# MICROSTRUCTURE, CRYSTAL IMPERFECTIONS AND ULTRASONIC STUDIESOF SPRAYED NANOSIZED Cu<sub>2-x</sub>S<sub>x</sub>OAND Cu<sub>2-y</sub>Cr<sub>y</sub>OTHIN FILMS

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In the current work,  $Cu_{2-x}S_xO(x = 0.05, 0.1 \text{ and } 0.2)$  and  $Cu_{2-y}Cr_yO$  (y = 0.03 and 0.06) composite thin films were deposited on a heated glass substrate using spray pyrolysis technique. The effect of S and Cr doping on microstructure, crystal defects and mechanical properties of  $Cu_2O$  nanoparticles was studied. X-ray diffraction results reveal that the single phase of  $Cu_2O$  has a cubic structure without any other phases related S and Cr.Scherrer and Williamson and Hall methods were used to determine the parameters of the microstructure by analyzing the X-ray diffraction line profile.Some important parameters such as crystallite size, microstrain, average residual stress, number of crystallite/cm<sup>2</sup> and dislocation density were studied. Analysis of microstructure and crystal imprefications revealed that all the parameters studied were increased by increasing the concentration of S in  $Cu_{2-x}S_xO$ ; conversely, when adding a Cr element to  $Cu_{2-y}Cr_yO$ . The Mechanical properties of the films was observed by ultrasonic technique deduced that the doping of  $Cu_2O$  thin film with S caused good quality of crystallinity. The doped films can be used for optoelectronic applications.

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# **1. Introduction**

The development of semiconductor metal oxide thin film is one of the interstitial materials p-n junction based optoelectronic devices. Recently,  $Cu_2O$  nanostructure has been very attractive researchers due to its interesting electrical and optical properties.  $Cu_2O$  is a cubic structure semiconductor with a narrow optical band gap (Eg) of 1.10 - 1.71eV [1]. It exhibits p-type conductivity due to the excess of oxygen or copper vacancies in its structure.  $Cu_2O$  has been used in many important fields, of science and technology such as gas sensing, magnetic strogemedia, photocatalysis and in photo electrochemical cells [2-6]. Also,  $Cu_2O$  is considered as one of the best choices as anodes for Na-ion batteries owing to their high theoretical capacity [7-8].Polycrystalline structures with Nano size crystallite have higher surface free energy at the grain boundaries than that of the structures made of micrometric grains. Different techniques to prepare  $Cu_2O$  thin films from such as gas phase deposition techniques [9], wet-chemical method [10] and electrode position route [11, 12] has been developed for the synthesis of  $Cu_2O$  with different microstructures. Among these methods, spray pyrolysis deposition, which presents a gentle, simple and economical method with the advantage of allowing patterned and controlled crystal growth, has shown the advantage to control the crystallization of large area metal oxide films.

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copper element that has three cases of oxidations, Cu<sup>+</sup>, Cu<sup>+2</sup> and Cu<sup>+3</sup> which acceptsadds other elements to the presence of each of the holes and electrons [13]. Using propylene glycol monoethyl ether and diethanolamine as a solvent and stabilizer Wu et al. enables to prepare Sn doped CuO films by spin coating technique [14] as well as Jayaprakash et al. develop Zn doped CuO nanocluster of grapes like morphology by a sol-gel method [13]. Kikuchi et al. also studied structural and electrical properties of the pulsed laser deposited Ni-doped Cu<sub>2</sub>O thin films [15]. Furthermore, magnetic and optical properties of Ni-doped CuO nanoparticles were carried out [16, 17]. Recently, Chiang et al. found that the electrical conductivity of CuO increased by about two orders of magnitude at adding some elements such as Li, Ni, Co, Ag, Zn and Mg and hence a significant increase in the photocurrent density [18]. In addition, Khmissi et al. also investigated the structural, morphology, optical properties and wettability of spin-coated deposited Ni-doped and (La,Ni) co-doping CuO thin films [19]. Chromium (Cr) is an element with electronic configuration [Ar]  $3d^5 4s^1$  that matches the electronic distribution of Cu is [Ar]  $3d^{10} 4s^1$ . So, Cr can trap the electrons and reduce the recombination of photogenerated electron-hole pairs [20]. Hence, doping with Cr can affect the optoelectronic properties of Cu<sub>2</sub>O.

Based on the literature, few reports on Ni-doped CuO nanoparticles [15-17] and La-doped CuO NPs [21]. The microstructural and optical properties of Cu<sub>2</sub>O NPs are not discussed in detail in previous works. Moreover, there are no reports on sulfur and chromium doped Cu<sub>2</sub>O thin films.Since the copper and chromium are neighboring to each other in the periodic table of elements and their ionic radii are different between them  $[Cu^{+2} (0.073nm) \text{ and } Cr^{+2} (0.052nm)]$ . But the sulfur element has a smaller ionic radii (0.037nm) than both ionic radii of Cu<sup>+2</sup> and Cr<sup>+2</sup>. It is meaningful to dope Cu<sub>2</sub>O with two different elements. Even the replacement of copper by S and Cr in the Cu<sub>2</sub>O unit cell may cause minor modifications compared with other elements. This could affect the crystallinity and optical properties of the Cu<sub>2</sub>O by spray pyrolysis method as well as S and Cr doped thin films. In this work, the influence of doping S and Cr on the microstructure and mechanical properties of Cu<sub>2</sub>O thin films was studded. The ultimate aim of this investigation is to use for optoelectronic applications.

#### 2. Experimental details

#### 2.1 Thin film preparation

Cu<sub>2</sub>O thin films have been deposited onto ultrasonic cleaned glass substrates using spray pyrolysis technique (SPT) using 0.1 mole of cupric acetate (Cu (CH<sub>3</sub>COO)<sub>2</sub>,H<sub>2</sub>O) which was dissolved in deionized 20 ml distilled water. Cu (II) acetate monohydrate dissolved in isopropyl alcohol and diethanolamine (DEA,  $C_4H11NO_2$ ), then glycerol was added to the solution. Aqueous solution of thiourea (NH<sub>2</sub>CSNH<sub>2</sub>) (Mw =76.12g/mol) and CrCl<sub>3.6</sub> (H<sub>2</sub>O) (Mw =266.436g/mol), as precursors for the S and Cr sources was taken for doping of Cu<sub>2</sub>O thin films. The S and Cr additives were controlled to obtain the following compositions;  $Cu_2O$  (pure),  $Cu_2xS_xO$  (x=0.05, 0.1 and 0.2) and Cu<sub>2-v</sub>Cr<sub>v</sub>O (y=0.03 and 0.06). The precursor solution was filtered using 0.45  $\mu$ m syringe filters before spraying. The glass substrate was cleaned by distilled water using the ultrasonic bath cleaner for 5 min, after that, the substrates were washed using acetone for 10 min to remove any organic impurities. Then the substrates were cleaned again using distilled water for 5 min, before washing the substrates with ethanol for 10 min to remove any other organic contaminants. After these operations, the glass was ready to use. The distance between substrate to spray nozzle was 19 cm and air pressure was 1 bar. The solution was sprayed onto the ultrasonically cleaned glass substrates heated at 300°C temperatures. The substrate temperature was recorded with the indium tin oxide glass substrate. The flow rate of the solution during spraying was adjusted at about 1 ml/min and was kept constant throughout the experiment and the spray time was 12 min. The films were dried in the furnace at 60 °C for 10 min. Finally, to crystalline the films, all samples were annealed at 500 °C in air at a heating rate of 5 °C/min and cooled down to room temperature. The film thickness was recorded using weighing methods and mechanical stylus method.

### 2.2 Thin film characterization

The prepared oxides samples were characterized by a high resolution x-ray diffraction (XRD) (JEOL model JSDX-60PA) for phase identification using Cu,  $K_{\alpha}$  radiation ( $\lambda$ =0.154184nm, 40kV, 40mA ,with attached Ni-filtered). Continuous scanning was applied with a slow counter speed (1°/min) and small time constant (1sec) for two theta range from 10 to 80°.

# 2.3 Ultrasonic technique

At room temperature, ultrasonic technique was used to study the prepared specimens of  $Cu_2O$  thin film, which were doped with Sulfur (S) (5%, 10% and 20%) and Chromium (Cr) (3% and 6%). The ultrasonic equipment was formed of flaw detector (USIP 20 – Krautkramer Branson), oscilloscope (54615B – hp), normal ultrasonic transducer of 4 MHz frequency (S12 HB4 - Karl Deutsch) and shear ultrasonic transducer of 4 MHz frequency (MB4y - Karl Deutsch).

The longitudinal, shear ultrasonic velocities and ultrasonic attenuation were measured by using pulse echo technique:direct contact transducer coupling from one specimen side acted both as transmitter and receiver of echoes. Ultrasonic measurements clarified the doping effect on  $Cu_2O$  thin film microstructure.

### 2.4 Determination of microstructure parameters

Microstructural parameters (crystallite size, microstrain and residual stress) play a crucial role in the behavior of materials and their physical properties especially the microstructural properties. Their importance is ascribed to the macroscopic characteristics and their potential usages in the advanced technological applications. X-ray diffraction line profile analysis (XRDLPA) is considered to be one of the most accurate techniques to determine the microstructure parameters of the prepared samples. The line broadening x-ray line profiles is usually described by a result of the small size of the crystalline [18, 22] as well as the non-uniform displacements strain of the atoms with respect to their reference lattice positions [23]. The line shape caused by lattice distortions in crystallization, which is revealed that the broadening of a diffraction peak with indices hkl. The integral breadth, values (area under the peak /maximum intensity of peak) of the characterized peaks were measured. It is a convolution of an instrument and a physical factor. This can be represented as follows:

$$I_{obs}(2\theta) = I_{exp}(2\theta) * I_{S}(2\theta) + background$$
(1)

where (\*) is a convolution operator. The functions  $I_{obs}$ ,  $I_{exp}$  and  $I_s$  are the broadening profiles of (i) the observed, (ii) the instrumental factor and (iii) the pure sample ( $\beta$ ), noting that, these three broadening profiles are functions in the diffraction angle  $2\theta$ . The corrected Lorentzian (Couchy) and Gaussian distribution of the integral breadth are given by:

$$\beta_{\rm L} = B - b \tag{2}$$

$$\beta_G^2 = B^2 - b^2 \tag{3}$$

where B and b are the broadening and instrumental factors, respectively. In this study, the exact microstructure parameters of the samples was determined in two ways: Firstly; the average crystallite size (D) is calculated by using Scherrer's equation as follows [24]:

$$D = K \lambda / \beta \cos\theta \tag{4}$$

Where the constant K is taken to be 0.94,  $\lambda$  the wavelength of x-ray used and  $\beta$  the broadening of pure specimen correction of the diffraction peak. The internal micorstrain,  $\langle \epsilon \rangle$  in the film is calculated according to the relation:

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$$\left\langle \varepsilon \right\rangle = \frac{\beta \cot \theta}{4} \tag{5}$$

Secondly, the Williamson-Hall method is used in the case of samples containing many xray diffraction peaks, as in the current samples. This fundamental difference was that both of the microstructural causing a small crystallite size and microstrain were combined to expand the reflection broadening.Depending on the different positions, the separation between the crystallite size and microstrain broadening analysis are performed using the Williamson and Hall (W-H) method. The equation of this method is given in the following equation [25-27]:

$$\beta_{hkl} = \beta_{strain} + \beta_{crystallite \ size} \tag{6}$$

$$\beta_{hkl} = \left(\frac{k\lambda}{D\cos\theta}\right) + 4\langle\varepsilon\rangle \tan\theta \tag{7}$$

Rearrangement equation (7) gives

$$\beta_{hkl}\cos\theta = \left(\frac{k\lambda}{D}\right) + 4\langle\varepsilon\rangle\sin\theta \tag{8}$$

where  $\beta_{hkl}$  is the pure broadening of the sample,  $\theta$  is the diffraction angle, k is the shape factor and in our case it is equal 0.94. The incident X-ray wavelength  $\lambda$  is ( $\lambda = 0.154184$  nm), D is the crystallite size and  $\langle \varepsilon \rangle$  is the average microstrain.

Residual internal stress is another important factor that depends on the structure and affects the properties of the microstructure of crystalline materials. It is defined as a normal stress that affects the normal surface of the plane and the shear stress resulting from perpendicular stress actions of the same plane. In measuring residual internal stress using X-ray diffraction, the strain in crystal lattice is determined by the residual stress associated with the elastic constants, assuming linear distortion of the appropriate crystal lattice plane. The uniform stress deformity model strain is calculated from the Hook's law maintenance line, which is a proportional to stress and strain by  $\sigma = Y\epsilon$ , where  $\sigma$  is the stress and Y is the Young's modulus. Apply Hook's law approximation to equation (8):

$$\beta_{hkl}\cos\theta = \left(\frac{k\lambda}{D}\right) + 4\left(\frac{\sigma}{Y_{hkl}}\right)\sin\theta \tag{9}$$

The energy density of a crystal was calculated from a model called Uniform Deformation Energy Density Model (UDEDM). From equation (8) we need to implicit that crystals are to be homogeneous and isotropic nature. The energy density,  $E_d$  can be calculated from  $E_d = \langle \varepsilon^2 \rangle Y_{hkl}/2$ using Hook's law. The equation (8) can be modified according the energy and strain relation:

$$\beta_{hkl}\cos\theta = \left(\frac{k\lambda}{D}\right) + 4\left(\frac{2E_d}{Y_{hkl}}\right)^{1/2}\sin\theta \tag{10}$$

Here equation (8) stands for UDM where it is assumed that the strain is uniform in all crystalline directions.  $\beta \cos\theta$  was plotted with respect to  $4\sin\theta$  for investigated samples. From the slope and y-intercept of the fitted line ware calculated the microstrainand crystallite size. Therefore, it can be evaluated the  $\sigma = \epsilon Y$  and the energy density  $E_d = \langle \epsilon^2 \rangle Y_{hkl}/2$ . Where the Young's modulus of Cu<sub>2</sub>O is 116.5GPa[28].

# **3.Results and discussion**

# **3.1X-ray diffraction analysis**

Cu<sub>2</sub>O crystallizes in a cubic structure with a two sublattice, face-centered cubic of copper cations and body centered cubic of oxygen anions. Oxygen atoms occupy tetrahedral interstitial positions relative to the sublattice of copper, so that the tetrahedron is the oxygen coordination of copper, while copper is coordinated by two neighboring oxygen. Effect of adding sulfur and chromium elements on crystalline features of Cu<sub>2-x</sub>S<sub>x</sub>O and Cu<sub>2-y</sub>Cr<sub>y</sub>O samples thin films prepared at 0.05M as shown in Figure 1. All the lines that appeared of these samples can be matched with the characteristic lines of polycrystalline  $Cu_2O$  has a cubic crystal structure (JCPDS no. 65-3288). It is clear that, the five lines at  $2\theta$ =29.44, 36.40, 42.48, 61.65 and 73.30° which can be ascribed to the (110), (111), (200), (220) and (311) diffractions of Cu<sub>2</sub>O phase. The intensities of the peaks were continuously decreased with increasing the sulfur ratio contents. This indicates that the degree of crystallization of the samples decreases with the increase in ratio sulfurdoped. Similarly, the characteristic lines of the Cu<sub>2</sub>O did not change position with the addition of the Cr element, but decreases the intensity of x-ray diffraction. This confirms that, the S and Cr ions are effectively substituted Cu sites within Cu<sub>2</sub>O lattice without affecting the crystal structure of the parent Cu<sub>2</sub>O. This is due to the shortdistance between the two of copper atoms equal to 3.02Å and the total diameters equal to 1.56 Å, so there are internal spaces between the two atoms of copper equal to 1.46 Å. Also, the internal space between each of the Cu and O atoms equal to 1.84 Å, thus the sulfur atom filled the interstitial between each of the copper and oxygen because the smaller diameter of sulfur atom is equal to 0.37 Å. Similarly, when adding Cr-atoms (3% and 6%), since the shortest atomic distance between Cu and O atoms equal to 3.68 Å and the bond length between two atoms of copper equal to 3.02 Å, as well as the Cr atoms have a diameter of 0.52 Å. Thus, it occupies the unit cell of the Cu<sub>2</sub>O and therefore did not affect the XRD pattern of the resulting Cu<sub>2</sub>O.



Fig. 1. The diffractograms of Cu<sub>2</sub>O thin films at different doping S and Cr ratios.

### 3.2 Effect of S and Cr on the lattice parameters

To calculate the average of lattice parameters (*a*) and also the value of interplaner spacing (*d*) of the diffraction angles for a number of five characteristic lines of  $Cu_{2-x}S_xO$  and  $Cu_{2-y}Cr_yO$  samples uses the following relation:

$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2)}{a^2} \tag{11}$$

Bragg's law is used to determine the  $2\theta$  value  $\lambda = 2d_{(hkl)}\sin\theta_{(hkl)}$ . The interplanarspacing, the lattice parameters values and unit volume are mentioned in the Table 1 and represented in Fig. 2.



Fig. 2(A). Interplanerspacing (Å), determined from x-ray diffraction pattern for undoped and S, Cr-doped Cu<sub>2</sub>O NPs.
 (B). Lattice constants a (Å), determined from x-ray diffraction pattern for undoped and S, Cr-doped Cu<sub>2</sub>O NPs.



Fig. 3(A). Volume of unit cell (Å<sup>3</sup>) determined from x-ray diffraction pattern for undoped and S,Cr-doped Cu<sub>2</sub>O NPs.
(B). lattice strain (Δa/a<sub>o</sub>) determined from x-ray diffraction pattern for undoped and S,Cr-doped Cu<sub>2</sub>O NPs.

Table 1.XRD data analysis of  $Cu_{2-x}S_xO$  and  $Cu_{2-y}Cr_yO$  thin films; 20 value of plane (111), d-value, lattice parameter values ( $a_o$ ) using Nelson–Riley extrapolation method, the change in the lattice parameter ( $\Delta a=a-a_o$ ), the lattice strain ( $\Delta a/a$ ) and volume of unit cell (where  $a_o = 4.2696$  Å according to JCPDS card number 65-3288).

Sample	2θ (Degree)	d(Å)	Lattice parameter a (Å)	$\begin{array}{c} \Delta a \times 10^{-3} \\ (\text{\AA}) \end{array}$	Lattice strain ( $\Delta a/a$ )	Volume of unit cell (Å <sup>3</sup> )
Pure Cu <sub>2</sub> O	36.36	2.4709	4.2796	10.00	$2.342 \times 10^{-3}$	78.385
Cu <sub>2</sub> O: 5% S	36.38	2.4696	4.2774	7.80	1.827x10 <sup>-3</sup>	78.260
Cu <sub>2</sub> O:10% S	36.40	2.4683	4.2751	5.50	1.288x10 <sup>-3</sup>	78.136
Cu <sub>2</sub> O:20% S	36.42	2.4669	4.2728	3.20	7.495x10 <sup>-4</sup>	78.011
Cu <sub>2</sub> O:3% Cr	36.34	2.4718	4.2819	12.30	2.880x10 <sup>-3</sup>	78.507
Cu <sub>2</sub> O:6% Cr	36.32	2.4735	4.2842	14.60	3.419x10 <sup>-3</sup>	78.634

The slightly decreasing values of the interplaner, d, are clearly attributable to the effect of the internal or surface interface energy of the prepared samples that reduce the surface area of the lattice unit cell of the formed undoped Cu<sub>2</sub>O and doping samples by S ions. The difference in the valence values of the sulfer and copper elements also plays an important role in the shrinkage of

the unit cell obtained from the unit cell of  $Cu_{2-x}S_xO$  compound. This is due to, the unit cell will suffer shrinkage in its dimensions. It should also be noted from Figure (2) that d-values are almost linear decrease when S is increasing in complex  $Cu_{2-x}S_xO$  samples. The lattice parameters valuescan be fitted to describe their decrease by increasing content S according to the following equation;

$$a(Å) = 4.2792 - 0.03377 X$$
(12)

where X is the S -content ratio  $(0.00 \le X \le 0.2)$  in the  $Cu_{2-x}S_xO$  samples. This indicates that deflation occurs in a similar way in all directions. In general, copper oxide nanoparticles contain many oxygen vacancies and lattice disorders. Due to the interaction of S ions with excess oxygen, resulting in decreased vacancy until network constants are reduced. There is also a dangling bond, which should be considered. These dangling bonds will react strongly with oxygen ions in the surrounding area, resulting in reduced lattice dimensions.

On the other hand, Fig. 2 depicts the change in the lattice constants  $\Delta a(\text{Å})$  of the S -doped Cu<sub>2</sub>O. As is evident, these changes are very small (in order  $10^{-3}$  Å), tend to decrease with increasing S -content. Hence and from above one can summarize that the lattice constants of investigated sample are compatible with the Vegard's law [29 -31].

In addition, the calculated volume of unit cell of  $Cu_{2-x}S_xO$  was determined and listed in Table 1 as shown in Fig. 3. Volume of unit cell values can be fitted to describe their decrease by increasing content S according to the following equation:

$$V(Å^3) = 78.36 - 1.850 X$$
 (13)

where X is the S -content ratio  $(0.00 \le X \le 0.2)$  in the  $Cu_{2,x}S_xO$  samples. It is obvious that the volume of the unit cell decreased from 78.385Å<sup>3</sup> to 78.011Å<sup>3</sup> with increasing S-ratio (X) from 0.00 to 0.2, respectively, confirming on the shrinkage of the lattice unit cell of the prepared  $Cu_{2,x}S_xO$ -NPs. This is evidence of shrinkage of the unit cell construction of  $Cu_2O$  with the addition of S element due to replacing the Cu atom in the unit cell with the smaller diameters. Where the atomic radius of the Cu element is 145pm while the atomic radius of S element is 87pm.

On the contrary when adding the Cr element which has the atomic radius (166pm) greater than the radius of the atoms of the copper element to the  $Cu_{2-y}Cr_yO$  compound. There is a shift towards the lower diffraction angle and thus an increase in the amount of the interplanar spacing and the amount of the lattice parameter which in turn cause the increase of the volume of unit cell of  $Cu_{2-y}Cr_yO$  extends from 78.507 to 78.634Å<sup>3</sup> with the Cr-ratio varying from 0.03 to 0.06, respectively.

 and (200), the degree of the orientation, σ(hkl) of standard (0.2474), interfacial tension, Ti(N/m)and volumetric mass density, ρ (g/cm<sup>3</sup>).

 Texture coefficient &
 Scherrer's

Table 2. The experimental data estimated of  $Cu_{2,v}S_xO$  and  $Cu_{2,v}C_vO$  thin films; TC of the two planes (111)

	Tex	ture coefficien	nt &	Scherrer's	W-H method		
Sampla	the	orientation de	gree	method	w-minethou	Density,	
Sample	(111)	(200)	σ <sub>(111)</sub>	Ti	Ti	$\rho$ (g/cm <sup>3</sup> )	
	(111)			(N/m)	(N/m)		
Pure Cu <sub>2</sub> O	0.669	1.068	1.694	3.800	5.915	6.062	
Cu <sub>2</sub> O: 5% S	0.703	1.071	1.628	3.557	5.272	6.072	
Cu <sub>2</sub> O:10% S	0.763	1.152	1.604	2.839	5.680	6.081	
Cu <sub>2</sub> O:20% S	0.947	1.427	1.588	1.819	2.428	6.091	
Cu <sub>2</sub> O:3% Cr	0.669	1.069	1.567	4.694	7.251	6.110	
Cu <sub>2</sub> O:6% Cr	0.602	1.176	1.546	5.648	9.118	6.139	

### 3.3The lattice strain and interfacial tension

The strain is a terminology used to express the distortion that occurs in the dimensions of the material sample relative to the original length. There are two types of strain, namely, uniform and non-uniform strains. The regular strain causes an expansion or contraction of the unit cell in an isotropic way [32]. This leads to some changes in the lattice parameters of the unit cell, thus causing a shift in the observed peaks. While the irregular strain leads to regular shift of atoms from their original locations and thus causes peak broadening [33]. The irregular strain arises due to the presence of many defects within the material, such as point defects, plastic deformation and bad crystallization of the material. The strain observed in the current  $Cu_{2x}S_xO$  and  $Cu_{2y}Cr_yO$ -NPs samples was an irregular strain, causing the XRD peaks to shift from their original locations as well as it causes them a broadening. This strain can be expressed along three dimension of the cell unit as  $(\Delta a/a)$ . They are sometimes called lattice strains or relative changes in the lattice constants. The lattice strain of the present samples Cu<sub>2-x</sub>S<sub>x</sub>O and Cu<sub>2-y</sub>Cr<sub>y</sub>O was found to be a non-uniform strain, causing the shift to XRD peaks from their original positions. The calculated values of these strains are recorded in Table 1. It can be easily observed that the behavior of the lattice stains  $(\Delta a/a)$  is reduced as a function of S-content, indicating that changes in the unit cell are constant in all directions and thus the unit cell can maintain its regular shape [34].

On the other hand, the crystalline tendency of the  $Cu_{2-x}S_xO$  and  $Cu_{2-y}Cr_yO$ -NPs samples is known as a spherical interface called  $T_i$ . Quantitative data about this tension, and its energy in previous literature, whether experimental or theoretical, are very rare. Solliard and Flueli can evaluate the interstitial tension,  $T_i$  using this equation[35-37]:

$$\frac{\Delta a}{a_0} = -\frac{4}{3} \frac{T_i}{KD} \tag{14}$$

\

$$T_i = \frac{3KD}{4} \left(\frac{\Delta a}{a_o}\right) \tag{15}$$

where K is the bulk modulus of Cu<sub>2</sub>O (K = 105.7 GPa) [28] and D is the crystallite size value. Accordingly, this interfacial tension was calculated in (N/m) and then included in Table 2. It was noted that  $T_i$ -values decreased of the present Cu<sub>2-x</sub>S<sub>x</sub>Osamples when S-content increased, which is due to the decreased value of the lattice strain. Although the values of crystalline size D increased, this increase is very small compared to the rapid decrease of values ( $\Delta a/a$ ). In addition, since  $T_i$  is defined as the energy per unit area of the crystallite size, since the values of D have increased, interferacial energy has decreased.

#### 3.4 Calculation of volumetric mass density from X-ray data

The importance of knowing the density of the prepared polycrystalline thin films of  $Cu_{2-x}S_xO$  and  $Cu_{2-y}Cr_yO$  samples have been theoretically calculated from measurements of XRD according to the relationship [38,39];

$$\rho = \frac{nM_w}{NV} \tag{16}$$

where, *n* is the number of molecular per unit cell,  $M_w$  is the molecular weight of  $S_xCu_{2-x}O$  and  $Cr_yCu_{2-y}O$ , V is the volume of a unit cell and N is Avogadro's number (6.0228x10<sup>23</sup>molecule/mol). The obtained theoretical value of the density is recorded in Table 1. We found that the density value of composite was almost consistent with the Vergard'slaw where the Cu<sub>2</sub>O density was equal 6.00 g/cm<sup>3</sup> and the density of S and Cr elements was 2.07g/cm<sup>3</sup> and 7.19g/cm<sup>3</sup>, respectively.

#### 3.5 Preferred orientation and texture coefficient

The texture coefficient,TC of  $Cu_{2-x}S_xO$  and  $Cu_{2-y}Cr_yO$  films can be estimated from the peak intensities using the method of Harris for polycrystalline fiber texture analysis [40, 41]. The degree of the preferred orientation, that is the orientation parameter of a certain crystal plane (hkl) in a polycrystalline film, can be determined from the following equation (Harris method);

$$TC = \frac{I_{(hkl)}/I_{o(hkl)}}{\frac{1}{N}\sum_{n} I_{(hkl)}/I_{o(hkl)}}$$
(17)

where  $I_{(hkl)}$  and  $I_{o(hkl)}$  are the measured intensity and standard integrated intensity (JCPDS number 65-3288) for (hkl) reflection, respectively, and N is the number of reflections observed. Since the texture coefficient measures the relative degree of preferred orientation during crystal plane growth of Cu<sub>2-x</sub>S<sub>x</sub>O and Cu<sub>2-y</sub>Cr<sub>y</sub>O thin films. The texture coefficient (TC) represents the texture of a particular plane, deviation of which from unity implies the preferred growth. TC for (111) and (200) planes are calculated using equation (13) and obtained values are recorded in Table 2. As seen from data, there is a clear difference between (111) and (200) peak intensity due to increasing of the doping ratios. It is observed that TC of (200) plane increases this suggests that a preferential orientation of Cu<sub>2</sub>O lattice plane is indicated a perpendicular alignment of the X-axis of the particles [41, 42].

On the hand, the degree of the orientation ( $\sigma$ ) of Cu<sub>2-x</sub>S<sub>x</sub>O and Cu<sub>2-y</sub>Cr<sub>y</sub>O films for a certain direction plane canbeestimated from the standard deviation of all TC<sub>i</sub>values, using the following equation [43–45]:

$$\sigma_{(hkl)} = \sqrt{\sum_{i=1}^{N} (TC_i - TC_{i0})^2}$$
(18)

where TC<sub>i</sub> is the texture coefficient of the plane (i), TC<sub>io</sub> is the texture coefficient of the standard sample in accordance with JCPDS card number 65-3288. The number N is the number of the observed planes. It is worthy to mention that the zero value of  $\sigma$  indicates that the sample is randomly orientated. But, if ( $\sigma$ ) has larger values, this suggests that the sample has a better orientation along this plane. The estimated  $\sigma$ values for the diraction plane (111) and (200) were recorded in Table 2. It is observed that the computed  $\sigma$ -values decreased with increasing S and Cr contents. This result confirms that the crystallization process decreased in the<111> direction when the S and Cr addition was increased as obtained before.

### **3.6Determination of microstructural studies**

The crystallite size and microstrain plays a crucial role in the behavior of the material and its physical properties, especially the microstructural properties. Their importance is due to their ascribed to the macroscopic characteristics and potential uses in advanced technological applications. Scherrer formula maintained in equations 4 and 5 is one of the most accurate techniques for determining the crystallite size and microstrain. It can be used successfully to determine the sample purity broadening at each x-ray diffraction peak. Also, Williamson Hole in Equation (8) is the favorite method to be used in the case of samples containing several x-ray diffraction peaks, as in present samples. Which is treated the pure peak broadening as the sum contributions of both the crystallite size and the microstrain. They supposed that the microstrain which presented in the sample is uniform, i.e. they considered the sample has the isotropic nature. Thus, from equation (8), if a graph is plotted between ( $\beta \cos \theta$ ) on the Y-axis against (4 sin  $\theta$ ) on the X-axis, then a straight line will be obtained. From the intercept part and the slope, it can calculate the average of crystallite size, D and the average of microstrain  $< \epsilon >$ , respectively. Plotting of ( $\beta \cos \theta$ ) versus ( $4 \sin \theta$ ) have been represented for the present Cu<sub>2-x</sub>S<sub>x</sub>O and Cu<sub>2-y</sub>Cr<sub>y</sub>O samples in Figs. (4a &b). The obtained values of the average crystallite size and the average microstrain according to Scherrer and W-H methodscalculations were tabulated in Table 3.

Clearly the values obtained from the crystallite size increased by increasing the content S and Cr-ratio of  $Cu_{2-x}S_xO$  and  $Cu_{2-y}Cr_yO$  NPs. The most important observation is that all samples are nanosized whether Scherrer and W-H are used, although there are slight differences in D values. The increasing values of D may be due to the S-ions is inserted within the  $Cu_2O$  unit cell, which helps S-ions to form larger crystalline clusters. Figure 5 illustrates this increasing variation in the crystallite size calculated by Scherrer, W-H method for  $Cu_{2-x}S_xO$  and  $Cu_{2-y}Cr_yO$  thin films. This result confirms that advances improve crystallization and at the same time increase the

crystals size. While with the addition of Cr-element, it leads to a decrease in crystalline agglomeration. These results correspond to the crystallite size values obtained from the field emission scanning electron microscope of many authors in the previous literature [46, 47].



Fig. 4(A). Variation of  $(\beta \cos \theta)$  versus  $(4 \sin \theta)$  for the present S doped Cu<sub>2</sub>O samples B). Variation of  $(\beta \cos \theta)$  versus  $(4 \sin \theta)$  for the present Cr doped Cu<sub>2</sub>O samples.

The mean values of the microstrain,  $< \epsilon >$  for the current  $Cu_{2-x}S_xO$  and  $Cu_{2-y}Cr_yO$  samples were obtained directly from the slope of straight line as shown in Fig. 4 (a and b) and their estimated values are listed in Table 3 and are represented in Fig. 6. The behavior of  $<\epsilon>$  values comes with is contrary to the behavior of D values, which decreases with increasing S or Cr content. This result can be attributed to the decreasing volume occupied by the atoms arranged in a featured agglomerate crystalline. This behavior has been observed in previous literature [48, 49].



Fig. 5.Plotting of the crystallite size against the S and Cr content for the present Cu<sub>2</sub>O-NP samples, using the calculations of Crystallite size is achieved Scherrer and W-H methods.



Fig. 6.Plotting of the microstrain against the S and Cr content for the present Cu<sub>2</sub>O-NP samples, using the calculations of Crystallite size is achieved Scherrer and W-H methods.

### 3.7 Dislocation density and Number of crystallite per unit volume

The strength and ductility of materials is controlled through dislocations. Dislocation density ( $\delta$ ) is defined, along the length of the dislocation lines per unit volume. In this study, the density dislocation of Cu<sub>2-x</sub>S<sub>x</sub>O and Cu<sub>2-y</sub>Cr<sub>y</sub>O thin films is estimated from the following relationship[25, 49]:

$$\delta = \frac{1}{D^2} \tag{19}$$

It is known that, the calculated value of  $\delta$  is attributed to the amount of defects in a crystal growth of Cu<sub>2-x</sub>S<sub>x</sub>O and Cu<sub>2-y</sub>Cr<sub>y</sub>O thin films. Dislocation density as a function of S and Cr-content were calculated and recorded in Table 3 and depicted in Figs. (7-a). It is observed reveals that, the  $\delta$  values were depending on the number of S and Cr-atoms of Cu<sub>2-x</sub>S<sub>x</sub>O and Cu<sub>2-y</sub>Cr<sub>y</sub>O compound. This result is the logic in which the XRD showed that the formed phase was partially crystallized so that the defects of the lines would easily occur. These results are consistent with data obtained by others for CdSand like phase thin films [25, 50, 51].

In addition, the crystalline number of each unit volume depends on the following parameters: crystallite size, crystallite shape, crystalline equality and the degree of agglomeration of thin films. It can determine the best size and shape of the crystallites with the density and type of atoms found in crystalline clusters. If the current atoms are light, the crystallites will be medium sized and contain the largest volume of crystalline clusters or agglomerate. In the case of high density atoms (in a range of less than 100 nm), the size of crystals or aggregates may be less. The number of crystals per unit volume (N) for  $Cu_{2-x}S_xO$  and  $Cu_{2-y}Cr_yO$  thin films was calculated from the estimated values of the crystallite size (D), using the following formula[52, 53]:

$$N = \frac{t}{D^3} \tag{20}$$

where the film thickness (t  $\approx$ 75nm). These calculated values for N were listed as a function for S and Cr in Table 3 and illustrated in Fig. (7-b). It was observed that for all samples examined from different S content, the number of crystals per unit volume was increased by adding S element. This is due to that, the reduction in the crystallite size of Cu<sub>2-x</sub>S<sub>x</sub>O matrix when someone adds more S to the matrix [54]. Conversely, with the addition of the Cr element in the Cu<sub>2-y</sub>Cr<sub>y</sub>O compound, where the N value decreases with the increase of the Cr-content.

<b></b>	Scherrer's method						W-H method							
Sample		<8>	Sx10 <sup>8</sup>	E <sub>d</sub>		Nx10 <sup>18</sup>	$\delta x 10^{14}$		<3>	Sx10 <sup>8</sup>	E <sub>d</sub>		Nx10 <sup>18</sup>	$\delta x 10^{14}$
~	D(nm)	x10 <sup>-3</sup>	N/cm <sup>2</sup>	x10 <sup>+</sup> J/cm <sup>3</sup>	nx10 <sup>4</sup>	cryst/m <sup>2</sup>	line/m <sup>2</sup>	D(nm)	x10 <sup>-3</sup>	N/cm <sup>2</sup>	x10 <sup>+</sup> J/cm <sup>3</sup>	nx10 <sup>4</sup>	cryst/m <sup>2</sup>	line/m <sup>2</sup>
Pure Cu <sub>2</sub> O	20.47	8.236	9.55	2.19	5.729	8.278	2.387	31.86	5.321	6.17	1.76	21.602	2.195	9.852
Cu <sub>2</sub> O: 5% S	24.56	7.699	8.93	2.11	9.912	4.792	1.657	36.40	4.706	5.45	1.65	32.267	1.472	7.547
Cu <sub>2</sub> O: 10%S	27.81	7.164	8.31	2.04	14.413	3.301	1.293	39.22	4.457	5.17	1.61	40.427	1.177	6.501
Cu <sub>2</sub> O: 20%S	30.62	6.630	7.69	1.96	19.269	2.473	1.067	40.86	3.993	4.63	1.52	45.787	1.041	5.989
Cu <sub>2</sub> O: 3% Cr	20.56	5.563	6.45	1.79	5.796	8.169	2.366	31.76	3.699	4.29	1.46	21.366	2.216	9.914
Cu <sub>2</sub> O: 6% Cr	24.74	3.967	4.60	1.52	10.083	4.689	1.634	33.64	3.178	3.69	1.35	25.349	1.865	8.837

Table 3. The average crystallite size, D, the average microstrain,  $\langle \varepsilon \rangle$ , the total stress,  $\sigma$  and the energy density, u, number of unit crystal per crystallite size, the number of crystallite and the dislocation density of Cu2-xSxO and Cu2-yCryO thin films, calculated according to W-H and Scherrer's methods.



Fig. 7(A).Plotting of the dislocation density against the S and Cr content for the present Cu<sub>2</sub>O-NP samples, using the calculations of Crystallite size is achieved Scherrer and W-H methods.
(B). Number of crystallite per unit volume against the S and Cr content for the present Cu<sub>2</sub>O-NP samples, using the calculations of Crystallite size is achieved Scherrer and W-H methods.

# 3.8The strain energy density and the number of unit cell

The value of the strain energy density within the thin  $E_d$  depends on the Young's of the modulus of the Cu<sub>2</sub>O film and the volume of the unit cell, V and the internal microstrain, < $\epsilon$ >. The energy density of this strain can be calculated as follows [55, 56]:

$$E_d = \frac{S^2}{2Y} = \frac{1}{2}S\langle\varepsilon\rangle = \frac{1}{2}Y\langle\varepsilon\rangle^2$$
(21)

The values of the strain energy density,  $E_d (J/m^3)$  were calculated and then tabulated in Table 3 and represented in Fig. 8 (a). From Williamson-Hall and Scherrer methods, it can observe that in the two cases, the strain energy decreased when S and Cr-content was increased. This decreasing is attributed to the decreasing of the average microstrain and the total internal stress.

Furthermore, in order to estimate the number of unit cell per crystallite size (n) of  $Cu_{2-x}S_xO$  and  $Cu_{2-y}Cr_yO$  nanocrystals using the following relation [57]:

$$n = \frac{\pi D^3}{6V} \tag{22}$$

where V represents the volume of unit cell and D is the size of the crystallite. The calculated values of (n) for the different of S and Cr content are shown in Table (3) and represented in Fig. (8-b). It was observed that the number of unit cells, n increases with increasing doping of S but decreases with Cr -ions. Similarly, these data are consistent with the findings found in literature [57].



Fig. 8.Plotting of the strain energy density and the number of unit cell per cluster against the S, (A) and Cr (B) content for the present  $Cu_2O$ -NP samples, using the calculations of Crystallite size is achieved Scherrer and W-H methods.

#### 4. Ultrasonic measurements

### 4.1 Longitudinal and shear ultrasonic velocities measurements

Due to the very short propagation pathways in the material, measurements of ultrasonic delay times were performed across waveguides, which contacted with the medium under investigation. Ultrasonic velocities of the longitudinal as well as shear ultrasonic waves can be derived from transit time ( $\Delta$ t) and sample thickness (d), can be determined from the following expression [58];

$$C = 2d / \Delta t \tag{23}$$

where d is the distance between the tips of the waveguides, $\Delta t$  is the delay time of the ultrasonic wave in the waveguides.

	Long	gitudinal	Shea		
Sample	Transit time (Δt), (±0.03ns), ns	velocity(C <sub>L</sub> ), (±30m/s), m/s	Transit time (Δt), (±0.03ns), ns	velocity(Cs), (±30m/s), m/s	Density (ρ), g/cm <sup>3</sup>
Pure Cu <sub>2</sub> O	0.41	3951	0.51	3176	6.065412
Cu <sub>2</sub> O: 5% S	0.45	4089	0.58	3272	6.070142
Cu <sub>2</sub> O:10% S	0.62	4355	0.74	3649	6.087702
Cu <sub>2</sub> O:20% S	0.71	4732	0.86	3907	6.112301
Cu <sub>2</sub> O:3% Cr	0.59	3831	0.72	3139	6.193211
Cu <sub>2</sub> O:6% Cr	0.67	4328	0.80	3625	6.321581

Table 4.Experimental data of the longitudinal, shear ultrasonic velocity and density of  $Cu_{2-x}S_xO$  and  $Cu_{2-y}Cr_yO$  thin films.

From the results shown in Table 4, it can be observed that ultrasonic velocities have increased as the percentage of S and Cr doping increases. This is due to increasing the crystalline size with the addition of the S element as the increase of the crystalline agglomeration increases the density of the composite, which in turn increases the bulk modules expansion which increases the velocity of acoustic waves in the Cu<sub>2</sub>O thin films [59].

#### **4.2 Density (ρ) measurement**

The density ( $\rho$ ) of the prepared specimens was measured by the following formula [58]:

$$\rho = W_s \rho_w / (W_s - W_w) \tag{24}$$

where  $W_s$  and  $W_w$  are weights of specimen in air and in water respectively, while  $\rho_w$  is the density of water. Table 5 shows the density ( $\rho$ ) measurements for different Cu<sub>2</sub>O thin films with different S concentration.From Table 4, the density was increased as the dopant (Cr and S) increased. When the concentration of the dopant increased the thin film's grains became more interconnected, uniform and compact [60]. So both the internal gaps and the thin film's volume decreased, causing the increment in thin film's densities.

## 4.3 Bulk modulus

The bulk modulus (K) of a substance is a measure of how incompressible/resistant to compressibility that substance is. It is defined as the ratio of the infinitesimal pressure increase to the resulting relative decrease of the volume[60]. It can be calculated by the following formula [58]:

$$K = \rho \left[ \left( C_{L} \right)^{2} - \left( \frac{4}{3} \left( C_{s} \right)^{2} \right) \right]$$
(25)

where  $\rho$  is the specimen's density,  $C_L$  is the ultrasonic longitudinal velocity and  $C_S$  is the ultrasonic shear velocity.



Fig. 9.Bulk modulus (K) variation with respect to different S and Cr concentration in Cu<sub>2</sub>O thin films.

Sample	Bulk modulus (GPa)	Attenuation coefficient,α (dB/cm)		
Pure Cu <sub>2</sub> O	13.11	12.42		
Cu <sub>2</sub> O: 5% S	14.84	11.64		
Cu <sub>2</sub> O:10% S	7.38	7.26		
Cu <sub>2</sub> O:20% S	12.46	4.92		
Cu <sub>2</sub> O:3% Cr	9.53	8.83		
Cu <sub>2</sub> O:6% Cr	7.65	7.24		

Table 5. Estimated the Bulk modulus and attenuation coefficient of  $Cu_{2,v}S_xO$  and  $Cu_{2,v}Cr_vO$  thin films.

From Fig.9, the bulk modulus decreases with respect to S content in the prepared Cu<sub>2</sub>O thin films (Cu<sub>2</sub>O-5%S, Cu<sub>2</sub>O-10%S) but it increases again at Cu<sub>2</sub>O-20%S. Sulfur (5% and 10%) may cause increment in compressibility of Cu<sub>2</sub>O thin films so cause decrement of bulk modulus, but sulfur of 20% may cause some alteration in the crystallinity or in the structure of the films. Also, the bulk modulus decreases with respect to Cr content in the prepared Cu<sub>2</sub>O thin films (Cu<sub>2</sub>O-3%Cr, Cu<sub>2</sub>O-6%Cr). Chromium may cause increment in compressibility of Cu<sub>2</sub>O thin films so cause decrement of bulk modulus.

# 4.4 Ultrasonic attenuation

The ultrasonic attenuation coefficient ( $\alpha$ ) of longitudinal ultrasonic waves was determined in each specimen at room temperature and a frequency of 4 MHz by measuring the height of 2 consecutive echoes as [60]:

$$\alpha = (1/2d)\ln(h_1/h_2)$$
(26)

where d is the thickness of the specimen and  $h_1$  and  $h_2$  are the heights of the first and second echoes, respectively [61]. The attenuation measurements are accurate to  $\pm 0.2$  dB/cm.



Fig. 10.Attenuation coefficient (a) variation with different S and Cr concentrations in  $Cu_2O$  thin films.

From Fig.10, it can be seen that the attenuation coefficient ( $\alpha$ ) is decreased with respect to increment in sulfur percentage in the prepared Cu<sub>2</sub>O thin films. Sulfur caused strengthens in the thin film structure so the attenuation was decreased and also, Sulfur improved the prepared Cu<sub>2</sub>O thin films. It can be seen that the attenuation coefficient ( $\alpha$ ) is decreased with respect to increment in chromium percentage in the prepared Cu<sub>2</sub>O thin films (Fig. 10). Chromium is one of the transition metal, which may cause good gap filling with Cu<sub>2</sub>O thin films. Therefore, it may be said that chromium caused strengthens in the thin film structure and improved them.

# **5.** Conclusions

Cubic crystal shaces of  $Cu_2O$  nanoparticles were successfully manufactured at room temperature by using pyrolysis technique using Cu (II) as a primary material. The effect of S and Cr on the microstructural, crystal defects and mechanical properties were studded. With no change the peaks position, the intensities of the XRD peaks were decreased with increasing the S and Cr ratio contents. This confirms that, the S and Cr ions are effectively substituted Cu sites within  $Cu_2O$  lattice without affecting the crystal structure of the parent  $Cu_2O$  and also, indicates that the degree of crystallization of the samples decreases with the increase in ratio S and Cr doping.

The obtained results of the density ( $\rho$ ) for Cu<sub>2</sub>O doped S and Cr measurements by XRD are in good agreement with ultrasonic measurements. The bulk modulus of Cu<sub>2</sub>O films decreases with S and Cr doping content, this may cause increment in compressibility of Cu<sub>2</sub>O thin films. The attenuation coefficient ( $\alpha$ ) is decreased with increasing S and Cr percentage in the prepared Cu<sub>2</sub>O thin films. Sulfur caused strengthens in the thin film structure so the attenuation was decreased.

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