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Effect of zinc on structural and some optical properties of CdS thin films

Foaad Shakir Hashim, Majeed Ali Habeeb, Ihsan Razooqi Ghanim
University of Babylon, college of education for pure sciences, department of physics
E-mail: majeed_ali74@yahoo.com

Abstract

This research deals with the study of the structural and optical properties of pure and Zinc doped CdS films with different doping ratios (3,6 and 9) % volume percentage. Thin films of CdS were deposited on glass substrates at temperature 400^{o}C by using of chemical spray pyrolysis with spray rate 3ml/sec and with different thickness. The structural properties for the prepared films were studied through test of X-Ray diffraction and it appeared that the films are polycrystalline having hexagonal structure. it is also showed the film prepared has a preferred orientation along (002).The grain size was found to be decreased with increasing (Zn) concentration, on the other hand the atomic force microcopy (AFM) showed an decrease in (RMS) values with increasing (Zn) concentration, also the optical properties of these films were studied by measuring transmission and absorption spectra as a function of wavelength, and it was found that the transmittance increases with increasing (Zn) concentration, as well as the optical energy gap increases with increasing (Zn) concentration.

Keywords: thin films, optical energy gap, structural properties.

1. Introduction:

The term of thin films is used to describe a layer or several layers of atoms for a certain substance whose thickness ranges between 10nm and less than 1 μm [1].The interest in thin films raised from the wide range of use and application in electronic equipments and devices. These films have been used in various fields such as of manufacturing (p-n) junctions, rectifiers, mirrors with two types ordinary and thermally, reflected and anti-reflected coating, photograph, integrated circuits, and optical communications as light emitting diodes, detectors solar cells, ….. , etc. This leads to study of electronic and optical properties of thin films.[2,3]

Semiconductors differ from insulators only in the width of the forbidden band (E_g). An insulator has a forbidden gap is so wide that very few electrons cross it at room temperature, whereas a semiconductor possesses a narrow gap which allows a considerable amount of electrons to the conduction band. At room temperature the semiconductors have conductivity in the range of $(10^{-8}\text{-}10^{3})\Omega^{-1}.cm^{-1}$[4] .

Cadmium sulfide is a direct band gap semiconductor of about 2.4 eV. It exists near the photon energy of maximum solar radiation spectrum, it causes absorption in the short wavelength side, and has a high absorption coefficient ($10^{5}cm^{-1}$) within the solar radiation to generate carriers across the band gap with wavelength less than (0.520 μm) [5]. The refractive index of CdS is 2.3 ,2.26 and dielectric constant 8.64[6,7] .

Cadmium sulfide is an ideal material for making a photovoltaic p-n junction with p-type CIS, CGS. CdS is naturally n-type with a wide optical band-gap and close lattice match to CIS[8]. It is usually used as a very suitable window layers which are prepared as thin as possible to avoid optical transition losses [9,10].

A number of film deposition methods such as Thermal Evaporation in Vacuum Deposition (TEVD) ,Sputtering technique, Chemical Vapor Deposition (CVD) , Pulse Laser Deposition (PLD) , Thermal Pyrolysis Deposition (TPD) , have been used for preparing II-VI compound . Among these , spray pyrolysis is one of the most used methods[11] .

2. Basic relation

The equation for the energy gap[12] is given by :

$$\alpha h\upsilon = B\,(h\,\upsilon - E_g^{\ opt.})^{\ r} \qquad [1]$$

Where: $E_g^{opt.}$: optical energy gap. B: constant depended on type of material. r: exponential constant, its value depended on type of transition, r =1/2 for the allowed direct transition. r =3/2 for the forbidden direct transition.

The transmittance part of incident light T is depending on α through the following eq.[13]

$$T = \exp(-2.303\ A) \qquad [2]$$

Where A is the absorption . Thus the absorption coefficient α corresponding to any wavelength λ can be calculated[13] by applying the relation:

$$\alpha = 2.303\ A/t \qquad [4]$$

Where t is the thickness.

3. Experimental work

CdS and CdS:Zn thin films were prepared onto glass substrate at 400°C by chemical spray pyrolysis with different doping concentration (3,6,9 %) volume percentage of Zn. The films were prepared by mixing aqueous cadmium nitrate-4-hydral solution $Cd(NO_3)_2.4H_2O$ with aqueous thiourea solution $CS(NH_2)_2$. Zinc doped CdS films were deposited by adding Aqueous zinc chloride solution as a dopant source to the solution. The spray rate was optimized to 3 ml/min through the nozzle to ensures a uniform film thickness. Glass substrates of 2.5 cm x 3.8 cm, are placed on the surface of heater when sprayed. The heater used was a hot plate with controller.

$$Cd(NO_3)_2.4H_2O + CS(NH_2)_2 \longrightarrow CdS + CO_2 + 6H_2O + 2N_2O$$

The film thickness was measured using BLK-CXR-SR-25 (BLACK-Comet Models Super Range 200-1100nm) and The Weight Method. The crystal structure of CdS films was determined by X-ray diffraction. Atomic Force Microscopy AFM (AA3000 SPM) was used to study the surface morphology of the film. Optical properties of the films were determined by (shimadzu, UV-1800 °A) spectrophotometer.

4. Result and discussion

4.1 XRD diffraction and AFM analysis

The X-ray diffraction (XRD) analysis has been performed on the CdS:Zn thin films to ascertain the crystal structure and the crystal orientation. The XRD patterns of as-deposited films with different doping concentration (0,3,6 and 9 %) of Zn onto cleaned glass substrate at 400°C and thickness 260nm are shown in Figs. (1,a,b,c and d). The peaks of the XRD were observed between 20° and 60° at room temperature. A comparison of the peak position (2θ) values of American Standard for Testing Materials (ASTM) card (03-0932) with XRD spectra data suggests that all films have (wurtzite) hexagonal structure and exhibit polycrystalline structure. It can be observed from diffractograms that the preferred crystallographic orientation of the crystallites in CdS:Zn films gradually changes from (002) to (100) with the change in the value of Zn from 0 to 9%. This result is in agreement with those of Ibrahim [14], and Perez [15]. The spectrum of CdS and CdS:3%Zn thin films exhibited peaks at (100), (002), (101), (102), (110) and(112) with a preferential orientation of (002) plane, and for CdS:6% and 9% Zn thin films exhibited peaks at (100), (002), (101), (102), (110) and(112) with a preferential orientation of (100) plane. Changes that have occurred in the intensity of the main peaks are scribed to the rotation of some crystalline grains during the preparation processes. The average crystallite size of the prepared samples measured at thickness 260 nm comes to be 17nm,11nm,10.5nm, and 9nm for doping concentration (0, 3,6 and 9 %) of Zn respectively. the crystallite size is found to decrease with the increase in Zn composition. Therefore, it has been found that when the strain increases the crystallite size decrease, because of the delayed crystal growth which is due to the pressures that can increase the lattice energy and reduce the driving force to growth .

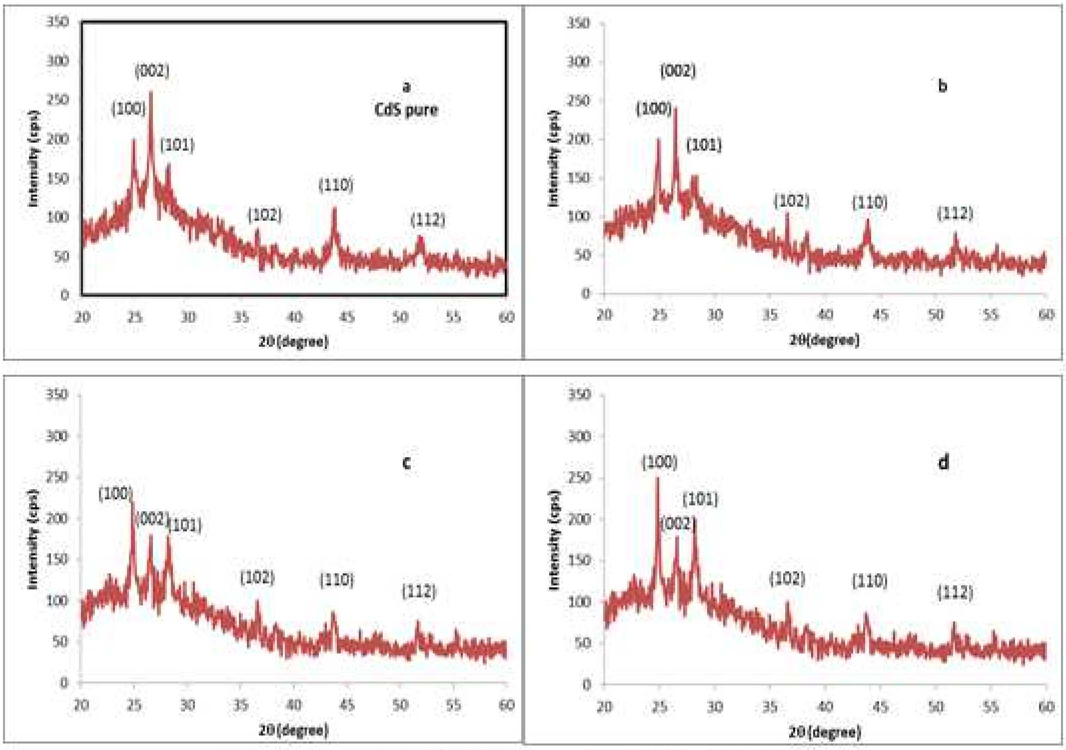
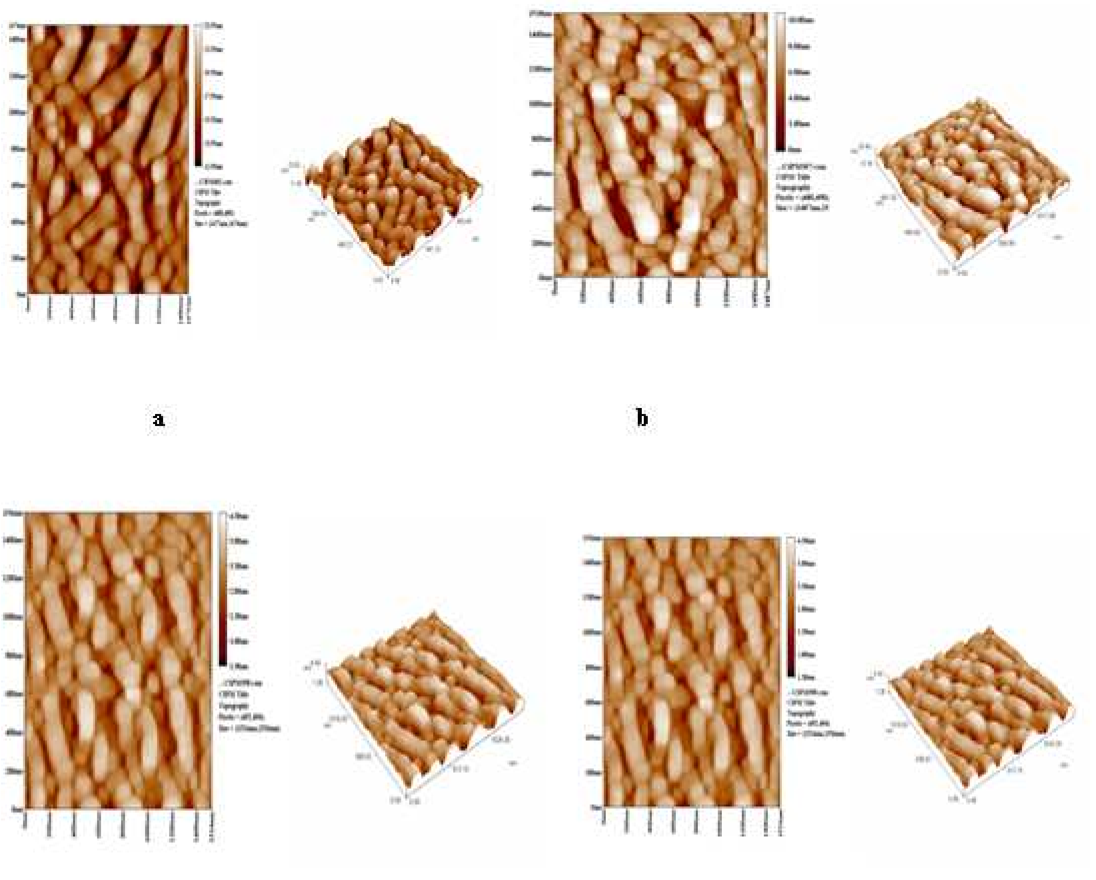


Fig.(1,a,b,c and d): XRD for deposited CdS:Zn=(0,3,6,9%)

The 2D and 3D AFM surface images films (160 nm) taken for CdS and CdS:Zn thin films with various contain of Zn were shown in Figs. (2,a,b,c and d).



a b

c d

Fig.(2,a,b,c and d): AFM images for thin films deposited from CdS:Zn=(0,3,6,9%),2D & 3D.

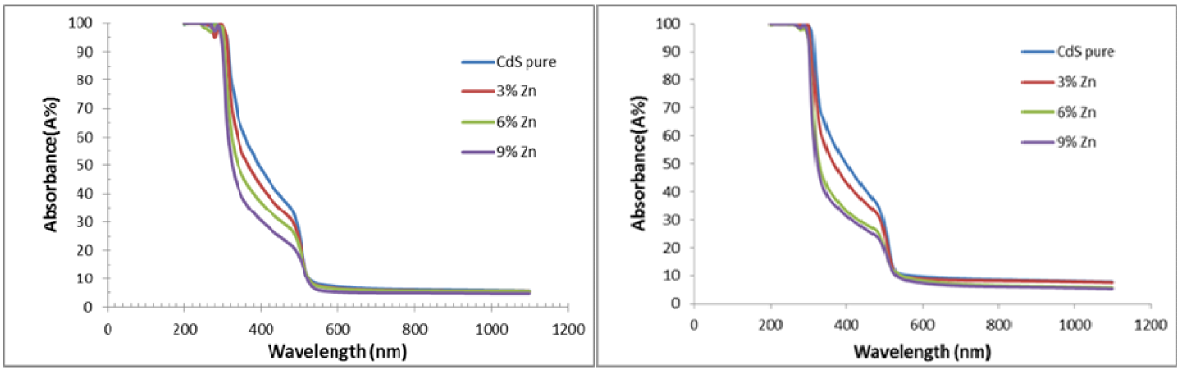
Out of the figures above it can be noticed that a familiar granular structure with crystallite size around some of nanometers, a root mean square (RMS) roughness ranged of (1.84 – 0.358) nm, and a maximum peak to peak height, Sz (ten point height) ranged of (6.6 -1.15) nm which shows that the surface of films is highly smooth, as shown in table (1).

Table (1): AFM data for films prepared from CdS:Zn.

Concentration Of Zn(%)	**Roughness average Sa(nm)**	**Root mean square Sq(nm)**	**Ten point height Sz(nm)**
0	1.840	2.30	6.60
3	1.620	2.04	6.14
6	0.856	1.06	3.89
9	0.358	0.44	1.15

4.2 Optical properties

The optical absorbsion spectra CdS and CdS:Zn thin films, we can be seen from Figs.(3,a&b) displays the variation of Absorbance spectra with wavelength of CdS:Zn thin films measured at thickness of 160 and 260 nm respectively. From the plots it can be justified that the films show higher absorption on the shorter wavelength side (ultraviolet region). The absorption edges of the films were observed to shift towards shorter wavelengths, which is indicated the increase of the optical band gap[16], with respect with the increasing of Zn concentration. The films show low absorption on the higher wavelength side (visible range). This behavior can be explained as follows: at high wavelength the incident photon do not have enough energy to interact with atoms, thus the photon will transmitted, while when the wavelength decreases (at the neighborhood of the fundamental absorption edge), the interaction between incident photon and material will occur, and the photon will absorbance[17].



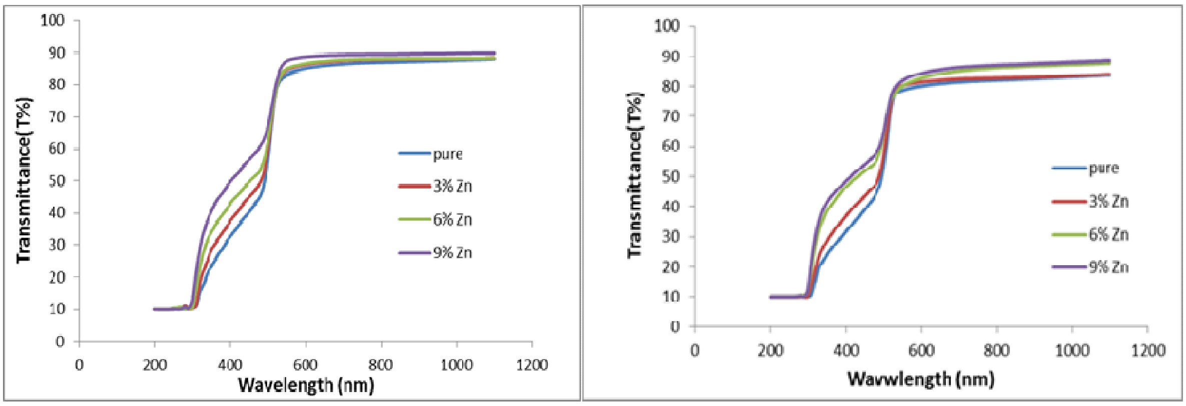
a b

Fig.(3, a &b): Absorbance spectra of CdS:Zn thin films measured at thickness of 160 and 260 nm respectively

Figs.(4, a&b) displays the optical transmittance spectra for the deposited CdS:Zn thin films measured at thickness of 160 and 260 nm respectively. The films at thickness of 160 nm as in Fig.(4, a), exhibit very high optical (87% - 90%) transmission in the visible range, depends upon radiation energy and the doping concentration of Zn within the films, which is important for its applications as a window layers in solar cells. The sharp absorption edge corresponding to the band gap confirms the good quality of grown films. The blue shift occurs in absorption edge (corresponding to the band gap) in CdS:Zn thin films with the increase in doping concentration of Zn within the films.

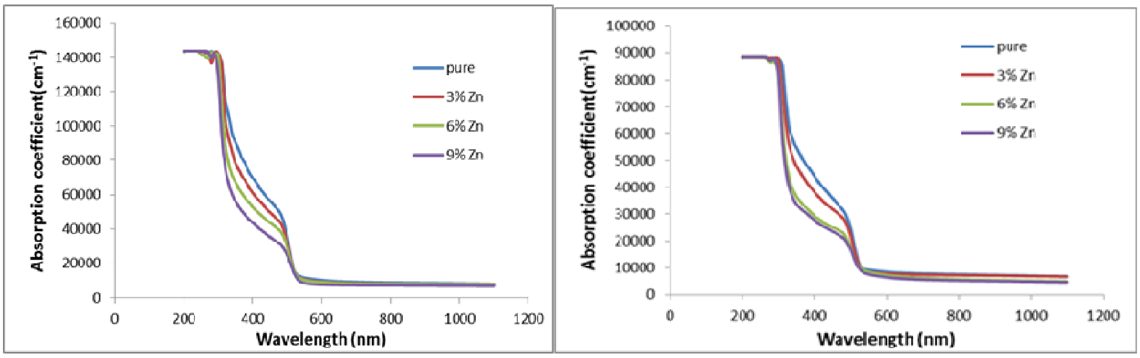
The films at thickness of 260 nm as in Fig. (4, b), exhibit high optical (82% - 87%) transmission in the visible range. The optical study indicates that the transmittance values in the visible range decreases with the increasing of thickness for all investigated samples. This behavior is attributed to the increase the number of atoms with thickness, that leads to the increase the number of collisions between incident photon and atoms which lead to the increasing of absorbance and decreasing transmittance [18]. Also may be attributed to the creation of level at the energy band by increasing thickness.

Figs.(5, a&b) show the optical absorption coefficient as a function of incident wave length on CdS and CdS:Zn thin films at different doping concentration (3,6 and 9 %) of Zn onto cleaned glass substrate at 400°C and the thickness was about 160 and 260 nm respectively. We can evidently see that all films has a value of absorption coefficient ($\alpha > 10^4$ cm^{-1}) which causes the increase of the probability of the occurrence direct transitions . The absorption coefficient was decreased with increased thickness. The absorption coefficient value depends on absorptivity and theoretically its relation is reversed with the film thickness.



a b

Fig.(4, a&b):Transmittance spectra of CdS:Zn films measured at thickness of of 160 and 260 nm respectively.

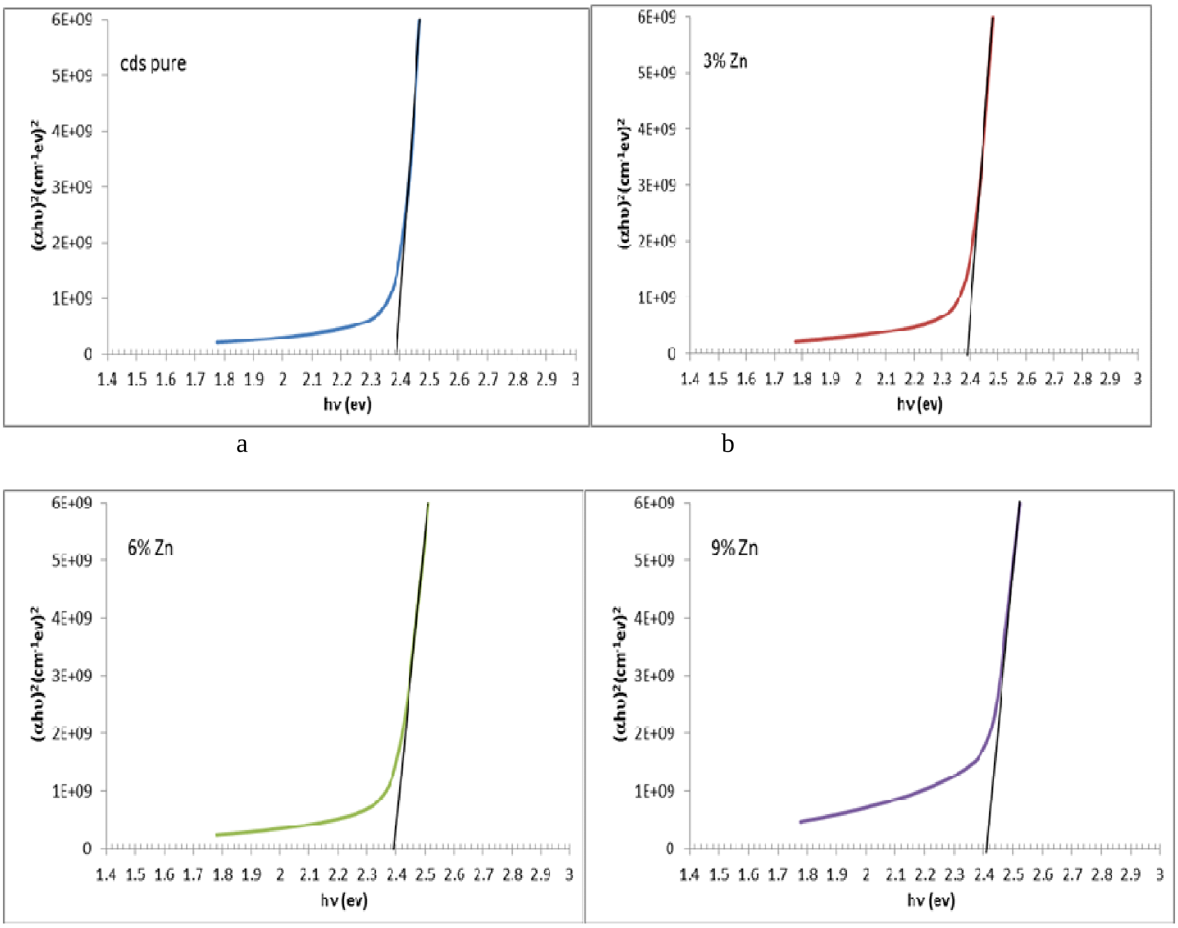


a b

Fig. (5, a&b): The absorption coefficient as a function of wave length for CdS:Zn thin films measured at thickness 160 and 260 nm respectively

Figs. (6,a,b,c and d) and (7,a,b,c,d). Extrapolating the straight line of the plot $(\alpha h\nu)^2$ versus $(h\nu)$ for zero absorption coefficient value ($\alpha = 0$) give the energy band gap value. The linear nature of the plots at the absorption edge confirmed that CdS:Zn is a semiconductor with direct band gap. The value of optical energy gap , which have been determined for CdS & CdS:3,6 and 9 % Zn films at $(\alpha h\nu)^2=0$, were equal 2.39, 2.393, 2.98 & 2.413 eV and 2.38, 2.39, 2.393 & 2.4 eV for 160 and 260 nm thicknesses respectively.

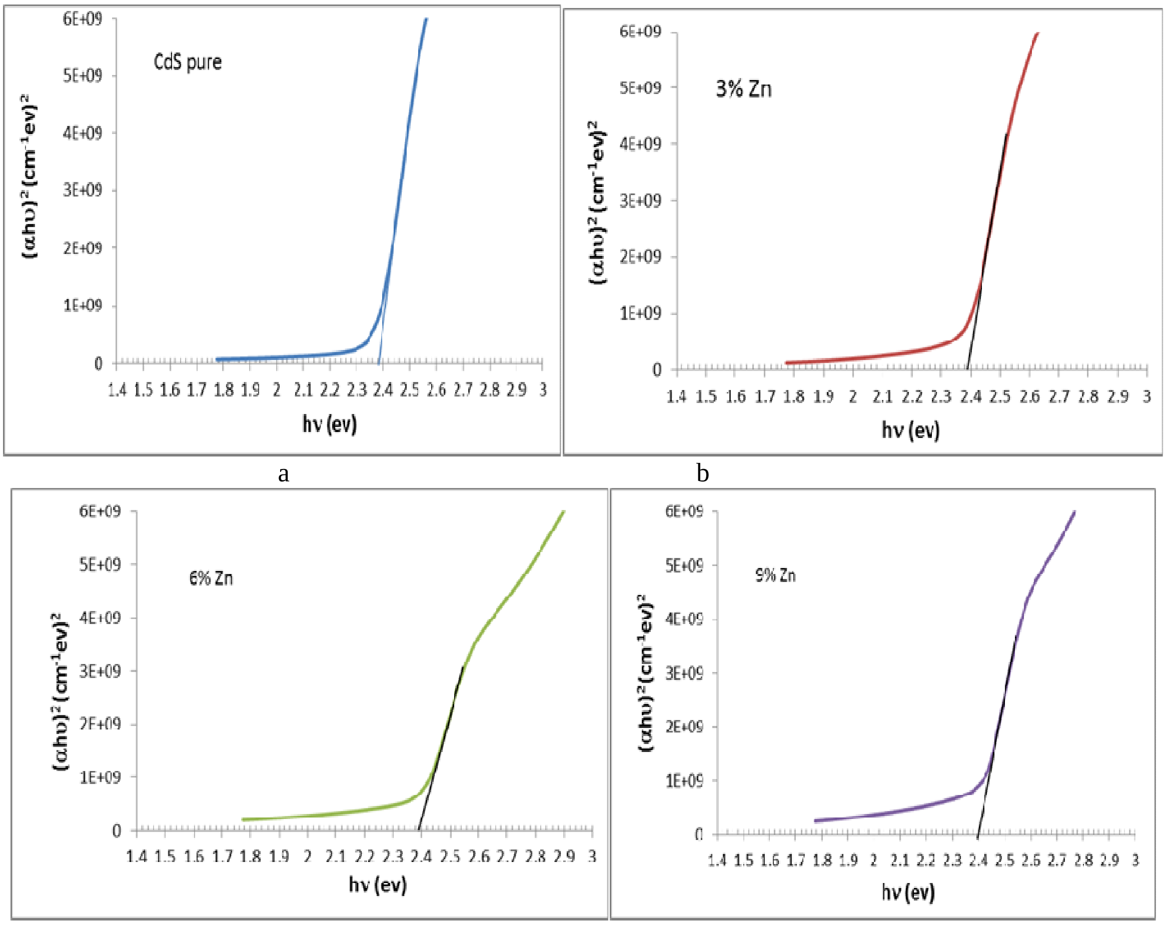
The increase in optical energy gap upon doping with Zn has been explained by splitting of the tail levels from the band. Increase in band gap can also occur by filling the lower-lying conduction (valence) band levels with electrons (holes), thereby requiring a larger photon energy to promote an electron from the valence to the conduction band (Burstein–Moss shift)[19,20].



a b

c d

Fig. (6,a,b,c and d): Variation of $(\alpha h\nu)^2$ versus photon energy (hν) of CdS thin films at thickness 160 nm with different Zn concentration



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c d

Fig. (7,a,b,c and d): Variation of $(\alpha h\nu)^2$ versus photon energy (hν) of CdS thin films at thickness 260 nm with different Zn concentration

5. Conclusion

1- From X-ray diffraction investigation observed crystalline structure of CdS and CdS:Zn films have (polycrystalline) structure and synthesis (hexagonal).

2- The doping with Zn did not effect on the nature of crystal structure of CdS.

3- The average crystallite size estimated from XRD data indicate that the crystallite size within the structures of the nanoparticles, as well as crystallite size decrease with increasing the doping concentration.

4- Transmittance of CdS & CdS:Zn films is ranged of 82-87% & 87-90% in the visible and near IR regions for thickness of 160 and 260 nm respectively, and high absorbance in UV region which makes it suitable as a window in solar cell.

5- The transition happen in these films are allowed direct transition.

6- Optical energy gap increase with increasing doping concentration.

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