J Nanostruct 12(4): 921-931, Autumn 2022

RESEARCH PAPER

Preparation and Study of the Effect of Cobalt and Magnesium on the Structural and Optical Properties of Cadmium Sulfide Compound

Muaamar Hasan Idan [1]*, Raheem G. Khadum Hussain [1] and M. A. Mohammed [2]

[1] *Department of Physics, College of Science, University of Babylon, Babel, Iraq*

[2] *Department of Soil Sciences and Water Resource ,College of Agriculture, University of Al-Qadisiyah, Al-Qadisiyah, Iraq*

ARTICLE INFO

Article History:
Received 27 July 2022
Accepted 16 September 2022
Published 01 October 2022

Keywords:
Cadmium Sulfide
Cobalt
Magnesium
Optical Properties

ABSTRACT

The compound cadmium, magnesium and cobalt sulfide was prepared in liquid form at the concentration of each of them respectively (0.1, 0.5 and 0.5) M. Where all the films were prepared CdS, CdS:Mg , CdS:CO , CdS:Mg:CO using spray pyrolysis thermochemical technique. Solutions were deposited on glass bases at a fixed settling temperature of 450 °C and at a fixed spray rate of 15 sprays within 15 minutes. The thickness of the films that were prepared was 150 nm. Results showed that they are polycrystalline, and their grain size decreases when cobalt and magnesium are added to the cadmium sulfide compound, while the width of the curve increases with atomic FHWM because it is an inverse relationship between the grain size and full width at half maximum (FHWM). Also, the results showed that all the prepared films have high surface homogeneity and are free of cracks and needle holes that induce films during their preparation. In addition, results scanning electron microscope showed that the particle size decreases when cobalt and magnesium are added to the cadmium sulfide compound, and this result is identical to the results of X-ray diffraction. The optical properties of all the prepared films were studied, where the absorbance was measured as a function of wavelength and the absorption coefficient was calculated from the absorbance spectrum, as well as the energy gap values were calculated. The results showed that the absorbance spectrum behaves visually similar to all the prepared films and that the absorbance values decrease when cobalt and magnesium are added to the cadmium sulfide compound. While the results of the absorption coefficient showed that it behaves similar to the absorption spectrum due to the direct relationship between them, in addition to that, the values of the absorption coefficient showed that it is greater than (10000/cm), and this means that direct electronic transitions occur. By knowing the absorption coefficient, the values of the direct energy gap were calculated, and it was shown that its values increase when cobalt and magnesium are added to the cadmium sulfide compound.

How to cite this article
Idan M H., Hussain R G K., Mohammed M A. Preparation and Study of the Effect of Cobalt and Magnesium on the Structural and Optical Properties of Cadmium Sulfide Compound. J Nanostruct, 2022; 12(4):921-931. DOI: 10.22052/JNS.2022.04.014

* *Corresponding Author Email: moeny7216@gmail.com*

INTRODUCTION

It is an important II–VI semiconductor (Eg = 2.42 eV (515 nm) at room temperature) with many excellent physical and chemical properties, which has promising applications in multiple technical fields including photochemical catalysis, gas sensor, detectors for laser and infrared, solar cells, non-linear optical materials, various luminescence devices, optoelectronic devices and so on; it is also the most promising candidate among II–VI compounds for detonation of lasers and infrared rays. Hydrothermal/solvothermal methods, thermal decomposition, etc.[1] can all be used to produce CdS in powder or thin film form[1,2]. CdS nanoparticles and their optical properties have received considerable attention in the last few decades. Due to the possibility of fine-tuning particle properties through manipulation of their sizes and shapes, new experimental methodologies that produce nanoparticles with extremely low size- and shape-dispersion are needed. For example, solvothermal method with cadmium chloride and thiourea in ethylenediamine solution prepared sea-urchin like cadmium sulfide nanoparticles with nanorod-based architecture [3]. There are two ways to synthesize CdS nanorods: using thioglycolic acid to form CdS nanorod bundles and non-ionic surfactants to form micro emulsion [4]. There have been numerous studies on cadmium sulfide nanoparticles, which have been produced using a variety of methods and starting materials.

Magnesium is one of the lightest metals in the world. Magnesium is 1.6 times less dense than aluminum and 4.5 times less dense than steel, at 1.74g/cm^3[5]. Because of its higher elastic modulus and compressive yield strength than other commonly used metallic implants, magnesium has a higher fracture toughness than ceramic biomaterials like hydroxyapatite. Additionally, magnesium is a vital component of human metabolism and is found in bone tissue naturally. Approximately half of the body's magnesium is stored in bone tissue, making it the fourth most abundant metal cation. Symbolized by Co and having an atomic number of 27, cobalt is a chemical element. For the most part, the Earth's crust contains only chemically combined cobalt, except for small deposits found in alloys of natural meteoric iron[5]. Reductive smelting yields a hard, lustrous, silver-gray metal as the free element. Blue pigments (cobalt blue) have been used since ancient times to make jewelry and paints, but the color was later thought to be due to the known metal bismuth [6]. Kobold ore (German for goblin ore) had long been used by miners for some of the blue-pigment generating minerals because they were low in known metals and produced toxic arsenic-containing fumes when melted. It wasn't until 1735 that the first metal discovered since ancient times was discovered from such ores, and it was named for a kobold[2-5].

MATERIALS AND METHODS

The materials that used cadmium acetate $(CH_3COO)_2Cd_2H_2O$, Thiourea CH_4N_2S , Magnesium acetate $(CH_3COO)_2Mg_4H_2O$, Cobalt acetate $(CH_3COO)_2CO_4H_2O$ and Salt-free ionic water (H_2O).

Prepared Thin Films

The compound cadmium sulfide (CdS) was prepared by dissolving each of cadmium by weight (13.32g) and sulfur(S) by weight(3.8g) in (100 ml) of distilled water in a glass container placed on a heater at a constant temperature of 60 C using a magnetic needle for a process of dissolution for a period of two hours.

Cobalt(CO) with a concentration of (0.5M) was prepared by dissolving cobalt by weight of (14.55g) in (100 ml) of distilled water in a glass container, using it placed on a heater at a constant temperature of 60 C, using the magnetic needle for the dissolution process for a period of two hours.

Magnesium(Mg) was prepared with a concentration of 0.5 M by dissolving magnesium by weight of(10.72g) in (100 ml) of distilled water in a glass container, using it placed on a heater at a constant temperature of 60 degrees Celsius, using the magnetic needle for the dissolution process, for a period of two hours.

The films were prepared (CdS),(CdS:CO), (CdS:Mg) and (CdS:Mg:CO) using the spray pyrolysis technique on glass bases with dimensions of 2 cm by 3 cm and at a fixed deposition temperature 450 ° C and a fixed spray rate of 15 sprays at a time rate of 15 minutes. All films prepared are 150 nm thick.

RESULTS AND DISCUSSION

Structure Properties

X-ray Diffraction Measurement (XRD)

Fig. 1 shows the results of the X-ray diffraction measurement for all the prepared films. The results showed that all the prepared films have a polycrystalline structure and that the prepared film CdS has a polycrystalline structure cuib and has three peaks representing Miller's coefficients at corresponding diffraction angles, while the prepared membrane cds:mg has a polycrystalline structure Cubic and tetragonal due to the appearance of new peaks due to the addition of magnesium to the cadmium sulfide compound, while the prepared membrane cds : co has a cubic and a orthorhombic structure due to the appearance of fine peaks due to the addition of cobalt to cadmium sulfide, while the prepared membrane cds : co : mg has a cubic, orthorhombic and tetragonal structure due to the appearance of peaks New ones are due to the addition of magnesium and cobalt to cadmium sulfide[5,6].

The distance(dhkl) between the atomic levels for all films prepared from X-ray diffraction pattern and Brack angles was calculated based on equation (1) and the results showed a somewhat similar approach with the theoretical values[7].

$$n\,\lambda = 2d \sin \theta B \quad (1)$$

Where n represent diffraction order and it take integer number such as (1, 2, 3…), Since: (λ): the wavelength of the incident X-ray, (d): The distance between two successive planes and (θB): Bragg's angle.

Also, the curve width of the full width half maximum (FWHM) was calculated for all the prepared films. The results showed that when cobalt and magnesium were added to cadmium sulfide, their value increased [6].

Table 1. Represents the X-ray diffraction results of the prepared thin film CdS .

NO.	Exp. Pos. [°2Th.]	Exp. d-spacing [Å]	FWHM (new)	HKL	Crystallite Size [nm]	Crystal system	Reference code Entry No.
1	26.5367	3.359	0.32	111	25.49685	cubic	
2	44.0229	2.057	0.155	202	55.26159	cubic	96-900-8840
3	52.1417	1.7542	0.125	311	70.72582	cubic	

Table 2. Represents the X-ray diffraction results of the prepared thin film CdS : Co.

NO.	Exp. Pos. [°2Th.]	Exp. d-spacing [Å]	FWHM (new)	HKL	Crystallite Size [nm]	Crystal system	Reference code Entry No.
1	19.3212	4.5941	0.19	101	42.39699	orthorhombic	96-100-8133
2	26.5367	3.359	0.3	111	27.19664	Cubic	96-900-0068
3	44.0229	2.057	0.225	202	38.0691	Cubic	96-900-0068
4	52.1417	1.7542	0.265	311	33.36124	Cubic	96-900-0068

Table 3. Represents the X-ray diffraction results of the prepared thin film CdS : Mg.

No.	Exp. Pos. [°2Th.]	Exp. d-spacing [Å]	FWHM (new)	HKL	Crystallite Size [nm]	Crystal system	Reference code Entry No.
1	26.4672	3.3677	0.37	111	22.04818	cubic	96-900-0109
2	28.2723	3.1566	0.25	112	32.75672	tetragonal	96-153-9502
3	43.9038	2.0623	0.175	202	48.92545	cubic	96-900-0068
4	47.7724	1.9039	0.205	105	42.36613	tetragonal	96-153-9502
5	51.9976	1.7587	0.19	311	46.50157	cubic	96-900-0068

Table 4. Represents the X-ray diffraction results of the prepared thin film CdS : Mg :CO.

No.	Exp. Pos. [°2Th.]	Exp. d-spacing [Å]	FWHM (new)	HKL	Crystallite Size [nm]	Crystal system	Reference code Entry No.
1	19.3212	4.5941	0.19	101	42.39699	orthorhombic	96-100-8133
2	26.4672	3.3677	0.37	111	22.04818	cubic	96-900-0109
3	28.2723	3.1566	0.25	112	32.75672	tetragonal	96-153-9502
4	43.9038	2.0623	0.175	202	48.92545	cubic	96-900-0068
5	47.7724	1.9039	0.205	105	42.36613	tetragonal	96-153-9502
6	51.9976	1.7587	0.19	311	46.50157	cubic	96-900-0068

The grain size(G) of all the prepared films was also calculated based on the sparks equation Scherer's equation (2). The results showed that when cobalt and magnesium were added to the cadmium sulfide compound, the average particle size decreased due to the addition of cobalt and magnesium in the form of an interstitial impurity in the cadmium sulfide lattice, and this leads to a decrease in the size granularity and an increase in the full width half maximum because the

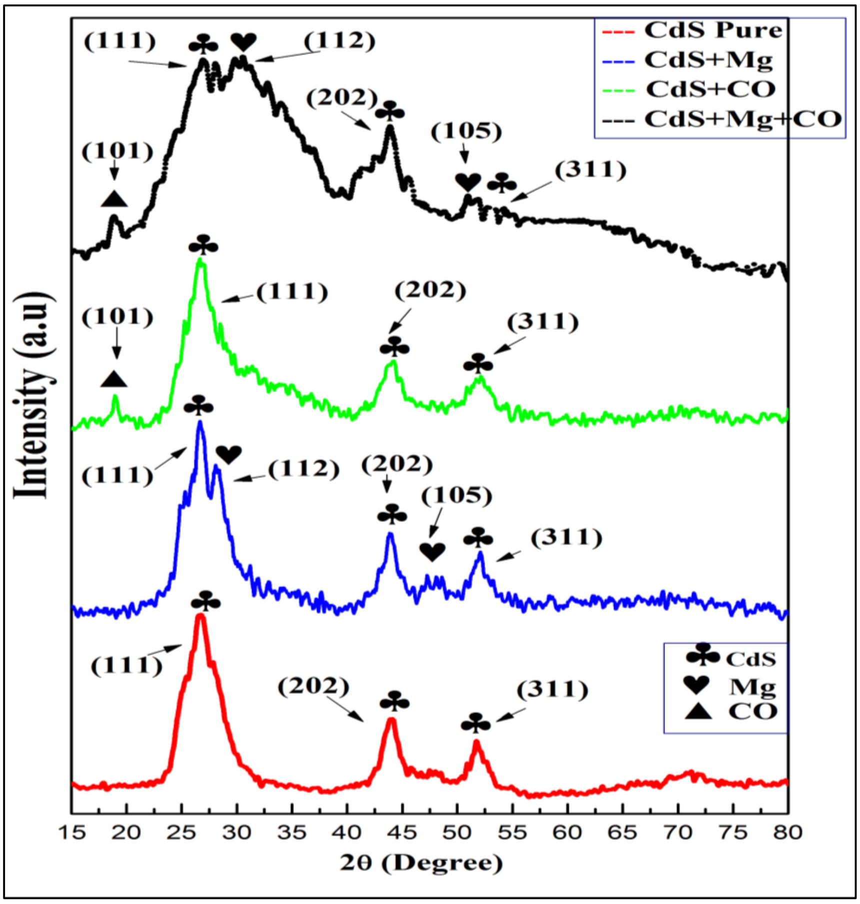

Fig. 1. Shows the X-ray diffraction measurement of all the prepared thin films.

relationship between them is inverse[5,7].

$$G = \frac{0.9\,\lambda}{\beta \cos \theta_B} \quad (2)$$

G : grain size, β: Full width half maximum particle size .

Tables. 1-4 show the results for all the prepared films obtained by measuring X-ray diffraction and we find that the obtained values are identical or close to some extent with the values given in American Standard of Testing Materials (ASTM).

Atomic Force Microscope (AFM)

Some parameters of thermal chemical spray pyrolysis technology such as spray rate, temperature and gas pressure have a direct effect on the nature of the prepared membrane surfaces and their homogeneity, and the difference in surface topography is due to the used technique and preparation conditions[7].

The topography of the prepared thin films surfaces was studied in two dimensions and in three dimensions. Figs. 2-5 shows AFM examination images for all the prepared membranes (CdS), (CdS:CO),(CdS: Mg) and (CdS:Mg:CO).We note through the images that all the prepared thin films surfaces have good crystalline regularity and good color homogeneity for all membrane surfaces, and this indicates that Crystalline homogeneity of the prepared films and high surface homogeneity, meaning there are no irregular gatherings. In addition, we note that it is free from defects, cracks and needle holes that occur in the films during preparation[4,8,9].

The Table 5. shows the values of the results of the surface roughness of the films and the square root of all the prepared films. It was found that when cobalt and magnesium were added to the cadmium sulfide compound, the surface roughness values and the mean square

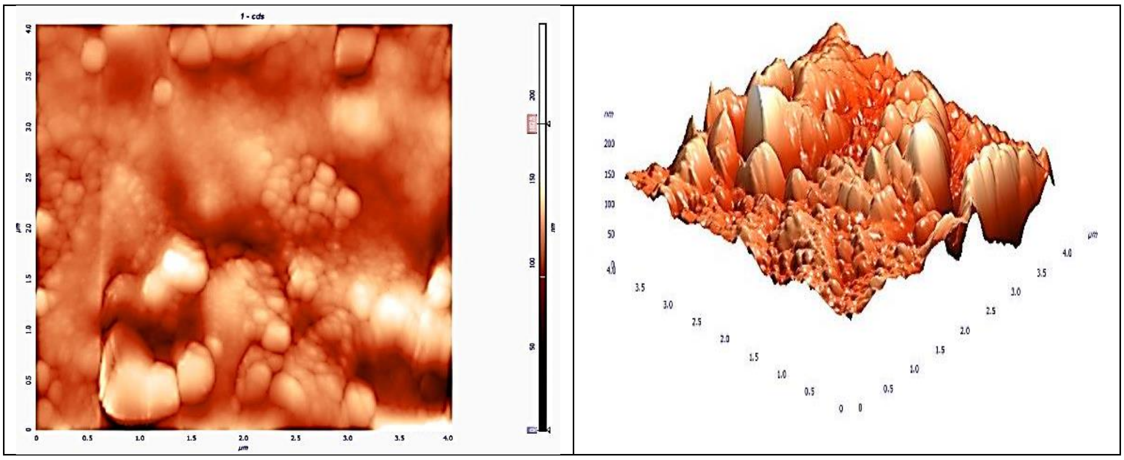

Fig. 2. Shows AFM examination images of the prepared thin film CdS.

Table 5. Shows the values of the results of the roughness of the thin films surfaces and the square root of all the prepared films.

Sample	Average Roughness, Sa	Root Mean Square, Sq
CdS	24.9756 nm	32.1346 nm
CdS : Mg	7.64472 nm	10.0448 nm
CdS : CO	8.58597 nm	10.7528 nm
CdS : CO : Mg	17.4414 nm	24.9562 nm

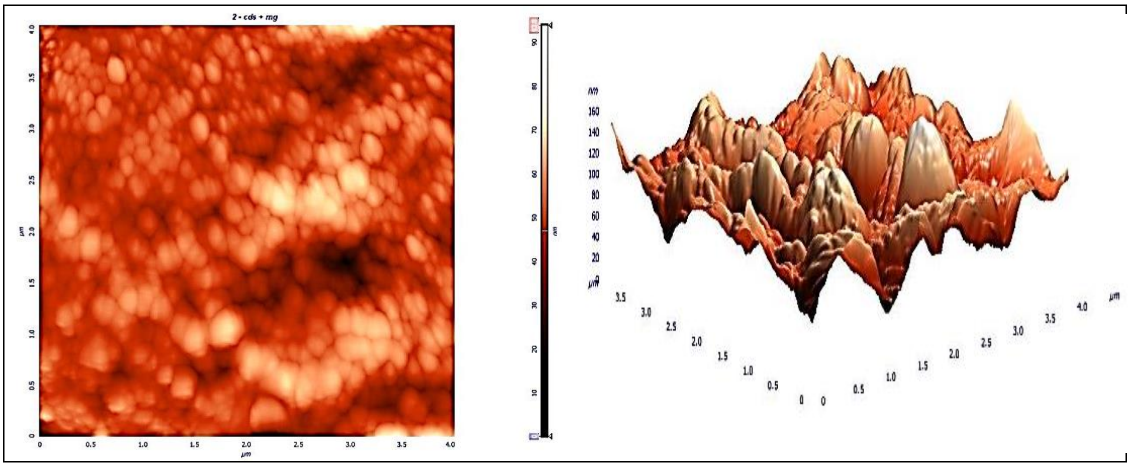

Fig. 3. Shows AFM examination images of the prepared thin film CdS : Mg.

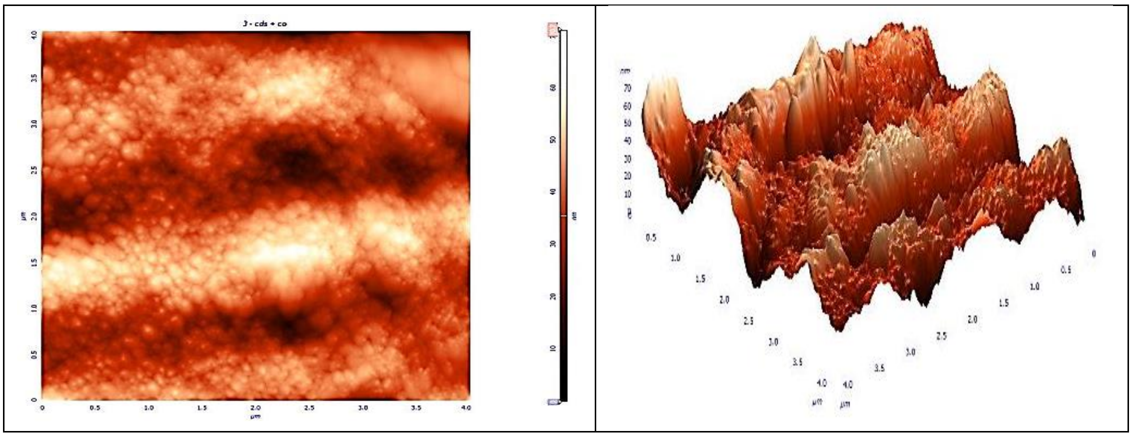

Fig. 4. Shows AFM examination images of the prepared thin film CdS : CO.

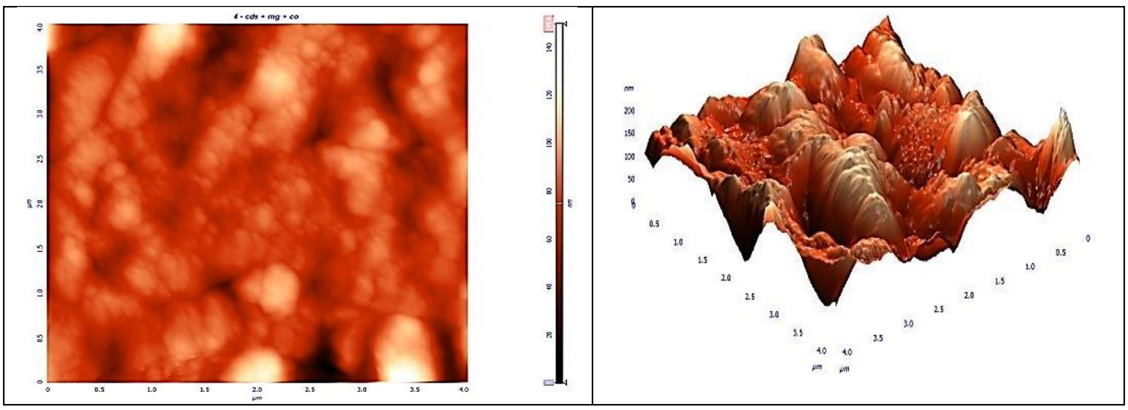

Fig. 5. Shows AFM examination images of the prepared thin film CdS : CO : Mg.

Table 6. Shows the particle size of all prepared films.

Prepared films	Particle Size D1nm
CdS	113.69
CdS : Mg	49.78
CdS : CO	67.54
CdS : CO : Mg	71.97

root of the surface roughness decreased due to the occurrence of crystal growth of grains perpendicular to the surface of the prepared films. This confirms that Cobalt and magnesium atoms are evenly and harmoniously distributed in the cadmium sulfide lattice, which makes them evenly arranged and improve their structural properties. These prepared films can be used in applications.

Scanning Electron Microscope (SEM)

The topography of the prepared membrane surfaces was studied using the Scanning Electron

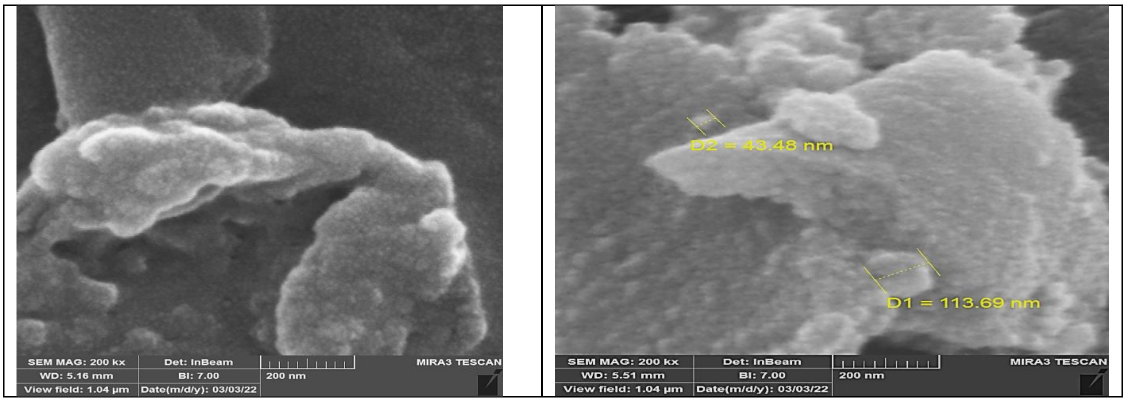

Fig. 6. Shows Scanning Electron Microscope images of the prepared thin film CdS .

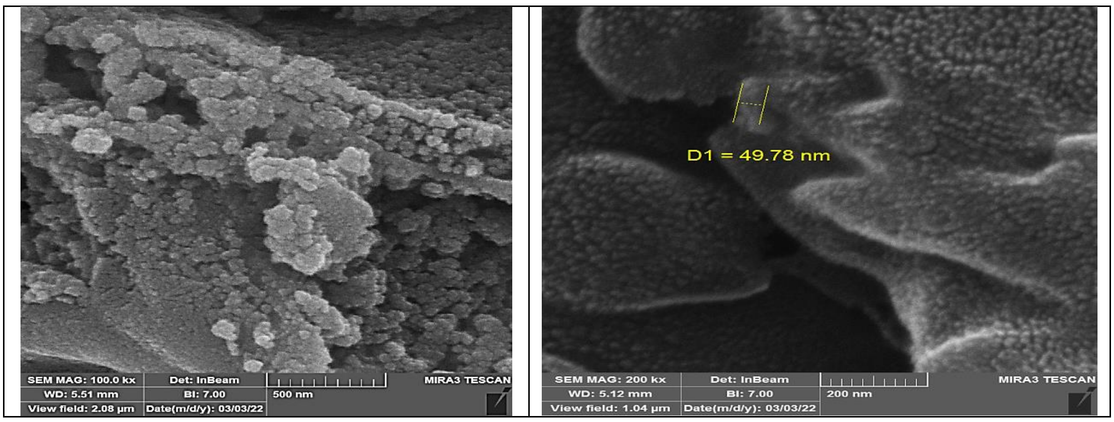

Fig. 7. Shows Scanning Electron Microscope images of the prepared thin film CdS : Mg.

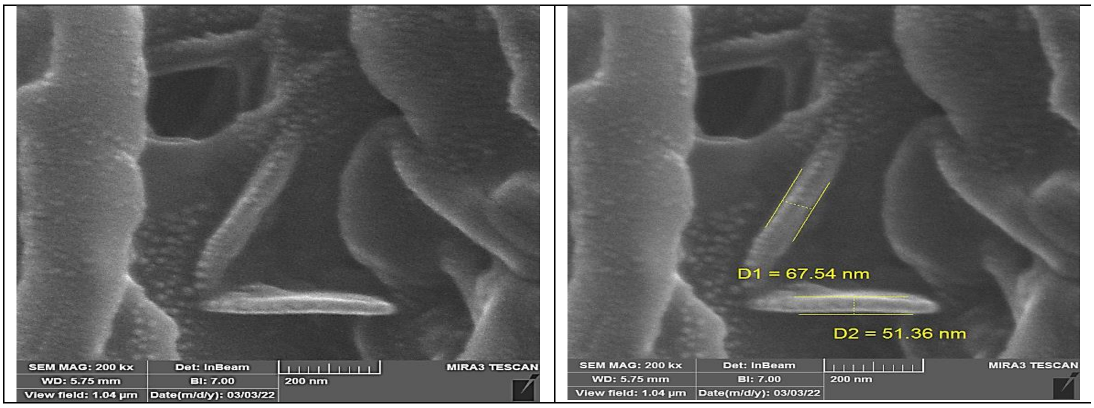

Fig. 8. Shows Scanning Electron Microscope images of the prepared thin film CdS :CO.

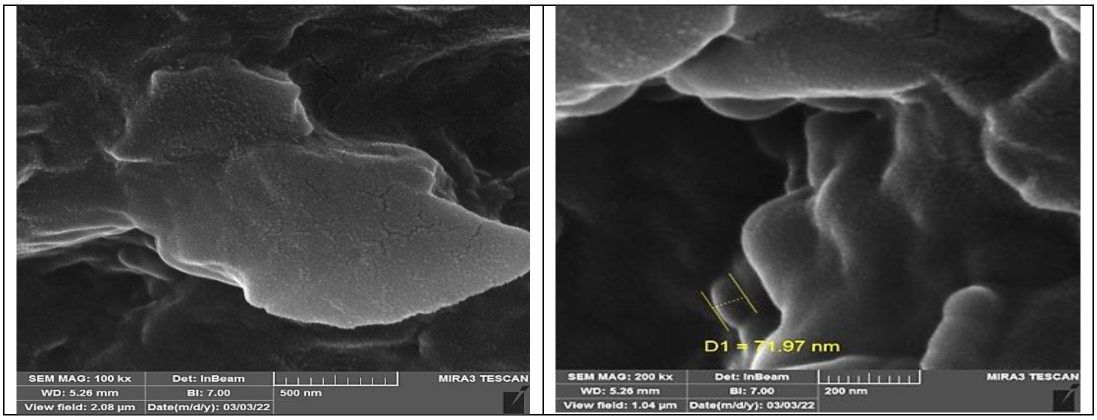

Fig. 9. Shows Scanning Electron Microscope images of the prepared thin film CdS:CO:Mg.

Microscope, which gives sufficient information about the topography and composition of the membrane surfaces. Good surface homogeneity and uniform distribution of cobalt and magnesium atoms added to the cadmium sulfide compound and free from crystalline defects. We note through the results of the scanning electron microscope image in Table 6. that the size of the particles decreases when cobalt and magnesium are added to the cadmium sulfide compound. Nucleation and thus an increase in nucleation centers and this leads to a smaller final granular size, in addition to that, the added cobalt and magnesium atoms do not increase nucleation, but rather act as barriers to the growth of the granules, and this indicates an improvement in crystallization levels and an improvement in its structural properties[10-13].

Optical Properties

Absorbance

The absorbance was measured using a visible spectrophotometer(uv) within the wavelength range from 200-1100 nm. Fig. 10 shows the absorbance spectrum as a function of the wavelength of all the prepared films (CdS) where we notice from the figure that the highest values of absorbance at short wavelengths i.e. the region have high energy and this indicates that the films The preparation is effective in the near ultraviolet and visible region, then we notice a rapid decrease in the absorption spectrum at wavelengths 575 nm[11,14]. We note that the absorbance spectrum of all the prepared films behaves similar optically and that the absorbance spectrum decreases with increasing wavelength.

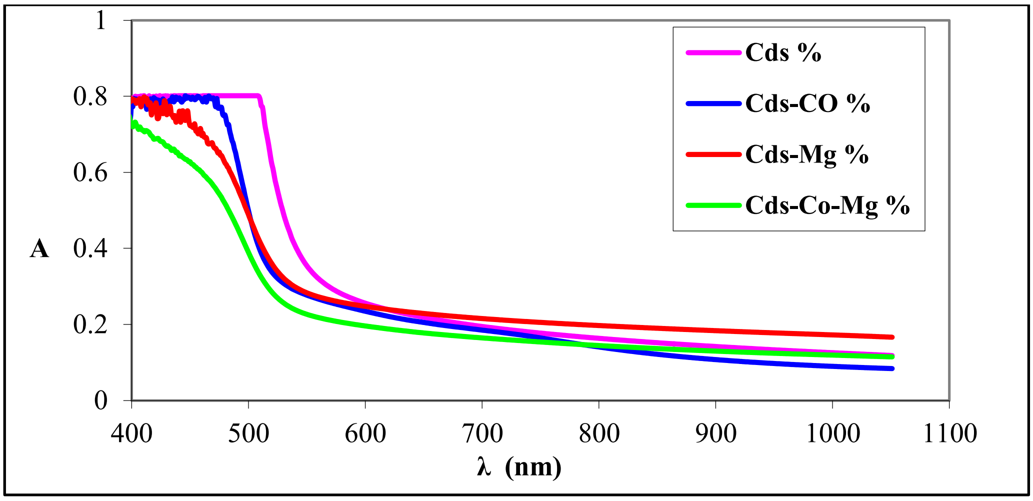

Fig. 10. Shows the Absorbance as a function of the wavelength for all the prepared films.

We find when adding cobalt and magnesium to the cadmium sulfide compound leads to a decrease in the absorbance values. The reason for this is the entry of cobalt and magnesium into the crystal structure of the cadmium sulfide compound, which leads to a change in the particle size as confirmed by X-ray diffraction measurements, which in turn leads to a decrease in the absorbance values[15].

Absorption Coefficient (α)

The absorption coefficient was calculated from the absorbance spectrum using Equation (3) Fig. 11 shows the spectrum of the absorption coefficient for all the prepared films as a function of the wavelength within the range from 400-1100 nm. We note that the prepared films behave visually similar to the absorption spectrum curves. The reason is due to the nature of the relationship between them. We note that the highest values of the absorption coefficient at short wavelengths and the lowest values absorption coefficient at long wavelengths[16].

$$\alpha = 2.303\ A^{o} / t \quad (3)$$

where : t / thick of thin film.

We note that the addition of cobalt and

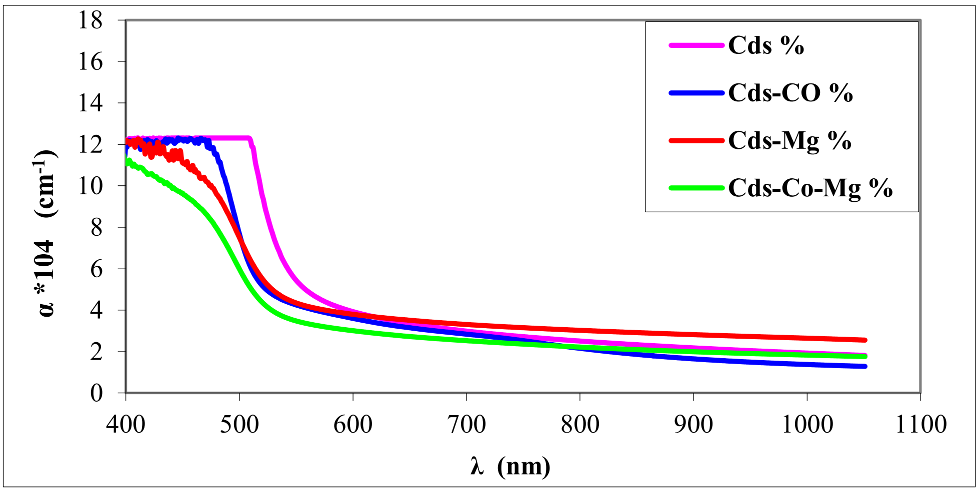

Fig. 11. Shows the absorption coefficient as a function of the wavelength for all the thin films.

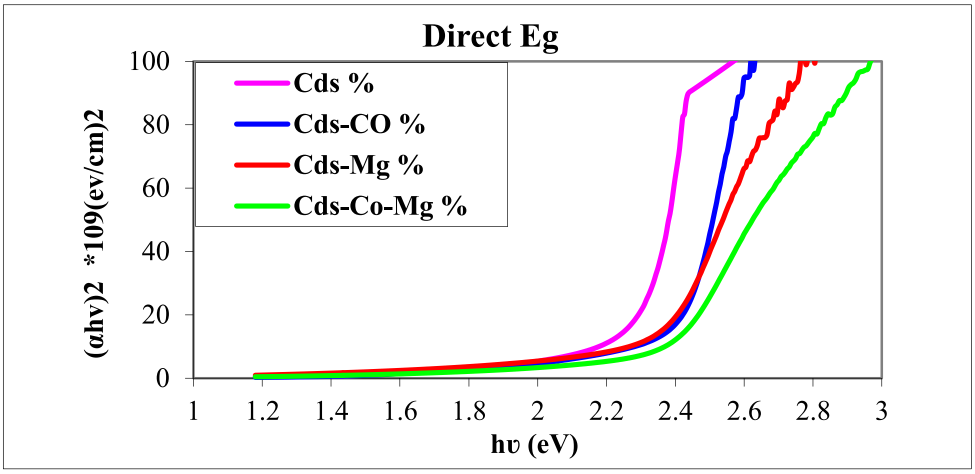

Fig. 12. Shows the direct energy gap values for all the prepared films.

Table 7. Energy gap values for all thin films.

Prepared films	Eg
CdS	2.22
CdS : Mg	2.29
CdS : CO	2.36
CdS : CO : Mg	2.38

magnesium to the cadmium sulfide compound led to a decrease in the values of the absorption coefficient. The reason is because the absorption coefficient is directly proportional to the absorbance, since the absorbance decreased, the absorption coefficient decreased [17]. We note that the values of the absorption coefficient of all the prepared films is greater than (10000/cm), and this indicates the occurrence of direct electronic transitions between the conduction band and the valence band[13,17].

Optical Energy Gap (Eg)

The direct optical energy gap of all the prepared films was calculated using Taoss equation (4)

$$h\nu\alpha = B(h\nu - Eg)^{r} \quad (4)$$

where :

α: absorption coefficient, measured in units (cm^{-1}) ,hv: the energy of the incident photon, Eg: Optical energy gap, r: the order of the optical transition and depends on the nature of the transition

The relationship between $h\nu\alpha^2$ and hv is drawn by extending a straight line whose extension is a transversal of the photon's energy axis. The value of the energy gap is determined from the point of intersection at which $h\nu\alpha^2 = 0$ and the Fig. 12 shows the energy gap of all the prepared films [17].

Table 7. shows the optical energy gap values for all the prepared films, where we notice that when cobalt and magnesium are added to the cadmium sulfide compound, the optical energy gap values increase and the reason for this is that the crystal growth is better when cobalt and magnesium are added, which also led to a decrease in the grain size and thus obtaining the phenomenon of quantum effect [16,18,19].

CONCLUSION

The results of X-ray diffraction measurements and AFM matched by the decrease in the particle size when cobalt and magnesium were added to the cadmium sulfide compound. All prepared films have good absorbance, they are effective in the visible region of the electromagnetic spectrum, so they can be used in the applications of optical detectors within this range. Through the results of the AFM measurement, it was shown that the surface roughness decreases when cobalt and magnesium are added, and this result confirms the possibility of using the prepared films as a sensor for some gases. By studying the optical properties, the results showed the type of electronic transitions between the conduction and valence bands are of direct type. By studying the optical properties, it was shown that all the prepared films fall within the energy gap range of semiconductor materials.

CONFLICT OF INTEREST

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

REFERENCES

1. Priya NS, Kamala SSP, Anbarasu V, Azhagan SA, Saravanakumar R. Characterization of CdS thin films and nanoparticles by a simple Chemical Bath Technique. Mater Lett. 2018;220:161-164.
2. Abdel-Galil A, Ali HE, Balboul MR. Influence of CdS nano-additives on optical, thermal and mechanical performance of CdS/polyvinyl alcohol nanocomposites. Optik. 2017;129:153-162.
3. Kumar NS, Kumar SKN, Yesappa L. Structural, optical and conductivity study of hydrothermally synthesized TiO_2 nanorods. Materials Research Express. 2020;7(1):015071.
4. Kok Sheng C. Investigation of Morphological, Structural and Electrical Properties of Cds/ PMMA Nanocomposite Film Prepared by Solution Casting Method. International Journal of Electrochemical Science. 2017:10023-10031.
5. Shalan AE, Barhoum A, Elseman AM, Rashad MM, Lira-Cantú M. Nanofibers as Promising Materials for New Generations of Solar Cells. Handbook of Nanofibers: Springer International Publishing; 2018. p. 1-33.
6. Hussien MSA, Mohammed MI, Yahia IS. Flexible photocatalytic membrane based on CdS/PMMA polymeric nanocomposite films: multifunctional materials. Environmental Science and Pollution Research. 2020;27(36):45225-45237.
7. Murugesan R, Sivakumar S, Karthik K, Anandan P, Haris M. Effect of Mg/Co on the properties of CdS thin films deposited by spray pyrolysis technique. Current Applied Physics. 2019;19(10):1136-1144.
8. Son D-Y, Kim S-G, Seo J-Y, Lee S-H, Shin H, Lee D, et al. Universal Approach toward Hysteresis-Free Perovskite Solar Cell via Defect Engineering. Journal of the American Chemical Society. 2018;140(4):1358-1364.
9. Smith RP, Hwang AA-C, Beetz T, Helgren E. Introduction to semiconductor processing: Fabrication and characterization of p-n junction silicon solar cells. Am J Phys. 2018;86(10):740-746.
10. Khan MJI, Usmani MN, Kanwal Z, Akhtar P. Novel substitutional effects on optical properties of Cds:Co system (A theoretical study). Optik. 2018;156:817-824.
11. Alsultani MJ, Abed HH, Ghazi RA, Mohammed MA. Electrical Characterization of Thin Films $(TiO2:ZnO)_{1-x}(GO)_x$/ FTO Heterojunction Prepared by Spray Pyrolysis Technique. Journal of Physics: Conference Series. 2020;1591(1):012002.
12. Shkir M, Chandekar KV, Khan A, El-Toni AM, Ashraf IM, Benghanem M, et al. Structural, morphological, vibrational, optical, and nonlinear characteristics of spray pyrolyzed CdS thin films: Effect of Gd doping content. Materials Chemistry and Physics. 2020;255:123615.
13. Fard NE, Fazaeli R, Ghiasi R. Band Gap Energies and Photocatalytic Properties of CdS and Ag/CdS Nanoparticles for Azo Dye Degradation. Chemical Engineering & Technology. 2015;39(1):149-157.
14. Suo Z, Dai J, Gao S, Gao H. Effect of transition metals (Sc, Ti, V, Cr and Mn) doping on electronic structure and optical properties of CdS. Results in Physics. 2020;17:103058.
15. Mohammed MKA. Studying the Structural, Morphological, Optical, and Electrical Properties of CdS/PbS Thin Films for Photovoltaic Applications. Plasmonics. 2020;15(6):1989-1996.
16. Andhare DD, Patade SR, Kounsalye JS, Jadhav KM. Effect of Zn doping on structural, magnetic and optical properties of cobalt ferrite nanoparticles synthesized via. Co-precipitation method. Physica B: Condensed Matter. 2020;583:412051.
17. Shakil M, Inayat U, Arshad MI, Nabi G, Khalid NR, Tariq NH, et al. Influence of zinc and cadmium co-doping on optical and magnetic properties of cobalt ferrites. Ceram Int. 2020;46(6):7767-7773.
18. Kumar M, Singh B, Yadav P, Bhatt V, Kumar M, Singh K, et al. Effect of structural defects, surface roughness on sensing properties of Al doped ZnO thin films deposited by chemical spray pyrolysis technique. Ceram Int. 2017;43(4):3562-3568.
19. Khani P, Sahraei R, Sharifirad Z, Ghavidel E, Nourolahi H, Jawhar NN, et al. Improved chemical deposition of cobalt-doped CdS nanostructured thin films via nucleation-doping strategy: Surface and optical properties. Materials Science and Engineering: B. 2021;272:115328.