Structural, surface morphology and optical properties of annealing treated Copper Phthalocyanine doped Fullerene (CuPc: C_{60}) thin films

Ameer F. Abdulameer¹, Lamiaa K. Abbas¹, Noor S. Sadeq², Zaid G. Mohammadsalih³*

¹Department of Physics – College of Science – University of Baghdad
²Materials Science Branch- Applied Science Department- The University of Technology
³Applied Science Research Unit- Applied Science Department- The University of Technology

Corresponding author 100170@uotechnology.edu.iq

Abstract

The doping process with materials related to carbon has become a newly emerged approach for achieving an improvement in different physical properties for the obtained doped films. Thin films of CuPc: C_{60} with doping ratio of (100:1) were spin-coated onto pre-cleaned glass substrates at room temperature. The prepared films were annealed at different temperatures of (373, 423 and 473) K. The structural studies, using a specific diffractometry of annealed and as deposited samples showed a polymorphism structure and dominated by CuPc with preferential orientation of the plane (100) of (2θ = 7) except at temperature of 423K which indicated a small peak around (2θ = 31) for C_{60}. AFM remarks showed the existence of a compact packing film with a smooth surface. The FTIR spectra emphasized the bonding between CuPc and C_{60}. UV-Vis Absorption spectroscopy confirmed that the CuPc was dominating the optical properties with a small shift in Q band towards higher wavelengths.

Keywords: CuPc: C_{60}, doping, Structural, Surface Morphology and Optical Properties

1. Introduction

The doping of an organic semiconductor is achieved in different ways compared to its counterparts of inorganic semiconductors, such as silicon, due to the chemical properties as well as the different charge storage mechanisms related to organic ones [1]. There are four strategies to dope organic semiconductors [2], electrochemical, chemical, interfacial, and photo-doping. The absorption of photon is associated with range of photo-physical procedures that are contend for evaluating the responsivity. The coupling of acceptor with donor can promote the generation of free carriers as well as the charge separation. It is confirmed that the doping increases the conductivities by 5 - 6 orders [3], which is often lead to a device improvement. However, it is important referring to the fact that while chemical procedures permit charge carrier generation of the required sign, the photo-doping yields to the generation of charge carriers and demands a method to separate them.
The scientific fact related to the controlled molecular doping of organic materials was emerged in 1999 by Pfeiffer et al. [4, 5].

P-doping can be obtained by the addition of a dopant which represents an acceptor molecule. Electrons are showing transition from the HOMO related to the matrix to the LUMO of the dopant and free holes are generated on the HOMO of the matrix as clarified in Fig (1) [6, 7]. To attain an efficacious p-doping through an energetically preferential electron transition, the LUMO level of the dopant should be energetically deeper than the HOMO of the matrix. Therefore, C_{60} chosen as dopant for CuPc (Fig. (2) [7].

**p - doping**

![Diagram showing the principle of P-doping](image)

*Fig. (1) The precept of P-doping, from the HOMO of the matrix to the LUMO of the dopant, an electron transition should be occurred.*

![Energy diagram of CuPc and C_{60}](image)

*Fig. (2) Energy diagram of the CuPc and C_{60}*

The selection of a good solvent is an important parameter according to its influential role for the nano-morphology without altering the absorption spectra of the materials. Regardless the chemical specifications of the solvent, the time required to achieve volatility is considered as an important parameter [8]. On the other hand, when mixing two materials and aiming to ensure a homogeneous distribution of the dopant within the doped material, a successful selection of a co-solvent will lead to achieve the desired goal, because the use of different solvents may lead to heterogeneity in mixing when preparing films using the spin coating method due to the different densities of the different solvents.
It has been confirmed that annealing treatments, carried out after the deposition process, are occasionally allow the phase separation phenomena and enlargement in crystals dimension. Consequently, the charge carrier transport is expedited.

In this work, the copper Phthalocyanine CuPc is employed as an electron donor (doped material), which has shown a considerable absorption in the visible region [9, 10], while the fullerene C_{60} is used as an electron acceptor (dopant material) [11, 12]. Therefore, the collaborative employment of these materials is expected to be very promising as a photoactive layer for photon-to-electric energy conversion and other applications.

2. Experimental Details

The organic materials used in this study were CuPc (99%), and C_{60} (99.95%), purchased from Sigma-Aldrich all used as received. To prepare CuPc doped C_{60} with ratio of (100:1) solution, (15:0.15) mg dissolved for each milliliter of chloroform, and kept in a small closed glass tube, then stirred by a magnetic stirrer as shown in Fig. (2-2) for 30h with temperature of 40°C, then, filtration was performed for the mixture by employing filters of 0.45µm and 0.2µm, respectively. Finally, the mixture was stirred for 5h by magnetic stirring process for obtaining an identical solution.

CuPc:C_{60} deposited on a glass substrate using spin coater device with speed of 1000 rpm for 1 min. The resultant films were apparently good with a uniform thickness suitable for studying the physical properties which are studied under the influence of heat treatment for different temperature.

The structure of the CuPc:C_{60} thin films was analyzed and the intensity was recorded as a function of Bragg angle using X-ray diffractometric system (Shimadzu XRD 6000, Japan). Cu (Kα) was the used source of radiation which has a wavelength of λ = 1.5405 Å, the current was 30.0 mA and the voltage was 40 kV. The scanning angle 2θ was varied within the range of (30-300) with speed 5.0000(degree /min) and preset time = 0.24 (sec).

W.L Bragg was able to deduce his law which stands on the basis that the difference in path between two scattered rays of the same phase equals to whole numbers of X-ray wavelength, and it can be written as [13].

\[ n \lambda = 2 d \sin \Theta_B \] ...........................(1)

where \( \Theta_B \): Bragg's angel, \( \lambda \): wavelength in (nm), \( d \): inter-planer spacing, \( n \): spectrum order (n = 1, 2, 3 ...).

The average grain size (G.S) of crystalline material was calculated using Scherer relation [14].

\[ \text{G.S} = (0.9 \lambda) / \text{(FWHM Cos} \Theta) \] .................... (2)

where FWHM: Full Width at Half Maximum measured in radian.
Surface morphological measurements for the annealed and as deposited CuPc doped C₆₀ thin films were performed by using CSPM-AA3000 contact mode spectrometer, Angstrom, Advanced Inc. Company, USA.

FTIR spectra for the annealed and as deposited CuPc:C₆₀ thin films were attained by Thermo Scientific™ Nicolet™ iN™10, USA. Infrared Microscope was adjusted over the range of 400-4000 cm⁻¹ with resolution of 4 of the spectra obtained at room temperature and recorded in the transmittance mode.

Absorption represents the reduction taking place in the energy of electromagnetic radiation when entering a specified medium so when alight of intensity (I₀) incident on a film of thickness (t), when the intensity of transmittance ray (Iₓ) is given by [15].

\[ Iₓ = I₀ \exp (\alpha t) \]  \( \text{(3)} \)

Tauc plot is drawn to determine the optical gap for the semiconductor [16] by plotting the quantity \( \nu \) versus \((\alpha \nu)^{1/r}\), where \( \alpha \) is the absorption coefficient, and the value of \( r \) denotes the nature of the transition [17] which is equal to 1/2 in this study because of direct transitions of CuPc:C₆₀ blend.

\[ \alpha \nu = B (\nu - E_g)^{r} \]  \( \text{(4)} \)

A double beam type UV-visible spectrophotometer supplied by Japanese company (Shimadzu) was utilized to record the optical measurements of deposited and annealed CuPc: C₆₀ thin films on glass substrate in the wavelength range (300-800) nm.

3. Results and Discussion

Fig. (3) represents the patterns of X-ray diffraction of the as-deposited and heat treated CuPc: C₆₀ thin films which prepared by solution process using spin coating technique. The XRD patterns for all prepared and annealed films show that the structure is varied between polycrystalline and amorphous phases which is called polymorphism structure. They display a strong reflection at (001) orientation around \( 2\theta = 7^\circ \) and this peak belong to CuPc phase. Also, another small beak around \( 2\theta = 9.12^\circ \) can be seen.

It was observed that the well-defined peaks in this pattern correspond to the ordered CuPc crystalline structures. However, after the addition of C₆₀ nano-particles, the prevailing crystalline structure of CuPc phase is reduced as depicted in Figs. (3). For molecular CuPc, the sticking molecules of C₆₀ on the CuPc may lead to a strong alteration in its crystallinity. The XRD results indicate that as the temperature increases, the grain size is decrease. This means that the crystallization of the films is a function of annealing temperatures.
Fig. (3) The patterns of XRD for the as-deposited and annealed CuPc:C₆₀ thin films.

Table (1): The structural parameters of as-deposited and annealed CuPc:C₆₀ thin films.

| Sample  | 2θ (Deg.) | FWHM (Deg.) | d_hkl Exp. (Å) | G.S (nm) | d_hkl Std. (Å) | phase | hkl |
|---------|-----------|-------------|----------------|----------|----------------|-------|-----|
| R.T     | 7.000     | 0.424       | 12.6178        | 18.8     | 12.640         | CuPc  | (001) |
| Ta=373K | 6.993     | 0.469       | 12.6524        | 17.1     | 12.640         | CuPc  | (001) |
| Ta=423K | 6.980     | 0.471       | 12.6539        | 16.9     | 12.640         | CuPc  | (001) |
| Ta=473K | 7.013     | 0.657       | 12.5945        | 12.1     | 12.640         | CuPc  | (001) |

The AFM measurements for the as deposited and annealed CuPc: C₆₀ thin films are clarified in Fig. (4). The 3-D images clearly show the existence of a compact packing film with a smooth surface. In 2-D images the blended CuPc:C₆₀ films appear as a CuPc planar molecules blended with C₆₀ near-spherical shape molecules which confirm the formation of a good bulk heterojunction at the level of CuPc: C₆₀ which should improve exciton separation and charges transport and consequently enhances photocurrent and efficiency of the device. The morphology parameters listed in table (2).
Fig. (4) 2-D and 3-D Atomic force microscopy picture for CuPc:C$_{60}$ thin film. (a) As-deposited, (b) $T_a=373K$, (c) $T_a=423K$, (d) $T_a=473K$
Table (2): The parameters related to the morphology of the annealed as-deposited CuPc:C₆₀ thin films.

| Sample   | Average Diameter (nm) | Roughness Average (nm) | R.M.S | Peak to Peak (nm) |
|----------|-----------------------|------------------------|-------|-------------------|
| R.T      | 95.03                 | 2.13                   | 2.56  | 10.6              |
| Ta=373K  | 87.73                 | 0.483                  | 0.572 | 2.15              |
| Ta=423K  | 87.01                 | 1.88                   | 2.16  | 7.49              |
| Ta=473K  | 81.26                 | 7.24                   | 8.3   | 40.6              |

Fig. (5) Shows the FTIR patterns for as deposited and annealed CuPc:C₆₀ thin films at different temperature (373, 423 and 473 K). In this figure, peaks locations identified and match them with the standard values, which are achieved in previous researches. The peaks appear at (3758 for N-H bond, 3435 and 2346 for O-H bond, 2923 for C-H bond, 1630 for C=C aromatic bond, 1436 for C-N bond, 1036 for S=O bond, 764, 691 and 632 C-H out of plane bend vibration, 515, 462 for Cu-N bond). The peaks for O-H, in general, decrease with the increment of annealing temperature, while the peaks corresponding to C=C aromatic bond and C-N bond decrease at 373 K then increase at 423 and 473K.

Also, it can be indicated that most of the peaks experienced a slight increase in energy bonds with annealing temperature 373 K which demonstrates the increasing atoms packing with annealing. Increasing annealing temperature up to 423 and 473 K leads to decrease energy bonds, as shown in table (3) as a result of increasing atoms spacing with further annealing.

Fig. (5) FTIR transmittance spectra for as-deposited and annealed CuPc: C₆₀ Thin Films.
Table (3) FTIR bonds recorded at various annealing temperatures for CuPc:C60 thin films.

| Ta (K)   | N-H  | O-H  | C-H  | C=C  | C-N  | S=O  | C-H out of plane bend | Cu-N |
|----------|------|------|------|------|------|------|----------------------|------|
| As       | 3758 | 3435 | 3246 | 2923 | 1630 | -    | 1036                 | 764  |
| deposited|      |      |      |      |      |      |                      | 691  |
|          |      |      |      |      |      |      |                      | 632  |
| 373      | -    | 3438 | 2923 | 1617 | -    | 1047 | 751.18               | 506  |
| 423      | -    | 3432 | 2368 | 2924 | 1630 | -    | 1040                 | 670.48|
|          |      |      |      |      |      |      |                      | 662.49|
| 473      | 3752 | 3444 | 2359 | 2925 | 1729 | 1436 | 1054                 | 673.73|
|          |      |      |      |      | 1631 |      |                      | 467  |

The absorption spectra for copper Phthalocyanine doped fullerene thin films of thickness 100nm are given in the Fig (6). One can observe that the Q band absorption shifts towards longer wavelengths when annealing temperatures are increased. Present study shows Q and B bands.

All spectra display the existence of strong absorption bands in the range of 400 and 800 nm caused by the π-π* transitions of the conjugated macrocycle of 18 π-electrons. The high-energy side of the absorption spectrum shows a sharp absorption edge. The absorbance spectrum shows sharp increase in absorption at wavelength near the absorption edge of the threshold wavelength of the absorbance spectrum, the energy corresponds to this determines the optical band gap of the semiconductor material.

The values of $E_g^{opt}$ are measured using Tauc formula for finding the type of transition. Figs. (7) and (8) show that the relation yields linear dependence, which explains the allowed direct transition. Prior to the heat treatment, $(E_g^{opt})$ has a value of 1.858 eV in Q band, whilst it read 3.2 eV in B band. After performing annealing up to 373 K, it decreases to 1.78 eV and 3.14 eV respectively. The optical band gaps $E_g^{opt}$ for B and Q bands reduce with a higher annealing temperature of (373)K and it enhances again after heat treatment at 423K although it shows a smaller value compared to the value of $E_g^{opt}$ at normal conditions. The behaviour of decrement can be ascribed to the presence of localized states inside the gap due to the amorphous structure of CuPc:C60 after this temperature (373K).
The confirmed localized states and tails are associated to the variation in the structure to be amorphous according to the effect of annealing, which is a prevailing feature of the optical data on amorphous and polycrystalline semiconductors which is ascribed mainly to the structural disorder that can be found at the grain boundaries. However, after performing annealing at Ta=423K, the energy gap increases due to enhancement in structure at this temperature and reduce the localized states.

![Fig. (6) The absorbance of heat treated and as-deposited and CuPc:C₆₀ films as a function of wavelength](image)

*Fig. (6) The absorbance of heat treated and as-deposited and CuPc:C₆₀ films as a function of wavelength*

![Fig: (7) (αhv)² against (hv) of incident radiation for CuPc:C₆₀ films at various temperatures of annealing (B band)](image)

*Fig: (7) (αhv)² against (hv) of incident radiation for CuPc:C₆₀ films at various temperatures of annealing (B band).*
Fig: (8) $(\alpha h\nu)^2$ against $(h\nu)$ of incident radiation for CuPc:C60 films at various temperatures of annealing (Q band).

4. Conclusion

The copper Phthalocyanine was successfully doped with fullerene with good homogenous thin films; the annealing temperatures clearly affected the films characteristics by reducing the grain size as indicated by XRD and AFM measurements, which lead to increase in optical energy gap. The FTIR measurements confirmed the high thermal stability of the blended film as no decomposition appeared with the increment of the annealing temperature.

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