Investigation of the role of annealing time in the optical, structural and morphological properties of trinary CdZnS thin films prepared by chemical bath deposition

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In this paper, CdZnS nanocrystalline films have been deposited by using chemical bath deposition (CBD) technique on glassy substrates. After deposition process, the films were annealed at different period of time (30, 60 and 120 minute) using thermal furnace. Optical properties of CdZnS films such as absorbance and optical band gap, have been investigated. From this measurements, the bandgaps energies were found to be 3 eV, 2.69 eV, 2.5 eV and 2.2 eV for (0, 30, 60 and 120 minute) respectively. The optical energy gap decreased as the annealing time increased. In this study, the influence of annealing time on the structure, optical, and surface properties of CdZnS thin films was examined, and the results were thoroughly discussed. This demonstrates their potential applicability in optoelectronic and photovoltaic devices, among other things.

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Keywords: annealing time; CdZnS; trinary thin film; CBD

1. Introduction

In optoelectronics, ternary thin films have piqued interest because of their unusual properties and numerous potential uses. Trinary semiconductor thin films can be modified by modifying one or more of its components, which affects their optical, structural, and morphological qualities [1]. As a wide band-gap window material, Cadmium zinc sulfide (CdZnS) thin films have been used a lot. They have been used in hetero junction solar cell and in photo conductive device. Solar cells where CdS films have been shown to work well have seen a decrease in window absorption losses and an increase in the short circuit current when CdZnS films were used instead of CdS films. [2-8]. In addition, trinary mixtures CdZnS consider hopeful material for high-density optical record, as well as for visible or ultra violet laser diode, among other applications. These applications were founded on the crystal structure of CdZnS, which has essential absorption edge that can range from green to ultraviolet in wavelength., several applications have been developed. [9]. Several approaches, such as thermal evaporations [10], close-spaced sublimations [11], chemical-vapor deposition (CVD) [12], spray pyrolysis [13] Chemical bath deposition (CBD) has been modified to deposit CdZnS thin films. CBD is the most popular of these deposition approaches because of its cost-effectiveness and ease of use during the deposition process. In addition, by adjusting the bath conditions, it is possible to modify the optoelectronic properties of the resultant thin films [1]. In this paper, we investigated the effects of annealing time on the structural and optical properties of CdZnS thin film has been invented through CBD procedure.

2. Experimental work

Nanocrystalline CdZnS thin film is deposited on glass substrate by CBD process in a solution holding 0.1M 20ml of cadmium cloride CdCl2 and 0.1M/20 ml of Zinc nitride [Zn(NO)3] were used as a Cd and Zn source, correspondingly. Solution of ammonia was dropped to alter the pH of solution to 10 and the whole solution volume was 100ml. 20 ml of 0.1 M of thiourea has been dropped gently to the above mixture. After disturbed the solution by magnetic

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stirrer for 5 minute, the glass substrates were dipped in vertical way inside the glass beaker and then located on the hot plate under temp. of 70 oC for 60 min.

Then the samples removed from the solution and rinsed with distilled water to remove any remaining impurities before being placed on a drying rack to complete the process. Yellowish layer covers the substrate indicates preparation CdZnS thin film. The films annealed in oven in temperature around 200 C for 30, 60, 120 min to test the influence of annealing time on the properties of prepared films. Table 1 show the preparing information for all samples

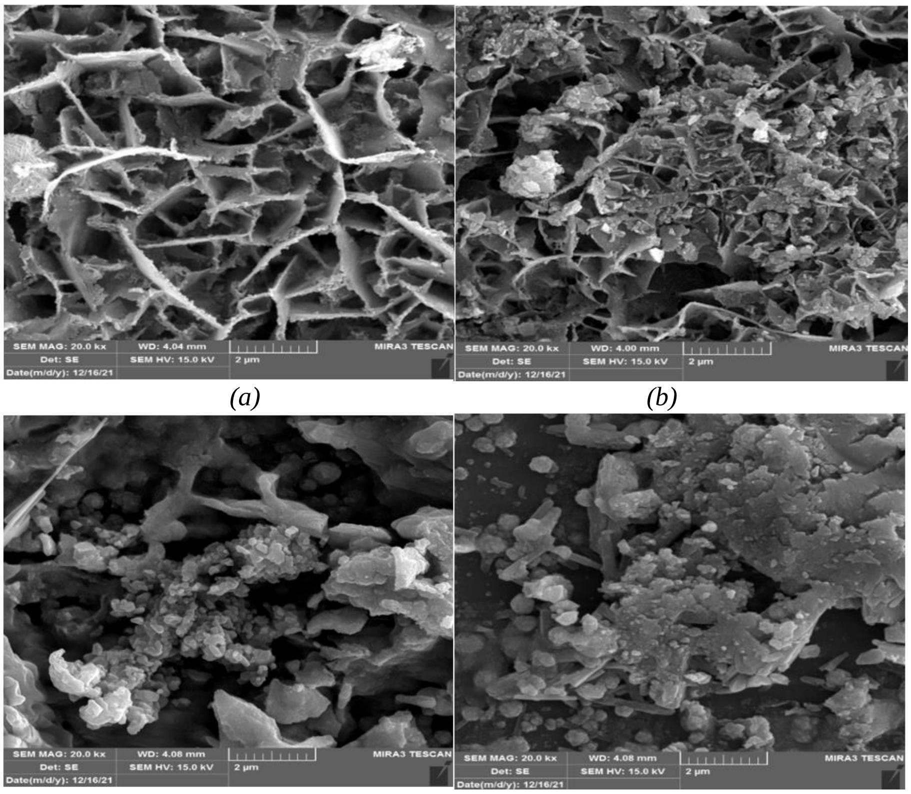
Cu-K radiation with a wavelength of 1.5418 is used to investigate the structural properties of CdZnS films, which are investigated using an X-ray diffractometer (XRD). The Scanning Electron Microscope was used to analyze the surface morphology (SEM). band gaps are calculated by measuring the absorption in a UV-VIS Spectrophotometer over a wavelength range of 350nm to 1000nm and calculating the results.

Table 1. Samples codes and procedure.

sample	Annealing temp. [^{O}C]	Annealing Time [min.]
CZS 1	0	0
CZS 2	200	30
CZS 3	200	60
CZS 4	200	120

3. Results and discussion

The surface properties of thin films are considered one of the most important basic properties for them to be used in many applications that depend on these properties, such as solar cells and sensors. The surface properties of the films were studied by a scanning electron field emission microscope. Figure 1 shows the microscope images for all films with different annealing times. It is observed from the figure that the morphology of the film without annealing is nano walls like these walls deform when the time of annealing was increased.



(a) *(b)*

(c) *(d)*

Fig. 2. FESEM images of CdZnS thin films annealed at different time

Figure 1. A shows the FESEM micrograph of as prepared CdZnS nanocrystalline thin film. The CdZnS is shaped as nano walls structures as exposed in the pictures [14,15]. In the SEM image after annealing, you can see sphere-shaped nanoparticles, a sign of increased crystallinity. When heated, the material's nanoparticles clump together to produce spherical grains that improve the material's crystallinity.

The XRD patterns of CdZnS thin films annealed at different time are shown in fig.2. the The hexagonal structure of CdZnS ternary thin films was seen in XRD patterns, which might be attributed to scattering from the (002), (110), and (112) plane, respectively. The reported diffraction peaks are consistent with the data on the standard JCPDS card, which is as follows: 49-1302 [16]. Because the (002) reflection is highest in the hexagonal phase, it follows that the c axis of CdZnS nanocrystals is almost always aligned with the surface of a thin film in this phase. The presence of low-intensity peaks in the XRD pattern indicates that the films are composed of tiny crystals, also known as nanocrystalline structures [17].

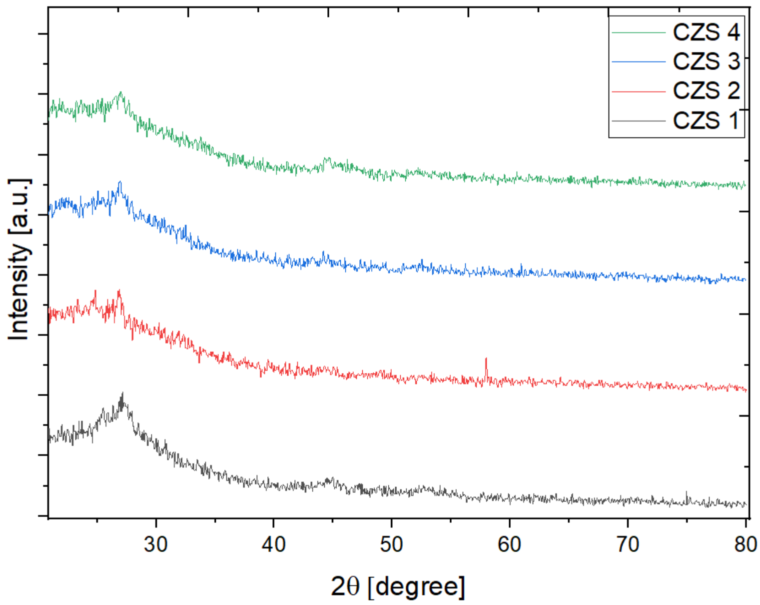


Fig. 2. X-ray diffractrograms of CdZnS thin films annealed at different time CZS 1 (0 min), CZS 2 (30 min), CZS 3 (60 min), CZS 4 (120 min).

Table 2. intensity, FWHM and inter atomic spacing of the CdZnS thin films.

sample	Pos. [°2Th.]	Planes	Height [cts]	FWHM [°2Th.]	d-spacing [Å]
CZS 1	27.2384	002	336.07	0.7872	3.27407
CZS 2	26.8318	002	245.27	0.3936	3.32275
CZS 3	26.8857	002	300.85	0.2952	3.31621
CZS 4	26.8386	002	206.97	0.9840	3.32193

The spectra of absorption for the prepared CdZnS nanocrystalline thin films have been investigated from 300nm to 1000nm. Figure 2 shows that the optical absorbance edge of CdZnS nanocrystalline thin films, for pristine film the edge appeared at around of 420 nm. This adge shifted to longer wavelength (red shift) because of the

The results of absorption spectra for prepared films was exposed that the designed thin films have small amount of absorption at region of visible and is more appropriate for the manufacture of solar cells. The optical bandgap (Eg) of CdZnS nanocrystalline thin films were calculated using the Tauc relation. Compared with the bandgap of CdS an increase in bandgap confirmed the formation of CdZnS compound [18]. the bandgaps energies were found to be 3 eV, 2.69 eV, 2.5 eV and 2.2 eV for (0, 30, 60 and 120 minute) respectively. The band gap decreased as the annealing time increased. The decreased band gap of the films after annealing was due to the improved crystalline nature of the material [19]. The nature of this band gap energy variation may be suggested as being suitable as a window material fabrication for solar cells.

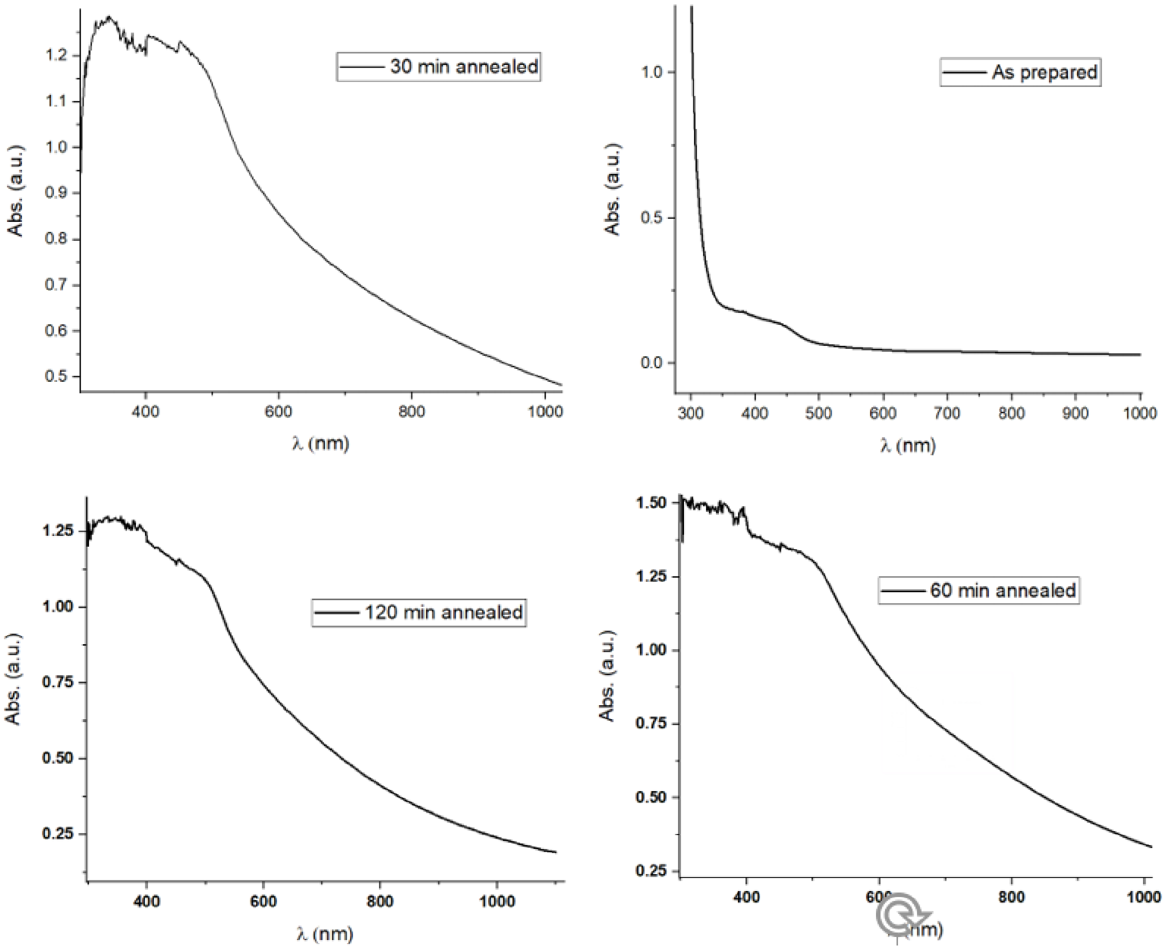


Fig. 3. UV-Visble absorption spectrums of CdZnS thin.

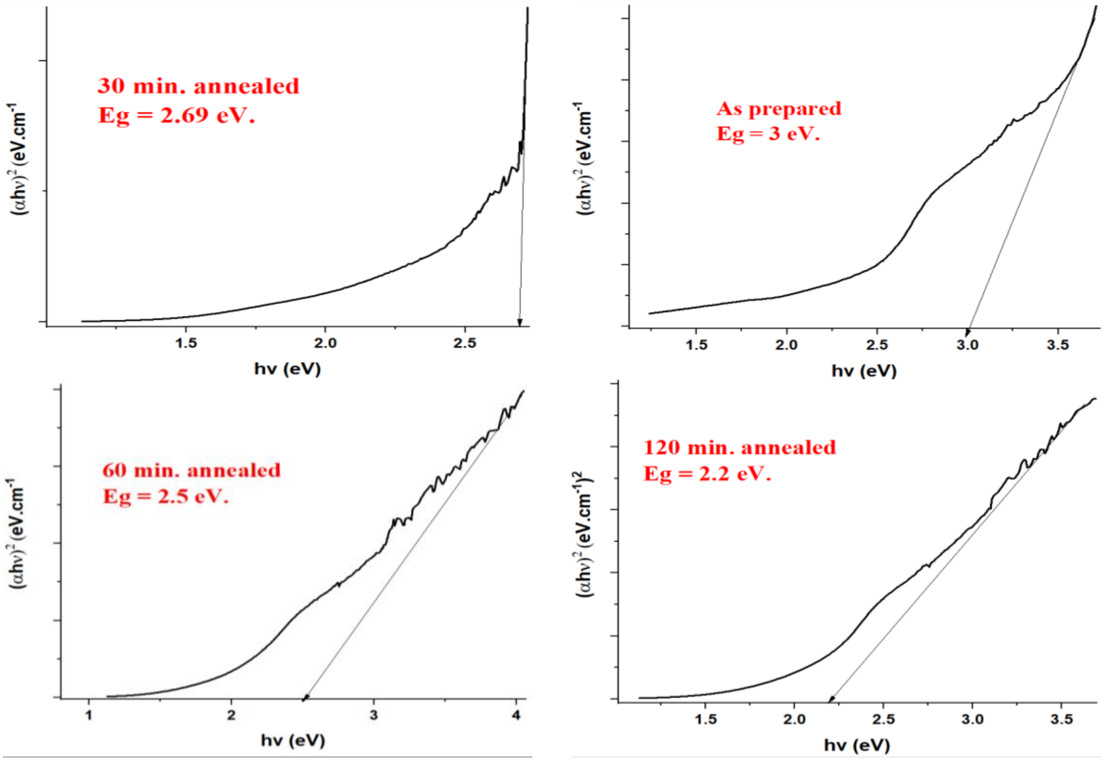


Fig. 4. energy gap of CdZnS films.

Fig. 5 characterizes the deviation in between energy gaps with time of annealing for thin films that was annealed at 200 C. also we can see from the figures above that energy gap decreases with increases the annealing time. Furthermore, decreasing of energy gap values through the annealing process may be founded on the increasing the grain sizes of the CdZnS films during annealing process [19,20].

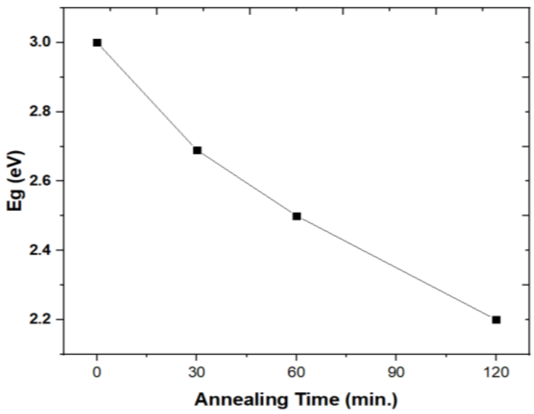


Fig. 5. Energy gap (Eg) with annealing time for films annealed at 200 C.

4. Conclusion

And by using the chemical bath method, nanocrystalline films were prepared from a tripartite semiconductor compound CdZnS with suitable parameters. The role of the heat treatment time and the annealing of the prepared films in controlling the optical properties such as the absorption spectrum as well as the direct energy gaps, as well as the effect of this time on the crystal structure of the prepared films were taken into consideration. It was concluded that there is no role for annealing on the crystal structure and the type of crystal system for the deposited films, but there is an important role and influence of annealing and its time on the optical properties, especially the energy gap. It has been observed that the energy gap always decreases when the heat treatment time is increased. And all the prepared films have a relatively wide energy gap that can act as windows in solar cells.

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