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# Optical and Morphological Studies of Copper Phthalocyanine Thin Films

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## ABSTRACT

Today the interest of electronics industry in new organic semiconductors (OSC) for the manufacture of optoelectronic devices has increased. Organic semiconductor thin films have also been used in various optoelectronics and microelectronic devices. Optical and morphological characterization of Copper phthalocyanine (CuPc) thin film vacuum deposited at different thickness was the aim of this work. Copper phthalocyanine thin films grown on glass substrates by thermal evaporation method were investigated using UV absorption spectroscopy with respect to different thickness. Dependence of absorbance on film thickness is studied. The samples prepared at different thicknesses are subjected to optical studies for the determination of the absorbance. The optical absorption properties of the films show strong dependence on film thickness. The surface morphology of the thin films was investigated using Scanning Electron Microscopy (SEM). In this paper, we reported both optical and morphological properties of copper phthalocyanine thin films. For that, we investigate the UV absorption spectrum at room temperature obtained from thermally evaporated thin films of these organic materials.

## KEYWORDS

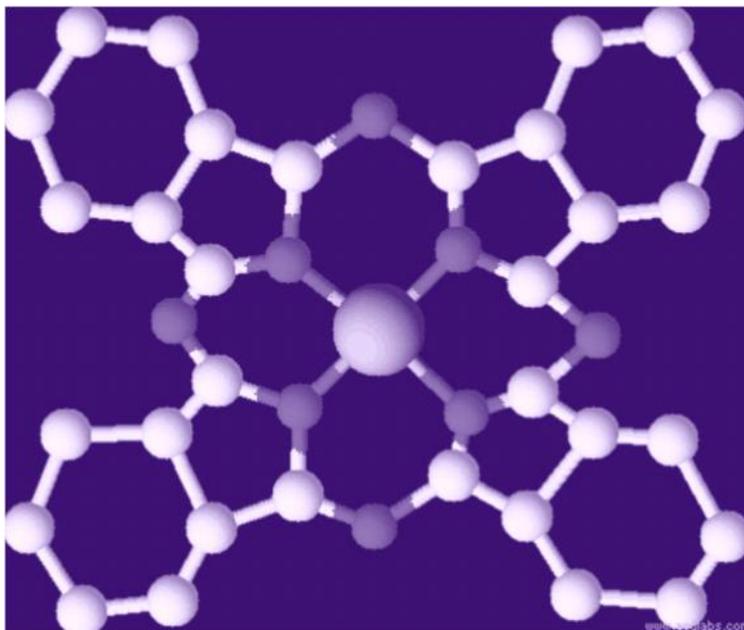
*Thin films, Organic semiconductors, Phthalocyanine, Vacuum deposition.*

## INTRODUCTION

Nowadays research into the applications of organic semiconductors has intensified rapidly. Organic semiconductors are very important class of materials having wide range of applications. Organic semiconductors have been proposed for successful application in optoelectronic devices. In the case of photo detectors, the use of organic semiconductors allows the fabrication of large area devices at relatively low cost and light in weight. Metal substituted (MPc) phthalocyanines are planar conjugated aromatic macrocycles forming molecular crystals with high conductivities, showing a rich absorption spectrum in the ultraviolet and visible ranges as well as effective catalytic properties. During the past decades, a great deal of interest has been focused on the synthesis of metallophthalocyanine and its derivatives due to their applications in many fields [1-8]. They are a class of macrocyclic compounds possessing a system of conjugated  $\pi$ -electrons. Their strong Q-band absorption and excellent photo induced charge generation efficiency facilitate their application in the xerographic photoreceptors of laser printers [9].

Phthalocyanines are organic semiconductors receiving considerable attention because of their suitability as an active layer for organic electronic devices. Phthalocyanines have become a major pigment in the dye industry because of their unique color, low manufacturing cost, high stability, and non-toxicity. Phthalocyanines derivatives can function as an active component in various optoelectronics applications. Because of the very good absorbance of these molecules in the ultraviolet region, there is a considerable interest in the characterization of phthalocyanine thin films. Since most of the phthalocyanines are found to exhibit very good optical absorption and emission in the 500-700 nm regions, they can be considered as suitable candidates for optical amplification in this region [10]. One of the most studied metal substituted phthalocyanines is copper phthalocyanine. Because of the interesting electronic properties of CuPc, we here

describe its film synthesis and optical properties. Although copper phthalocyanine is one of the most studied p-type organic semiconductors, few studies have addressed its molecular orientation and structure as a function of the film thickness. These materials are stable and its structure is reported to be monoclinic. CuPc, whose chemical formula is  $C_{32}H_{16}CuN_8$  are organic semiconductors with excellent chemical stability against heat, light etc. Fig. 1 shows the molecular structure of copper phthalocyanine molecule.



**Fig. 1. Molecular structure of Copper Phthalocyanine**

In this paper the optical and morphological properties of copper phthalocyanine thin films deposited at room temperature will be presented. Puigdollers et al. reported two absorption bands in the 300-450nm and in the 600-750nm regions in CuPc thin films [11]. The higher energy band occurring at around 650 nm is generally known as the Q band, and often exhibits vibrational structure in thin film. The intense band at 300-450nm, which gives the absorption edge, is related to direct electronic transition and is called the B band. The Q-band exists in the visible region of spectra while others B exist in the UV region of spectra. Optical properties were evaluated by absorbance and band gap measurements. Scanning Electron Microscopy (SEM) was used to study the dependence of the crystalline structure.

## EXPERIMENTAL

In a typical experiment, high purity copper phthalocyanine polymorphic was used as the starting material. Pure CuPc powder used in this work was purchased from Sigma Aldrich and no further purification was done. Thin films of CuPc with different thicknesses were prepared using Hind-Hivac thermal evaporation plant (Model No.12A4D) by thermal evaporation technique. Prior to loading into the evaporation chamber, glass substrates were successively cleaned in detergent, acetone, isopropanol and deionized water and dried in an oven. A molybdenum boat was used as a heating source. The source material is evaporated on to glass substrates from a molybdenum boat of dimension 75mm x 25mm x 1.3mm by resistive heating method. The substrate was located about 10 cm from the source and kept at room temperature. The evaporation process is performed within a vacuum chamber under  $2 \times 10^{-5}$  mbar with a deposition rate 3nm/min. The film thickness were deposited at room temperature were controlled by evaporation time and the resulting film thicknesses were measured using a crystal monitor. Fig.3 shows the evaporated thin film of phthalocyanine on a glass substrate. The absorbances of the films were measured at normal incidence in the spectral range 250-800 nm using a UV-VIS spectrophotometer (Model: UV-1600/1700 series, SHIMADZU).



**Fig. 2. Phthalocyanine thin film on glass substrate**

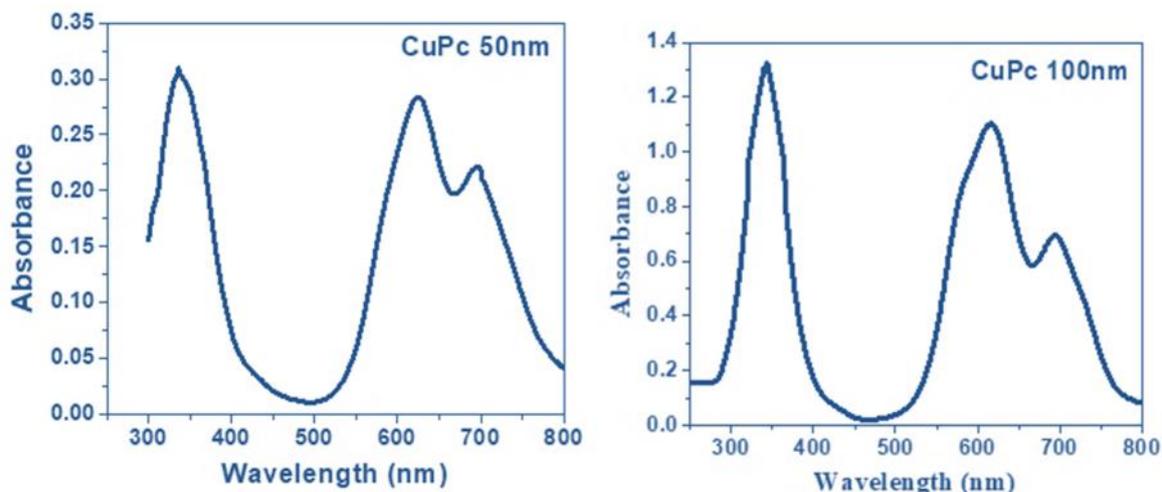
## RESULTS AND DISCUSSION

The research into the behavior of the organic semiconducting materials is normally carried out optically. That is, the absorbance properties are explored in optical method. The aim of this study was to fabricate and optically characterize CuPc thin films. The samples of CuPc films were prepared for two thicknesses as 50nm and 100nm. These films were prepared on a glass with base pressure of approximate  $10^{-5}$  mbar using thermal evaporation technique. The optical properties and spectral behavior of phthalocyanine films as a function of various thicknesses were studied at room temperature using UV - Visible absorption spectra. Increase in thickness, leads to increase in absorbance of films and shifts peak position of all bands towards low energy side of spectra [12]. The optical properties of thin films of metal phthalocyanine have been investigated in the spectral range 250-800 nm. The lower energy band, occurring at around 650 nm, is generally known as the Q band [13].

Copper phthalocyanine molecules have two main absorption bands in the visible/near-UV region of the spectrum. In the solid state, these bands are broadened and overlap so that phthalocyanines absorb light throughout the entire visible region of the electromagnetic spectrum [14]. Fig. 3 shows the optical absorption spectra of CuPc thin films deposited at different film thicknesses. It has been suggested that the UV-Vis spectrum of MPCs originates from the molecular orbitals within the aromatic 18  $\pi$ -electron system and from overlapping orbitals on the central metal. The optical band gap of the CuPc samples has been estimated by performing a fit to the exponential part of the spectra using the equation for allowed direct transitions [15,16]:

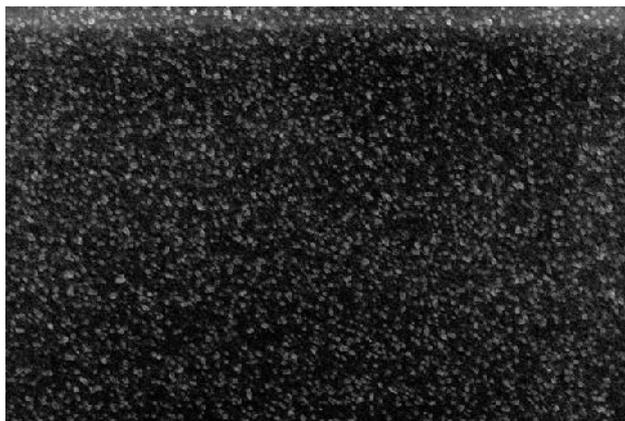
$$(\alpha h\nu) = A(h\nu - E_g)^2$$

where A is a constant and  $E_g$  is the optical band gap energy of the semiconductor. The band gap was calculated from the plot of  $(\alpha h\nu)^2$  versus  $h\nu$ . The values obtained for all the samples are around 1.63 eV and no conspicuous changes were observed as the function of thickness.



**Fig.3. Absorbance versus wavelength spectrum of CuPc thin film**

Fig. 3 shows the absorbance versus wavelength spectra of CuPc thin films with different thicknesses of 50nm and 100nm respectively. This study shows the, Q-band and B-bands in the absorption spectrum of CuPc thin films. From figure, it is clear that, there are distinct characterized peaks in the spectral distribution of absorbance of CuPc thin films for various thicknesses. It is observed that the peak of high intensity absorption maxima of Q band observed at 614nm. The band became prominent with increasing thickness, however there was no shift found with increasing film thickness. The absorption maxima of low energy peak of Q band observed at 697nm also become prominent with increasing film thickness. Also the maxima of B band observed at 342nm.



**Fig. 4. SEM images of Copper phthalocyanine thin film**

Fig. 4 presents a plan view SEM micrograph of the CuPc thin film grown by the thermal evaporation setup at room temperature. In this figure a kind of polycrystalline structure is observed, it corresponds to a three-dimensional growth. This structure of the film is uniform. The shape of the particles is spherical in nature. The particle size observed from the SEM images was in an order of 20 – 30 nm. The SEM micrographs reveal uniform and smooth featureless surfaces with no clear crystal grain structure.

## CONCLUSION

From the present work, we can conclude that the metal substituted phthalocyanine thin films of various thicknesses on glass substrate have been thermally evaporated successfully. The optical properties of copper phthalocyanine thin layers have been investigated using various film thicknesses. Copper phthalocyanine thin films deposited at different film thickness show polycrystalline structure. The absorption spectrum in the visible region consists of two distinct bands of copper phthalocyanine thin films deposited at room temperature using vacuum deposition. The Q and B bands are observed in the absorption spectrum of the films of CuPc materials at all different thicknesses. The main optical parameter, absorbance was found to be dependent of the film thickness for the two studied films. That is, the intensity of the Q and B bands are found increased with increasing thickness. Increasing film thickness does not allow any conspicuous changes in the band gap. However, no significant changes are observed in the morphological properties.

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