] and can easily be sublimed, resulting in high purity thin films without decomposition. 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 [2] and intense absorption in the visible spectrum make them suitable as chemical sensors [3-5], dyes [6] and colour filters [7]. They are used as materials for high density optical data recording due to their low heat conduction and excellent optical properties. Optical, electrical and structural properties of phthalocyanine thin films have been studied extensively because of their applications in various optical and electro-optical devices. They exhibit strong non-linear optical properties due to their spatially extended Pi-electron system [8] and find applications as active elements in photoconducting agents, photo-voltaic cell elements, solar cells, light emitting diodes and static induction transistors [9,10]. The halogenated phthalocyanines exhibit remarkable morphological and thermal stability over a larger temperature range compared to unhalogenated phthalocyanines [11]. The band gap determination is particularly useful to detect the impurity levels and defects when working with new compound semiconductors since radiative transitions in semiconductors involve localized defect levels. Electrons are excited from the valence band to the conduction band with the absorption of energy equal to the band gap of the material. The sudden fall in the absorption coefficient on the high energy side of the absorption spectra leads to the band edge in semiconductor systems. The electrical conductivity of phthalocyanine thin films changes due to the adsorption of gases such as oxygen. The development of thin film gas sensors is based upon the fabrication of reproducible and thermally stable sensing materials. It is seen that the behaviour of phthalocyanine thin films changes with various parameters such as evaporation rate, substrate temperature and post deposition annealing [12]. Hence the knowledge of the effect of air annealing and vacuum annealing on the electrical, optical and structural 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 [13-16], but relatively little work has been done on gallium phthalocyanine chloride thin films [17,18]. Within the large family of phthalocyanine compounds, gallium phthalocyanine chloride exhibits emission efficiencies strong enough to be considered as potential new infrared emitters [19]. These films are found to have a large absorption coefficient and, therefore, they may have an industrial application as a medium for optical disc. In the present work we study the electrical, optical and structural properties of GaPcCl thin films annealed at various temperatures to determine some fundamental parameters such as optical band gap, absorption coefficient, activation energy and grain size.

2. Experimental details

Gallium phthalocyanine chloride powder procured from Aldrich, USA was sublimed in vacuum using a Hind

Hivac 12A coating unit onto well cleaned microglass slides held at a pressure of 10^{-5} Torr. Thin films were prepared by resistive heating of the powder from a molybdenum boat and the evaporation rate was kept constant as 10-12 nm/min. Several films of same thickness and different thicknesses were prepared in the same experimental condition simultaneously by arranging a series of substrates horizontally and keeping the evaporating source to one side but well below the specimen plane. The reproducibility of the results was confirmed by making several such depositions under more or less the same deposition conditions. Thickness of the film was determined by Tolansky's multiple beam interference technique [20].

GaPcCl thin films of thickness 430±5 nm were annealed in air for 1 hour at different temperatures in a furnace whose temperature could be controlled by a controller cum recorder. Another set of films was annealed in vacuum for 1 hour at 348 K, 398 K, 448 K and 498 K. UV- Visible absorption spectra were recorded using a Shimadzu 160 A UV –Visible spectro-photometer. The absorption edge was analyzed to get the optical band gap of GaPcCl. For electrical conductivity studies evaporated silver was used as the contact electrode. Thin copper strands were fixed by silver paste and the film was placed onto a hollow copper block in the conductivity cell which is heated. The temperature of the sample was measured using Chromel- Alumel thermocouple. The electrical conductivity studies were done in the temperature range 300-525 K. The resistance was noted at regular intervals of 5K using a programmable Keithley electrometer (Model No 617). The change of conductivity during cooling of the sample from 525 -330 K was also studied. To avoid any possible contamination, measurements were performed in vacuum at 10^{-3} Torr.

3. Results and discussion

3.1 Optical Studies

The study of optical absorption is a useful method for investigating the induced transition and providing information about the band structure in the materials. Optical studies are done to determine the energy band gap and the effect of annealing on the band gap. The principle of this technique is that photons with energies higher than the band gap energy will be absorbed and electrons are excited from the valence band to the conduction band with the absorption of energy equal to the band gap of the material. The rapid drop in the absorption coefficient on the high energy side of the absorption spectra leads to the band edge in semiconductors. The transition type is also important to be defined for the material characterization. The optical absorption spectra of films annealed in air at temperatures 348 K, 398K, 448 K and 498 K over a wavelength range of 300-900 nm are shown in Fig. 1.

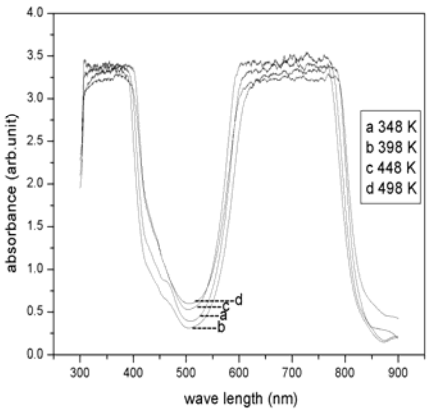

Fig. 1. Optical absorption spectra of GaPcCl thin films of thickness 430±5 nm annealed in air at different temperatures.

The spectrum of phthalocyanine is believed to originate from orbitals within the aromatic 18π electron system and from overlapping orbitals on the central metal atom [21]. The conjugated ring system of the phthalocyanines comprises forty atoms. Each carbon atom in a conjugated system has three nearest neighbors with which it forms three equivalent sigma bonds made from the sp^2 hybridization of three valence atomic orbitals of the carbon atom: 2s, $2p_x$ and $2p_y$. For such a hybridization state, the fourth orbital $2p_z$ lies perpendicular to the σ bond plane. It is the lateral overlap of these out of plane $2p_z$ atomic orbitals gives the π bonds. As π orbitals overlap is weaker than s orbitals overlap, the energy spacing between bonding and anti-bonding molecular orbitals is larger for π to π^* than for σ to σ^*. The π and π^* molecular orbitals are the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) respectively in terms of molecular physics. They are also the valence and conduction bands of semiconductor physics. In phthalocyanines the direct electronic transition from π to π^* orbitals in the energy range 300-450 nm results in an intense band called B-band (Soret band) which corresponds to the fundamental absorption from which the energy band gap is obtained [22]. The Q-band appeared in the 600-800 nm range gives onset energy [23]. The fundamental absorption edge was analyzed within the one electron theory of Bardeen [24] to obtain information about direct or indirect interband transitions. The absorption coefficient α was calculated using the relation

$$\alpha = 2.303\ A/t \tag{1}$$

where A is the absorbance of the film and t is its thickness. For direct allowed transition, the absorption coefficient α is related to the photon energy hν by the relation

$$\alpha = \alpha_o\,(h\nu - Eg)^{1/2} \tag{2}$$

where Eg is the optical band gap and α_o a constant. A satisfactory straight line fit is obtained for α^2 as a function of hν, showing the existence of a direct band gap. For the film annealed in air at 498 K the absorption coefficient is obtained as 17.70×10^4 cm^{-1}. The value of absorption coefficient α greater than 10^4 cm^{-1} obtained is also related to direct inter-band transitions. By plotting α^2 versus hν and extrapolating to zero absorption, the band gap *Eg* is obtained. Plot of α^2 versus hν for air annealed GaPcCl films is shown in Fig. 2. The absorbance spectra and α^2 vs. hν graph for vacuum annealed GaPcCl thin films of thickness 430± 5 nm are shown in Figs 3 and 4, respectively.

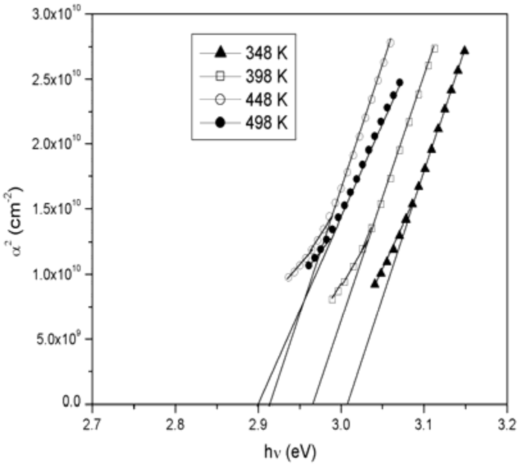

Fig. 2. Plot of α^2 vs. hν for GaPcCl thin films annealed in air at different temperatures.

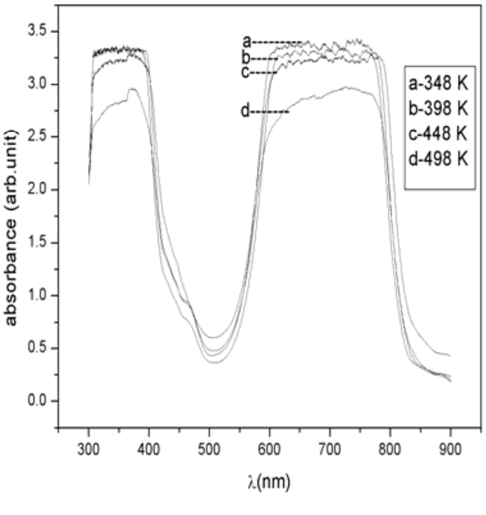

Fig. 3. Optical absorption spectra of GaPcCl thin films of thickness 430±5 nm annealed in vacuum at different temperatures.

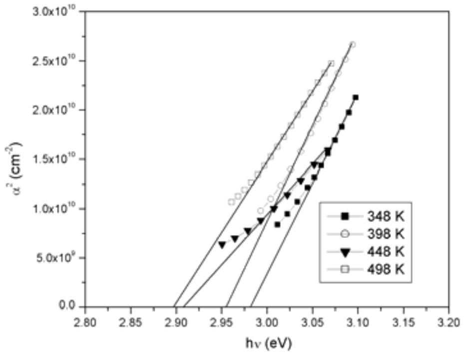

Fig. 4. Plot of α^2 vs. hν for GaPcCl thin films annealed in vacuum at different temperatures.

The values of fundamental and onset energy gaps are determined from the graph and are given in Table 1.

Table 1. Fundamental energy gap and onset energy gap of GaPcCl thin films annealed at different temperatures

Gallium phthalocyanine Chloride		Fundamental energy gap (eV)	Onset energy gap(eV)
Air annealing temperature K	348	3.01	1.55
	398	2.96	1.54
	448	2.92	1.53
	498	2.90	1.52
Vacuum annealing temperature (K)	348	2.98	1.54
	398	2.95	1.54
	448	2.91	1.53
	498	2.90	1.52

For the film annealed in vacuum at 448 K, a reduction in intensity of peak was observed. In the case of GaPcCl thin films two broad bands namely B band with absorption peak in the 300-400 nm region and Q band in the 580-780 nm region were observed. That is Q band is broader than B band. The considerable inhomogeneous broadening obtained is attributed to the high concentration of defects in evaporated phthalocyanine thin films. It is seen from the figure that not only the position of the peaks shifted towards higher frequencies, but the widths of these peaks also have changed. For both air annealed and vacuum annealed films the optical band gap is shifted to lower energies as the annealing temperature increases. This red shift of the B-band with increase in annealing temperature is due to sintering of nano-crystallites into effectively larger crystallites. From the XRD studies also it is seen that the grain size and hence the crystalline nature increase with annealing temperature. The phthalocyanine molecules are arranged in stalks of parallel molecules [25]. In metal phthalocyanines, the central metal atom is in a position of nearest approach to nitrogen atoms in parallel molecules and this increases the overlap between parallel pairs of molecules. Hence any crystal phase change would affect the energy gap between conduction and valence bands [26].

3.2 Electrical Studies

Semiconducting properties of phthalocyanines are first observed by Eley [27]. The electrical conductivity σ of a film of resistance R, length l, breadth b and thickness t is given by

$$\sigma = l/Rbt \tag{3}$$

The electrical conductivity can also be expressed as

$$\sigma = \sigma_0 \exp(-E/k_B T) \tag{4}$$

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. Graph of ln σ vs. 1000/T for vacuum annealed films and films of various thicknesses are shown in Figs. 5, 6 and 7, respectively.

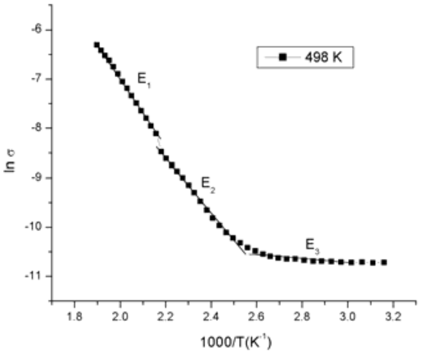

Fig. 5 . Plot of ln σ vs. 1000/T for GaPcCl films annealed in vacuum at 498 K.

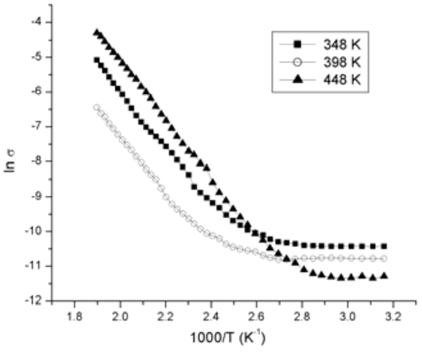

Fig. 6. Plot of ln σ vs 1000/T for GaPcCl films of thickness 342 nm annealed in vacuum at different temperatures.

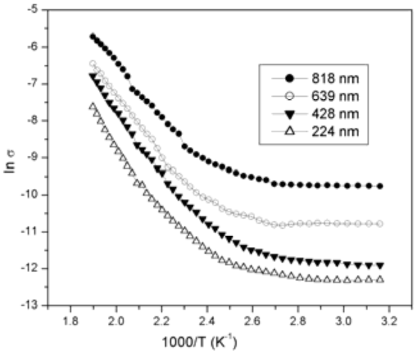

Fig. 7. Plot of ln σ vs 1000/T for GaPcCl films of different thicknesses.

Each curve has three different slopes in the lower and higher temperature regions. From the slopes of these graphs of activation energies are evaluated and collected in Table 2.

Table 2. Variation of activation energy with film thickness and heat treatment.

Gallium phthalocyanine Chloride		Activation Energy (eV)		
		E_1	E_2	E_3
Film thickness (nm)	224	0.89	0.52	0.15
	428	0.74	0.52	0.15
	639	0.70	0.54	0.16
	818	0.60	0.53	0.16
Vacuum annealing temperature (K)	348	0.79	0.61	0.44
	398	0.73	0.65	0.33
	448	0.69	0.57	0.16
	498	0.61	0.50	0.09

The activation energy was determined within an accuracy of ±0.01eV in all measurements. As shown by Belgachi and Collins [28], 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 are obtained at T > 460 K, between 410- 460 K and between 360 - 410 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 and E_2 and E_3 are associated with a short lived charge transfer between impurity and the complex [29]. In the low temperature range conductivity is due to hopping of charge carriers between the neighbors in the localized states near the Fermi level. As temperature increases the activation energy also increases. The change in the slope and hence the activation energy is interpreted as a change from extrinsic to intrinsic conduction. As thickness increases the activation energy E_1 is found to decrease. However E_2 and E_3 are not notably affected by thickness of the film. The decrease in the activation energy indicates an increase in the electrical conductivity and hence conductivity increases with thickness. A similar behaviour has been reported for H_2Pc thin films also [30]. The intrinsic activation energy E_1 decreases with increase in annealing temperature also. The lowering of activation energy is influenced by the structure of the film and the distribution of trap levels. Activation energies associated with impurity conduction E_2 and E_3 also decrease with annealing temperature. It seems that annealing improves the quality of the film, releasing strains and removing some defects. Hence a more continuous curve is obtained as the annealing temperature increases.

4. Structural studies

The XRD spectra for as-deposited and air annealed GaPcCl films are shown in Fig.8.

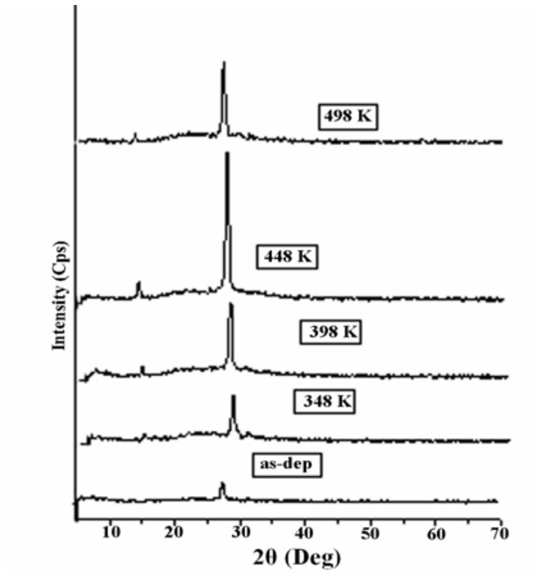

Fig. 8. XRD of GaPcCl thin films annealed in air at various temperatures.

For the as-deposited film there is only one peak at 2θ= 27.307°. For the annealed samples one smaller peak is also observed. For the sample annealed at 75°C the peaks are observed at 2θ =13.715° and 27.296°. For all annealed films, the same peaks are observed but with some shifts. The most intense peak was found to be at 2θ ≈ 27.307° for all samples. The intensity of this peak is found to increase as the annealing temperature increases. For the film annealed at 225°C this peak has been back shifted to 2θ =27.208° and the main peak intensity is obtained as 111 Cps. The increase in the main peak intensity, and also the increase in the number of the obtained peaks with annealing temperature indicate a slight increase in the crystalline nature of the films. The shape of the peaks, that is, the value of the full width at half maximum (FWHM) of the peaks, also reflects the degree of crystallinity .The larger the crystals of a given material, the sharper the peaks on the XRD spectra [31].

The grain size L of the film is calculated using the Scherrer equation [32]

$$L = K\lambda / b \operatorname{Cos} \theta$$

Where λ is the wave length of the X –ray beam (λ =0.15425 nm of Cu $K_{\alpha 1}$), b is the value of the full width at half maximum (FWHM) of the most intense peak, θ is the corresponding Bragg angle and K is Scherrer constant. The value of K, in general, depends on the crystallite shape and it is assigned a value of 0.9 for phthalocyanine films [33]. The grain sizes, corresponding to the as-deposited and annealed films are calculated and given in Table 3.

Table 3. Observed interplanar distance (d), position of the most intense peak (2θ), FWHM (b), maximum intensity and grain size(L) for GaPcCl thin films.

Annealing temp. (K)	d (Å)	2θ deg.	FWHM (b) $\times 10^{-3}$ rad	Max. Intensity Cps	Grain Size nm
As deposited	3.2594	27.307	9.330	27.8	15.308
348	3.2651	27.296	8.443	63.8	16.920
398	3.2766	27.178	8.373	116	17.057
448	3.2618	27.319	8.164	243	17.499
498	3.2752	27.208	7.327	111	19.495

It is clearly shown that as the annealing temperature increases, the FWHM decreases, providing that the crystallite size increases from 15.31 nm for the as-deposited sample to 19.50 nm for the sample annealed at 498 K. The noticed decrease in the FWHM and the increase in the crystallite size, due to air annealing, are in agreement with the results previously obtained for many metal phthalocyanines. The increase in the crystallinity may be due to the relief of stress in the crystals at the entry of tie molecules.

5. Conclusions

Absorption spectra of GaPcCl thin films show two absorption bands which we have identified as the fundamental absorption at high energies (B-band) and the exciton absorption at low energies (Q- band). The transition type is defined to be allowed direct transition and the optical band gap is red-shifted from 3.01 to 2.90 eV as the annealing temperature increases from 348-498K. Since the interactions of the molecules are of Vander Waals type, the rearrangement of molecules alters the energy gap. The activation energy is calculated from the electrical conductivity studies. There are three activation energies, which are due to the intrinsic charge carriers (E_1) and the impurity scatterings (E_2 and E_3). Thermal annealing treatment for a sufficiently long period of time may cause migration or diffusion of some atoms leading to a stable phase. It is found that, as the film thickness increases the intrinsic activation energy decreases. Thus films having desired activation energy can be prepared by adjusting the thickness of the film during deposition.

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