

Photoconducting properties of hierarchical rod like structure nanostructured $Cd_{1-x}Zn_xS$ thin films prepared by chemical bath deposition technique

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Abstract

Nanostructured hierarchical rod shape $Cd_{1-x}Zn_xS$ ($x=0.2, 0.4, 0.6, \text{ and } 0.8$) thin films has been prepared by chemical bath deposition technique. The CBD is relatively simple, inexpensive and convenient for large area deposition. Nanostructured $Cd_{1-x}Zn_xS$ thin films were deposited on glass substrate by chemical bath deposition technique have been investigated by different analytical technique. The influence of Zn composition on structural, surface morphology, optical and electrical properties of thin films was investigated. It was observed that as Zn composition of the films significantly effect on crystallite size, grain size, optical band gap energy. The result are discussed and interpreted.

Keywords: CdS thin films; chemical bath deposition technique, TEP, electrical conductivity, photoconducting property.

1.INTRODUCTION

Semiconducting thin films exhibit novel electrical, mechanical, chemical and optical properties In recent years, current interest in the creation of semiconducting thin films on surfaces by a variety of self-organizing techniques has focused on their application in photoconducting and molecular electronics [1]. Nanostructured semiconductors of group II-IV have potential applications in many technical fields [2] . The growth of ternary semiconductors thin films has been studied very extensively

in the recent years, since these films play an important role in the fabrication of solar cells due to their favorable electrical and optical properties [3]. Sulphides of cadmium and zinc have been utilized in various optoelectronic devices. It is of great technological interest that cadmium zinc sulphides (CdZnS) thin films have been used as a wide band gap window material in heterojunction solar cell and in photoconductive devices [4].

Photoconductivity studies of II-VI compounds are quite important due to their broad applications in photovoltaic solar energy and thin film transistor electronics [5]. Photoconductivity by visible light in polycrystalline semiconductor films has been reported by many researchers studying a wide range of materials. Photo decay and photo response properties are employed for investigation of photoconductive materials and photovoltaic structures [6]. In order to obtain CdZnS films, there are several deposition methods like vacuum evaporation [7], solution growth technique [8].

Among these techniques, CBD presents many advantages: inexpensive, simple equipment, low temperature (<100°C), and large-area deposition. So it is well suited for the manufacture of photovoltaic devices [9]. In recent year's major attention have been given to the investigation of electrical and optical properties of CdZnS thin films. Additionally, photosensor applications, switching properties of photoresponse, photo decaying properties should be studied.

In this work, nanostructured $Cd_{1-x}Zn_xS$ thin films were prepared by chemical bath deposition technique. Phase purity and surface morphology properties were studied using X-ray diffractogram (XRD) and scanning electron microscope (SEM). Chemical composition was examined using energy dispersive spectrophotometer (EDAX). Optical band gap property was investigated using UV-spectroscopy. Electrical conductivity measured by two probe method. Thermoelectric power set up (TEP) used to determine type of material. This work reports the effect of Zn content on structural,

microstructural, electrical and optical properties of these films. Photoconducting properties were studied using photoconducting setup at different applied voltage and filters.

EXPERIMENTAL DETAILS

The physical properties of the nanostructured $Cd_{1-x}Zn_xS$ films are dependent upon the growth parameters such as the bath temperature, the relative concentrations of the various reactants in the solution the pH value and the type of substrate. The chemical bath deposition technique was used to deposit the thin films of nanostructured $Cd_{1-x}Zn_xS$ on glass substrate. The starting materials used were cadmium sulphate and thiourea (Made: Sd-fine 99.99% purified). For the deposition of $Cd_{1-x}Zn_xS$ thin films a well cleaned glass substrate was immersed vertically in the solution and temperature of bath maintained at 60 to 80 °C for 1 to 3 hours. Triethanolamine (TEA) was used as a complexing agent. Ammonia solutions were used to adjust pH of the reaction mixture. The composition of Zn was varied from 0.2 to 0.8. As prepared nanostructured $Cd_{1-x}Zn_xS$ samples referred as S1, S2, S3, and S4. Finally, the substrates then washed with distilled water and annealed at temperature 200 °C. In order to obtain good quality of thin films, following parameter were adjust such as deposition time, temperature of deposition, pH of the solution is adjust by addition of liquid ammonia drop in the prepared solution. The optimum value of time, temperature and pH were tabulated in Table 1.

Table 1. Optimum parameter to obtain nanostructured $Cd_{1-x}Zn_xS$ thin films

Deposition parameter	Optimum value / item
Deposition time	70 min.
pH	10
Concentration of precursor cadmium sulphate, zinc sulphate, thiourea	0.1 M
Solvent	Deionized water

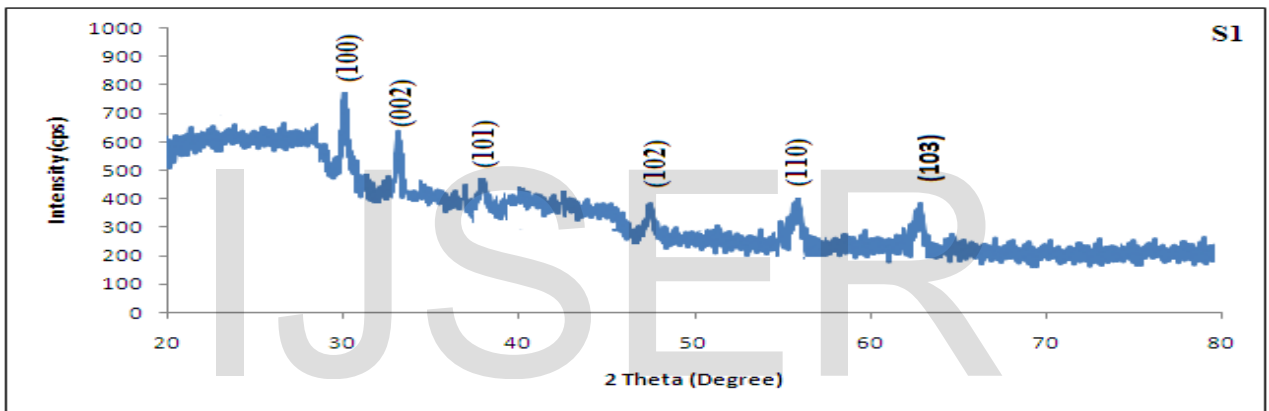
Zn composition	0.2, 0.4, 0.6, 0.8
Deposition temperature	70 °C

3. RESULTS AND DISCUSSION

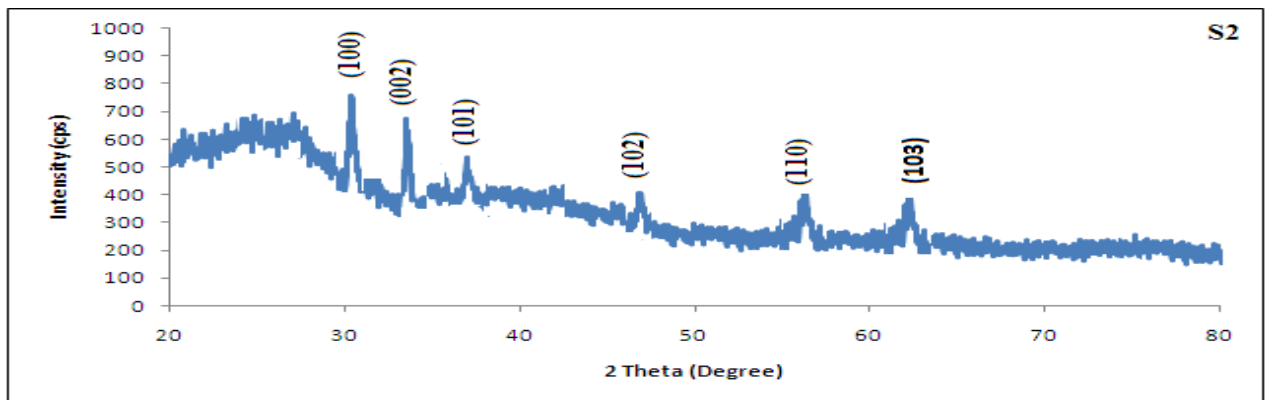
3.1. Structural properties

3.1.1. X-ray diffraction:

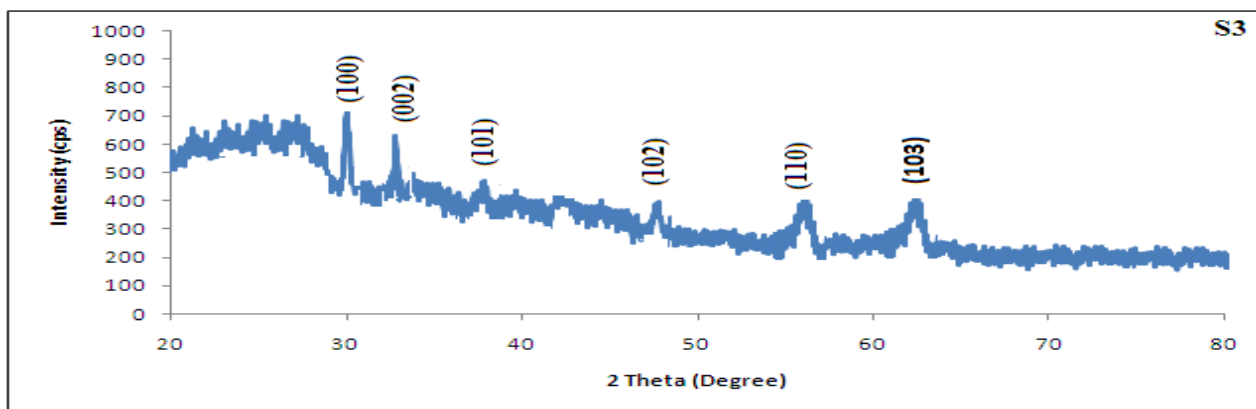
The phase purity of the film was analyzed with X-ray diffractogram (Miniflex Model, Rigaku, Japan) using $\text{CuK}\alpha$ radiation with a wavelength of 1.542 Å.



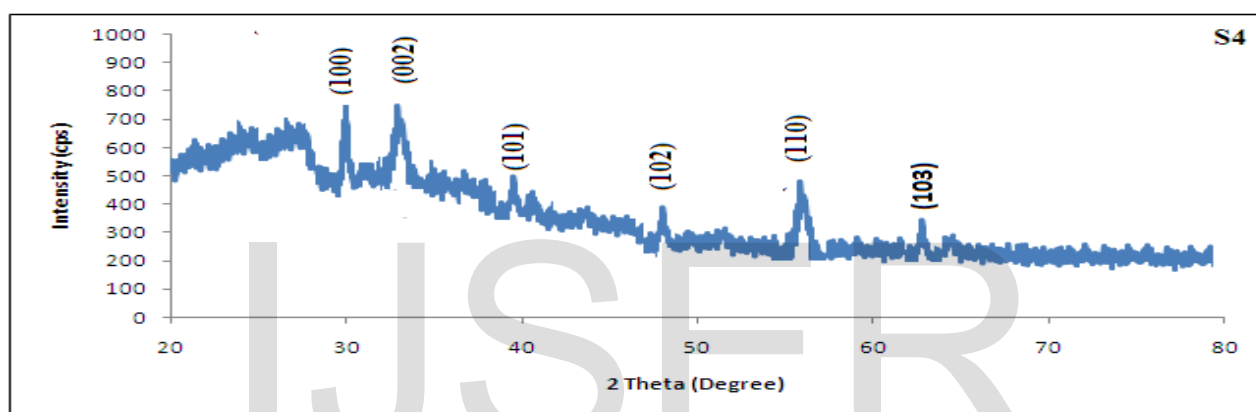
(a)



(b)



(c)



(d)

Figure. 1. (a), (b), (c) and (d) shows X-ray diffractogram of nanostructured $Cd_{1-x}Zn_xS$ thin films.

The structural characterization is very important in explaining structural, microstructural and electrical properties of $Cd_{1-x}Zn_xS$ thin films. The X-ray diffraction patterns were recorded from 20 to 80° as shown in Fig. 1 (a) – (d). The XRD results show that all the films were nanocrystalline in nature. These XRD patterns conform the formation and composition of alloy of $Cd_{1-x}Zn_xS$ ternary system with $x = 0.2, 0.4, 0.6$ and 0.8 . The presence of sharp peaks indicates polycrystalline structure of synthesis films. It is observed from Fig. 2 (a), (b), (c) and (d) that, the observed peaks (100), (002), (101), (102), (110) and (110) are match with standard JCPDS data of CdZnS.

The average crystallite size of $Cd_{1-x}Zn_xS$ thin film samples were calculated by using the Scherrer formula,

$$D = 0.9\lambda/\beta\cos\theta \text{ ----- (1)}$$

Where, D = Average crystallite size

λ = X-ray wavelength (1.542 Å)

β = FWHM of the peak

θ = Diffraction peak position.

The average crystallite size was presented in Figure 3 (a).

Dislocation density values were calculated using the standard relations [10].

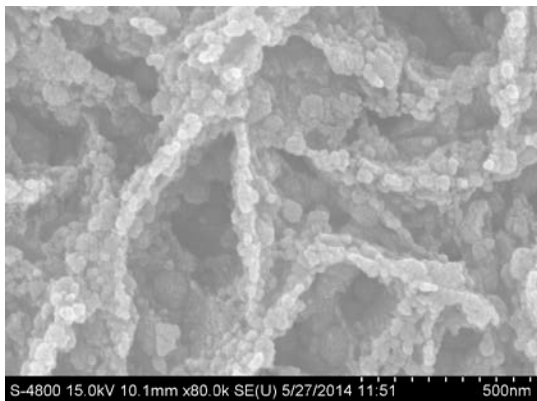
$$\text{Dislocation density } (\delta) = 1/D^2 \text{ ----- (2)}$$

The dislocation density value were tabulated in Figure 4.

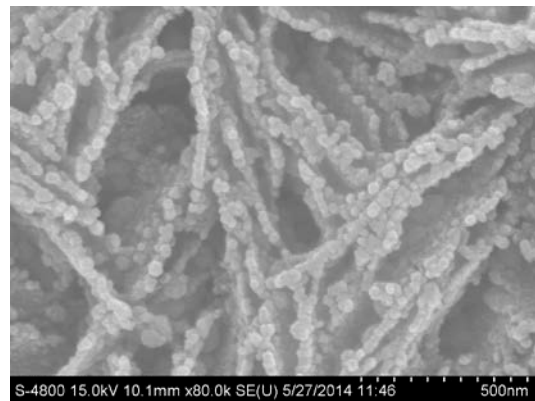
3.2. Microstructure Study

3.2.1. Field emission Scanning electron microscope

The surface morphology of the prepared film was analyzed using a field emission scanning electron microscope coupled with energy dispersive X-ray analysis (EDAX) (FE-SEM, JEOL. JED 6300).



(S1)



(S2)

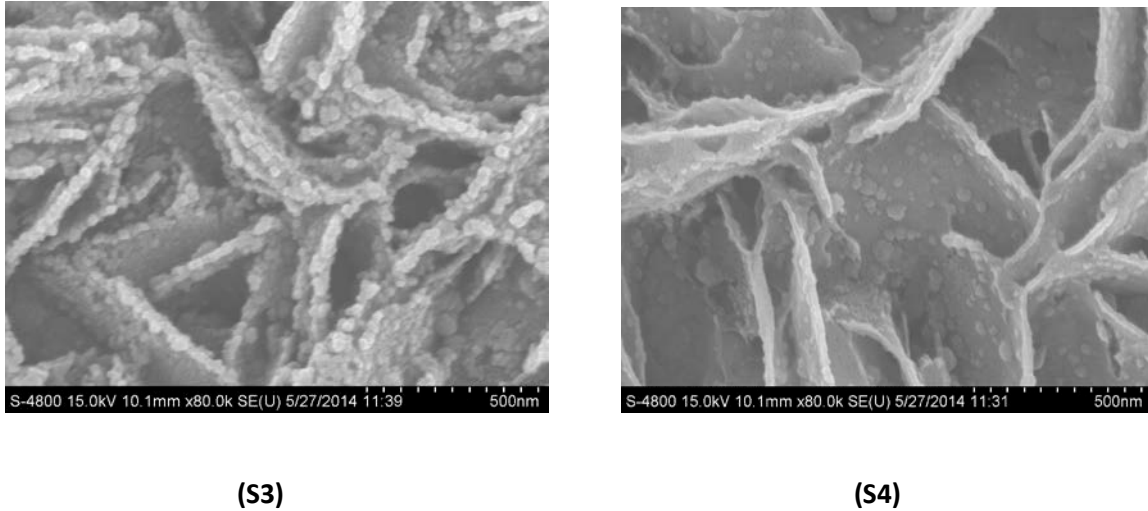


Figure. 2. FE-SEM images of nanostructured $Cd_{1-x}Zn_xS$ thin film sample S1, S2, S3 and S4

FE-SEM imaged of nanostructured $Cd_{1-x}Zn_xS$ thin films were represented in Fig.3. Scanning electron microscope resolve nanoparticle associated with the film even at high magnification of “15E+3” Fig 2(a) (b) (c) and (d) shows the hierarchical formation of the particle for $Cd_{1-x}Zn_{1-x}S$ thin film. In fig. 2(a) shows agglomerations of the grains. Grain size was given in Figure 3 (b).

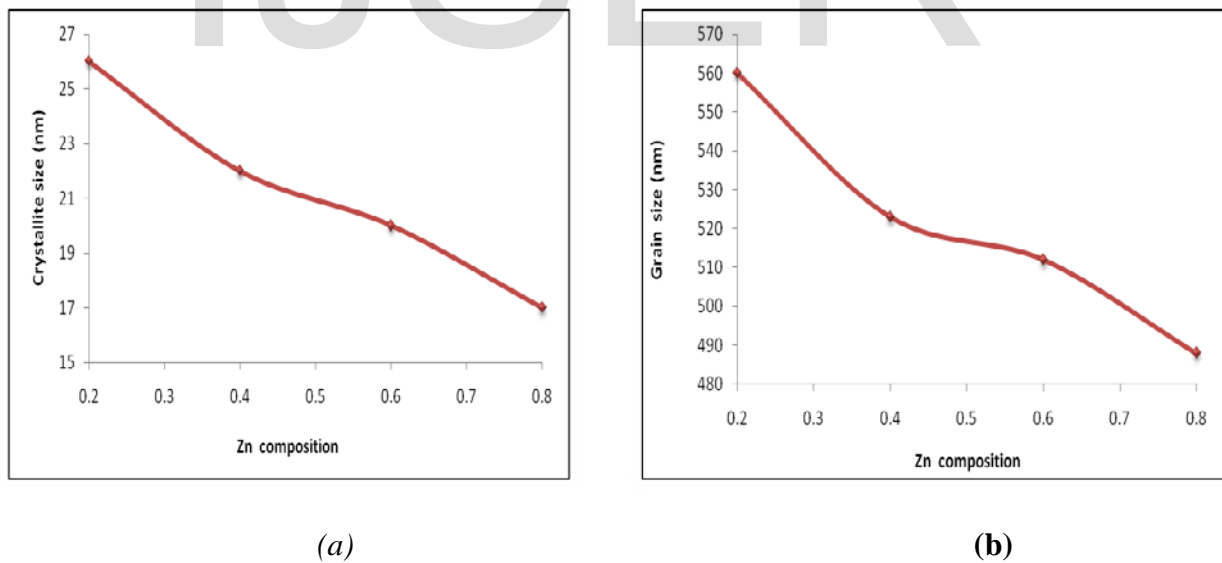


Figure. 3. (a) and (b) Variation of crystallite size and grain size with Zn composition

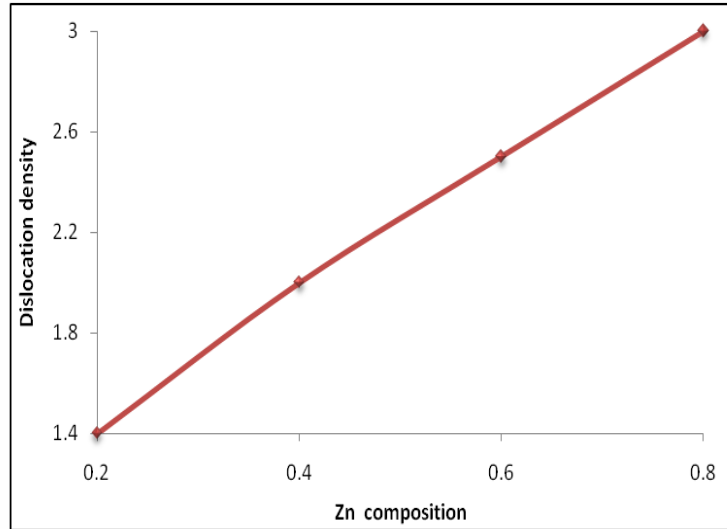


Figure. 4. Variation of dislocation density with Zn composition

It is also clear from Figure 3 (a), (b) and (c), that crystalline size, grain size goes on decreasing with increase in Zn composition in the thin films while value of dislocation density increase. This may be due to the change in structural and surface morphology with increase in Zn composition, which leads to minimum imperfection.

3.3. Quantitative elemental analysis (EDAX)

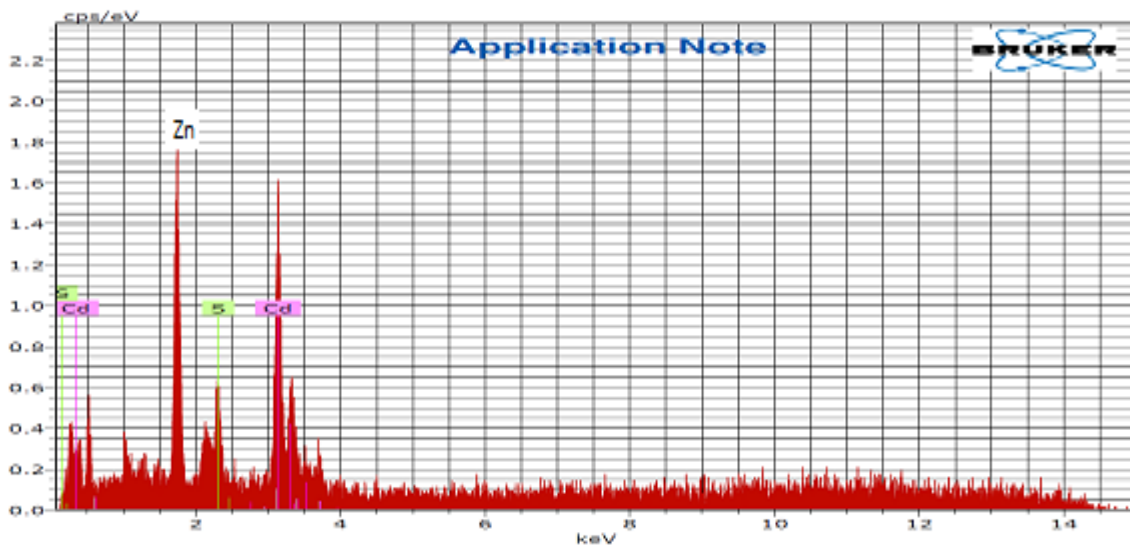


Figure. 5. EDAX of nanostructured Cd_{1-x}Zn_xS thin film sample (S3)

The quantitative elemental composition of $Cd_{1-x}Zn_xS$ thin film were analyzed using an energy dispersive spectrometer. Fig.5 shows as the prepared $Cd_{1-x}Zn_xS$ thin film was nonstoichiometric in nature.

Table 2. Quantative elemental analysis as prepared $Cd_{1-x}Zn_xS$ thin films

Element	Observed							
	S1		S2		S3		S4	
	wt %	at %	wt %	at %	wt %	at %	wt %	at %
Cd	57.29	35.63	49.88	30.85	47.38	29.15	40.35	25.14
S	16.82	36.67	14.38	32.44	13.84	29.85	09.85	21.52
Zn	25.90	27.70	35.74	31.16	38.78	41.01	49.80	53.34
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Table 2 indicate that the formation of $Cd_{1-x}Zn_xS$ thin films. It shows nonstoichiometric formation. From Table 2 it was observed that as composition of Zn ($x=0.2$ to 0.8) in $Cd_{1-x}Zn_xS$ increases at % of Zn increased.

3.4. Optical properties using UV-spectroscopy

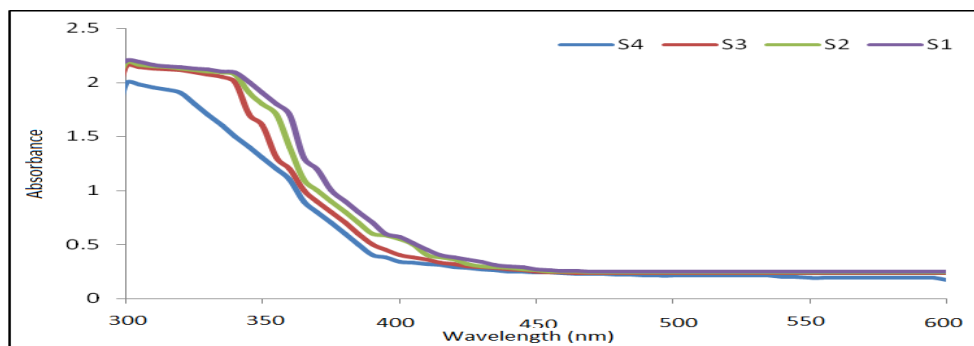


Figure. 6. Variation of absorbance with the wavelength (λ) nm for samples S1, S2, S3 and

S4.

The optical absorbance of the films were measured using UV-visible-2450 spectrophotometer at room temperature. Optical absorption studies of hierarchical $Cd_{1-x}Zn_xS$ thin films were carried out in the wavelength (λ) range 300-600 nm. The variation of absorbance with wavelength (λ) as shown in Fig.6. The band gap energies of the samples were calculated from the absorption edges of the spectra [11]. The slope drawn from the start of an absorption edge (the onset of absorbance) and horizontal tangent had drawn on absorption minimum and intercepted each other at some point.

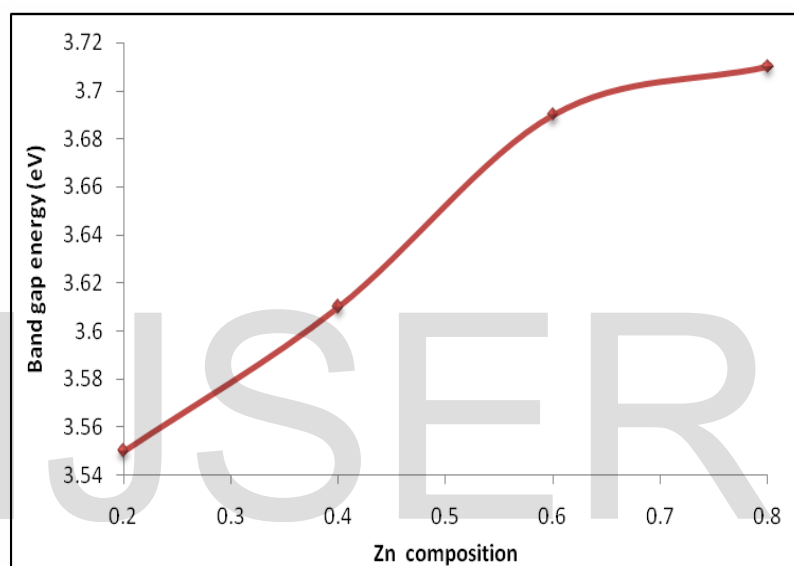


Figure. 7. The variation of energy gap of the nanostructured $Cd_{1-x}Zn_xS$ as function of Zn composition

The effects of Zn composition on the band gap (E_g) values of the nanostructured $Cd_{1-x}Zn_xS$ films have been studied and is shown in Figure 7. It can be seen that the band gap energy varies with Zn composition in a nonlinear way. In the present case of nanostructured $Cd_{1-x}Zn_xS$ thin films, E_g values vary from 3.55 to 3.71 eV for $x=0.2$ to 0.8 in a nonlinear way. This change in the band gap energy of $Cd_{1-x}Zn_xS$ by addition of Zn shows the formation of a continuous series of solid solutions [12]. Optical band gap energies of the samples were observed to be slightly varying from 3.55 to 3.71 eV. It is well known that a significant increase in the band gap energy is possible when the size of crystallites reaches the

size of the quantum dots. It seen that the slightly increase in the optical band gap energy of the films with increasing film in Zn can be attributed to the increase in the crystalline and grain size.

3.5. Electrical properties

3.5.1. Thermoelectric power measurements:

The *p*-type or *n*-type semiconductivity of nanostructured $Cd_{1-x}Zn_xS$ thin films was confirmed by measuring the thermoelectric power of the thin film samples. The thermoelectric power (TEP) was measured as a function of temperature in the range between 320 and 440 K.

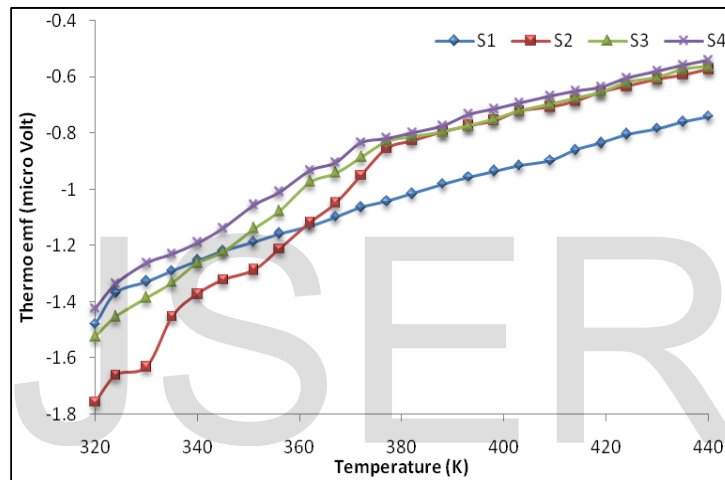


Figure. 8. Variation of the thermo emf with temperature

For nanostructured $Cd_{1-x}Zn_xS$ material, conduction electrons originate from ionized defects such as oxygen vacancies, rendering *n*-type conductivity. The variation of the thermo emf with temperature difference for all the samples is shown in Fig. 8. TEP increases with increase in temperature for all the samples. Nanostructured $Cd_{1-x}Zn_xS$ thin films were observed to be the *n*-type material.

3.5.2. Electrical conductivity

Fig.9 shows the variation of $\log(\sigma)$ with operating temperature. The conductivity of each sample is observed to be increasing with an increase in temperature. The increase in conductivity with

increase in temperature could be attributed to negative temperature coefficient of resistance and semiconducting nature of nanostructured $Cd_{1-x}Zn_xS$ thin films.

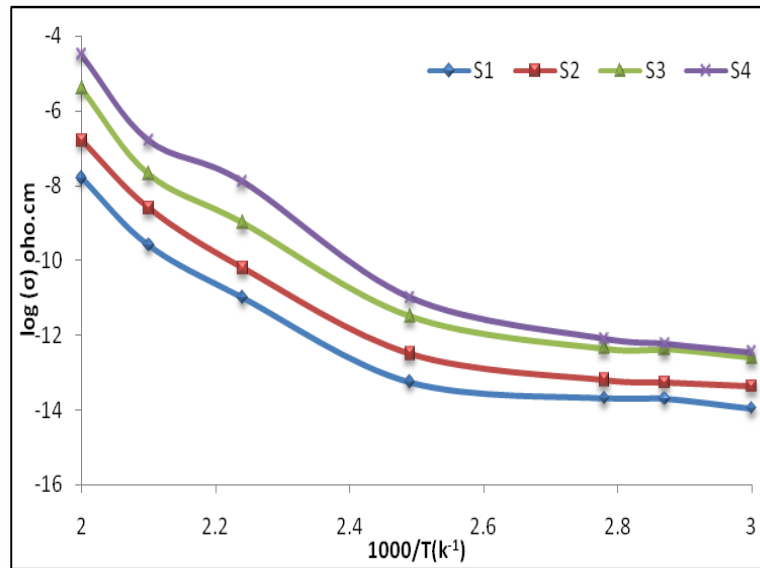


Figure. 9. Temperature dependence of the conductivity of nanostructured $Cd_{1-x}Zn_xS$

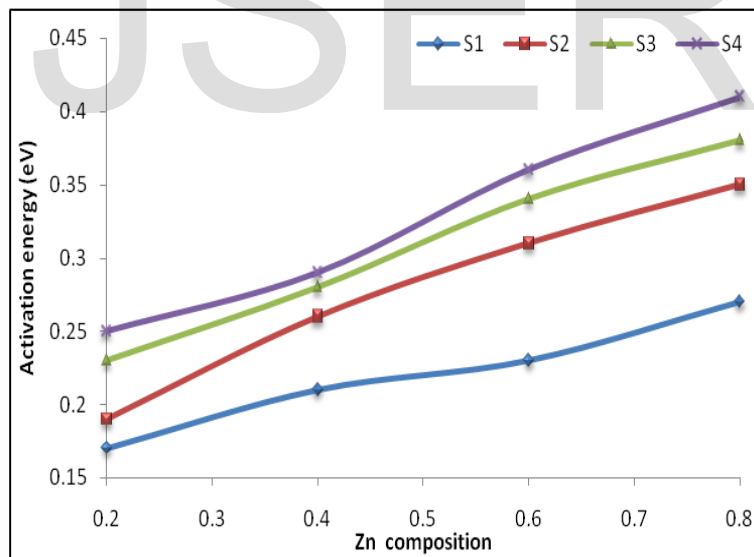


Figure. 10. Composition dependence of the activation energy in nanostructured $Cd_{1-x}Zn_xS$ thin films

Activation energy has been determined using the slope of this Figure 9 for each composition of Zn. It was found that the activation energy of $Cd_{1-x}Zn_xS$ ($x=0.2, 0.4, 0.6$ and 0.8) thin films was

observed to be increases linearly with increasing Zn composition as shown in Figure 10. An increase in the activation energy of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ ($x=0.2, 0.4, 0.6$ and 0.8) thin films with increasing composition of Zn in CdS is suggestive of the fact that the conduction is due to thermally assisted tunneling of the charge carrier in the localized state, which are present in the band gap[13] .

4. Photoconducting Application of nanostructured $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films:

4.1. I-V characteristics of thin film

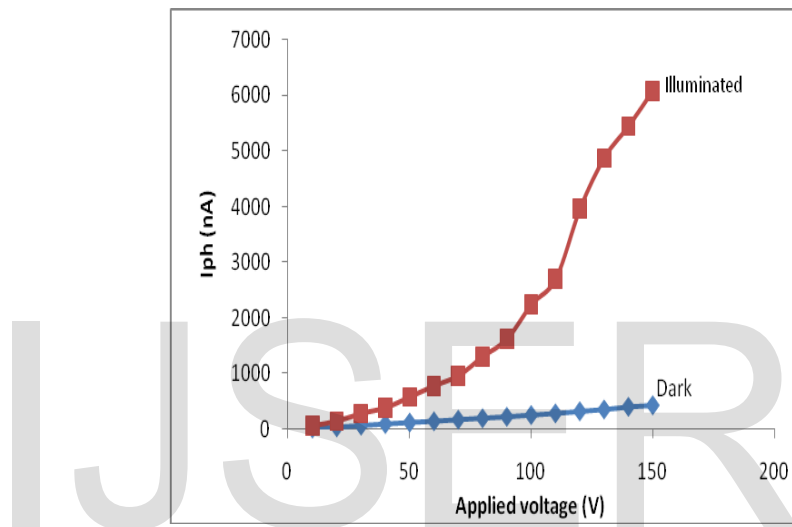


Figure. 11. I-V characteristics of the films.

Fig.11 depicts the I-V characteristics of nanostructured $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films, the symmetrical nature of the I-V characteristics for particular samples shows that the contact was ohmic in nature. It show the semiconducting property of the synthesized nanostructured $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films.

4.2. Measurement of spectral response for thin film

Fig.12 gives typical example of nanostructured $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin film as a function of incident light at different wavelength. It is seen that the photocurrent increases with wavelength and attains a maximum and then decreases. The maximum photoconductivity is at $\lambda= 480$ nm. Which corresponds to the band gap of thin film. We conclude that photosensitivity is dependent on the wavelength of the incident light. It is called spectral response characteristics.

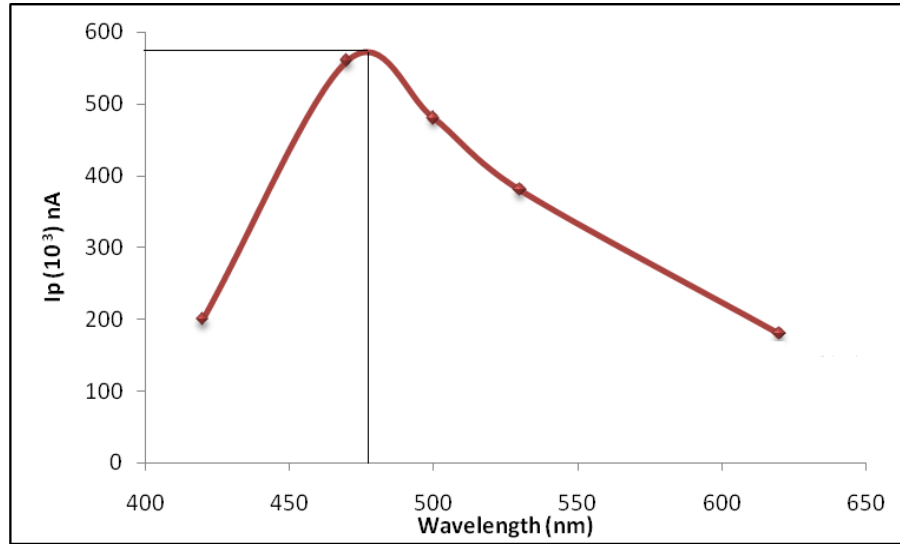


Figure. 12. Measurement of spectral response ($\lambda= 480 \text{ nm}$) for nanostructured $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin film.

The variation of photocurrent of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films with varying applied voltage in Fig.13. The plot shows that there is a linear dependence of photocurrent with applied voltages. The measurement results were investigate and regions where ohmic conduction mechanism

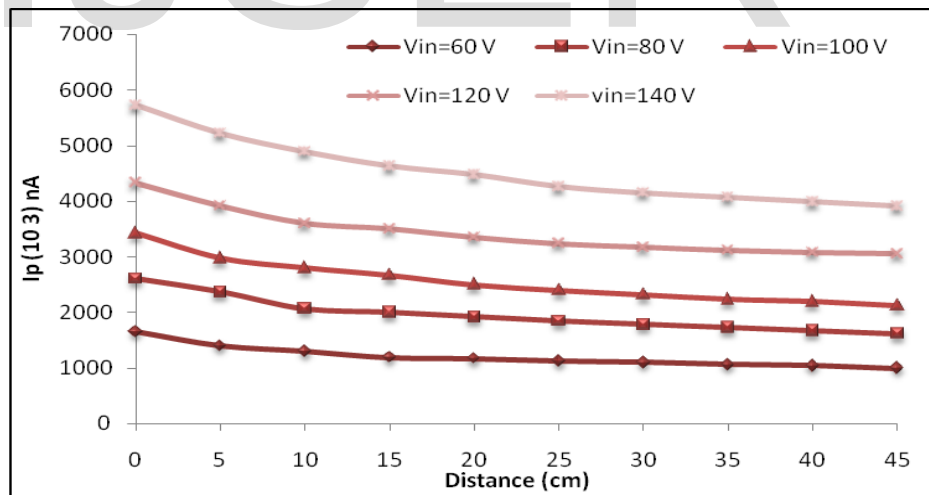


Figure. 13. Variation of photocurrent for nanostructured $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin film at different applied voltage

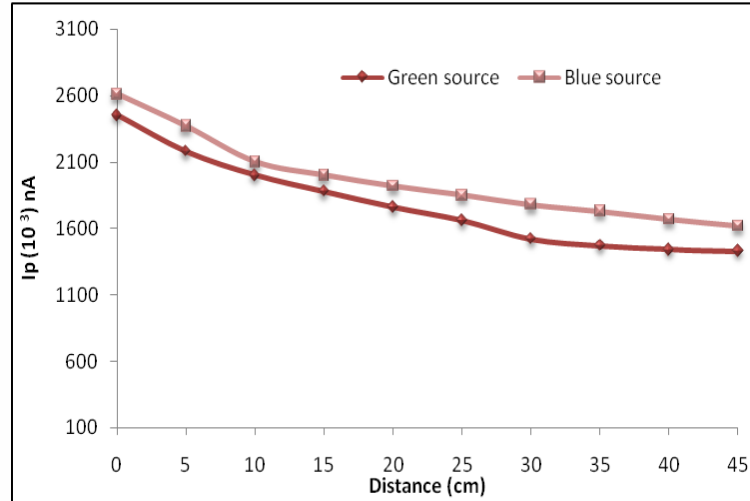


Figure. 14. Measurement of photocurrent for nanostructured $Cd_{1-x}Zn_xS$ thin film by using different source of light with distance

When the intensity of the white light goes down fewer valence electrons are promoted into the conduction band. As a result resistance of the photocell increases. As the distance increases that is as intensity goes down (Fig.14). The resistance becomes larger. The variation of measured resistance because of different colors of light hitting the photo-resistor may be dependent on several factors.

As the color (energy) of the light source changes, assuming a fixed distance, changes its resistance. It was observed that average value of resistor for blue color source is $31M\Omega$ and for green color source $42M\Omega$.

4.3. Rise and decay characteristics of nanostructured $Cd_{1-x}Zn_xS$ thin film:

The intensity of light falls on the film, the photocurrent is high and increases with respect to time that is the growth of current and is also called 'ON' condition, and when intensity of light is switched off, then the photocurrent is decreases as time called decay of current is also called 'OFF' condition (Shown in Fig.15). When light is illuminated on the film, the photocurrent is high. Initially high value of photocurrent is due to the absorption of photon by film, which excites the electrons from the valence band to conduction band. Most of the electrons are from the surface of the $Cd_{1-x}Zn_xS$ film

which moves from valence band to the conduction band, it increases the process of pair generation initially, which in turn increases the carrier concentration, resulting in high photocurrent.

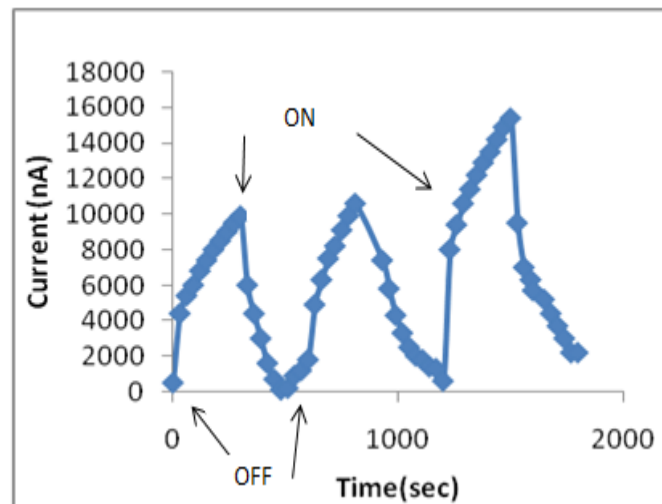


Figure. 15. Variation of rise and decay of nanostructured $Cd_{1-x}Zn_xS$ thin film

The photocurrent rise and decay characteristic is another important aspect for characterization of defects in film. Slow rise and decay of photocurrent upon illumination which are accurately measured. The photocurrent is dependent on the wavelength of excitation and increases as applied voltages. In present study, the deposited films show a slow rise and decay of photocurrent indeed always indicates the existence of high defect density in the films.

To measure the rise and decay of photo conductivity with time, light was turn on and rise of current was measured as function of time. While when light was turned off and the decay of current as function of time. By plotting the graph of photo conductivity (photo current) and time, it is clear from the characteristics that the photo current initially rises fast then becomes slows, saturating after certain time. The behavior of rise and decay curves is similar at different intensities. When light is turned off, initially photo current decreases fast and after a few seconds it decrease steadily with respect to time

Nanostructured $Cd_{1-x}Zn_xS$ thin films have certain time decay in responding to incident light. The response speed is an important point in designing detector as rapidly changing light levels and on-off switches. The response speed varies considerably with the light level. The higher incident light level, the faster the response speed. Also $Cd_{1-x}Zn_xS$ kept in darkness exhibit slower response than kept as a brighter light level.

5. Conclusions

The deposition conditions are optimized to obtain nanostructured $Cd_{1-x}Zn_xS$ thin films. The structural investigation using XRD reveals that formation of nanostructured $Cd_{1-x}Zn_xS$ thin films. Our study have shown that as Zn composition in the film goes on increases, decreasing crystallite size, grain size with increasing optical band gap energy, dislocation density and activation energy. Microstructural properties confirm that the as-prepared nanostructured $Cd_{1-x}Zn_xS$ thin films were hierarchical rod like structure. The elemental analysis conferred that as prepared $Cd_{1-x}Zn_xS$ thin films were nonstoichiometric in nature. Electrical conductivity increases with increase temperature of the nanostructured $Cd_{1-x}Zn_xS$ thin films, indicating semiconducting nature. TEP measurement indicates that as prepared nanostructured $Cd_{1-x}Zn_xS$ thin films are *n* type. Nanostructured $Cd_{1-x}Zn_xS$ photoconductor behaves like an ohmic resistance that depends upon the intensity of source. The photo decay methods are employed both for investigation of the photo sensitive, photovoltaic's and photo switching devices. The time response of photocurrent for nanostructured $Cd_{1-x}Zn_xS$ for several cycles as the light was turned ON-OFF, shows photo response properties and shows high photosensitivity and hence $Cd_{1-x}Zn_xS$ is used for opto-electronics, photo sensor applications.

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Reference

- [1] S. M. Patil and P. H. Pawar, pH dependent structural, optical and electrical properties of chemically deposited CdS thin films, Scholars Research Library, (2014);5 (3):40-48.
- [2] I. Akyuz, Salihkose, F. Atay, F. B. Vildan, Some physical properties of chemically sprayed $Zn_{1-x}Cd_xS$ semiconductor films Material science semiconductor processing, (2007);10: 103-111.
- [3] J. Zhou, X. Wu, G. Teeter, CBD $Cd_{1-x}Zn_xS$ thin films and their application in CdTe solar cells, Physica Status Solidi (B), (2014); 241: 775–778.
- [4] M. A. Green, K. Emery, Y. Hishikawa, and W. Warta, Solar cell efficiency tables (version 37), Progress in Photovoltaics, (2011); 19: 84–92.
- [5] S. Bhushan, T. Chandra, Stability Effect In Photoconducting Studies of Some Chemically Deposited CdS, (Cd-Pb)S and (Cd-Zn)S Films, Turk J. Phys.; (2008);32:21-29.
- [6] T. Pisarkiewicz, Photodecay method in investigation of materials and photovoltaic structures, Optoelectronics review; (2008); 12(1): 33-40.
- [7] L. C. Burton and T.L. Hench, $Zn_xCd_{1-x}S$ films for use in heterojunction solar cells, Applied Physics Letters, 9(1976);29:612–614.
- [8] K. Nagam, M. Ani, V. Reddy, Y. Lingappa, K. T. Ramakrishna, Reddy, R. W. Miles, Physical properties of $Zn_xCd_{1-x}S$ nanocrystalline layers synthesized by solution growth method, International journal of Optoelectronics Engineering, (2012); 2(2):1-4.

- [9] T. Yamaguchi, Y. Yamamoto, T. Tanaka , Y. Demizu , and A.Yoshida , (Cd, Zn)S thin films prepared by chemical bath deposition for photovoltaic devices, Thin Solid Films, (1996);281(1);375–378.
- [10]R. H. Bari , S. B. Patil, Studies on spray pyrolysed nanostructured SnO₂ thin films for H₂ gas sensing application, International Letters of Chemistry, Physics and Astronomy, (2014); 17(2) ;125-141.
- [11]R. H. Bari, V. Ganeshen , S. Potdar , L. A. Patil , Structural, optical and electrical properties of chemically deposited copper selenide films, Bulletin of material Science,(2009); 32(1):37-42.
- [12]W. Li, J.Yang , Z.Sun , L. Feng , J.Zhang and L.Wu L, Preparation and characterization of Coevaporated Cd_{1-x}Zn_xS thin films, International journal of photoenergy,(2011); Article ID 969214: 1-5.
- [13] D. Patidar , N. Saxena , S. K. Sharma , T. P. Sharma , Conduction mechanism in CdZnS thick films, Optoelectronic and advanced material-rapid communication,(2007);1:329-332.

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