EFFECT OF ANNEALING TEMPERATURE ON THE OPTICAL PROPERTIES OF COPPER PHTHALOCYANINE (CUPC) THIN FILMS PREPARED BY VACUUM EVAPORATION METHOD

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ABSTRACT:
Thin films of copper phthalocyanine CuPC with different thicknesses (200,215,235,255) nanometers have been prepared by using the technique of thermal evaporation in a vacuum (PVD) on soda glass substrates. The film, with a thickness of 255 nm, was thermally treated (vacuum-annealing) with different annealing temperatures (300,373,473) in order to study the effect of the annealing temperature on the optical properties of this film. Before and after the annealing process, the effect of the annealing temperature Ta on the optical properties of those films within the visible part of the optical spectrum was studied in order to take advantage of the absorbance and transmittance spectrum of the films and to know the value of the absorption and extinction coefficient. The values of each of the absorbance, transmittance and optical band energy were calculated, and these values were found to change with the change of thickness as well as with the change of the annealing temperature.

Keywords: Copper Phthalocyanine, Absorbance, Transmissivity, extinction coefficient, Energy band gap.

I. INTRODUCTION:
The semiconductor properties of organic semiconductors are due to the existence of conjugated double bonds in their molecular structure, where Π orbitals are the orbitals most relevant to the photoelectric characteristic of organic semiconductors [1]. The reason that makes organic semiconductors attractive and a candidate for optoelectronic applications is the flexibility of producing new molecules with desirable specifications by changing the atomic arrangement or functional groups of these compounds, which leads to a change in the electronic properties of the molecules [2].

Metallic phthalocyanine (MPC) is an important class of materials for optoelectronic device applications. Several metallic phthalocyanines have been investigated for various applications such as thin-film transistors, photovoltaic cells as well as gas sensors [3].

Copper phthalocyanine (CuPC) is a positive-type organic semiconductor, that is stable in air and can be used in many organic applications such as field-effect devices as well as in organic solar cells in addition to many other applications. The optical absorption properties of thin films in general are considered one of the basic and important parameters for estimating the suitability of any material for optoelectronic applications. Through this research, the effect of annealing temperature on the optical properties of copper phthalocyanine films was studied.

The absorption region B or the so-called Soret band [4,5] which is caused by the transition (π → π*) appears with a peak position in the range (330-335) nm where this value depends on the nature of the substrate as well as on the conditions and value of the annealing temperature. The absorption band in the visible region of each film sample is known as the Q-band which is the result of the π→π* transition [5], the peak is doubled due to Davidoff splitting [6].
II. EXPERIMENTS:

The copper phthalocyanine powder (Pigment 85%, Baoji Guokang Bio-Technology Co., Limited, Baoji City, China) was kept in a molybdenum boat through which the powder was heated by a high current (current rating 100 A) whose intensity is controlled by a special converter. The transformer is capable of providing current (150 A) at voltage (20 V), i.e., used to provide additional current to heat the molybdenum boat through which the powder CuPC is vaporized. Prior to the fumigation (evaporation) process of copper phthalocyanine powder, the material is carefully vacuumed at a low temperature for approximately 45 minutes using a closed shutter. CuPC thin films were deposited at room temperature on previously cleaned glass substrates, under pressure ($10^{-6}$ Torr) using a coating unit (12 A 4D Hind Hivac, India). A rotary motor is used in order to maintain the thickness of the film within the required value. The rate of the evaporation process was also controlled to keep it constant during the evaporation of thin films. The thickness of the films obtained is within (200,215,235,255) nanometers, where the thickness of the films was measured using the optical method. The film, with a thickness of (255) nm, was annealed at different temperatures (300,373) K using a vacuum furnace (annealing-vacuum) for one hour. By observing the films obtained, the adhesion of the films to the substrate appears to be highly good. The prepared samples were studied for their optical properties under the same conditions (similar environment) where optical measurements were made using a visible spectrophotometer (Shimadzu 160 A). The transmittance spectra were recorded, then the absorption edge was analyzed in order to obtain the optical bandgap value. The effect of the annealing temperature on the optical bandgap value was studied.

III. RESULTS AND DISCUSSION:

3.1 Thin film thickness effect

Figure 1 shows the change in the transmittance value of CuPc thin films of different thicknesses. From the figure, we conclude that the value of the permeability varies with the thickness of the thin films. Organic molecules in general and phthalocyanine molecules (PC) and their derivatives in particular show abnormal optical properties due to their distinctive aromatic ring structure, which has two types of energy bands as it is known, (Q-band) is one of the bands, which is equal to the α-band in porphyrin And the other is called (B-band) or (soret-band), which is equivalent to γ, in porphyrins. The origin of Q-band and B-band is the product of transition from a1u to Eg instance (n → π*) and a2u Eg instance (π → π*) instance respectively [7]. The reason for the high-energy peak of the (Q-Band) is assigned to the first transition of (π→π*) over the large phthalocyanine (PC) cycle [8]. The low-energy (Q-band) peak seen during the plot was variously interpreted as resulting from a second transition (π→π*) [8].

![Figure 1. The change of transmittance value with wavelength for CuPC films of different thicknesses.](image-url)
Through Figs 2 and 3 it can be observed that a variation in the value of the absorbance (A) as well as the extinction coefficient ($k_f$) with the wavelength of CuPc thin films of different thicknesses. It can be concluded from the graph that the absorption and extinction coefficients vary in value as the value of the thickness of the thin films is changed.

In copper phthalocyanine (CuPc) films there is an absorption peak appearing in the near ultraviolet (UV), B-band (soret band) below 470 nm where the transition ($\pi \rightarrow \pi^*$) occurs. The Q-band transition ($n \rightarrow \pi^*$) appears in the visible region at about (570–660) nm. We note that this band contains double peaks for all samples resulting from exciton formation [10]. By observing the peak positions in the transmittance and reflection spectra in the absorption region, the structure of copper phthalocyanine films was stable. The refractive index and the absorption index are practically independent of the thickness of the thin films.

Absorption coefficient, this parameter depends on the wavelength of CuPc precipitated films of different thicknesses as well as of the annealed films; As shown in Figure 4.
Figure 4. The change of the absorption coefficient value with the wavelength of CuPC films of different thicknesses.

As this figure shows, the absorption coefficient of CuPc thin films is shown by the strong absorption in the Q and B bands for the wavelength region between 610 nm and 750 nm for Q band and between 320 nm and 380 nm for B with a sharp edge in the long term of the length side the wavelength is from (710 nm) to (790 nm) for the Q-band and from (350 nm) to (390 nm) for the B band for unplasticized films of different thicknesses.

Figure 5. The change of the extinction coefficient with the wavelength of CuPC films of different thicknesses.

The optical energy gap, in order for the electron to become free in the conduction band, it must leave the valence band and this needs to obtain sufficient energy equal to the value of the energy gap. We can measure the energy gap by determining the absorbance. The optical bandgap (Eg) values of CuPc thin films for the edges of the B and Q bands were determined using the Tauc equation for the permissible direct transition. The UV visible
spectrum gives the absorption edge of a band called the B-band or Soret which appears in the UV region between 350-370 nm as shown in Figure 2. The UV visible spectrum gives the absorption edge of a band called the B-band or Soret which appears in the UV region between 350-370 nm as shown in Figure (6). The other known band is shown As (Q-band) in the visible region between (630-710) nm as shown in Figure 4 and for different thicknesses When the thickness increases, we notice a decrease in the value of the optical bandgap as shown in Table (1) Which is in agreement with previous studies [11], This behavior of the films was due to the growth of the grain size, as well as the decrease of the impurity states near the bands.

![Figure 6](image)

**Table 1. Optical bandgap value of CuPc thin films with respect to the change of film thickness**

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>Energy gap (ev) B-band</th>
<th>Energy gap (ev) Q-band</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Q₁</td>
</tr>
<tr>
<td>200</td>
<td>3.25</td>
<td>1.75</td>
</tr>
<tr>
<td>215</td>
<td>3.20</td>
<td>1.72</td>
</tr>
<tr>
<td>235</td>
<td>3.16</td>
<td>1.69</td>
</tr>
<tr>
<td>255</td>
<td>3.10</td>
<td>1.67</td>
</tr>
</tbody>
</table>

3.1 Annealing temperature effect :

Figure 7 shows the transmittance spectrum of CuPc films at different annealing temperatures. It can be seen that at longer wavelengths (λ > 900 nm) all films of copper phthalocyanine become transparent and do not scatter or absorb any light, while at shorter wavelengths (λ < 900 nm) the presence of absorption can be seen. The transmittance value increases slightly with increasing annealing temperatures (298, 343) K for both B and Q bands and the transmittance decreases slightly at (423) K, which may be due to the phase change of CuPc films. The differences of the transmittance value with the annealing temperature of the Q band are larger than the differences in the B band, and this is in agreement with previous studies [12].
Figure 7. Optical transmittance (T) spectra of CuPc films at different annealing temperatures.

The annealing process at 300 K and 373 K increases the absorption of the films compared to that of precipitated ones and also shifts the peak positions of all bands towards the lower energy side of the spectra. This may be due to the loss that occurs as a result of the unstable conformation on the surfaces of the thin copper phthalocyanine films. Some researchers mentioned that the unstable conformation layer may be present on the CuPc films and can only be removed by heat treatment (annealing process) [13].

Figures 8 and 9 show the change in the value of the absorbance as well as the extinction coefficient with the wavelength of CuPc films that were annealed at different temperatures, and through the graph the spectrum reveals that both the absorbance and extinction coefficient of the thin films increase with the increase in the annealing temperature.

Figure 8. Optical absorption spectra of CuPc films at different annealing temperatures.
Figure 9. extinction coefficient of CuPc films at different annealing temperatures.

Figure 10 shows the photon energy value of CuPc films of 255 nm thickness annealed at different temperatures. We notice from the graph that the optical energy gap decreases slightly with the increase in the annealing temperature before reaching (473) K, and this change may be attributed to the increase of defects around the grain boundary or due to the decrease in the local states in the band gap, and the increase in the value of the optical energy gap relative to the annealing temperature at (473) K is due to the shift from the β phase to the α phase, which agrees with studies [14] and is shown in Table (2).

![Graph showing extinction coefficient of CuPc films at different annealing temperatures.]

Table 2. Optical bandgap values for CuPc thin films and annealing at different temperatures.

<table>
<thead>
<tr>
<th>T_a (K)</th>
<th>Energy gap (eV) B-band</th>
<th>Energy gap (eV) Q-band</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Q1</td>
<td>Q2</td>
</tr>
<tr>
<td>300</td>
<td>3.35</td>
<td>1.81</td>
</tr>
<tr>
<td>373</td>
<td>3.31</td>
<td>1.78</td>
</tr>
<tr>
<td>473</td>
<td>3.40</td>
<td>1.84</td>
</tr>
</tbody>
</table>

Table 4 shows the optical bandgap values of CuPc films, it can be concluded from the obtained results and fixed in the table that these films only have the allowed transition [15]. In general, the phthalocyanine dye absorbs light...
on both sides of the bluish-green area and can be used as photoconductors as well as chromatic filters [16]. Optical analysis of CuPc confirms the above result.

IV. CONCLUSION:

The value of the optical band gap decreases with the increase in the thickness of the thin film. Also, the value of the optical bandgap decreases at the annealing temperature 300 and 373 K, and increases at (473 K). The value of the absorption and extinction coefficients varies with wavelength and increases with increasing thickness of the thin film and annealing temperature (300, 373 K) and decreases at (473 K). The optical band gap decreases with the increase in the thickness of the films and decreases with the increase in the annealing temperature. The optical results obtained for these films indicate that copper phthalocyanine is likely to be used as a material in photovoltaic applications.

REFERENCES: