



OPTICAL AND ELECTRICAL CHARACTERIZATIONS OF SILICON PHTHALOCYANINE DICHLORIDE THIN FILMS

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Abstract

The phthalocyanines [Pc] are a class of planar aromatic organic compounds that have hetero-aromatic system and readily form complexes with many groups and transition metals. The versatility, architectural flexibility, non-toxicity and ease of processing make them eligible for use in microelectronics and also in nano-technology.

The present paper discusses the optical and electrical characterizations of Silicon Phthalocyanine dichloride thin films. It is observed that the electrical and optical properties of phthalocyanines are critically dependent on film morphology, which in turn is determined by preparation parameters such as deposition rate, substrate temperature and post deposition annealing. The direct optical transition takes place in these films. The optical energy gap remains unaffected due to annealing both in air and vacuum. For longer wavelength greater than 800nm, the film becomes transparent. The film also shows anomalous dispersion.

The variation of thermal activation energy with thickness and annealing temperature is studied. An Arrhenius plot shows two linear regions. Activation energy increases with increase of annealing temperature in air and vacuum. By optimizing the growth conditions, the applicability of this halogenated metal phthalocyanine as active layer in organic semiconductor thin film devices can be improved.

Keywords: Phthalocyanines, Optical Properties, Optical Band Gap, Thermal Activation Energy.

1. Introduction

Phthalocyanines (Pc) are small organic molecules which have been successfully used in organic photoreceptors, sensors, light emitting diodes, display devices in mobile phones and TV screens, photo sensitizers in laser printers, active layer in Schottky diodes and in organic thin film transistors by their high symmetry, planarity, electron delocalization and are used as an active layer for electronic devices [1-6]. For the fundamental understanding as well as for the device fabrication, the study of characteristics of the materials is important. This can be carried out in different ways- viz. optical, electrical and structural studies. It is observed that the electrical, optical and structural properties of phthalocyanines are critically dependent on film morphology, which in turn is determined by ambient parameters such as deposition rate, substrate temperature and post deposition annealing [7]. There is evidence that halogenated MPC's may exhibit properties suitable for gas sensing applications [8]. The present work is focused on the optical and electrical characterization of Silicon Phthalocyanine dichloride (SiPcCl₂) thin films.

2. Experimental Details

Spectroscopically pure SiPcCl₂ (C₃₂H₁₆N₈Cl₂Si) powder is used as the source material for the preparation of thin films. The result of elemental analysis of C, H and N of the sample agreed well with the calculated values (C=62.31%, H=2.22%, N=18.26%). Thin films of suitable thickness are deposited onto thoroughly cleaned rectangular glass substrates by vacuum sublimation from a resistively heated molybdenum boat using a "Hind Hi- Vac 12A" coating system at room temperature at a pressure of 10⁻⁵Torr. The thickness of the films is measured by Tolansky's multiple beam interference technique [9]. Thin films prepared at room temperature have been annealed in air and vacuum at different temperature for one hour. UV- Visible absorption, Reflection and Transmission spectra are recorded in the wavelength range 300 to 900 nm using the Shimadzu 160A UV-Visible Spectrophotometer. The electrical conductivity studies are done at a pressure of 10⁻³Torr to avoid the possible contamination in the temperature range 323 K to 523 K and the resistance is measured. Since phthalocyanines are photosensitive, measurements are done in darkness [10].

3. Results and Discussions

3.1. Optical Studies

The optical properties of a material provide important information on the electronic structures, localized states and type of optical transitions. Typical absorption spectrum of as deposited sample is given in figure 1.

The molecular spectra in Pc's originate essentially from the molecular orbitals within the aromatic 18 π electron system and



from the overlapping orbital on the central metal atom [11]. All the absorption spectra consist of two main bands B-band (Soret band) and Q-band. It is clear from the absorption spectrum that the film is transparent above 800 nm. The B (Soret) band consists of an absorption peak around 377 nm. The Q-band is sharp and consists of two peaks, one at 670 nm and another strong peak at 746 nm. This type of absorption spectrum is reported in the case of InPcCl [12]. It can be also seen that the annealing process had an influence on the absorption coefficient of the investigated film. Annealing produces subsequent decrease in the absorption but the peak position of the energy remains the same. The absorption coefficient α is calculated and is related to the energy band gap E_g and the photon energy $h\nu$ by the relation.

$$r = r_0 (h\nu - E_g)^n \quad (1)$$

where $n=1/2$ for direct allowed transition and $n=2$ for indirect allowed transition.

A satisfactory linear fit is obtained for the plot of α^2 versus $h\nu$ as in figure 2, indicating the presence of direct energy gap ($n=1/2$). The extrapolation on energy axis at $\alpha^2 = 0$ gives energy band gap of 3.10 eV for SiPcCl₂ thin films of thickness 210 nm within an accuracy of ± 0.01 eV. The value remains constant for both air-annealing and vacuum annealing (Table 1). Due to weak Van der Waal's interaction between the molecules in the film, their optical properties are not significantly changed when compared with free molecules. The same type of spectra is seen in the case of other halogenated MPC's like Aluminium Phthalocyanine chloride, Indium Phthalocyanine chloride and Titanium Phthalocyanine dichloride thin films [8,12,13].

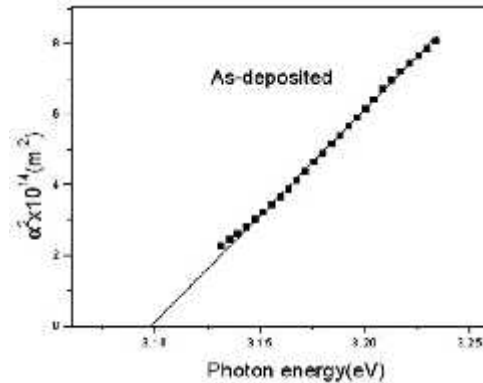
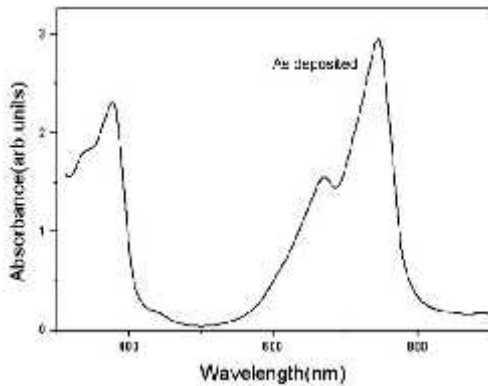


Fig 1. Absorption Spectrum of as Deposited Fig 2. Plot of r^2 versus $H\epsilon$ for as Deposited Thin Film

Table 1. Fundamental and Excitonic Energy Gaps of Sipcl₂ Thin Films at Different Annealing Temperatures

Annealing Temperature (K)	Air Annealing		Vacuum Annealing	
	Fundamental Energy gap (eV)	Excitonic Energy gap (eV)	Fundamental Energy gap (eV)	Excitonic Energy gap (eV)
303	3.10	1.60	3.10	1.60
373	3.09	1.59	3.10	1.60
423	3.09	1.60	3.09	1.60
473	3.09	1.60	3.07	1.58

The fundamental optical parameters of SiPcCl₂ are determined from the transmittance and reflectance spectra of as deposited SiPcCl₂ thin film. The inequality $R+T<1$ at shorter wavelength ($\lambda<900$ nm) shows the existence of absorption. The reflectivity R of an absorbing medium of indices n and k in air for normal incidence is given by

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

where n is the refractive index and k is the extinction coefficient.



Thus by knowing R and k, n is calculated. The optical properties of the film are characterized by the complex refractive index ($N=n-ik$) and complex dielectric constant ($\epsilon=\epsilon_1-i\epsilon_2$). The real part ϵ_1 generally relates to the dispersion, while the imaginary part ϵ_2 gives a measure of the dissipation rate of the wave in the medium. The two parameters are related to n and k through the equation.

$$v_1 = n^2 - k^2 \quad v_2 = 2nk \quad (3)$$

The values of k, n, ϵ_1 , ϵ_2 are calculated from the transmission and the reflectivity data using these equations. The dependence of photon energy with n and k and ϵ_1 and ϵ_2 are plotted in figures 5 and 6 respectively. The values of n_{max} (4.09) and ϵ_{1max} (16.55) occur at 1.60eV.

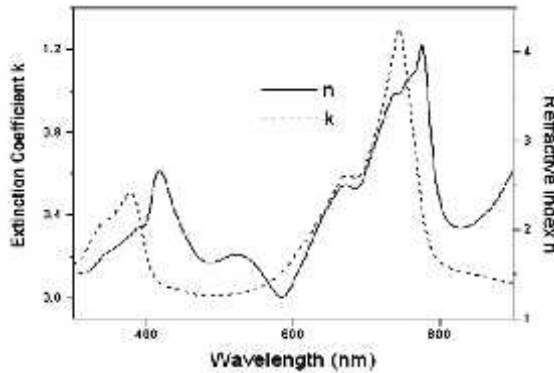


Fig.3. Plot of extinction coefficient (k)

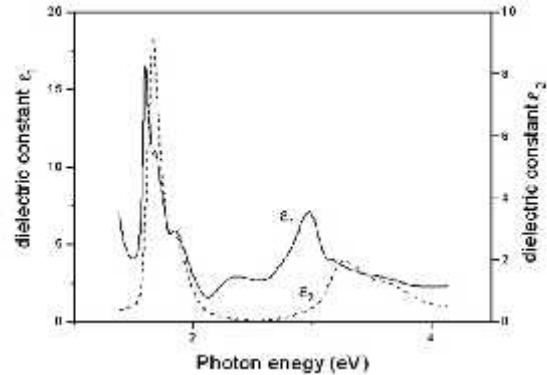


Fig 4. Spectral distribution of the real (v_1) Refractive index (n) as a function of photon and Imaginary (v_2) parts of dielectric constant energy

3.2. Electrical Studies

In the case of Pc thin films, the electrical conductivity σ at absolute temperature T is given by the relation

$$\uparrow = \uparrow_0 \exp(-E/k_B T) \quad (4)$$

Where σ_0 is pre-exponential factor, E is the thermal activation energy and k_B is Boltzmann's constant.

The Arrhenius plots ($\ln \sigma$ versus $1000/T$) yields a straight line whose slope can be used to calculate the thermal activation energy E. Figure 5 and 6 gives the Arrhenius plot for SiPcCl₂ thin films of different thicknesses and air annealed samples respectively. In the case of SiPcCl₂ thin films, there are two linear regions for the Arrhenius plot and the corresponding activation energies E_1 and E_2 that confirms the existence of trap levels. The change in the slope and hence the activation energy is because of the change from intrinsic to extrinsic conduction [8]. According to Davis and Mott [14], the formation of localized states has an important role in the conduction of charge carriers. In the extrinsic region, the charge carriers move by hopping along with ions and electrons.

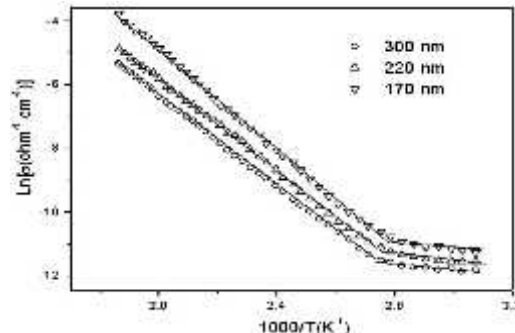
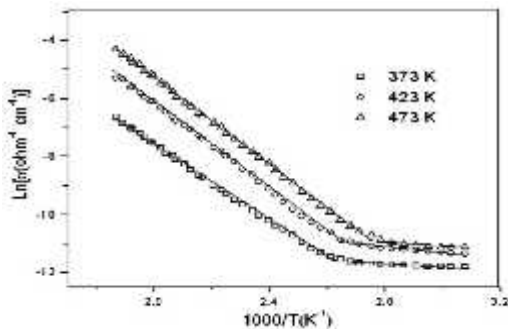


Fig 5. $\ln \uparrow$ versus $1000/T$ for films of different thicknesses Fig 6. $\ln \uparrow$ versus $1000/T$ for air annealed film

The activation energy E_1 in the higher temperature region is found to be due to intrinsic majority carriers (holes) whereas the activation energy E_2 in the lower temperature region is due to different trap levels present in the forbidden gap. As the



thickness of the film increases crystallite size of the film increases which in turn cause decreases in the activation energy. The variation of thermal activation energy with annealing temperatures in air and thickness is given in Tables 2 and 3. As the annealing temperature both in air and vacuum increases, activation energy increases. The increase in E_1 can be attributed to better film ordering due to air annealing [12].

Table2. Activation Energy for Air Annealed Film

Annealing Temperature(K)	Activation energy (eV)	
	E_1	E_2
373	0.57	0.04
423	0.64	0.08
473	0.66	0.10

Table 3. Activation Energy for Films of Different Thicknesses

Film Thickness (nm)	Activation energy (eV)	
	E_1	E_2
170	0.67	0.09
220	0.62	0.07
300	0.60	0.05

Activation energy increases with the annealing temperature in vacuum annealing. The desorption of oxygen in vacuum annealing causes an increase in resistance. Thus the electrical conductivity decreases and hence the activation increases. As deposited sample may contain different kinds of defects such as vacancies, grain boundaries and dislocations which can be partially annealed out by the heat treatment, results in a decrease in the density of defects [12].

4. Conclusion

Optical investigations of SiPcCl₂ thin films are done with respect to post deposition annealing. Absorption spectra shows the existence of two absorption region, which are identified as B-band and Q-band. The fundamental energy gap and the onset gap remains the same. The dependence of electrical conduction on thickness and post deposition annealing in air and vacuum for SiPcCl₂ thin films is studied and activation energies are found out. The conduction mechanism is free band type in the intrinsic region and hopping type in the extrinsic region. The improvement in the size of crystallites with increase of thickness decreases the activation energy. The annealing in vacuum produces desorption of oxygen from it. By optimizing these parameters, these thin films can be used to fabricate organic semiconductor devices.

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