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Optical and surface morphological studies on CuPcOC$_8$ thin films prepared by physical vapour deposition

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2,3,9,10,16,17,23,24-copper octakis (octyloxy) phthalocyanine (CuPcOC$_8$) thin films deposited at room temperature have exhibited a change in their surface morphology with the post deposition annealing temperature under normal atmosphere.These films have been characterised by optical absorption also. SEM images have shown densely packed nano particles and nano-rod like structures on the substrates annealed at different temperatures. The optical transition was found to be direct allowed and the direct energy gap changed with the annealing temperature. The results of optical and surface morphological studies on CuPcOC$_8$ have been discussed.

Keywords: *copper octakis (octyloxy) phthalocyanine; absorption spectra; annealing temperature; optical band gap; Davydov splitting; surface morphology*

1. Introduction

Research on organic semiconducting thin films has become increasingly important for applications in optical as well as electronic devices, such as light emitting diodes [1], field-effect transistors [2]. Phthalocyanines (Pc's) are well-known organic semiconductors [3–5] and one of the promising materials for organic solar cells [6–11]. These materials are chemically and thermally stable [8, 9] and attempts have been made to use thin films of these materials as molecular components in a number of electronic and optoelectronic devices [7, 12–14]. High rectification ratio has been observed in copper (II) phthalocyanine photo-detector [15]. The photo conducting behaviour [16] and the persistence in photoconductivity [17] of phthalocyanine nanostructured thin films have been studied very recently. The structure, morphology, electronic and optical properties of the films are crucial for their technological applications [15–19]. Recently, studies on the orientation of substituted Pc's on gold have attracted attention of researchers [20, 21]. Among the substituted Pc's, copper (II) ph-

thalocyanine has been found to have superior properties [22–25] than the others.

2,3,9,10,16,17,23,24-copper octakis (octyloxy) phthalocyanine (CuPcOC$_8$) consists of side chains with eight carbon units. It is well known that incorporating substituents onto the Pc ring is the most important method used to tune the physiochemical, electrochemical and spectroscopic properties of phthalocyanine derivatives. Thus far, various kinds of different substituents such as alkyl, alkoxy and thioalkoxy groups have been introduced onto the peripheral and/or nonperipheral positions of the Pc ligand [26]. Because of their large conjugated molecular structure, together with strong π-π interactions between aromatic rings, Pc derivatives have also been used as sample building blocks for ordered molecular systems [27]. Octakis (octyloxy) substituted Pc's show self assembling behavior. Through a self assembling process, functional molecules can self-assemble into a well defined monolayer with various patterns. By accurately controlling the self assembled monolayer, the development of electronic devices is expected. Prior to our studies, only a few data have been available on octa substituted Pc having different functionalities [28–33]. The present work is an at-

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tempt to study the optical and surface morphological properties of CuPcOC$_8$ thin films.

2. Experimental procedure

The CuPcOC$_8$ powder (Fig. 1) used in this study was obtained from Sigma Aldrich Chemicals (USA). Thin CuPcOC$_8$ films were prepared by conventional thermal evaporation technique using a high vacuum coating unit (Hind HiVac 12A4D). The micro glass slides (75 mm × 25 mm × 1.3 mm) that were used as substrates were cleaned before coating, using a liquid detergent, dilute nitric acid, distilled water, acetone and hot air. Thin films were deposited from a molybdenum boat in a vacuum of 1.33×10^{-2} Pa during deposition; the deposition rate was controlled at 2.5 nms^{-1} using a quartz crystal thickness monitor. Further it was cross checked by Tolansky's multiple beam interference technique [34]. The temperature of the substrate was kept at room temperature. The samples were annealed in air for 1 hour at temperatures 323, 373, 423, 473 and 523 K. After annealing the temperature was slowly reduced to the ambient temperature. The absorption spectra of the films deposited onto micro glass slides were recorded on a spectrophotometer (UV-2401 PC, Shimadzu, Japan) in the wavelength range of 200 – 900 nm. All the spectra were taken at room temperature. JEOL JSM-6390 Scanning Electron Microscope was used to record the scanning electron micrograph images of the CuPcOC$_8$ thin films.

3. Results and discussion

3.1. Optical studies

The spectral properties of the Pc's resulted from an aromatic cyclic conjugated π-electron system with 18-electrons, very similar to that of porphyrins, which are very important chromophores in biological light harvesting system and photoreaction centres. The absorption spectra of the as deposited CuPcOC$_8$ thin films of 250 nm thickness and the film after annealing are shown in Fig. 2. It has been suggested that UV-Vis spectra of MPc's originate from the molecular orbitals within the
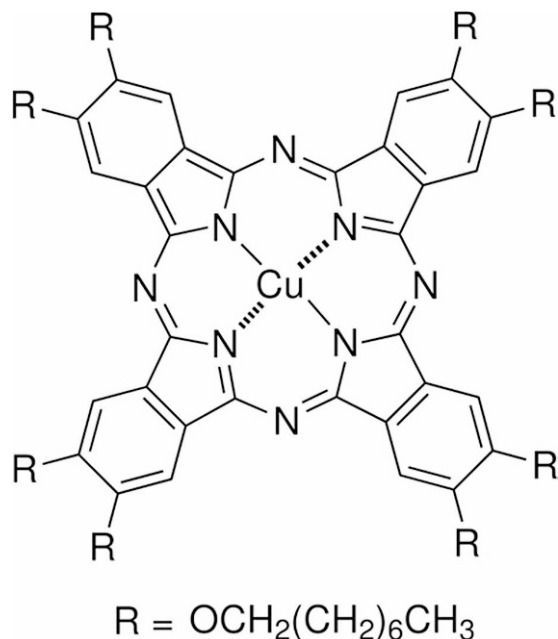

Fig. 1. Molecular structure of CuPcOC$_8$.

aromatic 18 π-electron system and from overlapping orbitals on the central metal [35]. In the near UV-region, the B-band or Soret band [35, 36], representing the $\pi \rightarrow \pi^*$ transition, appears with a peak position in the range of 330 – 345 nm, depending on the annealing temperature of the film. The absorption band in the visible region for each sample of the film, known as the Q-band (representing the $\pi \rightarrow \pi^*$ transition) [36], has a doublet due to Davydov splitting [37]. The position of the absorption peaks, including the amount of Davydov splitting for the different sample films, are shown in Table 1. From Table 1 and Fig. 2, it is clear that the position and relative intensity of the peaks and the amount of Davydov splitting depend on the annealing temperature. The extent of Davydov splitting is related to the differences in the relative orientation of molecules which are close enough to give electronic transitions, namely interactions between the transition dipole moments from adjacent molecules. The high tendency of the self ordering of Pc molecules could be one of the main reasons for anisotropy in the film morphology, depending on the annealing condition. For the as deposited film the intensity of the higher peak is larger than that of the lower-energy peak. This
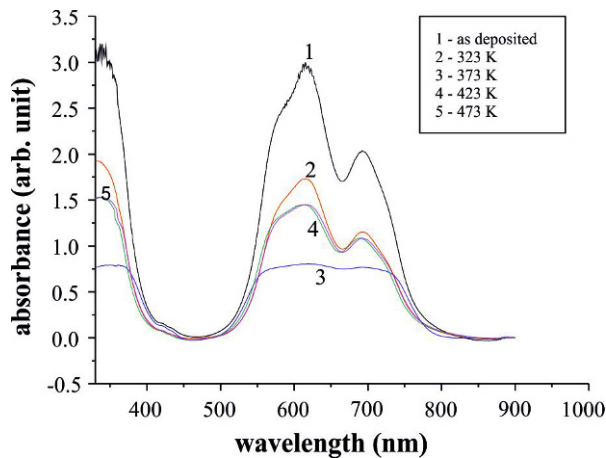
Fig. 2. Optical absorption spectra of CuPcOC$_8$ thin films

Fig. 3. Typical plot of α^2 vs. energy of CuPcOC$_8$ thin film.

behaviour represents the typical features of the α-phase of CuPcOC$_8$ [38]. Similar behaviour was noticed for annealing the CuPcOC$_8$ film up to about 323 K. For annealing at 373 K, the intensity of the higher energy peak becomes smaller and the curve becomes flat, which confirms the formation of the β-phase of CuPcOC$_8$ [38]. For annealing at 423 K and 473 K, the observed peaks are located at the same position, but their intensity is found to be less than that of the α-phase (up to 323 K) which also confirms the β-phase of CuPcOC$_8$ [39].

The variation in absorption coefficient (α) with photon energy ($h\nu$) for band-to-band transition is obtained [40] as:

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

where α_0 is a constant; E is the energy gap and n determines the type of transitions, which is equal to 0.5, 2 or 3/2 for direct, indirect or forbidden transitions, respectively. The dependence of $(\alpha)^{1/n}$ on photon energy ($h\nu$) for onset gaps have been plotted from transmission spectra of CuPcOC$_8$ thin films. For different values of n, the best fit was obtained for n = 0.5, as shown in Fig. 3. The corresponding direct allowed onset energies for different annealing temperatures are listed in Table 1. From Table 1, it has been found that the energy gap changes with an increase in annealing temperature. The changes in energy gap at different annealing temperatures are attributed to the changes in the crystal structure of these films.
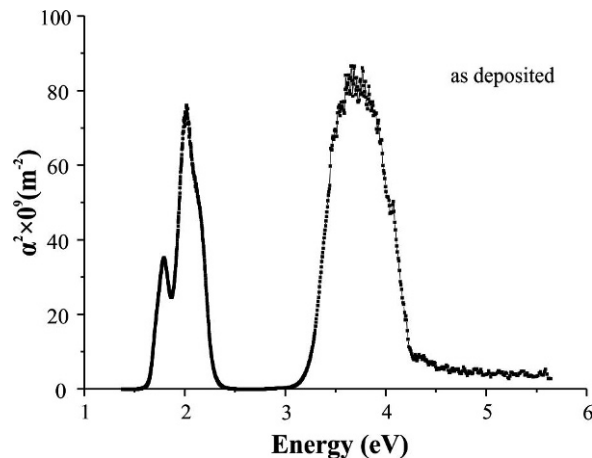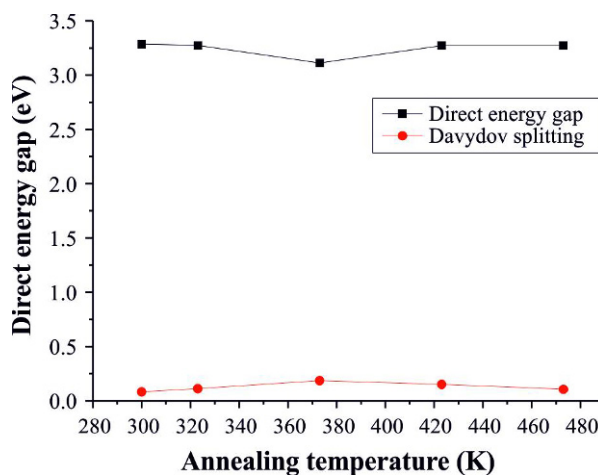

Fig. 4. Variation of Davydov splitting and direct energy gap with annealing temperature.

The plot of Davydov splitting and the direct energy gap versus annealing temperature of the thin film is shown in Fig. 4. Here we observe that the band gap decreases with annealing temperature up to 373 K, which is the transition point. The amount of Davydov splitting is low in this phase. When the β-phase occurs, the band gap remains constant and the amount of Davydov splitting increases to a maximum. Davydov splitting is the splitting of bands in the electronic (or vibrational) spectra of crystals due to the presence of more than one (interacting) equivalent molecular entity in the unit cell. The extent of Davydov splitting depends on the interaction between the transition dipole moments

Table 1. Positions of absorption peak, Davydov splitting and the direct energy gap for $CuPcOC_8$ thin films.

Annealing temperature (K)	Position of absorption peaks (nm)	Davydov splitting (eV)	Direct energy gap (eV)
As deposited	338 615 693	0.08	1.68 1.77 3.29
323 K	337 616 693	0.11	1.66 1.77 3.27
373 K	351 610 696	0.19	1.43 1.61 3.11
423 K	349 616 694	0.15	1.66 1.81 3.27
473 K	340 616 694	0.11	1.68 1.78 3.27

from adjacent molecules. $CuPcOC_8$ thin film deposited at room temperature shows the interaction of the α-phase. The crystal structure of the thin film annealed at 373 K shows the β-phase. At annealing temperatures above room temperature but below 373 K, the transition from crystalline α-phase to the β-phase occurs in the $CuPcOC_8$ thin film. In fact, annealing causes a change in the crystalline phase as well as distortion of the unit cell [38]. As a result, a change in the Davydov splitting is observed with a change in the annealing temperature. The lower value of Davydov splitting in the α-phase could be due to the reduced interaction between the transition dipole moments from adjacent molecules. The change in the crystal structure of the $CuPcOC_8$ thin film with annealing temperature is a possible reason behind the observed change in the band gap with annealing temperature.

3.2. Surface morphological studies

The SEM images of the $CuPcOC_8$ thin film annealed at different temperatures are shown in Fig. 5. Fig. 5(a) shows the SEM image of as deposited $CuPcOC_8$ film at room temperature. Most of the particles are almost spherical in shape and the average size is nearly 42 nm. Fig. 5(b) shows the surface morphology of the film annealed at 373 K. Clearly from this figure, the same types of particles are observed as in Fig. 5(a), but the aggregation of particles can be observed. Fig. 5(c) shows the surface morphology of the $CuPcOC_8$ film annealed at 473 K. Here the film is found to be formed uniformly with vertical nanorods of $CuPcOC_8$ of almost square and rectangular cross sections. Fig. 5(d) represents the same type of ver-

tical nanorods bent over the surface for a $CuPcOC_8$ film annealed at 523 K. The breadth of the rod is about 89 nm. The cross section of the nanorods in this case is also square and rectangular in shape.

Thus the SEM images show the phase change. Thin films deposited at room temperature are in the α-phase. At annealing temperatures above 373 K, a β-phase in $CuPcOC_8$ thin film has been observed. This experiment demonstrates that the phase transition starts at a temperature of 373 K. Thus the SEM images confirm the phase transition of $CuPcOC_8$ thin films which is observed in the optical absorption spectra. The similar behaviour was also observed in the case of CuPc by S. Karan et al. [41].

4. Conclusions

For the growth of $CuPcOC_8$ thin films by vacuum evaporation, the optical property and surface morphology of the thin films were influenced strongly by the post-deposition annealing temperature. With an increase in annealing temperature, the band gap and the amount of Davydov splitting remained almost constant in the α-phase and started to decrease when the β-phase occurred. At low annealing temperatures, most of the nanoparticles were spherical in shape. When the annealing temperature increased, nanorods were observed. Thus the SEM images also showed the phase transition of $CuPcOC_8$ thin films.

(a) as deposited

(b) annealed at 373K

(c) annealed at 473 K

(d) annealed at 523 K
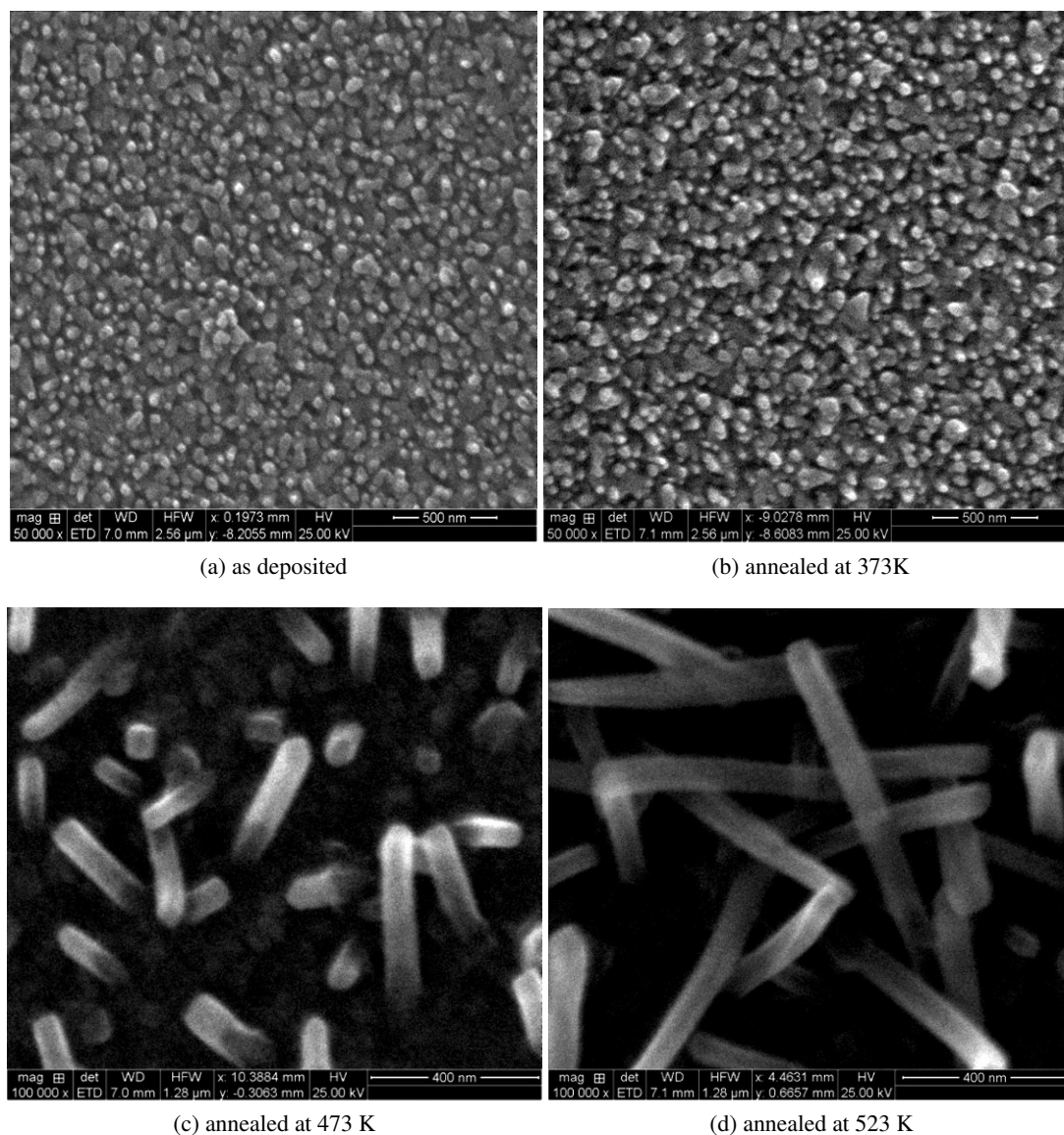
Fig. 5. SEM images of CuPcOC$_8$ thin films (magnification 50 000 × (for a, b) and 100 000 × (for c, d)).

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