http://www.e-journals.net

ISSN: 0973-4945; CODEN ECJHAO
E-Journal of Chemistry
2012, **9(1),** 294-300

Effect of Vacuum Annealing on the Optoelectric and Morphological Properties of $F_{16}CuPc$ Thin Films

RAJI KOSHY and C.S.MENON

School of Pure and Applied Physics
Mahatma Gandhi University, Kottayam, Kerala-686560, India
rajirose23@yahoo.com

Received 10 March 2011; Accepted 15 July 2011

Abstract: The effect of vacuum annealing temperature on optical and electrical properties of vacuum evaporated $F_{16}CuPc$ thin films have been studied spectrophotometer and Kiethely electrometer respectively. The band gap energy both fundamental and excitonic remains unchanged when the annealing temperature increased. The optical constants of thin films are obtained by means of thin film spectrophotometry. From the electrical study, the activation energies of the films, in the intrinsic region and impurity region have been determined from the Arrhenious plots of $\ln\sigma$ *versus* 1000/T. Optical data have been obtained from both absorption and reflectivity spectra over the wavelength range 200-800 nm. The absorption coefficient α and extinction coefficient k are estimated from the spectrum. The mechanism of optical absorption follows the rule of direct transition. Using α and k, the refractive index and the dielectric constants are determined. The SEM investigations are $F_{16}CuPc$ thin films are expected to find application in the fabrication of optoelectronic devices such as organic transistors and LED devices.

Keywords: Thermal evaporation, Vacuum annealing, Thin films, Optical properties, Electrical properties, SEM

Introduction

In recent years, organic semiconductors have attracted a great deal of attention due to their potential use in a wide range of technological applications. Due to their interesting physical properties combined with the low material cost make this particular family of organic compounds a strong candidate for the electronic and optoelectronic devices. Phthalocyanines (Pcs) represent one of the most promising candidates for ordered organic thin films. As these systems possess advantageous attributes such as chemical stability and excellent film growth which results in optimized electronic properties. Many of these materials incorporating different metals have been investigated for gas sensing[1],

photovoltaic devices[2,3], thin film transistors[4], organic light emitting diodes[5] and Schottky diodes[6]. The light absorbing properties of phthalocyanines in the visible and infra red regions are of significant importance because of the current interest in the conversion of solar to electrical energy[7]. Hexadecafluorophthalocyanines attracted interest as a possible *n*-type organic semiconductor with high electron mobility and good stability characteristics[8,9]. This suggests that hexadecafluorophthalocyanines are useful to develop organic bipolar devices such as transistors and electroluminescent diodes[10]. Among various phthalocyanines, copper hexadecafluoro phthalocyanine has received considerably less attention. This article brings out the results of the optical band gap, refractive index and dielectric constants, from the absorption co-efficient and extinction co-efficient of $F_{16}CuPc$ thin films, which is essential for the fabrication of electronic devices. From the electrical studies we estimate the values of activation energies in the intrinsic and extrinsic regions. In the paper we also investigate the morphological properties of the $F_{16}CuPc$ thin films. Results show that $F_{16}CuPc$ is highly stable against heat, high energy radiations and atmospheric air.

Experimental

Copper hexadecafluoro phthalocyanine, procured from Sigma- Aldrich Chemicals (USA), was purified by the train –sublimation technique using nitrogen as the carrier[11] and was used as the source material for thermal evaporation. Thin films of $F_{16}CuPc$ were prepared on a glass substrate using a Hind Hivac 12A4 evaporation plant. Glass slides with dimensions 5 cm x 1.15 cm x 0.1 cm were used as substrates. Evaporation of the material was done at a base pressure of 10^{-5} Torr using a molybdenum boat. 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 deposition was controlled at 10^{-13} nm per minute. $F_{16}CuPc$ thin films 60±5 nm thick were annealed in vacuum for 1 h at 373,423 and 473 K for 1 h in vacuum at a base pressure of 10^{-3} Torr. The thickness of the film is measured using a Dektac thickness profilometer and is cross checked with a Tolansky's multiple beam interference technique. The absorption spectra of $F_{16}CuPc$ 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. The surface morphology of the thin films is studied using the JOEL JSM scanning electron microscopy images.

Results and Discussion

Optical properties

The optical properties of a material are important, as they provide information on the electronic structures, localized states and type of optical transitions. The optical absorption spectra of all the prepared samples of $F_{16}CuPc$ in the wavelength range 200-900 nm are recorded. Typical absorption spectrums of as-deposited and vacuum-annealed samples are given in Figure 1.

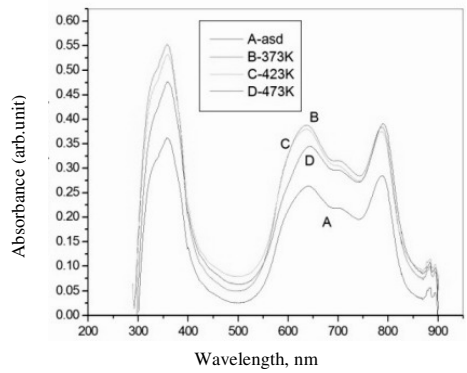


Figure 1. Plot of absorbance *versus* wavelength for $F_{16}CuPc$ thin films as-deposited form and different vacuum annealing temperature

The molecular spectra in Pc's originate essentially from the molecular orbital's within the aromatic 18 π electron system and from the overlapping orbital on the central metal atom[12]. All the absorption spectra consists of two main bands B band (Soret band) and Q band. The electronic transitions from the π- π^* orbitals result in intense band in the UV region called B band positioned at 358 nm which gives the fundamental absorption edge, while broad band that appeared in the visible region called Q band, which split up into two, positioned at 638 nm and 792 nm gives the excitonic energy[13]. The fundamental absorption edge is analyzed within the framework of one electron theory of Bardeen *et.al*[14]. Using this theory, energy band gaps of a number of MPc's have been found out[13,15]. The absorption coefficient α is calculated and is related to the band gap Eg and photon energy hν according to the relation[16].

$$\alpha = \alpha_0 (h\nu - E_g)^n \quad (1)$$

Where n= ½ for direct allowed transitions and n=2 for indirect allowed transitions Figure 2 shows the plots of variation of α^2 with hν for $F_{16}CuPc$ thin film deposited at room temperature of the as-deposited and vacuum annealed temperatures. A satisfactory fit is obtained for α^2 *vs.* hν indicating the presence of a direct band gap. The intercept on the energy axis gives the energy band gap. A band gap of (3.06±0.01 eV) is obtained. The absorption at lower energy side is related to singlet exactions and has been confirmed for many other phthalocyanines[17]. The variation in band gap energy with annealing temperature is given in Table 1.

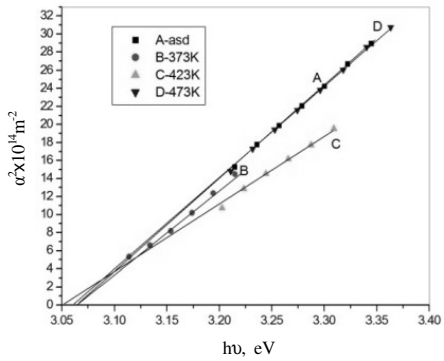


Figure 2. Plot of α^2 *versus* photon energy hν for $F_{16}CuPc$ thin films annealed in vacuum (fundamental gap)

Table 1. Variation in band gap energy with annealing temperature

Annealing Temperature, K	Fundamental Band gap eV	Excitonic Band gap eV	
		1	2
as deposited	3.06	1.61	1.50
373 K	3.06	1.60	1.50
423 K	3.05	1.61	1.50
473 K	3.06	1.60	1.50

The fundamental optical parameters of $F_{16}CuPc$ are determined from the reflectance spectra of as-deposited and annealed thin films of thickness 60 nm recorded in the range 200-800 nm

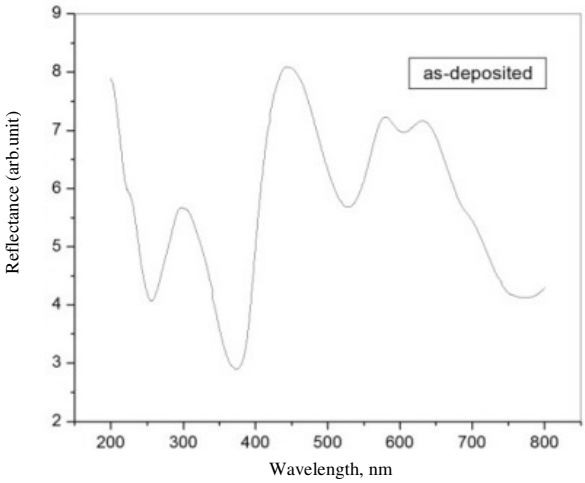


Figure 3. Reflectance *versus* wavelength for as-deposited $F_{16}CuPc$ thin film

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

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

Thus by knowing the R and k, n is calculated. 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 dissipative rate of the wave in the medium[15].

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 $F_{16}CuPc$ 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. The two parameters are related to n and k through the equation

$$\varepsilon_1 = n^2 - k^2, \qquad \varepsilon_2 = 2nk \tag{4, 5}$$

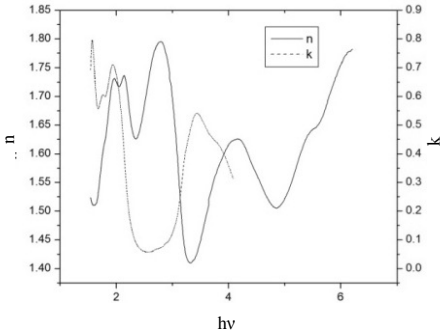


Figure 4. Plot of refractive index n and extinction coefficient k *versus* photon energy for as deposited $F_{16}CuPc$ thin film

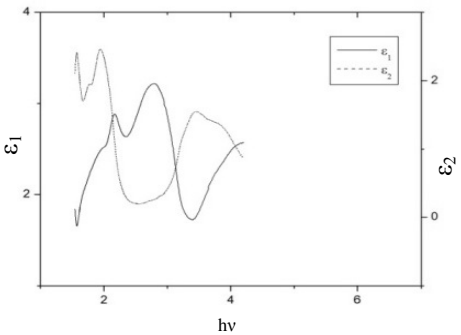


Figure 5. Plot of real and imaginary parts of the dielectric constant *versus* photon energy for as deposited $F_{16}CuPc$ thin film

It is observed that these parameters vary with photon energy. The refractive index n has a maximum value of 1.793 at 2.797 eV for the $F_{16}CuPc$ thin film.The extinction coefficient k has a maximum value of 0.786 at 1.562 eV. The real part ε_1 shows a maximum value of 3.208 at 2.775 eV while imaginary part ε_2 has a maximum value of 2.414 at 1.958 eV. It is observed that these parameters vary with photon energy.

Electrical studies

Electrical conductivity studies on $F_{16}CuPc$ thin films of 60±5 nm thickness are used to determine thermal activation energy and to study the effect of vacuum annealing temperature on the activation energy. In inorganic semiconductors the semiconducting properties are brought about by thermal excitation, impurities, lattice defects and nonstochiometry. Holes in the valence band and electrons in the conduction band contribute the electrical conductivity. The electrical conductivity σ can be expressed as

$$\sigma = \sigma_0 \exp(-E_a/k_b T) \tag{6}$$

Where σ is the conductivity at temperature T, E_a is the thermal activation energy, k_b is the Boltzmann constant and σ_0 is a pre-exponential factor. Arrhenius plots of lnσ *vs*. 1000/T of $F_{16}CuPc$ thin films are made to study the dependence of the conduction mechanism on vacuum annealing temperature 473 K and as-deposited form are given Figure 6 (a) and (b)

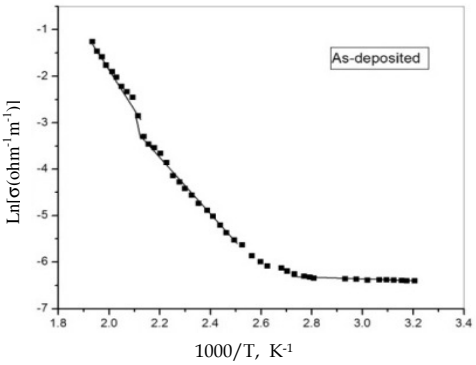


Figure 6(a). Plot of lnσ *vs*. 1000/T for the as-deposited film

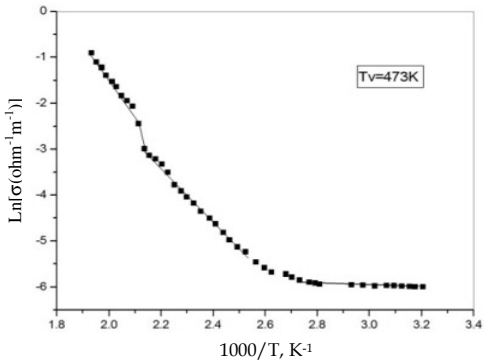


Figure 6(b). Plot of lnσ *vs*. 1000/T for the film annealed at 473 K

The activation energy E_1 is associated with an intrinsic generation process. It is based on the assumption of electron hole pair production via thermal transition from a valance band to the conduction band and may occur in several organic solids. The phthalocyanine owes their intrinsic conductivity to the partial charge transfer from phthalocyanine ring to the central ion. E_2 and E_3 are the activation energy needed to excite the carriers from the corresponding trap levels to conduction band and are associated with the impurity conduction[18]. The activation energies E_1, E_2 and E_3 obtained are collected in Table 2.

Table 2. Variations of activation energies with annealing temperatures

Annealing Temperature, K	Activation Energy±0.01, eV		
	E_1	E_2	E_3
As-deposited	0.53	0.39	0.01
373 K	0.55	0.42	0.01
423 K	0.59	0.44	0.01
473 K	0.62	0.46	0.02

The intrinsic activation energy E_1, increases with increase in annealing temperature. This is attributed to better ordering of the film due to annealing. The value of E_2 and E_3 and its corresponding increase with increase in annealing temperature are attributed to the different distribution of shallow trapping states.

Surface morphological studies

Morphology and crystal growth in organic thin films have much influence on their recording efficiency and optical properties[19]. Surface topography and micro structural features of thin films are controlled by film preparation procedures[20]. It is well known that the morphology of vacuum sublimed organic films varies with deposition parameters[21]. The SEM micrographs shown in Figure 7 a and b display the development of the surface morphology of 165 nm thick $F_{16}CuPc$ films as-deposited form and annealed at 473 K in vacuum.

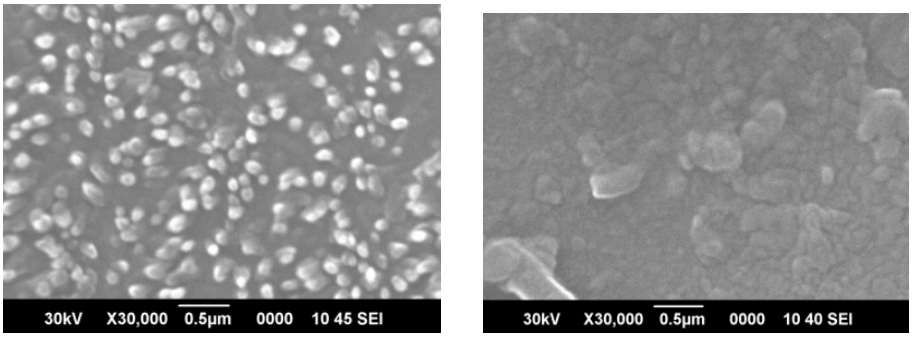


Figure 7. (a) and (b) SEM images of as-deposited and annealed at 473 K in vacuum respectively.

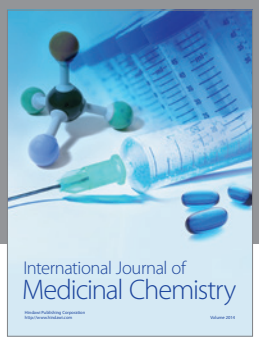
The size of the microcrystalline grains is found to decrease with increase of annealing temperature. As annealing temperature increases agglomerated forms of the particles and cloudy nature is obtained. The fine grain crystallite on the as-deposited films is transformed to a structure of nature with agglomerated form. The microcrystalline grain boundaries of $F_{16}CuPc$ thin films annealed in air increases with increase of temperature. These films are polycrystalline in nature.

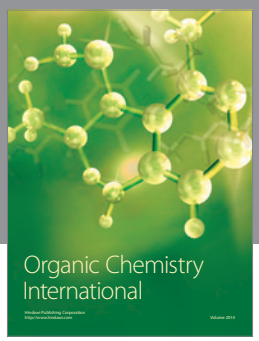
Conclusion

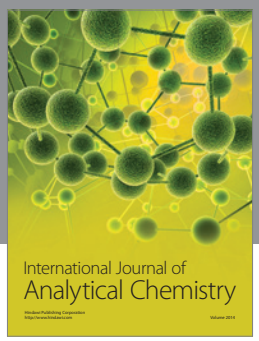
Electrical, optical and surface morphological studies of $F_{16}CuPc$ thin films have been studied with respect to post deposition vacuum annealing. Fundamental optical parameters have been determined from both absorption and reflection data. A direct allowed transition is observed. The optical band gap energy is 3.06±0.01 eV and excitonic energy gap also remains unchanged under different heat treatments. Electrical conductivity by thermal activation process is found to involve different conduction mechanisms. The activation energies in the intrinsic region are observed to increase with increase in vacuum annealing temperature. The increase in activation energy is due to the reversible change in molecular interactions observed in fluorinated phthalocyanines, which are *n*-type semiconductors. In $F_{16}CuPc$ thin films the fluorine atoms are help to block the penetration of moisture. The increase in activation energy is due to the decrease in interaction of molecular π-systems of the fluorinated phthalocyanine. This decrease in interaction leads to an increased barrier of charge transport in the film and hence the increase in activation energy. From the SEM study reveals that the size of the microcrystalline grains is found to decrease with increase of annealing temperature. As annealing temperature is increased a cloudy nature of film is observed.$F_{16}CuPc$ thin films are the potential candidates for the fabrication of molecular electronic devices. In future there is find application on the fabrication and characteristic study of *p-n* junction diodes using CuPc and $F_{16}CuPc$ thin films.

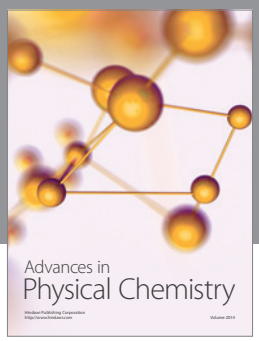
References

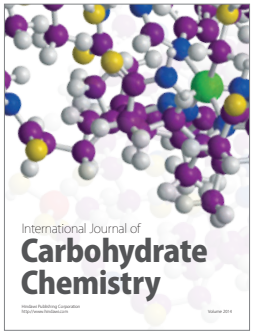
1. Miyata T, Kawaguchi S, Ishii M and Minami T, *Thin Solid Films*, 2003, **425**, 225.
2. Pfeiffer M, Beyer A, Fritz T and Leo K, *Appl Phys Lett.,* 1998, **73**, 3202.
3. Nelson J*, Mat Sci.,* 2002, **6**, 87-95.
4. Joseph C M and Menon C S, *Mater Lett*., 2002, **52(3)**, 220-222.
5. Hohnholz D, Steinbrecher S and Hanack M, *J Mol Struct*., 2000, **521**, 231.
6. Rajesh K R and Menon C S, *Semicond Sci Technol*., 2005, **20** , 464-468.
7. Kobayashi N, *Coord Chem Rev*., 2001, **219**, 99-221.
8. Bao Z, Lovinger A J and Brown J, *J Am Chem Soc*., 1998, **120**, 207-208.
9. Hipps K W, Louis Schudiero, Dan E Barlow and Manning P Cooke, *J Am Chem Soc*., February, 2002.
10. Alonso M I, Garriga M, Ossd J O, Schreiber F, Barrena E and Dosch H, *J Chem Phys.*, 2003, **119**, 6335-6340.
11. Riad A S, *Physica B*, 1999, **270**, 148-156.
12. Moser F H and Thomas A L, The Phthalocyanines, Vols.1 and 2, CRC Press, Boca Raton F L, 1983.
13. EI-Nahass M M, Abd-Ei Rahman K F, Al-Ghamdi A A and Asiri A M, *Physica B*, 2004, **344,** 398-406
14. Bardeen J, Slatt F J and Hall L T, Photoconductivity Conference, Wiley, New York 1965.
15. Azim-Araghi M E and Krier A, *Pure Appl Opt.*, 1997, **6**, 443-453
16. Tauc J, Grigorovici.R and Vancu A, *Phys Stat Solidi*, 1996, **15,** 627.
17. Lucia. E A and Verderame F D, *J Chem Phys*, 1968, **48**, 2674.
18. Hassan A K and Gould R D, *J Phys Condens Matter*., 1989, **1**, 6679.
19. Hisao Yanagi, Takashi Kouzeki and Michio Ashda*, J Appl Phys.*, 1992, **71(10),** 5146.
20. Yuh-Lang Leea, Wen-Ching Tsaib and Jer-Ru Maab, *Appl Surface Sci*., 2001, **173**, 352.
21. Hsieh C J, Liv C J and Ju Y H, *Thin Solid Films*, 1998, **322**, 98-103.











Hindawi

Submit your manuscripts at
http://www.hindawi.com