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Investigation of the Annealing and Cu Doping Effect on Structural and Optical Properties of CdZnS Nanomaterial Deposited by Ultrasonic Spray Pyrolysis

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ABSTRACT

This study investigates doped CdZnS thin films synthesized through the ultrasonic spray pyrolysis technique, followed by annealing at temperatures of 400 and 500 °C. X-ray diffraction analysis demonstrated that both undoped CdZnS and Cu-doped CdZnS thin films exhibit cubic crystal structures, with a preferred orientation along the (111) plane. Scanning electron microscopy (SEM) measurements indicated that the CdZnS thin film has a smooth surface, whereas the Cu-doped CdZnS film shows clustered particles, attributed to the effect of copper doping acting as an activator metal ion. Electron dispersive scanning (EDS) analysis confirmed that the Cd, Zn, and S elements are present in acceptable chemical stoichiometry (Cd + Zn/S = 1:1), with a ratio of 3:1, consistent with the molar amounts used in the precursor solutions. The band gap of the CdZnS thin film decreased from 3.12 to 2.56 eV after annealing at 500 °C, attributed to an increase in crystal size. In contrast, the band gap of the Cu-doped CdZnS thin film decreased from 2.51 to 2.22 eV, lower than that of pure CdZnS, due to the formation of additional phases such as zinc oxide and copper oxide within the CdZnS host structure during annealing.

Keywords: Ultrasonic spray pyrolysis, CdZnS thin film, Annealing, Band gap energy.

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Introduction

The II-VI compound group holds significant importance in the field of material science due to their specific bandgap spanning from UV to IR light wavelengths. These compounds are composed of elements from group II (like zinc, cadmium, and mercury) and group VI (including oxygen, sulfur, selenium, and tellurium). Their appeal to scientists lies in their direct bandgap energy, typically falling between 1.5 to 3.7 eV, which makes them highly suitable for optical applications. They exhibit exceptional optical absorption characteristics, capable of absorbing 99% of incident light with just a 1µm thickness, making them a focus of extensive research [1, 2].

There are many methods to produce CdZnS thin film like chemical bath deposition (CBD) [3,4], thermal vacuum evaporation technique (PVD) [5], electrodeposition technique [7,8], and ultrasonic spray pyrolysis (USP) [9, 10]. Among these techniques, USP technique is the most preferred one, it is easy, and many layers can be deposited.

Previous studies reported that CdZnS thin film could be doped with cationic metals such as Cu, Zn, Ag, and Al or anionic metals such as B, Cl, and Fe, etc. In our study doping by copper ions has been used to improve the electro-optical properties and to increase the efficiency of photocatalytic activity by enhancing the electron transition [11], [12, 13, 14, 15, 16, 17].

In this study, first, pure CdZnS ternary and Cu-doped CdZnS quaternary thin film samples were fabricated by the USP technique and then annealed at 400 and 500 °C, to investigate of annealing effect on the crystal structures, surface morphology, chemical composition, and optical properties of the fabricated samples.

Materials and Methods

To fabricate the CdZnS thin films, zinc chloride (ZnCl2), cadmium chloride (CdCl2), and thiourea (CH_4N_2S) salts were used as precursor materials. First, 0.3 M of ZnCl2 was dissolved in 20 ml of distilled water, and after 10 minutes, two drops of hydrochloric acid (HCl) was added to this solution to prevent oxychloride formation. Then, 0.6 M of thiourea was dissolved in a separate beaker with 10 ml of distilled water and mixed with the ZnCl2 solution. Subsequently, 0.1 M of CdCl2 was dissolved in 20 ml of distilled water in another beaker. This solution was then poured into the first prepared solution, and the mixture was stirred with a magnetic stirrer for two hours until it became completely homogeneous. This solution was divided into two separate beakers: one for the preparation of pure CdZnS thin films and the other for the preparation of Cu-doped CdZnS thin film samples, to which 2 mg of copper sulfate (CuSO4.5H2O) was added.

The glass substrate cleaning process involved using ethanol, acetone, and ethanol sequentially. The Sono-Tek Flexi Coat, equipped with a nitrogen gas generator, was utilized in an ultrasonic spray pyrolysis (USP) deposition system. Other optimization parameters were set as follows: nitrogen pressure at 2.5 kg/cm², substrate-to-nozzle distance at 12 cm, and solution flow rate at 0.5 ml/minute. Doped and undoped CdZnS thin films were produced on substrates with a 10 × 10 cm² deposition area at a substrate temperature of 275 °C in an ambiance containing 3% oxygen. Both thin films were annealed at 400 °C and 500 °C, respectively, using an oven supplied with nitrogen gas and excess sulfur (sulfurization) to improve crystallinity【18,19】.

The structural properties of CdZnS and CdZnS: Cu thin films were studied by using Bruker D8 Advanced Twin-twin XRD system with the Cu-Kα radiation with a wavelength of 1.5406 Å and 2θ ranging from 20° to 80°. Morphology and elemental analyses of the films were examined by FEI Quanta FEG 250 Scanning Electron Microscope (SEM) which attached an EDAX EDS system. Optical characterization was also held by using Perkin Elmer Lambda 950 UV/Vis spectrophotometer in between 300 – 1000 nm wavelength.

Glutathione (GSH) is a tripeptide found within cells. It plays a critical role in neutralizing free radicals and reactive oxygen species (ROS), thereby preventing oxidative stress and maintaining cellular homeostasis. It is a central component in preserving redox homeostasis (the oxidative state within cells) [11]. The balance between oxidized glutathione (GSSG) and reduced glutathione (GSH) determines a cell's capacity to cope with oxidative stress. This ensures that cells function healthily and prevent the onset of pathological conditions. Therefore, GSH and its metabolism are considered potential therapeutic targets in many diseases associated with oxidative stress [12, 13].

Malondialdehyde (MDA), a by-product of lipid peroxidation, is also considered an indicator of oxidative damage. It is used to assess the extent and effects of oxidative damage to membrane lipids [14, 15].

In particular, in research and clinical studies, the examination of GSH and MDA aids in understanding oxidative damage and elucidating cellular mechanisms at the cellular level. In this study, the effects of toluene exposure-induced oxidative stress in rats were investigated. Additionally, it was assessed whether resveratrol plays a protective role against these adverse effects. Levels of MDA, an indicator of lipid peroxidation, and GSH, which plays a significant role in cellular antioxidant defense, were analyzed.

Results and Discussion

X-Ray Diffraction Measurements

The XRD patterns recorded for CdZnS and CdZnS: Cu thin films deposited on glass substrates for as-grown and annealed samples at 400 °C and 500 °C are given in Figures 1. a) and b), respectively. It can be seen, all the planes displayed in cubic structure and polycrystalline in nature. The major peak of cubic structure for both films CdZnS and CdZnS: Cu were found at 2θ values of 28.62° and 28.39°, respectively, which are attributed (111) directional plane as a preferred plane orientation. Scherer's equation [19](Eq.1) has been applied to calculate the average crystal size.

$$D=0.92\lambda/B\cos\theta \quad (1)$$

Where λ =1.5406 Å for CuKα , B is full width at half maximum (FWHM) and θ is Bragg's angle. Crystal size was Calculated of CdZnS and Cu-doped thin films are listed in Table 1 and 2, respectively.

Table 1. Crystal size for CdZnS and CdZnS : Cu doping thin films.

Sample	peak position for (111) indices	FWHM (deg)	Average of crystal size A°
Undoped sample as grown	28.62°	0.784	116.2
Undoped sample annealed 400 °C	28.72°	0.735	124.0
Undoped sample annealed 500 °C	28.28	0.692	131.5
Doped sample as grown	28.39°	3.515	26.0
Doped sample annealed 400 °C	28.21°	3.084	29.5
Doped sample annealed 500 °C	27.92°	3.352	27.2

Table 1 shows that the crystal size of CdZnS and CdZnS: Cu doping thin films increases with annealing temperature due to the reduction of structural defects within the lattice by applying extra thermal energy [19, 21, 22], but this trend is disrupted after annealing at 500 °C for copper doping thin film. This is due to the substitution of Cu^{2+} ions, which have a smaller ionic radius (0.73 Å) compared to Cd^{2+} ions (0.97 Å). Cu^{2+} ions can easily enter the CdZnS lattice, causing distortion in the CdZnS lattice structure, which aligns with previous reports in the literature [22,23].

Figure 1.a) shows that the improvement of the main diffraction peak intensity of CdZnS thin film depended on the increase of the annealing temperature, this improvement might be attributed by the high thermal energy helps the atoms to move to the correct position in the lattice. As a result the defects will be reduced that leads to re re-crystallization in the lattice [19, 21 ,22]. Whereas Figure 1.b) shows that after annealing the samples up to 500 °C, it is clear there is a disruption of the main diffraction peak for CdZnS: Cu thin film, and a slight shifting for the major peak (111). This reason is argued by

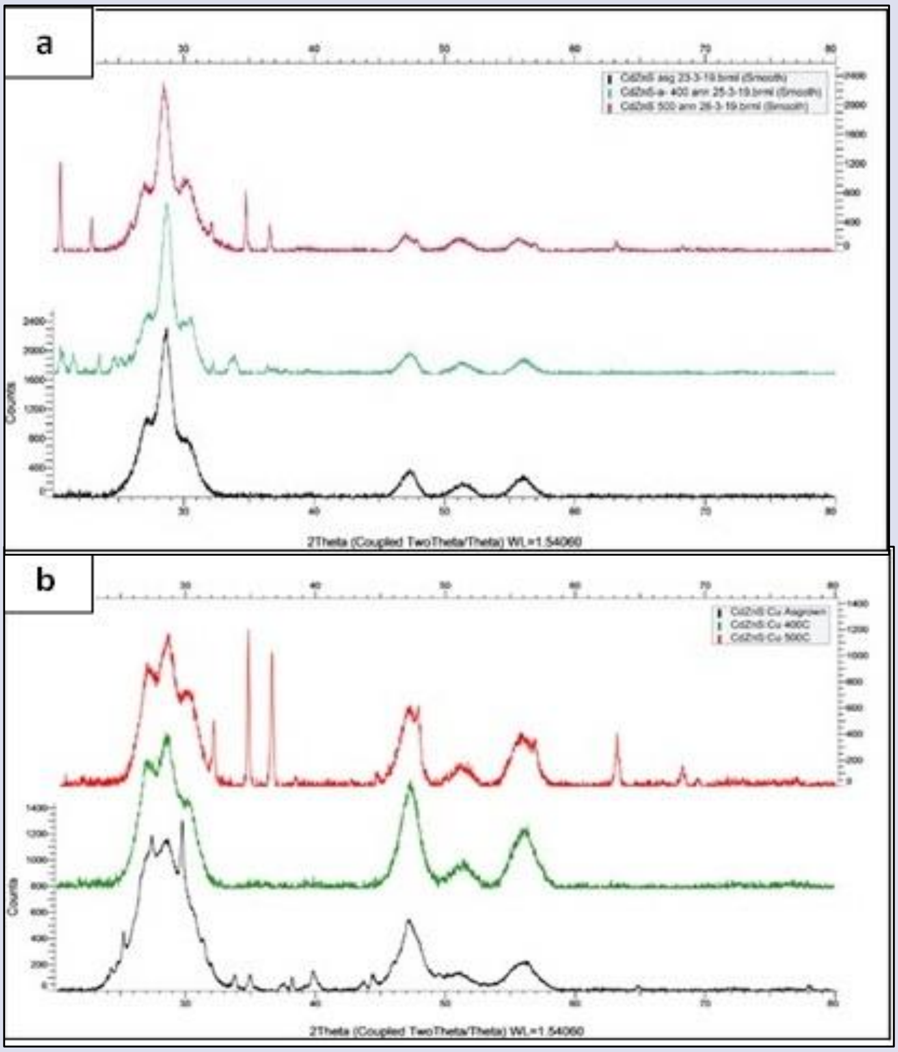


Figure 1. (A) GSH levels in rat lung. (B) GSH levels in rat serum

the oxidization and with copper oxide crystal structure has been generated to take its poison inside the hostel crystal, however all the peaks matching with CdZnS structure PDF 01-079-7040 library, it is in consistent with the literatures reported [23, 24, 25].

Surface Morphology Analysis

Figure 2. a) and b) represents images of scanning electron microscopy (SEM) for the surface of CdZnS and CdZnS:Cu thin films, respectively.

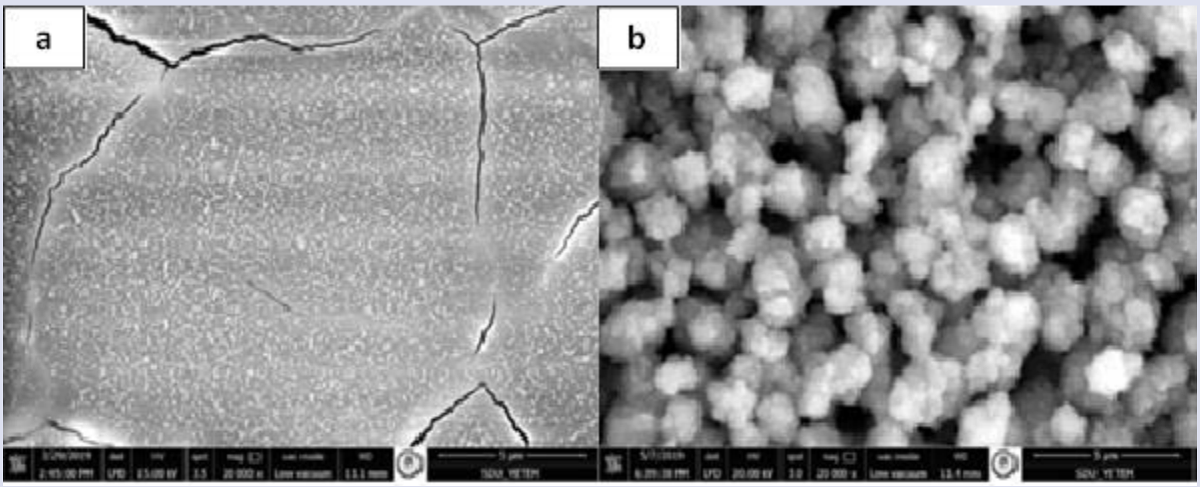


Figure 2. As grown SEM images of a) CdZnS and, b) CdZnS: Cu thin films

SEM images shows that the surface of CdZnS thin film has smooth and a few cracks, whereas the surface of CdZnS: Cu thin film has clusters, due to the effect of doped copper metal which was added to the precursor solution and generated agglomerated particles.

The energy dispersive spectroscopy (EDS) system is followed by SEM measurements, and the elemental composition analysis of the CdZnS and CdZnS: Cu thin films for as grown, annealed at 400 °C and 500 °C, respectively, are given in Table 3. and 4. It was observed that Cd, Zn, and S elemental compositions are approximately the same for CdZnS and CdZnS: Cu thin films. Although there were slight differences in their concentrations due to the deposition process was not homogeneous. However, all the elements in both films are closed to be aimed composition with the acceptable chemical stoichiometry (Cd+Zn/S =1:1), and the ratio of Zn: Cd = 3:1, according to the amount of molarity which has been used. After annealing under sulfur resulted in an excess number of sulfur elements in the thin film structure as expected. It is also clear that the crystallographic results gained from XRD and elemental composition results obtained from EDS measurements are in good agreement with each other.

Table 3. EDS measurements as atomic percentage(A%) of CdZnS and Cu doping thin film as grown, and annealed at 400 °C and 500 °C.

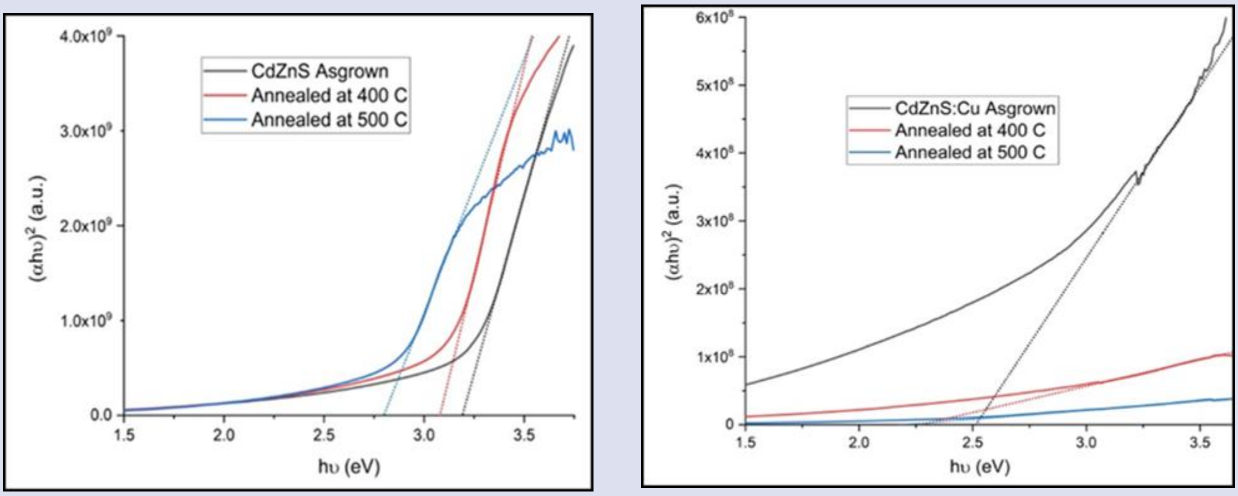
Samples	S	Cd	Zn	Cu	Zn/Cd	Zn+Cd/S
undoped sample as grown	39.07	8.36	33.3	--	3.98	1.06
undoped sample annealed 400 °C	40.05	9.09	38.13	--	4.19	1.17
undoped sample annealed 500 °C	36.62	8.07	39.5	--	4.89	1.29
doped sample as grown	33.55	7.78	30.6	0.36	3.933	1.14
doped sample annealed 400 °C	30.98	7.97	36.3	0.45	4.55	1.42
doped sample annealed 500 °C	33.32	8.1	39.06	0.37	4.82	1.41

Optical Properties

Figure 3.a) and b) showed the Absorption spectra for both CdZnS and Cu doped respectively. The absorption spectra for both films were recorded by using UV-vis system at room temperature in the wavelength ranging from 300 -1000 nm, the result showed that the absorption spectrum is shifted to the blue region which exhibited lower absorption in the longer wavelength. The band gap energy was estimated with help of absorption spectra and by using Tauc relation [25] (Eq. 2)

$$\alpha h\nu = A\,(h\nu - E_g)^n \qquad \textbf{(2)}$$

Where α; is an absorption coefficient, hv; photon energy, E_g; band gap, A; constant and n = 1/2 for allowed direct band gap transition of CdZnS. By plotting the graph of $(\alpha h\nu)^2$ versus and applying the extrapolation method, the band gap energy values of the samples shown in the figure3



(a) (b)

Figure 3. Band gap energy of a) CdZnS and b) CdZnS: Cu doped thin films.

Figure 3.a) shows that an absorption edge is shifted to the blue region, which exhibited lower absorption in the longer wavelength, and optical band gap value decreased from 3.12, 3.01 to 2.56 eV for as grown, annealed sample at 400 °C and annealed sample at 500 °C, respectively. The decrease in the bandgap values arises from increasing of crystal size as is shown in Table 3. And quantum confinement which taking a place in the crystal structure [26, 27].

Figure 3.b) indicates that the energy band gap value of CdZnS: Cu thin film decreases with increasing annealing temperature. The bandgap energy values decrease from 2.51, 2.30, and 2.22 eV which is associated with an extra phase of zinc oxide and copper oxide, generated inside the host structure of CdZnS due to the effect of thermal metal oxidization. That will cause to shift toward lower energies. However, this is in agreement with the previous literatures reported related to metal doping to CdZnS thin films [28, 29].

Conclusion

CdZnS and Cu-doped thin films were fabricated by ultrasonic spray pyrolysis method and annealed at 400 and 500 °C to investigate the annealing effect on the crystal structures, surface morphology, chemical composition, and the optical properties of the fabricated samples, XRD, SEM, EDS, and UV-VIS measurements were conducted. XRD analysis showed that the CdZnS and Cu-doped CdZnS thin film samples have cubic crystal phase and polycrystalline structure. SEM measurements indicated that CdZnS thin film has a smooth surface, whereas CdZnS: Cu has cluster particles due to the effect of copper doping which presents as an activator metal ion. EDS analysis exhibited that all the components Cd, Zn, and S are composed in chemical stoichiometry (Cd+Zn/S =1:1), and the ratio of Zn: Cd = 3:1. After annealing at 500 °C, it was observed that the bandgap energy value of CdZnS thin film decreased from 3.12 to 2.56 eV due to an increase in crystal size , and at the same time bandgap energy of the CdZnS: Cu thin film was lower than pure CdZnS decreasing from 2.51 to 2.22 eV resulting from the associated to extra phases of zinc oxide and copper oxide, generated inside the host structure of CdZnS by annealing effect. This is evidence that doping by copper ions is playing a major strategic role in the enhancement of photocatalytic activity.

In addition, some studies can be carried out on the application of the USP deposited CdZnS thin films as a window layer for solar cells since their suitable band gap energy values can be changed by applying annealing and copper doping as required

Conflict of interest

There is no conflict of interest among the authors.

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