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Structural and Morphological Properties of as-Deposited and Heat - Treated Composite (CuPc/Alq3) Thin Films

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Abstract
In this work, an organic semiconductor of copper (II) phthalocyanine (CuPc) and Tris(8-hydroxyquinoline) aluminum (III) (Alq3) were entirely dissolved in chloroform with various mixing ratios (1:0,0.75:0.25,0.5:0.5,0.25:0.75,0:1) (w/w) to make thin films. They were deposited on a pre-cleaned glass using a spin-coating process and heat-treated at 473 K in vacuum. X-ray diffraction and a scanning electron microscope were used to investigate the films. XRD analysis reveals that CuPc/Alq3 composites have a polymorphic structure, with the exception of Alq3's amorphous structure, the crystallinity increases after annealing, but decreases when the concentration of Alq3 is increased. The quantity of (CuPc) rod-like structure and (Alq3) grain-like islands structure depends on the percentage of the combination. The compositional parameters of as-deposited and annealed thin films were explained using EDX data, which revealed that the sample was close to the nominal composition.

Keywords: Organic semiconductor, CuPc, Alq3, Structural and Morphological.

الخصائص التركيبية والسطحية لاغشية المزيج *(CuPc/Alq3)* المرسبة والمعالجة حرارياً

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الخلاصة
في هذه الدراسة، يتم ترسيب أشباه الموصلات العضوية لأغشية رقيقة من النحاس (II) فثالوسيانين (CuPc) والمنيوم ثلاثي هيدروكسي كينولين (Alq3) تم إذابته بالكامل في الكلوروفورم بنسب خلط مختلفة (1:0,0.75:0.25,0.5:0.5,0.25:0.75,0:1) (وزن / وزن) من خلال تقنية الطلاء الدوراني على طبقة زجاجية مُنظَّفة مسبقًا ومعالجتها بالحرارة عند 473 كلفن بمعزل عن الهواء، تم فحص الأفلام المنتجة بواسطة: حيود الأشعة السينية XRD، والمجهر الالكتروني الماسح SEM يظهر من قياس XRD أن عينات مزيج CuPc / Alq3 لها تركيب متعدد الأشكال عدا هيكل Alq3غير متبلور في الطبيعة , يزداد التبلور بعد عملية التلدين بينما يقل بعد زيادة تركيز Alq3 أظهرت صور SEM للأغشية الرقيقة لمزيج CuPc / Alq3 وجود هياكل شبيهة بالقضيب تمثل المادة العضوية (CuPc) والحبوب مثل الجزر تمثل (Alq3) والتي كميتها

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تعتمد على نسبة المزيج .اوضحت بيانات (EDX) الخصائص التركيبية للأغشية الرقيقة المحضرة عند درجة حرارة والملدنة , وأكدت أن العينات تحتوي على العناصر الأساسية المكونة لها.

1. Introduction

Heat, light, magnetic fields, and the presence of small amounts of impurities all impact semiconductor properties. Semiconductors are essential materials in electronic applications because of their sensitivity to these factors [1]. In general, there are two types of semiconductors: organic and inorganic. Organic semiconductors have a distinct bonding nature stronger than their inorganic counterparts. Compared to covalently bonded semiconductors like Si or GaAs, organic molecular crystals are van der Waals bonded solids, meaning less intermolecular bonding. Mechanical and thermodynamic qualities such as reduced hardness or a lower melting point are examples of the effects organic semiconductor. But, perhaps more importantly, there is a far weaker delocalization of electronic wave functions among nearby molecules; this has obvious ramifications for charge carrier transport and optical characteristics [2].

Metal phthalocyanine is found in the phthalocyanine ($C_{32}H_{18}N_8$) family of chemicals. Metals from every group of the Periodic Table have been substituted for the two hydrogen atoms (H_2Pc) in the molecule's core, resulting in the metal phthalocyanines, as shown in Figure 1 (a, b). Hydrogenated Copper-phthalocyanine (CuPc), with the chemical formula ($C_{32}H_{16}N_8Cu$), is a planar molecule having an inner porphyrin ring and four benzene rings symmetrically placed at each of its four corners [3] with one copper atom in the middle of the ring and 16 hydrogen atoms surrounding it. Phthalocyanines are difficult to dissolve in ordinary solvents (such as de-ionized water, ethanol, methanol etc.). Copper-phthalocyanine (CuPc) is an example of organic semiconductor. It is extremely stable both chemically and thermally [4]. It is important to produce electronic devices using simple techniques such as micro-drop coating, solution spinning, printing, and so on for large-scale device applications, primarily in the form of micro electro-machined devices (MEMs) [5].

Tris- (8-hydroxyquinoline) aluminum (Alq3) is commonly employed in LED and solar cells. It has been employed as an electron-emitting and/or transporting layer with success. Alq3 has recently been found to boost the lifetime and efficiency of organic solar cells when used as buffering and/or dopant layers. There are two geometric isomers of Alq3: facial and meridional [6], [7]. The levels of LUMO and HOMO are anticipated for the two isomers that are expected to influence the injection barrier and act as charge carrier traps [8], [9]. Organic and donor materials are the most promising materials for use in numerous bilayers or bulk heterojunction applications. Heat treatment [10] or chemical treatment can improve the characteristics of organic semiconductor materials [11], [12]. Researchers have been interested in various electronic applications such as organic light emitting diodes, organic thin film transistors, strain sensors, pressure sensors, humidity sensors, and organic solar cells for decades due to the low cost of organic semiconductors[13].

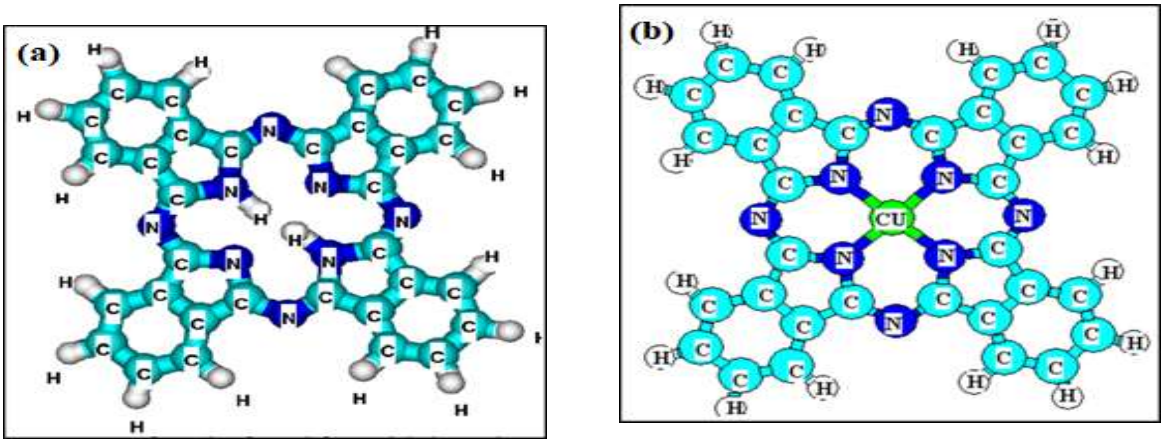


Figure 1: (a) Basic structural unit of a metal phthalocyanine molecule (b) Molecular structure of Copper (II) phthalocyanine CuPc [5]

2. Experimental

Copper (II) phthalocyanine (CuPc) and tris (8-hydroxyquinolinato) aluminum (Alq3) (purchased from Sigma Aldrich), without additional purification, were completely dissolved in chloroform at a concentration of 10 mg/ml to make the mix. CuPc/ Alq3 composite was made by combining CuPc and Alq3 of different mixing ratios(1:0, 0.75:0.25, 0.5:0.5, 0.25:0.75, 0:1) wt% , mixing them for 24 hours at room temperature using a magnetic stirrer. The spin-coating process was used to prepare the CuPc / Alq3 thin films; a small amount of the solution was dispensed on a glass substrate and spinning it with a speed of 3000 rpm. The spin speed is used to control the thickness of the composite films. The film was left to dry at room temperature for one day. Then they were put in an oven at 60^{o}C for 15min to remove the residual solvent that may have stayed inside the film as nano bubbles. The result is solid films. Following the pre-preparation of the films, the annealing process was carried out at 473K for 1 hour. Using an X–ray diffractometric system (Goniometer=PW3050/60), the structure of CuPc/ Alq3 thin films were analyzed, and the intensity as a function of Bragg angle was recorded. X–ray system 0.05deg step size, Time per steps = 1 second, λ= 1.54. Cu (K) was used as the radiation source, with a wavelength of 1.54nm, 30.0 mA current and 40 kV voltage. The scanning angle 2θ was changed between (5^{o}-50^{o}) at a speed of 5.0000 (degrees per minute) and a preset time of 0.24. (sec). The Bragg law is expressed as [14]:

$$\boldsymbol{n\,\lambda = 2\,d\,sin}\,(\Theta_{\boldsymbol{B}}) \qquad \text{.......(1)}$$

Where: Θ_B is the Bragg's angel, λ is the wavelength in (nm), d is the inter-planer spacing, and n is the spectrum order (n = 1, 2, 3 …).

The average grain size f crystallite can be estimated by the following relation:

$$\boldsymbol{G.S = (k\,\lambda)\,/\,(B\,Cos\,\theta)} \qquad \text{.......(2)}$$

Where: G.S is the average grain size of crystallite, k is a constant factor = 0.9, θ is the angle between incoming and reflected rays, and λ is the X-ray wavelength, which is 1.54 for Cu target. Using the X-Powder application, the Full Width at Half Maximum (FWHM) and grain size were estimated (ver. 21010.01.45)

Field Emission Scanning Electron Microscope (FESEM) and energy dispersive X-ray (EDX) analysis for as-deposited and heat treated thin films were employed to study the surface morphology and element concentration of materials, respectively. The TESCAN-Mira III scanning electron microscope was used to provide topographical and elemental information; a resolution of(1 nm at 30 keV and 2 nm at 1 keV) is possible with certain types of specimens.

3. Results and Discussion

3.1 X-Ray Analysis Measurements

XRD patterns for as-deposited CuPc/Alq3 composite thin films with different ratios (1:0, 0.75:0.25, 0.5:0.5, 0.25:0.75, 0:1) are shown in Figure 2. The thin film patterns for all the prepared samples showed a polymorphism structure, with a preferred peak at 2θ = 7.044, which is the same as the standard peak in the direction (001). Robinson and Klein [15] and Stella [16] both agreed that there is a big hump at about 23^0. In organic semiconductors, the films crystallize with a prominent peak in the (001) direction, indicating that this plane is favorable for crystal growth [17]. The XRD pattern of the as- deposited CuPc shows three diffraction peaks corresponding to reflecting surfaces hkl (001), (20-1), and (004) at 2θ of 7.025, 9.205, 28.439 with crystallite size of (24.1, 21.6, 42.1) nm, respectively. The XRD patterns of the annealed at 473K CuPc thin film, shown in Figure 3, exhibited the same peaks as that of the as-deposited films but with more crystallinity indicated by the higher intensity of the preferred peak (001) and the disappearance of the (004) peak. The structure precisely matched that of α-CuPc, which has space group C2/c and four molecules per unit cell of the monoclinic structure, according to the XRD pattern. This results agrees with that of Wang et al. [18].

The XRD pattern of the organic semiconductor CuPc/ Alq3 thin films of (0.75/0.25) mixing ratio shows a preferred peak at 2θ of 7.004, 9.205 with d-spacing of 12.5389, 9.5996 Å at room temperature, with crystalline sizes of 24.1, 31.5 nm, respectively, as shown in Figures 2 and 3.

The XRD pattern of organic semiconductor CuPc/Alq3 thin films of (0.5/0.5) mixing ratio are depicted in Figure 2. The favored homogenous construction in the middle of like-rod as well as grain similar Islands morphologies also displayed diverse characteristics in XRD pattern, The preferred peaks were at a 2θ of 7.004,9.205 with crystalline size 31.5,19.5, respectively. A novel structure with cluster semi-rods and grain aggregations was obtained that are larger than those seen in added proportions.

For CuPc/Alq3 thin films of (0.25/0.75) mixing ratio, the favored peaks of CuPc occurred with reduced intensity at a 2θ of 6.966, 9.049. With a smaller FWHM and a larger crystalline size of 29.2, 22.8 nm,. Figure 3 shows the XRD pattern of the annealed CuPc/Alq3 thin film at 473 K. With crystalline size of (23.0, 28.8) nm and 12.5794 Å, 9.6609 Å d-spacing, the preferred peak emerged at a (2θ) of 7.021, 9.147. The structure of Alq3 is amorphous in nature, with distinctive planes, according to XRD study. The crystallite size of as-deposited and post-annealing temperature, is shown in Table 1 (a,b).

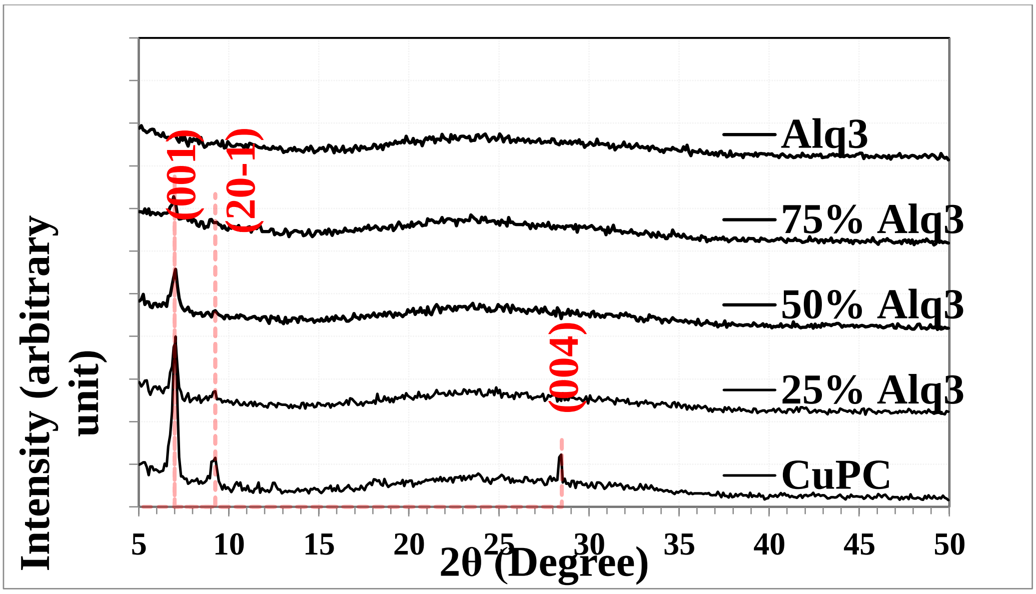


Figure 2: The XRD patterns for CuPc/Alq3 organic semiconductor thin layers in various ratios as-deposited at RT

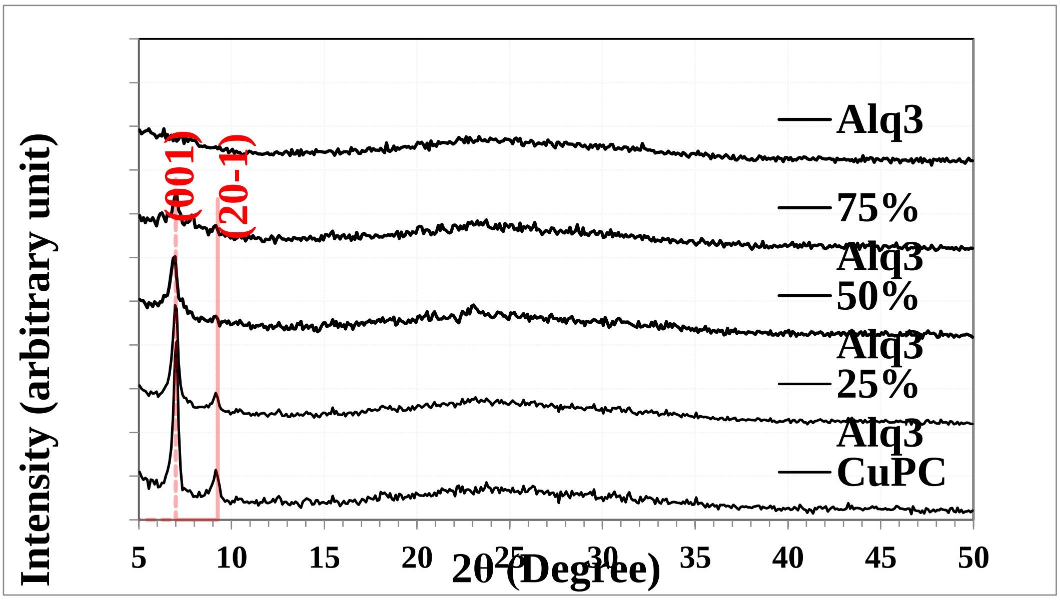


Figure 3: The XRD patterns for CuPc/Alq3 organic semiconductor thin layers in various ratios with thermally treated annealed at 473K.

Table 1: The 2Θ. D-spacing. FWHM. And Dimensions of crystallites, (a) At the RT

Sample	2θ (Deg.)	θ (rad)	FWHM (Deg.)	FWHM (rad)	d_{hkl} Exp.(Å)	G.S (nm)	phase	hkl
CuPC	7.025	0.06127	0.331	0.005773	12.5736	24.1	CuPc	(001)
	9.205	0.08029	0.370	0.006453	9.5996	21.6	CuPc	(20-1)
	28.439	0.24805	0.195	0.003396	3.1359	42.1	CuPc	(004)
25% Alq3	7.044	0.06144	0.331	0.005773	12.5389	24.1	CuPc	(001)
	9.205	0.08029	0.253	0.004415	9.5996	31.5	CuPc	(20-1)
50% Alq3	7.044	0.06144	0.409	0.007132	12.5389	19.5	CuPc	(001)
	9.205	0.08029	0.331	0.005773	9.5996	24.1	CuPc	(20-1)
75% Alq3	6.966	0.06076	0.273	0.004754	12.6789	29.2	CuPc	(001)
	9.049	0.07893	0.350	0.006113	9.7645	22.8	CuPc	(20-1)
Alq3	Amorphous							

(b) At (473 K)

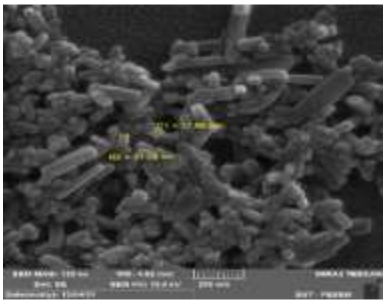
Sample	2θ (Deg.)	θ (rad)	FWHM (Deg.)	FWHM (rad)	d_{hkl} Exp.(Å)	G.S (nm)	phase	hkl
CuPC	7.039	0.06139	0.311	0.005425	12.5485	25.6	CuPc	(001)
	9.147	0.07978	0.346	0.006028	9.6609	23.1	CuPc	(20-1)
25% Alq3	6.970	0.06079	0.346	0.006028	12.6728	23.0	CuPc	(001)
	9.147	0.07978	0.294	0.005124	9.6609	27.1	CuPc	(20-1)
50% Alq3	6.918	0.06034	0.346	0.006028	12.7676	23.0	CuPc	(001)
	9.147	0.07978	0.276	0.004822	9.6609	28.8	CuPc	(20-1)
75% Alq3	7.021	0.06124	0.346	0.006028	12.5794	23.0	CuPc	(001)
	9.147	0.07978	0.276	0.004822	9.6609	28.8	CuPc	(20-1)
Alq3	Amorphous							

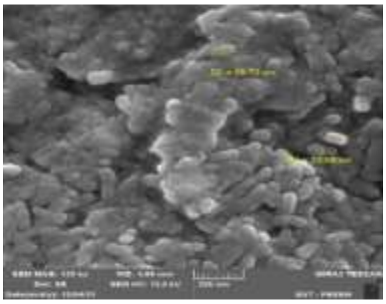
3.2 Morphological Analysis

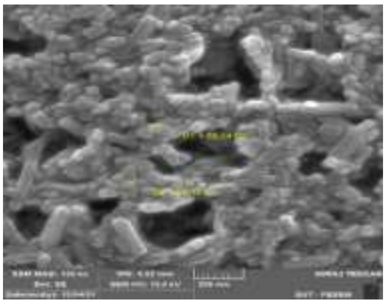
the surface morphology of the CuPc/Alq3 thin films were examined using a field emission scanning electron microscope. The pictures were taken with a scale of 200 nm and were noticeable at high magnification up to 135kX. Figure 4 (a) shows the surface morphology of the CuPc/Alq3 thin films at RT while, Figure 4 (b) depicts the surface morphology of the thin films annealed at 473K.

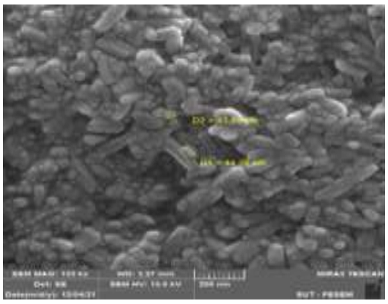
At room temperature, the surface characteristic of CuPc thin film are the rod-like forms. Wang et al. [18] revealed similar findings with diameters ranging from 30 to 60 nm. The FESEM images of the annealed thin films (Figure 4 (b)) show that the rod-like CuPc became evenly dispersed. The CuPc/Alq3 organic semiconductors thin films at (0.75/0.25) mixing ratio have similar CuPc surface composite together. Figures 4 (a)shows films that are thin which have been thermally treated, due to the binding of particles to one other, the semi-rod morphology transforms into equally dispersed in a given direction and morphology forms like-rod as seen in the Figure 4 (b). The CuPc/Alq3 organic semiconductors thin films at (0.5 /0.5) mixing ratio displayed diverse attributes from the best homogenous surface between rod-like of CuPc and grain like islands morphologies. As illustrated in Figure 4 (a), the distribution of Alq3 grain on CuPc that rod-like caused the disappearing characteristic of CuPc that rod.

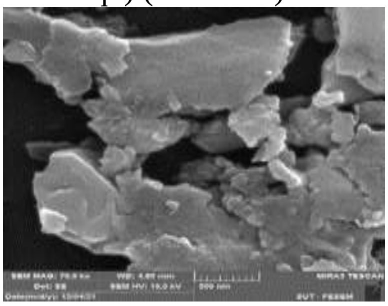
CuPc/Alq3 thin films (0.25/0.75) Alq3 particles all the bases were covered rods of CuPc and generated diverse architectures, as seen in the Figure 4 (a,b) . This fluctuates owing to Alq3 grain aggregation on CuPc rod, which covered the majority of them. These particles, as well as a little amount of particle aggregation, were found. Because particles are coupled to one other, the Alq3 morphology appears as clusters of grain like islands

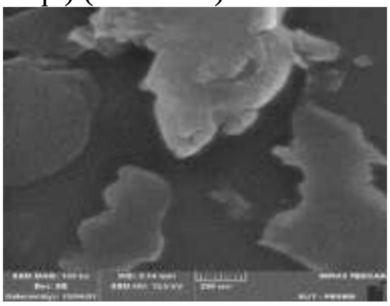

CuPc thin films

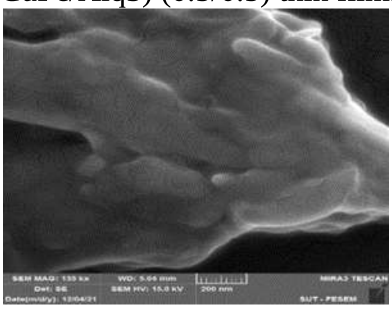

CuPc annealed thin films

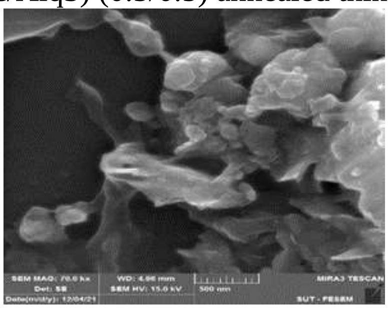

(CuPc/Alq3) (0.75/0.25) thin films

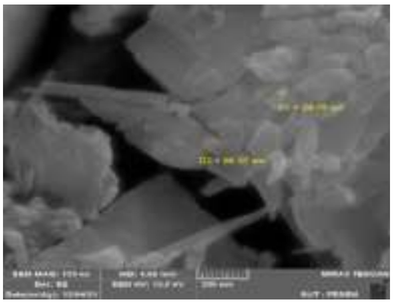

(CuPc/Alq3) (0.75/0.25) annealed thin films


(CuPc/Alq3) (0.5/0.5) thin films

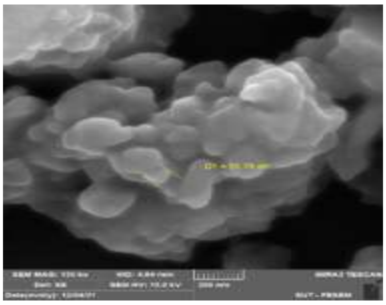

(CuPc/Alq3) (0.5/0.5) annealed thin films


(CuPc/Alq3) (0.25/0.75) thin films


(CuPc/Alq3) (0.25/0.75) annealed thin films



Alq3 thin films

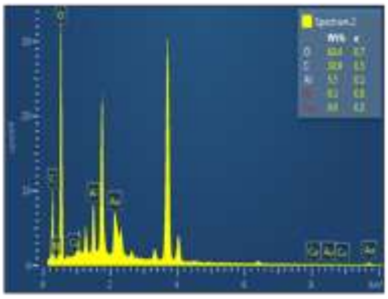


Alq3 annealed thin films

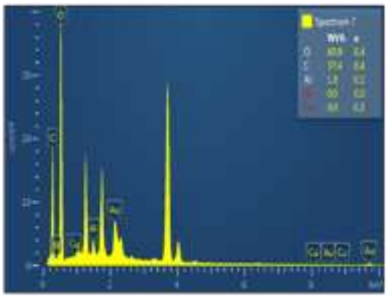
Figure 4: (a) As-deposited films (b) Annealed films

3.3 Composition Analysis

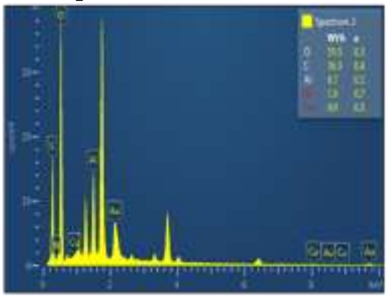
Energy Dispersive X-Ray Analysis (EDX), often known as EDS or EDAX, is a type of X-ray analysis. It is an x-ray method for determining a material's elemental makeup. The elemental composition of CuPc films deposited using the EDAX process at various CuPc and Alq3 mixing ratios in films was studied; it was found that copper (Cu) was quite poor. In this research, the elemental composition of (CuPc/Alq3) composite thin films made by spin coating process of as-deposited and thermally treated at annealing temperatures of (473 K) was determined by EDX for five distinct ratios (1/0, 0.75/0.25, 0.5/0.5, 0.25/0.75, and 0/1) wt %. The EDX spectrum confirmed the presence of the usual components C, N, O, and Cu, Al, in the CuPc films. The EDAX spectra of the CuPc and Alq3 films is shown in Figures 4 (a, b). The presence of the CuPc compound was confirmed by the emergence of the C peak in the EDX spectra of organic semiconductor thin films. Increasing the quantity of Alq3 in organic semiconductor films also raised the fraction of Al atoms in these thin films. Table 2 (a) and (b) indicates the elemental compositions of the as-deposited and annealed films, respectively.



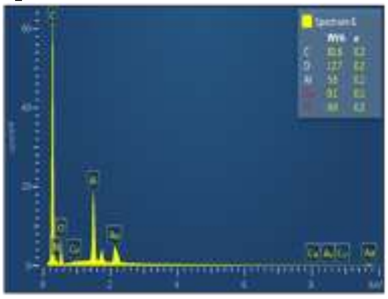
EDX spectra of CuPc thin films



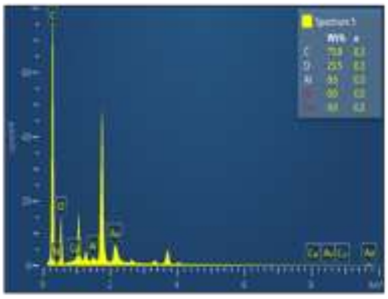
EDX spectra of CuPc annealed thin films



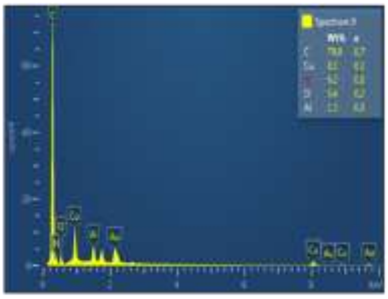
EDX spectra of (CuPc/Alq3) (0.75/0.25) thin films



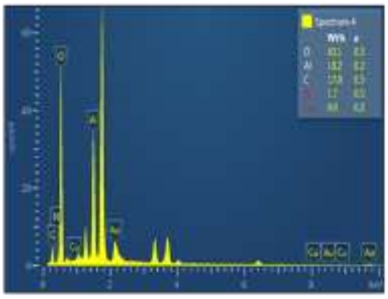
EDX spectra of (CuPc/Alq3) (0.75/0.25) annealed thin films



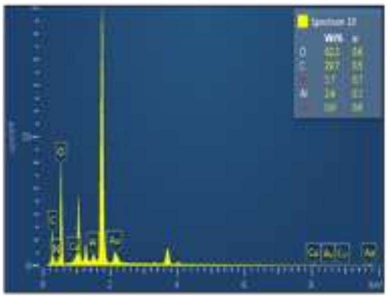
EDX spectra of (CuPc/Alq3) (0.5/0.5) thin films



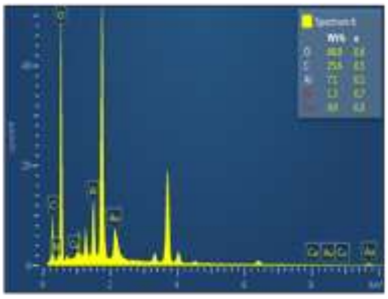
EDX spectra of (CuPc/Alq3) (0.5/0.5) annealed thin films



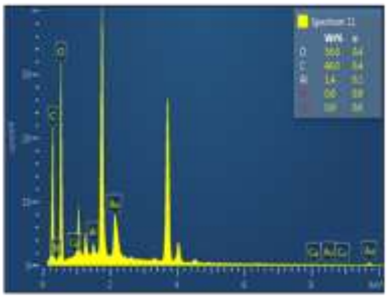
EDX spectra of (CuPc/Alq3) (0.25/0.75) thin films



EDX spectra of (CuPc/Alq3) (0.25/0.75) annealed thin films



EDX spectra of Alq3 thin films



EDX spectra of Alq3 annealed thin films

Figure 5 :(a) As-deposited films (b) Annealed films

Table 2 : (a) As-deposited films

Element	Line Type	Wt%	Atomic %
C	K series	30.85	38.03
N	K series	0.32	0.34
O	K series	63.37	58.64
Al	K series	5.46	2.99
Cu	L series	0.00	0.00
Total		100.00	100.00

Identify of composition material of CuPc thin films

Element	Line Type	Wt%	Atomic %
C	K series	36.26	44.09
N	K series	1.57	1.64
O	K series	55.51	50.66
Al	K series	6.66	3.61

(b) Annealed films

Element	Line Type	Wt%	Atomic %
C	K series	37.37	44.57
N	K series	0.00	0.00
O	K series	60.85	54.48
Al	K series	1.78	0.95
Cu	L series	0.00	0.00
Total		100.00	100.00

Identify of composition material of CuPc thin films

Element	Line Type	Wt%	Atomic %
C	K series	81.63	87.14
N	K series	0.00	0.00
O	K series	12.69	10.17
Al	K series	5.63	2.68

Cu	L series	0.00	0.00
Total		100.00	100.00

Identify of composition material of (CuPc/Alq3) (0.75/0.25) thin films

Cu	L series	0.05	0.01
Total		100.00	100.00

Identify of composition material of (CuPc/Alq3) (0.75/0.25) thin film

Element	**Line Type**	**Wt%**	**Atomic %**
C	K series	17.02	23.02
N	K series	1.75	2.02
O	K series	63.05	64.02
Al	K series	18.18	10.94
Cu	L series	0.00	0.00
Total		100.00	100.00

Identify of composition material of (CuPc/Alq3) (0.5/0.5) thin film

Element	**Line Type**	**Wt%**	**Atomic %**
C	K series	78.96	87.30
N	K series	6.17	5.85
O	K series	5.42	4.50
Al	K series	1.34	0.66
Cu	L series	8.11	1.69
Total		100.00	100.00

Identify of composition material of (CuPc/Alq3) (0.5/0.5) thin films

Element	**Line Type**	**Wt%**	**Atomic %**
C	K series	75.92	80.92
N	K series	0.00	0.00
O	K series	23.51	18.81
Al	K series	0.57	0.27
Cu	L series	0.00	0.00
Total		100.00	100.00

Identify of composition material of (CuPc/Alq3) (0.25/0.75) thin films

Element	**Line Type**	**Wt%**	**Atomic %**
C	K series	29.71	36.07
N	K series	5.69	5.92
O	K series	62.21	56.71
Al	K series	2.39	1.30
Cu	L series	0.00	0.00
Total		100.00	100.00

Identify of composition material of (CuPc/Alq3) (0.25/0.75) thin films

Element	**Line Type**	**Wt%**	**Atomic %**
C	K series	25.56	32.17
N	K series	1.34	1.45
O	K series	66.02	62.41
Al	K series	7.08	3.97
Cu	L series	0.00	0.00
Total		100.00	100.00

Identify of composition material of Alq3 thin films

Element	**Line Type**	**Wt%**	**Atomic %**
C	K series	43.95	51.35
N	K series	0.00	0.00
O	K series	54.63	47.91
Al	K series	1.42	0.74
Cu	L series	0.00	0.00
Total		100.00	100.00

Identify of composition material of annealing Alq3 thin films

4. Conclusion

The impact of Alq3 ratio in CuPc/ Alq3 composite on the structural properties was clear as indicated by the XRD patterns which revealed that the structure of as-deposited and annealed (CuPc:Alq3) composite thin films decreased in crystallinity after adding of Alq3 due to it is amorphous in nature. While, annealing process caused increase in the crystallinity of all prepared films. The surface morphology was also affected by adding of Alq3 to CuPc organic semiconductor and the morphology change from rod-like structure of CuPc to grain like islands with increasing the concentration of Alq3. The annealing temperature affected the aggregation of particles.

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