# Nanostructure Investigation of Organic Semiconductor Copper (II) PhthalocyanineTetrasolfonic Acid Tetrasodium Salt (CuPcTs) Thin Films by Structural and Surface Morphological Measurements

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***Abstract:*** *copper(II) phthalocyaninetetrasulfonic acid tetrasodium salt (CuPcTs) organic thin films which are prepared using spin coating on ITO/glass with speed rate of 1000 rpm for 1 min at different annealing temperatures (298, 373, 423, 473) K and then characterized byX-ray diffraction, atomic force microscope (AFM) and Field Emission Scanning Electron Microscope (FESEM),. The obtained results indicatedthat they had a polycrystalline structure with tetragonal of lattice parameters are $a=b=17.37A^0$, $c=12.79A^0$ and $\beta=90^0$. The prefer orientation of thin films is (001) plane. The average crystallite size decreased with increasing annealing temperature. This result was supported by morphologies measurements as in AFM and FESEM indicate the same behavior as in XRD.*

## I. Introduction

In general nanoparticles are formed by several to hundred thousand atoms and have an intermediate structure between a molecules and bulk, to determine the structure properties of nanoparticles many characterization techniques are used, The X-ray diffraction XRD is a specific tool to determine crystalline structural properties [1].

Field Emission Scanning Electron Microscopy (FESEM) and Atomic Force Microscopy (AFM) can detect surface structures and shapes of nanoparticles, the physical and chemical properties of particle can be very different from their bulks the surface to volume ratio of nanoparticles is much larger that of its bulk; so that the nanoparticles has more ratio of bonds on the surface, the large surface-volume ratio in a nanoparticle causes a structural deformation which can also change the physical properties of nanoparticles, In the past few years, the synthesis and physical characterization of nanoscale semiconductors have aroused much interest [2]

The structural properties of phthalocyanine thin films are dependent on various parameters such as preparation technique, substrate temperature and post-deposition annealing[2],For a several of experiments in the topics of scanning probe microscopy[3,4] spectroscopy[5] sensors[6] and electronics[7] there is a strong attractive to investigate Nano structure of organic metal phthalocyanine films.

Phthalocyanine (Pc) is planar aromatic macro-cyclic compound with dark green-blue color which forms coordination complexes with more than 70 metals including Cu, Al, Ni, Co, Fe and V etc. These compounds are formed by arranged carbon and nitrogen atoms which form four isoindole units with a cloud of 18 delocalized $\pi$ electrons [8],

Metal phthalocyanines (MPcs) are very well known dye pigments having likeness in structure with biological molecules chlorophyll and hemoglobin. They exist as a range of derivatives, where the polyaromatic ring is most commonly bound to a transition metal (MPc) or hydrogen ($H_2Pc$)[10], These materials have shown many properties e.g. chemically and thermally very stable [11, 12], most of these can easily form ordered thin films and show photoconductivity [10, 11]; exhibit catalytic activity [12] etc.

Copper (II) phthalocyaninetetrasulfonicacidtetrasodium salt (CuPcTs) is a typical example of water-soluble phthalocyanines. CuPcTs structure is very similar to CuPc except that polar $SO_3Na$ attached to the corners of benzene rings and makes this compound water soluble [13],

In this study, an organic compound Copper (II) phthalocyaninetetrasulfonic acid tetrasodium salt (CuPcTs) has been prepared on glass and ITO substratesand used to investigate its structural and surface morphology properties. Hence, the purpose of our work is to find the optimal temperature for which the film produces best nanostructural properties.

## II. Experimental work

Copper (II) phthalocyaninetetrasulfonic acid tetrasodium salt (CuPcTs) was purchased from Sigma-Aldrich and used without further purification. Its molecular formula is ($C_{32}H_{12}CuN_8O_{12}S_4Na_4$) and has 984.25 g/mol molecular weight. Molecular structure of CuPcTs is shown in Fig. (1), before starting the deposition, the glass substrate was put in an ultrasonic bath for 20 min using alcohol then acetone, followed by cleaning in distilled water.The substrate was dried in open air in a cleaned room.

CuPcTs powder has mixed with deionized water 50mg/ml to obtain CuPcTs Solution then it has put on a magnetic stirrer for 30min. after that Filtration process is used to the mixture by using 0.45µm and 0.2µm filters. And it has put on a magnetic stirrer for 30min to get a Homogenous solution.The resistivity of the used deionized water was ~15 MΩ-cm
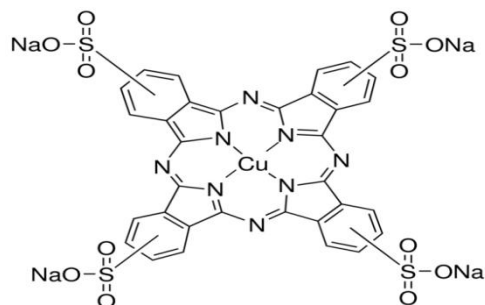


*Fig.(1) Molecular structure of Copper (II) phthalocyaninetetrasulfonic acid tetrasodium salt (CuTsPc).*

Thin film prepared by using spin coater type CHEMAT SCIENTIFIC SKW-4A2 spin coater.

The pattern of XRD has been plotted the intensity as a function ofBragg's angle .its analysis Using X–ray diffractometric system Shimadzu XRD 6000.

The source of radiation was Cu ($K_\alpha$) with wave length= 1.5405 Å, the current was 30.0 mA and the voltage 40 kV. The scanning angle 2θ varied in the range of ($3^o$-$30^o$) at5.0000(degree /min) speed andfor preset time = 0.24 (sec).

The lattice parameters of the films were calculated using the Bragg's formula[14]:

$$n\lambda = 2d \sin\theta \ldots\ldots\ldots (1)$$

Where n: spectrum order (1, 2, 3….), λ: wave length in (nm), d: inter planer spacing, θ: Bragg's angle.

The grain size (G.S) of the crystallites was calculated from the XRD using Scherer's relation[15]:

$$G.S(nm)= 0.9\lambda/FWHM \, Cos\theta \ldots\ldots.. (2)$$

Where: Full Width at Half Maximum.

Surface morphological measurements ofCuPcTs thin films with different annealing temperature were measuredusingcontact mode Atomic Force spectrometer, AFM micrograph provide good information about 2D, 3D images for all studied samples, roughness and grain size.

Field emission scanning electron microscopy (FESEM), supplied with Energy-Dispersive X-ray spectroscopic detector (EDX), type JSM-7600F produce by JEOL Ltd. Japan, which is used to get topographical and elemental information at magnifications of 10X to 300,000X, with virtually unlimited depth of field.

## III. Results and discussions

The XRD patterns (fig. 3)for as-deposited and annealed films show that the structure is polycrystalline and display a strong reflection at (001) orientation. Another peak distinguished in the XRD pattern of as-deposited and annealed film with Ta=373K which represents a reflection at (411) orientation, while this peak disappeared in XRD pattern of annealed films with Ta=423K and Ta=473K, this may be due to the change of crystallites orientation at this peak toward the preferred peak (001) under the effect of elevated temperature.

The XRD results indicate that as the temperature increase the grain size decrease and the crystallization of the films is a function of annealing temperatures. Actually, the most important tool to study the Nano materials is X-ray diffraction. A considerable broadening in X-ray diffraction lines will

occur when particle size is less than 100 nm. The broadening is due to the particle size and strain from diffraction pattern. This broadening is used to calculate the average particle size using Scherrer equation (2). This technique will lead to most accurate results.

The size, shape, lattice parameter determination and phase fraction analysis of the unit cell for any compound can be determined easily by XRD. The standard and experimental inter-planer distances (d), the full width at half maximum (FWHM), crystallites size (G.S) and Miller indices of the as-deposited and annealed CuPcTs thin films are listed in Table (1), while Table (2) shows the standard and calculated lattice constants (a, b and c) of CuPcTscrystallite.The results have good agreements with other measurements and with Robinson and Klein results [16] and with Stella, Marco [17], its result seems to indicate that the CuPc has grown with an amorphous micro-structure.

**Table(1): the structural parameters of as-deposited and annealed CuPcTs polycrystalline thin films.**

| T (k) | 2θ (Deg.) | FWHM (Deg.) | $d_{hkl}$ Exp.(Å) | G.S (nm) | $d_{hkl}$standard (Å) | hkl |
|-------|-----------|-------------|-------------------|----------|-----------------------|-----|
| 298 | 6.95 | 0.2411 | 12.6913 | 33.0 | 12.64 | (001) |
| | 23.86 | 0.3444 | 3.7249 | 23.6 | 3.71 | (411) |
| 373 | 6.95 | 0.3788 | 12.6913 | 21.0 | 12.64 | (001) |
| | 23.90 | 0.5166 | 3.7196 | 15.7 | 3.71 | (411) |
| 423 | 6.85 | 0.5510 | 12.8824 | 14.4 | 12.64 | (001) |
| 473 | 6.82 | 0.8610 | 12.9473 | 9.2 | 12.64 | (001) |

**Table (2): The lattice constants of CuPcTscrystallite.**

| parameters | Present results $A^0$ | Standard results $A^0$ | Error ratio% |
|------------|-----------------------|------------------------|--------------|
| a | 17.37 | 17.55 | 1.02% |
| b | 17.37 | 17.55 | 1.02% |
| c | 12.79 | 12.67 | 0.94% |
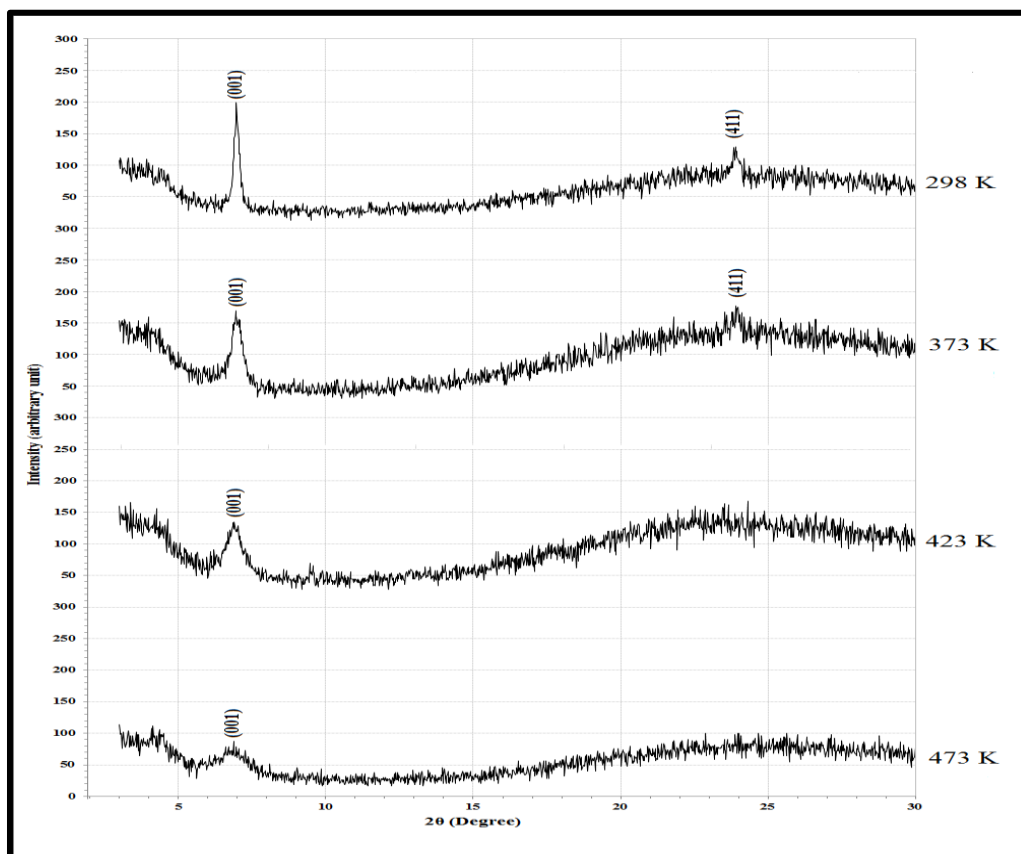


**Fig: (3) XRD pattern of as-deposited and annealed CuPcTs Thin Films.**

Surface morphology of CuPcTs thin films prepared at different annealing temperatures (298, 373, 423, and 473) K was determined by using Atomic Force Microscope (AFM) images shown in Fig.(4).The images show that the thin films havesmaller number of grain size and are homogeneously distributed, which indicates the crystalline nature of the film. The morphologies,grain sizeand roughness of thin films were examined by atomic force microscopy in order to provide a large surface inspection of the micro-structural arrays;it is found that the roughness mean square (rms) of the untreated film, 373K, 423K and 473K heat treated films is approximately 1.24nm, 0.954nm, 0.659nm and 0.444nm, respectively. As can be clearly seen without heat treatment, the CuPcTs film surface has bigger granular structure size corresponds to higher surface roughness. As the film treated with temperature, most part of the bigger structure has been reduced by the temperature and the grains diameter decrease with increasing the temperature, the smallest grains diameter indicated at annealing temperature of 473K. These results are good agreement with the results obtained from XRD measurements. As consequence of the above results, the peak to peak also decreased with increasing the temperature of heat treatment. Table (3) listed the parameters can be obtained from AFM measurements. The average grain size decreases as temperature increases.It has great agreements with P.Kalugasalam results [18], and there is disagreement with Mohammed T. Hussein[19], in their research the grain size and roughness increase with temperature increasing that's due to the nucleating behavior of the substance.

**Table (3) Grain size (nm), Roughness average (nm) and peak to peak (nm) of as-deposited and annealed CuPcTs thin films.**

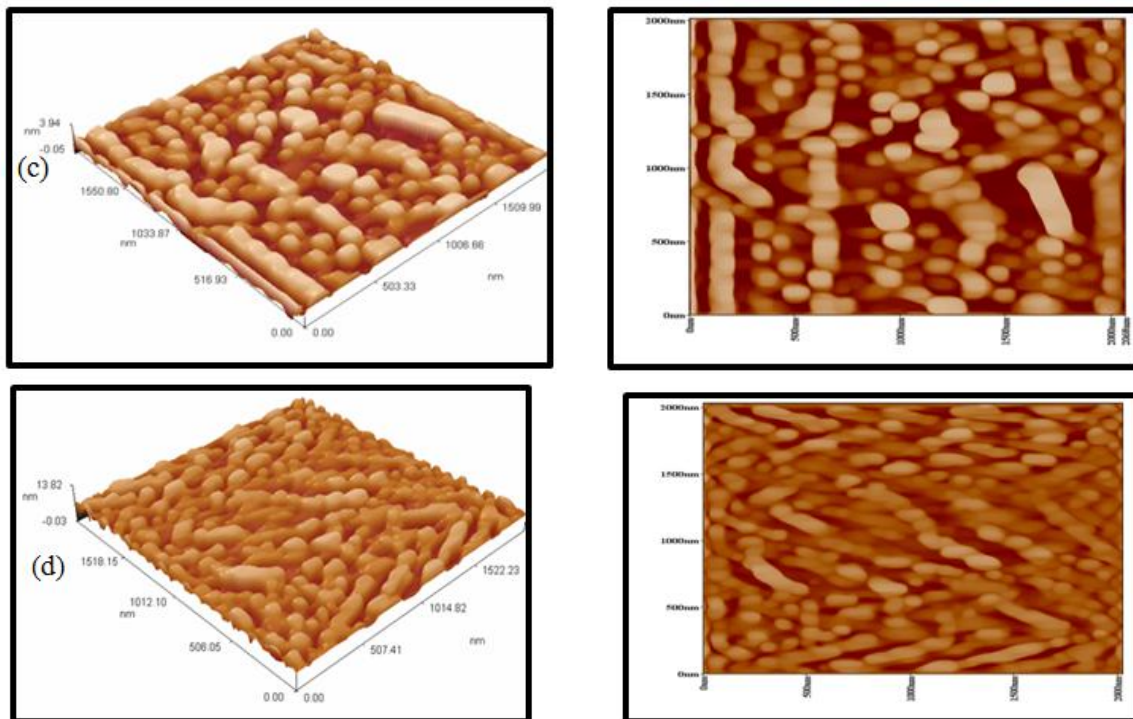| $T_a$ (k) | Grain size(nm) | Roughness average (nm) | (p-p)(nm) |
|---|---|---|---|
| 298 | 105.84 | 1.24 | 9.86 |
| 373 | 103.48 | 0.954 | 6.83 |
| 423 | 95.03 | 0.659 | 3.18 |
| 473 | 89.53 | 0.444 | 3.08 |
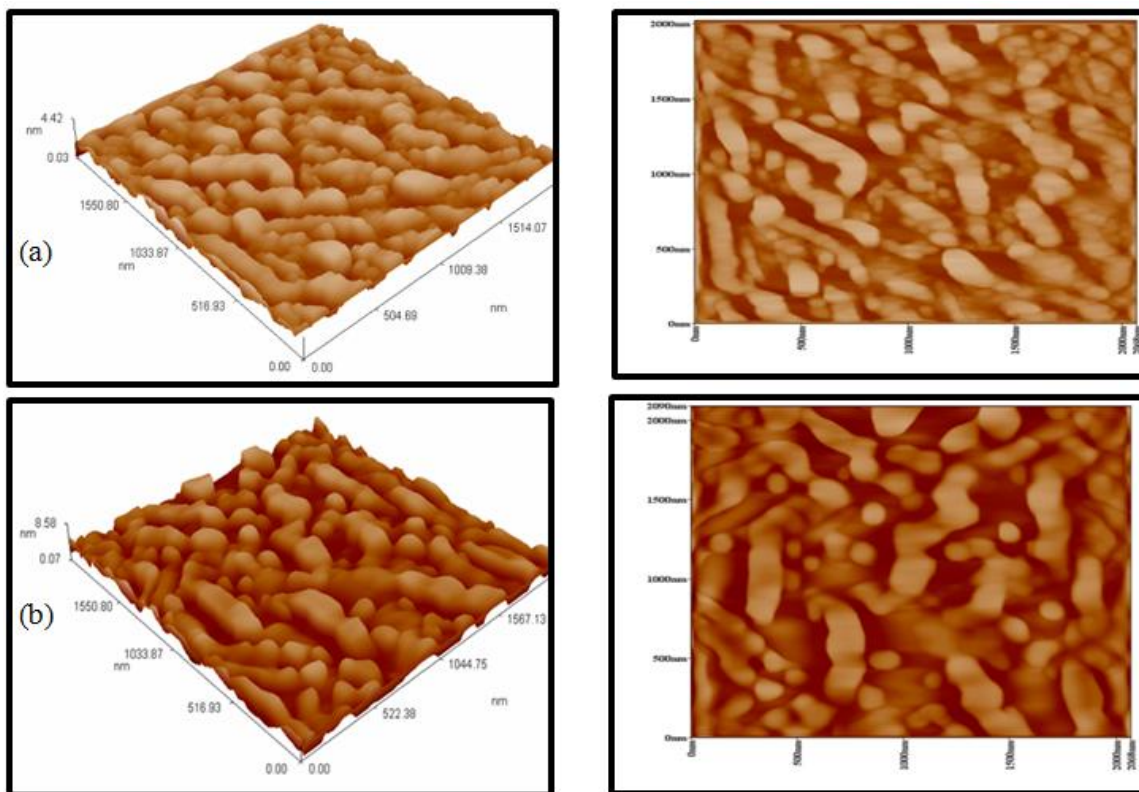
**Fig.(4): 3D&2D AFM images of CuPcTs thin films at (a) as-deposited thin film (b)Ta=373K (c) Ta=423K (d) Ta=473K**

The Field Emission scanning electron (FESEM) micrographs of thin films which annealed at 373K and 473K are shown in the Fig (5). The film morphology changes for the elevated annealing temperatures. All films of CuPcTs transformed into Nano grain size with diameter less than 100 nm for the film of annealing temperature 373 K as appear in Fig.(5-a). It is also observed that the shapes of grain like Islands are separated with increasing of annealing temperatures.
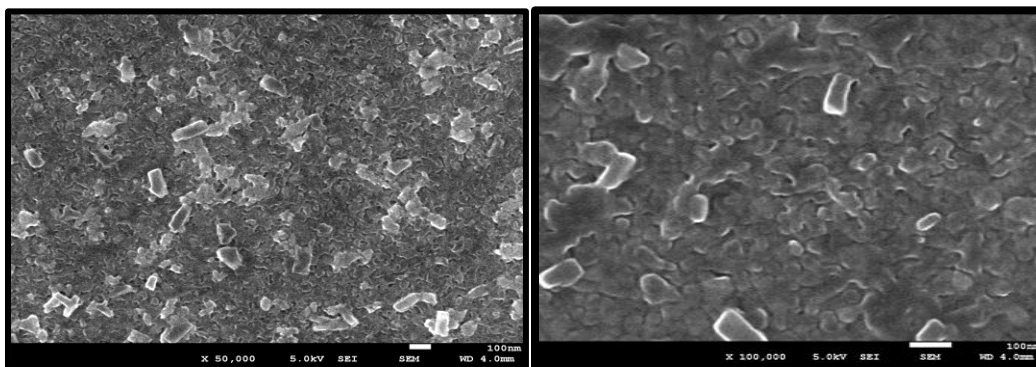


*(a)*
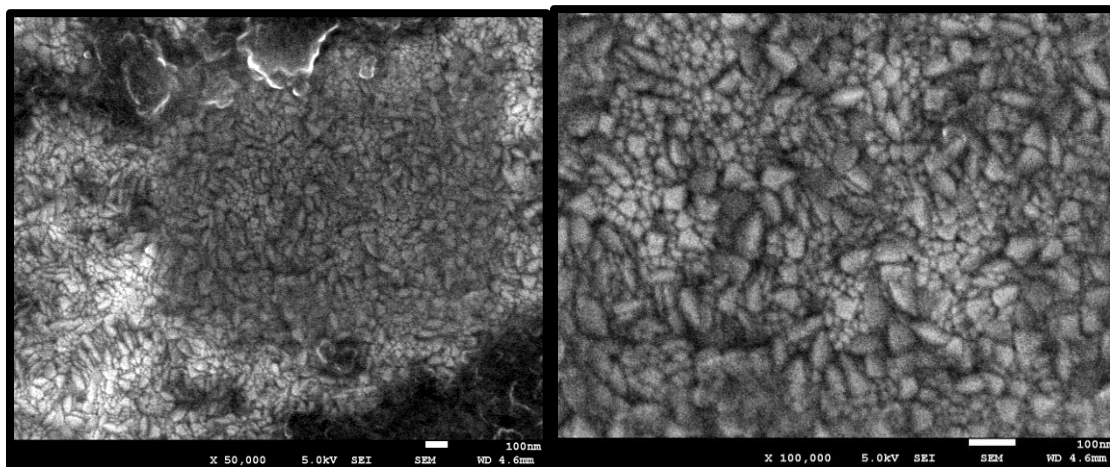
*(b)*

**Fig.(5) FESEM pictures x50000 & x100000 of CuPcTs Film deposited on ITO glass at(a) 373 K annealing temperature (b) 473K temperature**

EDX graph Fig. (6) Showing elemental ratios of C, N, O, Na, Al, Si, Ca, Cu and In of CuPcTs thin films prepared by spin coated and annealed ($T_a$=473K) CuPcTs thin film on ITO-glass. EDX is unable to determine the elemental ratio of hydrogen, so the elemental ratio of hydrogen in the CuPcTs is not mentioned. The elements Si, In and excess amount of O are belonging to ITO-glass substrate, and Mg may be attributed to contaminations. Table (4) represents the elements composition weight% and atomic% which are obtained from EDX result.
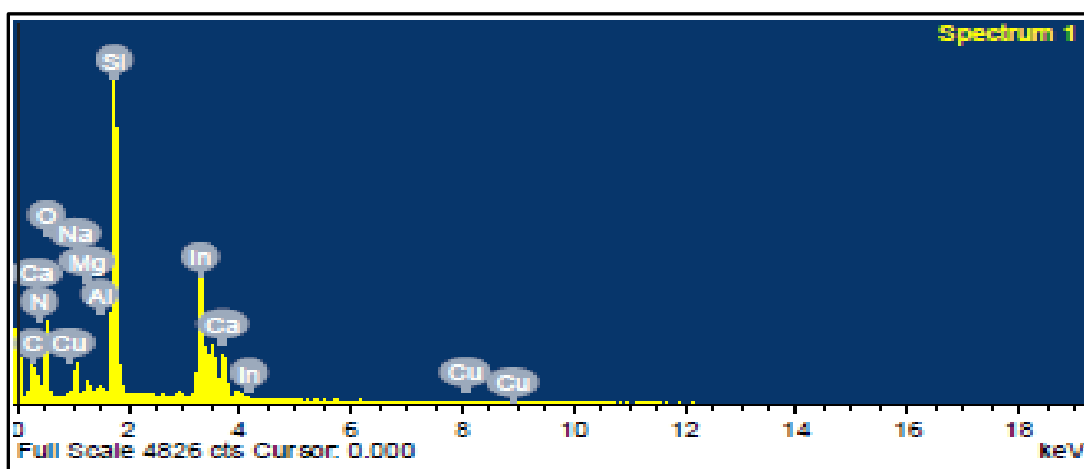


*Fig: (6) EDX result of annealed CuPcTs / ITO*

**Table (4) shows Elements composition Weight % and Atomic % from EDX result of annealed CuPcTs / ITO**

| elements | Weight% | Atomic% |
|---|---|---|
| C | 9.03 | 20.18 |
| N | 1.20 | 2.30 |
| O | 25.66 | 43.06 |
| Na | 2.82 | 3.29 |
| Al | 0.34 | 0.33 |
| Si | 19.43 | 18.58 |
| Ca | 3.79 | 2.54 |
| Cu | 0.57 | 0.32 |
| In | 36.14 | 8.45 |

# IV. Conclusions

The CuPcTs thin films deposited successfully using a spin-coating technique ,the morphological and structural properties of thin films modified by heat treatment.

The XRD measurements and the AFM topographic images showed of CuPcTs thin films indicated that polycrystalline structure with a tetragonal system and thin films transform to strong peak (001) influenced by annealing temperatures , and the grain size is decrease with increase of annealing temperature. The broadening in X-ray diffraction lines occur when particle size is less than 100 nm.

These structural characterizations confirm that substrate temperature allows us to control the structural organization of CuPcTsmolecules in their solid state, from which a large development of the properties by increasing the annealing temperatures, therefore, the best result can we getin achieve nanostructure at heat treatment for the film in 473 K.

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