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# Optical Studies of Metal Substituted Phthalocyanine Thin Films

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## ABSTRACT

Nowadays the interest of electronics industry in new organic semiconductors for the manufacture of optoelectronic devices has increased. Organic semiconductor (OSC) thin films have also been used in various optoelectronics and photovoltaic devices. The aim of this work is to study the influence of film thickness on the optical behavior of thermally evaporated metal substituted phthalocyanine thin films. Thin films of metal substituted phthalocyanines are deposited by thermal evaporation technique under high vacuum at room temperature. Dependence of absorbance on film thickness is studied. The samples prepared at different thicknesses are subjected to optical studies for the determination of the absorbances. In this paper, we reported the optical properties of two OSCs such as copper phthalocyanine (CuPc) and cobalt phthalocyanine (CoPc). 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 field effect transistors, Phthalocyanine, Thermal evaporation.*

## INTRODUCTION

Over the past thirty years, research into the applications of organic semiconductors has intensified rapidly. Organic semiconductors are a very important class of materials having wide range of applications. The characterization of organic semiconductors is receiving great attention because of the increased activity in their synthesis and potential use in a wide range of large area flexible, electronic, and photonic devices, such as photo detectors, organic field effect transistor, memory, organic light emitting diodes and sensors. The electronic conductivity of these materials lies between that of metals and insulators. OSCs have shown immense potential in terms of their numerous technological applications which were earlier dominated by inorganic semiconductors. Though their electron mobility is much lower than that of typical semiconductors, OSCs show promise in low-cost, flexible and lightweight semiconductor applications. Phthalocyanines (Pcs) are organic semiconductors receiving considerable attention because of their suitability as an active layer for organic electronic devices. Pc is an organic semiconductor has excellent stability against heat, light, moisture and oxygen.

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 [1]. The peaks in the absorption spectra are due to overlapping of electron orbitals created by the conjugated double bonds within the crystal structure of the film. These electrons are able to transfer energy throughout the structure [2]. These materials are stable and its structure is reported to be monoclinic. CoPc, whose chemical formula is  $C_{32}H_{16}CoN_8$  and CuPc, whose chemical formula is  $C_{32}H_{16}CuN_8$  are organic semiconductors with excellent chemical stability against heat,

light, moisture and oxygen, low heat conduction, and diversity of optical properties. Fig. 1 shows the molecular structure of phthalocyanine molecule.



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

In the present study, CoPc and CuPc thin films were deposited by vacuum deposition and their optical properties were studied. Puigdollers et al. reported two absorption bands in the 300-450nm and in the 600-750nm regions in CuPc thin films [3]. Similar behaviors of the absorption spectra are obtained for CoPc thin films [4]. 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.

## EXPERIMENTAL

The metal phthalocyanine powders with high purity used in this study are obtained from Sigma Aldrich chemicals. Thin films of both CoPc and CuPc with different thicknesses were prepared using Fillunger thermal coating system (Model: TCS-0204) by thermal evaporation technique. Before starting the deposition, the glass substrate was cleaned in an ultrasonic bath for 10 min using acetone followed by rinsing in deionized water. The substrate was dried in open air in a cleaned room. 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. During deposition, the pressure in the vacuum chamber was kept constant at about  $2 \times 10^{-5}$  mbar and the deposition rates of all the films were at about 5 nm/min. Also the substrate is placed at a distance of 10cm from the molybdenum boat. Thickness of the film is measured from the crystal monitor [5]. 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 DISCUSSIONS

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 CoPc and CuPc thin films. The samples of CoPc films were prepared for two thicknesses as 50nm and 150nm. Also 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 absorbance of films and shifts peak position of all bands towards low energy side of spectra [6].

To study the effect of thickness on optical properties, thin films of CuPc and CoPc are deposited on the substrates with different thickness at room temperature. Hsieh et al. stated that the characteristic of vacuum sublimed organic films varies with deposition parameters like thickness, substrate temperature and annealing [7]. 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. In the solid state, these bands are broadened and overlap so that phthalocyanines absorb light throughout the entire visible region of the electromagnetic spectrum [8]. 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 [9].

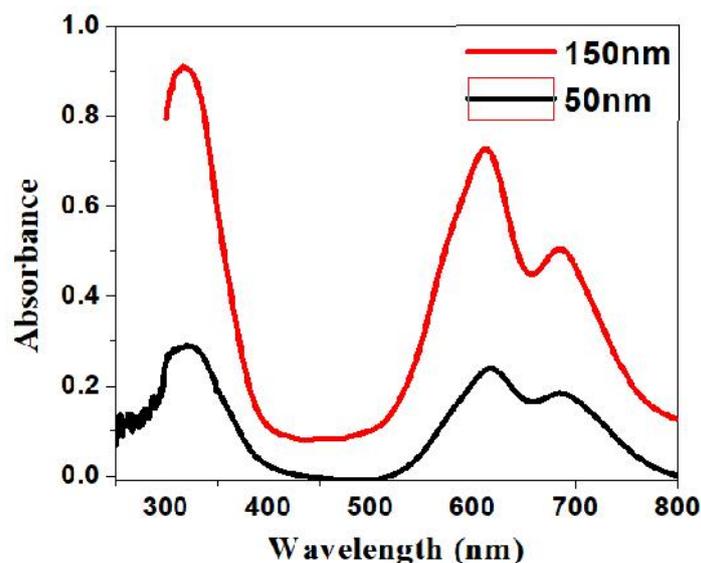
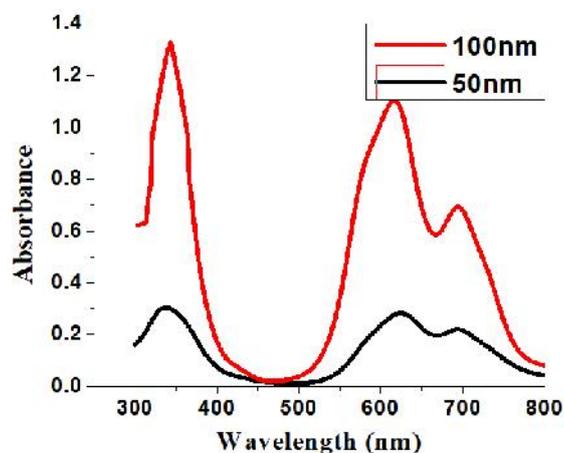


Fig.3. Absorbance versus wavelength spectrum of CoPc thin film

The absorbance spectra in the UV–VIS region of spectra for CoPc thin films of different thickness 50nm and 150nm shows that absorbance of films increases with increasing film thickness. CoPc molecules shown in figure have two main absorption bands in the UV-visible region of the spectrum, and this is agreement with many researchers [10,11]. In the Q-band region, it is noticed from figure that the doublets are the only features in absorbency spectra CoPc films [12,13]. These representing the first and second  $\pi - \pi^*$  transition appear at 688nm and 618nm respectively. In the near UV region a single peak is observed at 328nm (B-band). The high energy peak of the Q-band has been assigned to the first  $\pi - \pi^*$  transition on the metal phthalocyaninemacrocycle [14]. The low energy peak of the Q-band has been variously explained as a second  $\pi - \pi^*$  transition. The spectral distribution of absorbance in the wavelength range 250-800 nm for as deposited CoPc films with different thickness of 50nm and 150nm were shown in Fig.3.



**Fig.4. Absorbance versus wavelength spectrum of CuPc thin film**

Fig. 4 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.

## 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. Optical properties of the CoPc and CuPc thin films were studied with different film thickness at room temperature. The Q and B bands are observed in the absorption spectrum of the films of two 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.

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