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RESEARCH PAPER

Effect of Lithium on Structural and Optical Properties of Nanostructured CuS Thin Films

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ABSTRACT

In this study, the chemical bath deposition (CBD) strategy was applied for preparation of pure and Lithium-doped copper sulfide (CuS) thin film on glass. The CuCl2.2H2O, as a copper source and thiourea as a sulfur source were used. The structural, topographical, and optical properties of products were characterized via powder X-ray diffraction (XRD), atomic force microscopy (AFM), and UV-Vis spectroscopy. Results showed that the crystalline size is increased via Lithium doping, though the strain (%) parameter decrease from 30.39 to 27.47. Obtained results revealed that doing of lithium has a significant effect on the optical properties of prepared CuS-based thin films. The optical properties of samples was investigated through band gap calculation. The bands gap were calculated 2.4, 2.5, and 2.6 eV for CuS:3% Li, CuS:1% Li and pure CuS thin films respectively. Based on attractive properties of prepared thin films, Lithium-doped CuS thin film has potential application in optoelectronic fields.

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INTRODUCTION

Nanostructure-based semiconductors have been found more attention in recent years. Semiconductor Copper sulfide is one of the most promising materials which have attractive electrical, optical and catalytic properties [1-3]. The biocompatibility of CuS is a key properties which facilities application of CuS in the bio-related fields [4, 5]. Many reports have been focused on the CuS binary system in powder, bulk, and as thin films with different compositions and properties. These differences in the properties originated mainly by factors related to phases equilibria, because of a strong tendency of Cu and S to form several metastable and nonstoichiometric phases. The copper chalcogenide system is known to have five different stable phases at room temperature: chalcocite (Cu_2S), djurleite ($Cu_{1.95}S$), digenite ($Cu_{1.8}S$), anilite ($Cu_{1.75}S$), and covellite (CuS) with a crystal structure varying from hexagonal to orthogonal[6, 7].

The size-dependent properties of nanostructures lead to engineering different route for preparation of CuS nanostructures[8]. Till now various methods have been applied for synthesis of CuS nanostructures, such as hydrothermal [9], atomic layer deposition [10], photo chemical deposition [11], sonochemical [12], microwave

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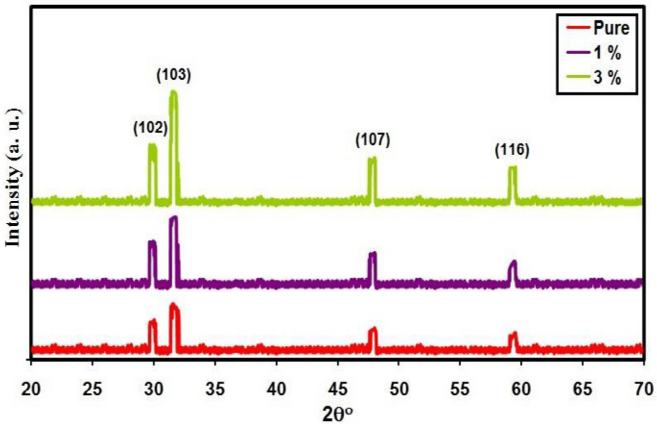

Fig. 1. XRD-patterns of the deposited films.

[13], microemulsion [14], spray pyrolysis [15], and chemical bath deposition (CBD) [16, 17]. CBD is a method to deposit thin films and nanomaterials, first described in 1869. Chemical bath deposition encompasses a variety of routes for producing functional films and coatings at relatively low temperature by immersing a substrate in a liquid solution.

Fayroz A.Sabahthe and et al. prepared CuS thin films via two processes; the first process called pyrolytic process to deposit CuS thin film on glass, ITO, Si and tungsten substrates using CW CO_2 laser beam (10.6 µm, 40 W) as the heat source rather than a heater, while the second process called photolytic process to deposit CuS thin film on glass substrate by apply the laser directly on the droplet after leaving the nozzle. They investigated all structural and morphological properties of prepared thin films and showed that prepared thin films can be applied as a pH sensors [18].

In another work, the microcrystal structure of copper sulfide (CuS) nano-structured ultra-thin film was prepared on glass substrate from aqueous ammonia solution and sodium hydroxide at 60 °C using a simple and cost-effective chemical bath deposition (CBD). The structural, morphological and optical properties of prepared thin film were characterized via powder X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), and UV-Vis spectroscopy[19].

The current study is about the grown of CuS and CuS:Li thin films by chemical bathe deposition (CBD). It likewise focuses on the effect on basic and optical properties it has including absorption coefficient (α), transmittance (T), and the films bandgap energy. Using AFM, the film surface morphology was talked about. Using XRD, the auxiliary portrayal was additionally contemplated.

MATERIALS AND METHODS

CuS films were prepared through CBD technique. The 10 ml triethanolamine, 8 ml salt (30%), and 10 ml NaOH (1M) were applied as a solution content. The 10 ml $CuCl_2.2H_2O$, as a copper source and 6 ml thiourea (1 M) as a sulfur source were dissolved in solution and make 100 ml in volume via deionized water. The temperature of reaction medium was set at the of 40 °C. The different content of Lithium Chloride as a dopant were added under stirring condition. After preparation of the CuS films, prepared thin films cleaned with deionized water and subsequently are dried by 40 °C temperature air. Thin films thickness were measured by weighing method and found to be 200 ±10 nm. The structural properties were examined by X-ray diffractometer (Shimadzu, model: XRD-6000, Japan). AFM (AA 3000 Scanning Probe Microscope) was used to study surface topography, then optical transmittance and absorbance were registered in the wavelength range (300-900nm) using UV-Visible spectrophotometer (Shimadzu Company Japan).

RESULTS AND DISCUSSIONS

The X- ray diffraction of CuS and CuS: Li films appear in Fig. 1. XRD pattern shows peaks at (2θ~ 29.28°, 31.78°, 47.82° and 59.4°) in correspondence to the planes (102), (103), (107) and (116) separately that are attributed to the hexagonal crystalline structures. These peaks agree with JCPDS 06-0464. The presence of

Table 1. Grain size, optical bandgap and structural parameters of the films.

Samples	(hkl) Plane	2θ (°)	FWHM (°)	Grain size (nm)	Optical bandgap (eV)	Dislocations density ($\times 10^{14}$)(lines/m^2)	Strain ($\times 10^{-4}$)
CuS	103	29.28	0.72	11.4	2.6	76.69	30.39
CuS: 1% Li	103	29.00	0.68	12.07	2.5	68.64	28.72
CuS:3% Li	103	28.70	0.65	12.62	2.4	62.78	27.47

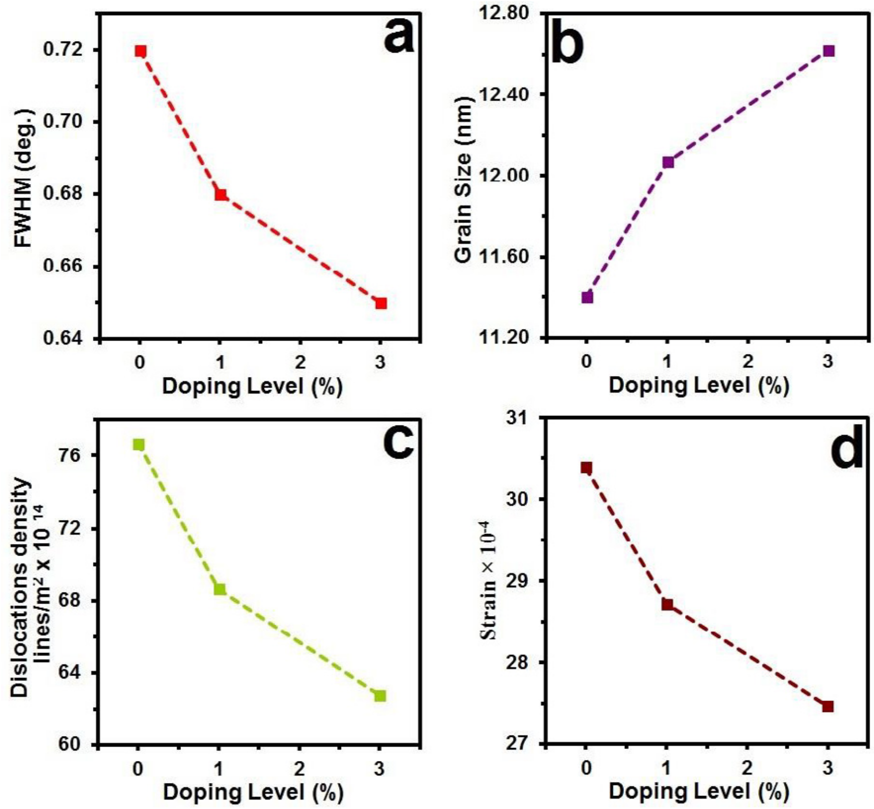

Fig. 2. FWHM (a) Grain size (b) Dislocation (c) Strain (d).

different peaks confirms the polycrystallinity of prepared films. The obtained rsults are in a good agreement with previous reports [20].

Scherrer's formula was applied for calculation of crystallite size, as follows [21]:

$$D = \frac{0.9\lambda}{\beta\cos\theta} \quad (1)$$

Where D is the crystallite size, λ represents the X-ray wavelength, β represents (FWHM) and θ is Bragg's angle. Table 1 shows the values of D which 11.40 nm and 12.62 nm for CuS and CuS:3%Li thin films, respectively. As well as shown, the crystalline size is increased via Lithium doping, though the strain (%) parameter diminishes from 30.39 to 27.47.

The following equation was utilized to measure the dislocation density (δ) in the thin Films.

$$\delta = \frac{1}{D^2} \quad (2)$$

The following equation was utilized to determine the strain (ε) in the thin Films.

$$\varepsilon = \frac{\beta\cos\theta}{4} \quad (3)$$

It is observed that the value of (ε) (Table 1) increases as doping Lithium increases. CuS film adheres well to the glass substrate. This will induce some lattice strain within the CuS film. The calculated structural parameters are shown in Table. 1

The correlation between FWHM, D, δ, strain, and dopant content is represented in Fig. 2. It

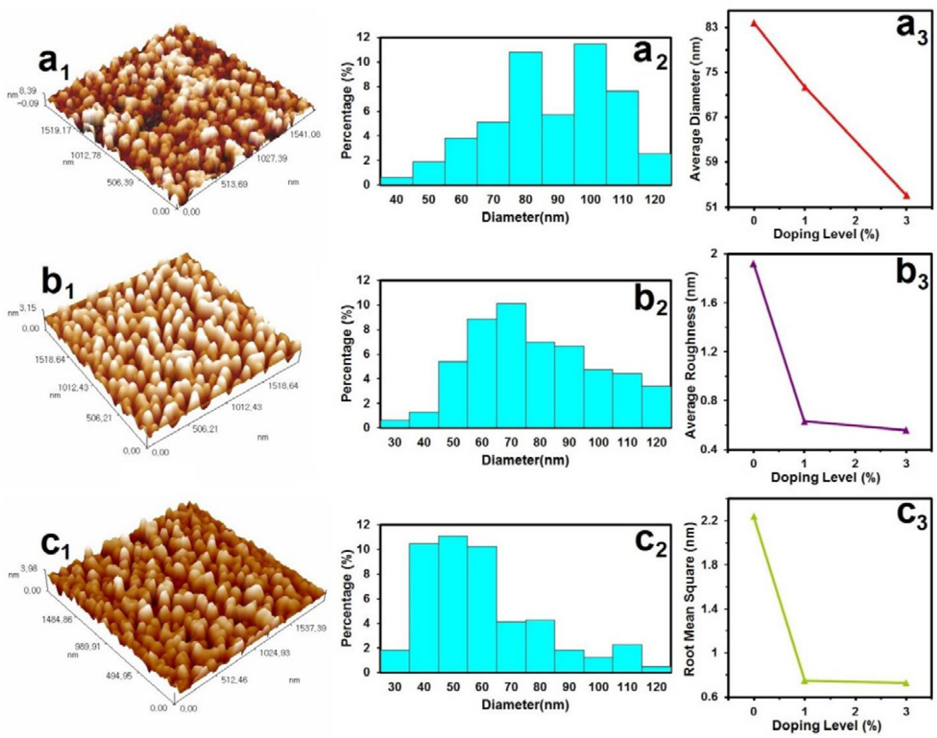

Fig. 3. AFM images of the prepared films (a_1, b_1 and c_1), granularly distributed (a_2, b_2 and c_2) and variation of AFM parameters via doping (a_3, b_3 and c_3).

Table 2. AFM parameters of the deposited films.

Samples	Average Diameter nm	Roughness Average (nm)	R. M. S. (nm)
CuS	83.81	1,92	2.24
CuS: 1% Li	72.40	0.62	0.75
CuS: 3% Li	53.15	0.58	0.73

also shows the different correlation between the size of the crystallite and other parameters. Fig. 2 demonstrates β, D, δ and ε strain versus doping content.

To investigation the surface topography of deposited films, an (AFM) was applied . 3D AFM image of CuS thin films are displayed in Fig. 3 (a_1, b_2 and c_1). It shows that the CuS thin films has larger particle size, which indicates the crystalline nature of the films is of high crystallinity and good surface morphology.

The root mean square roughness (R_{rms}) and average roughness (R_a) of prepared films are shown in Table 1. As can be seen the R_{rms} and R_a related to the dopant. The deposits materials surface morphology is studied through the use of atomic force microscope (AFM). The particle size of the nanoparticles is noted to be (83.81), (72.40) and (53.153) nm for CuS films grown at CuS: 1% Li and CuS: 3% Li, respectively. The R_{rms} value of 2.24 nm for as deposited CuS film, thin films decreased to 0.73.37 nm by decreased CuS: 3% Li, R_a roughness parameters as a function of dopant concentration were given in Fig. 3 (a_3, b_3,and c_3) respectively. Table (2) represent the values of AFM parameters.

Fig. 4 shows the transmittance spectra of the prepared samples. The results revealed that the normal transmission (T) in the noticeable region is about 75-55% at the wavelength around 600nm, which transmittance surpasses esteems that are accounted for somewhere else.

Using the equation 4, where absorption coefficient (α cm^{-1}) was calculated from absorbance (A), as follows:

$$\alpha = (2.303\times A)/t \quad (4)$$

Where (t) related to film thickness. Fig. 5

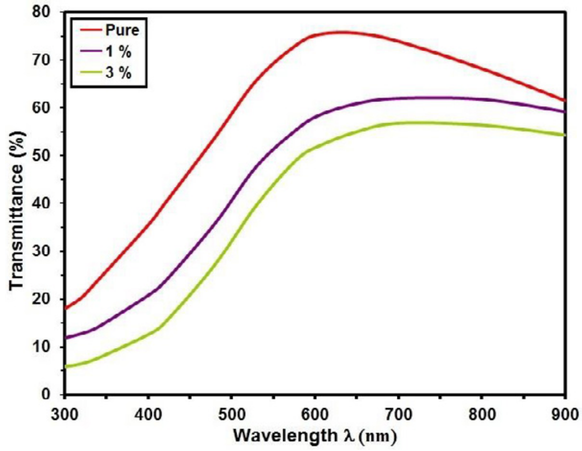

Fig. 4. Transmittance of the prepared films.

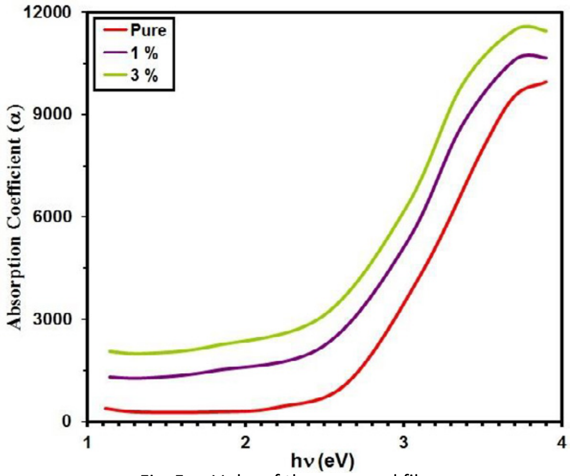

Fig. 5. α Vs hν of the prepared films.

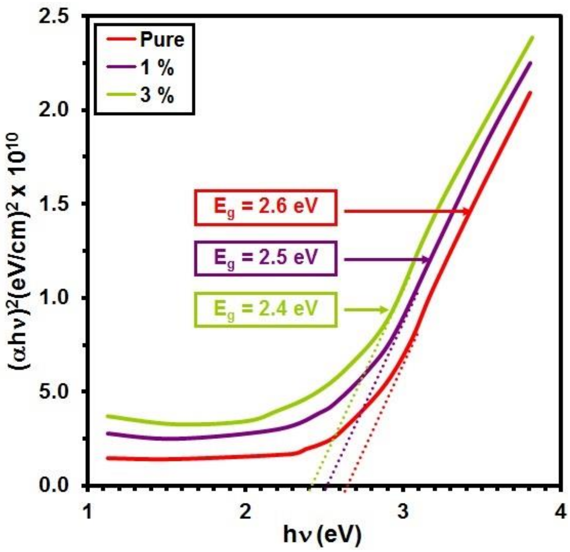

Fig. 6. $(\alpha h\nu)^2$ Vs hν of the prepared films.

demonstrates the relationship between the α versus photon energy. From Fig. 5, it can be found that the absorption coefficient of CuS thin films relayed on the Lithium-content and E_g increase as Lithium increases.

The optical band gap (E_g) of the CuS and CuS:Li thin films was calculated using the following equation:

$$(\alpha h\nu) = A\left(h\nu - E_g\right)^{\frac{1}{2}} \quad (5)$$

where hv is the photon energy, A is a constant, the plot of $(\alpha h\nu)^2$ and photon energy (hv), was shown in Fig. 6. From Fig. 6 it should be noted that the bandgap of the CuS thin films depends on the Lithium-content and E_g decreases as Li increase. The bandgap values of the synthesized nanocrystalline CuS and CuS:3% Li thin films are 2.6 and 2.5 eV, respectively. Table (1) represent the values of bandgap.

CONCLUSION

An appropriate CBD strategy was applied for preparation of CuS-based thin film on glass. The XRD pattern confirms polycrystalline hexagonal structure. The Grain size for pure CuS and CuS:3% Li were calculated 11.40 and12.62 nm respectively. Also the strain (%) for CuS and CuS:3% Li were calculated from 30.39 to 27.47. AFM analysis shows that presence of Lithium affect morphological properties of products. The particle size were determined 83.81, 73.40 and 53.15 nm for the CuS, CuS:1% Li and CuS:3% Li respectively. The optical properties of prepared samples was studied comprehensively. It was concluded that the optical transmittance reduce from 75% - 55% in the visible region wavelength, when the content of lithium was increased. Results showed that the band gap of products lead to decrease via increasing lithium content.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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