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STRUCTURAL AND OPTICAL PROPERTIES OF NANOCRYSTALLINE $Zn_{0.5}Cd_{0.5}S/CdS$ THIN FILMS FOR PHOTOVOLTAIC APPLICATIONS

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ABSTRACT

In the present work, structural and optical properties of nanocrystalline $Zn_{0.5}Cd_{0.5}S$, CdS and $Zn_{0.5}Cd_{0.5}S$ / CdS thin films have been investigated in order to use as window layer for photovoltaic application. Nanocrystalline $Zn_{0.5}Cd_{0.5}S$ and CdS films have been deposited on glass substrates using chemical bath deposition technique (CBD). The atomic force microscopy (AFM) images showed that the prepared nanocrystalline thin films are homogeneous and have nano size structures. XRD analysis showed that, the films have polycrystalline structure with (002) orientation. From the optical properties results, the films have high transmittance (70 %). The band gap is found to be higher as comparison with the bulk of the same films indicating blue shift with respect to the bulk value as a result of quantum size effect. The electrical properties results show that the resistivity of CdS, $Zn_{0.5}Cd_{0.5}S$ and $Zn_{0.5}Cd_{0.5}S$ / CdS was (3.50×10^2, 3.43×10^3 and 3.18×10^2 Ω cm) respectively.

Keywords: CBD technique, $Zn_xCd_{1-x}S$ thin films, Optical properties.

الخصائص التركيبية والبصرية لأغشية $Zn_{0.5}Cd_{0.5}S/CdS$ ذات التراكيب النانوية للتطبيقات الكهروضوئية

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الخلاصة

في هذا البحث، تمت دراسة الخصائص التركيبية والبصرية لأغشية $Zn_{0.5}Cd_{0.5}S$ و CdS و $Zn_{0.5}Cd_{0.5}S$ /CdS ذات التراكيب النانوية لغرض استخدامها كنافذة في التطبيقات الكهروضوئية حيث تم ترسيبها على ارضيات زجاجية باستخدام تقنية الحوض الكيميائي. أوضحت صور مجهر القوة الذرية للعينات المحضرة أن الأغشية متجانسة وذات تراكيب نانوية، فحوصات حيود الاشعة السينية بينت ان الأغشية المحضرة متعددة التبلور وذات اتجاه سائد (200). من خلال نتائج الخصائص البصرية فأن الأغشية ذات نفاذية بصرية اكبر من 70 % وان فجوة الطاقة البصرية للأغشية النانوية ذات قيمة اعلى مقارنة مع فجوة الطاقة البصرية للحالة المحسوسة (Bulk) نتيجة لتأثيرات التقييد الكمي. اما نتائج الخصائص الكهربائية فقد بينت ان المقاومية لأغشية CdS، $Zn_{0.5}Cd_{0.5}S$ و $Zn_xCd_{1-x}S$ / CdS كانت 3.50×10^2 ، 3.43×10^3 و 3.18×10^2 أوم سم على الترتيب.

الكلمات المفتاحية: تقنية الترسيب بالحوض الكيميائي، أغشية $Zn_xCd_{1-x}S$ ، الخصائص البصرية.

1. INTRODUCTION

Nanocrystalline semiconductors exhibit changes in the energy band structure, resulting in quantum size effects. Since the energy levels are confined to potential wells of small dimensions, the spacing's between the energy levels increase as the crystal becomes smaller [1]. The quantum size effect is theoretically classified into two types: one is the exciton confinement effect and the other is the independent confinement effect of electron and hole. When the radius of the microcrystal is sufficiently larger than the exciton Bohr radius, the exciton confinement effect occurs. On the other hand, when the radius is comparable or smaller than the exciton Bohr radius, the independent confinement of electrons and holes takes place [2]. Recent developments related to nanoengineered materials have demonstrated that nanostructure semiconductors offer increasingly greater flexibility and control in designing various nanoscale structures and devices. The main motivation is related to continuous trends towards increasing miniaturization of various structures and devices, improving dimensional precision and the high flexibility of controlling and designing various material properties by controlling the sizes of the nanostructures [3]. Porous silicon layers is regarded as nanomaterials which can be obtained by the electrochemical etching of silicon substrate in HF based electrolyte solution. Porous silicon is described as a network of void spaces within a nanostructured silicon matrix which has the capability to modify the optical properties of silicon in order to overcome the limitations of the intrinsic indirect silicon electronic bandgap. The morphology and size-scale of porous silicon features are highly dependent on the process parameters. The refractive index profile of porous silicon layers can be tailored by controlling the porosity of individual layers via current density during etching process [4]. Ternary alloy is an alloy made up of three different chemical elements; usually two cations and an anion and their band gap is a continuous function of composition [5,6]. Ternary compounds are found to be promising materials for optoelectronic device applications such as green light emitting devices and expected to improve the performance of thin film solar cells and photo electrochemical energy conversion [7,8]. $Zn_xCd_{1-x}S$ has a variable band gap energy of 2.4-3.7eV, is widely used in heterojunction solar cells, high density optical recording, blue and ultra violet laser diodes and in low-voltage cathode luminescence [9]. In solar cell systems, where CdS films have been demonstrated to be effective, the replacement of CdS with the higher band gap $Zn_xCd_{1-x}S$ alloys has led to a decrease in window absorption loss and an increase in the short circuit current [10]. $Zn_xCd_{1-x}S$ thin films have been prepared using various techniques, such as electrodeposition, chemical bath deposition, successive ionic layer adsorption and reaction (SILAR) and metal organic chemical vapor deposition. Among these techniques, chemical bath deposition is simple and cost-effective as compared to the others for large-area solar cell fabrication [11]. The objective of this work is to prepare nanocrystaline $Zn_xCd_{1-x}S$, CdS thin films and study the structural, morphological and optical properties for photovoltaic applications.

2. EXPERIMENTAL DETAILS

For preparing nanocrystalline $Zn_{0.5}Cd_{0.5}S$ and CdS thin films, analytical grade cadmium chloride (0.1M $CdCl_2$), zinc chloride (0.1M $ZnCl_2$) and thiourea (0.1M $CS(NH_2)_2$) are used. The appropriate quantity of $CdCl_2$, $ZnCl_2$ and $CS(NH_2)_2$ solutions are mixed slowly at room temperature in a 100 ml beaker with continuous stirring by using magnetic stirrer, and making alkaline by the addition of ammonia solution (NH_3OH) to adjust pH=10 of the reaction mixture by using pH meter, a beaker containing the reaction mixture is placed in a water bath at 75 ± 2 °C. Immediately, the clean glass slide is fixed vertically in the beaker for two hours of the deposition time.

Then the glass substrate was removed from the beaker and washed ultrasonically with distilled water to remove loosely adherent particles and then dried under sun light. The fabricated films are yellow, highly adherent, homogenous then were kept in a desiccator. The experimental details of the prepared films are present in the Table (1).

Table1: experimental details for prepared $Zn_{0.5}Cd_{0.5}S$ and CdS thin films

Samples	**$ZnCl_2$ (ml) (0.1M)**	**$CdCl_2$ (ml) (0.1M)**	**Bath conditions**
CdS	0	20	Vol. of $CS(NH_2)_2$= 20 ml of (0.1 M) Deposition time =2 hour ,Temperature = 75±2 °C, PH=10
$Zn_{0.5}Cd_{0.5}S$	10	10	

The reaction of formation of CdS film can be written as follows [12]:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \qquad \ldots\ldots\ldots\ldots\text{(1)}$$

$$Cd^{2+} + 4NH_3 \rightarrow Cd(NH_3)_4^{2+} \qquad \ldots\ \ldots\ldots\ \text{(2)}$$

$$(NH_2)_2CS + 2OH^- \rightarrow S^{2-} + {}_2H_2O + H_2CN_2 \qquad \ldots\ldots\ldots\ldots\text{(3)}$$

$$HS^- + OH^- \rightarrow S^{2-} + H_2O \qquad \ldots\ \ldots\ldots\ldots\text{(4)}$$

$$Cd(NH_3)_4^{2+} + S^{2-} \rightarrow CdS + 4NH3 \qquad \ldots\ldots\ldots\ldots\text{(5)}$$

In the presence of sufficient NH_3, the Cd salt exists predominantly in the form of $Cd(NH_3)_4^{2+}$. When the concentration product of Cd^{2+} and S^{2-} in solution exceeds the solubility product of CdS, 1.4×10^{-29} at 25°C, CdS precipitates. While, the reaction procedure for the formation of $Zn_xCd_{1-x}S$ may be described by the following steps: Ammonia ion formation [11]:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \qquad \ldots\ldots\ldots\ldots\text{(6)}$$

Ammonia solution is added to the Cd and Zn salt solutions to form cadmium tetra-amine ion $[Cd(NH_3)_4^{2+}]$ and zinc tetra-amine ion $[Zn(NH_3)_4^{2+}]$, respectively, as follows:

$$Cd^{2+} + 4NH_3 \rightarrow Cd(NH_3)_4^{2+} \qquad \ldots\ \ldots\ldots\ \text{(7)}$$

$$Zn^{2+} + 4NH_3 \rightarrow Zn(NH_3)_4^{2+} \qquad \ldots\ \ldots\ldots\ \text{(8)}$$

The sulfide ions are released due to the decomposition of thiourea in the alkaline medium, which is described by the following chemical reactions;

$$CS(NH_2)_2 + 3OH^{-} \rightarrow 2NH_3 + CO_3^{2-} + HS^{-} \quad \text{……...(9)}$$

$$HS^{-} + OH^{-} \rightarrow S^{2-} + H_2O \quad \text{..……..(10)}$$

All three of these source ions combine in the reaction mixture leading to the formation of CdZnS:

$$(1-x)[Cd(NH_3)_4^{2+}] + x[Zn(NH_3)_4^{2+}] + S^{2-} + NH_3 \rightarrow Zn_xCd_{1-x}S \quad \text{..…(11)}$$

3. RESULTS AND DISCUSSION

3.1 XRD ANALYSIS

Figure (1) shows the X-ray diffraction patterns of $Zn_{0.5}Cd_{0.5}S$, CdS and $Zn_{0.5}Cd_{0.5}S$/ CdS films deposited on glass substrates at pH=10 and constant temperature 75±2 ºC. XRD analysis reveals that the films were polycrystalline in nature with a prominent broad peak appear at an angle $2\theta = 26.68^o$ which correspond to (002) hexagonal structured. These peaks are quite broad, which is indicative of nanosize particle [12]. Also there are two peaks appear at an angles 44^o and 52^o corresponding to (220) and (311) plane of the hexagonal phase. From (002) peaks of the XRD patterns it is possible to evaluate the average grain size of the samples by using the Well-known Deby-scherrer formula [13]:

$$D_{hkl} = k\,\lambda / \beta \cos\theta \quad \text{……..(12)}$$

Where k =0.94, λ is the wavelength of X-ray, β is the full width at half the peak maximum in radians and θ is Bragg's angle. The X-ray characterization of the prepared films are summarized in Table (2). It is also observed that the structure of nanocrystalline $Zn_{0.5}Cd_{0.5}S$ / CdS thin films have higher intensity and sharper peaks as comparing with nanocrystalline $Zn_{0.5}Cd_{0.5}S$ and CdS thin films, this effect can be attributed to the increase of both, thickness and grain size of the structure of $Zn_{0.5}Cd_{0.5}S$ / CdS thin film.

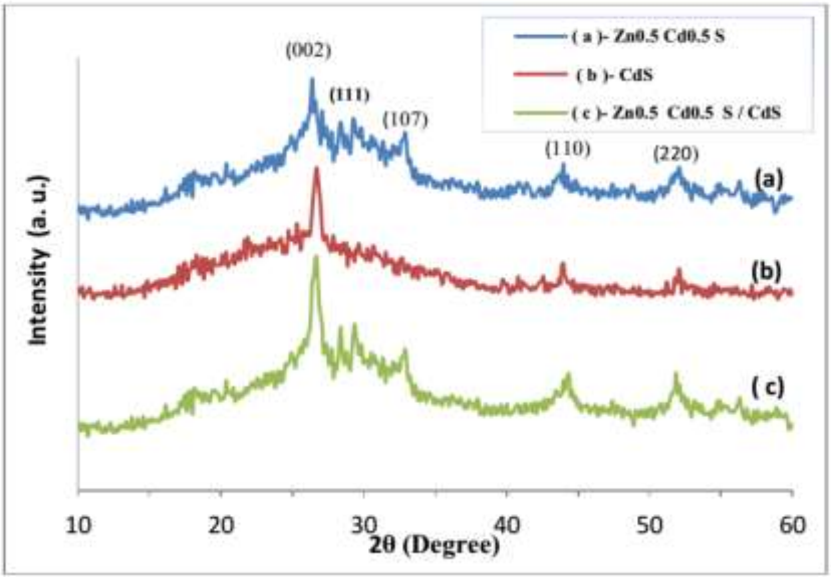

Figure 1: XRD spectra of nanocrystalline thin films
(a)- $Zn_{0.5}Cd_{0.5}S$, **(b)**- CdS and **(c)**- $Zn_{0.5}Cd_{0.5}S$ / CdS.

Table 2: XRD data of nanocrystallites $Zn_{0.5}Cd_{0.5}S$**,** CdS and $Zn_{0.5}Cd_{0.5}S$/CdS thin films.

Sample	2θ (degree)	d (nm)	(hkl)	FWHM	Grain size (nm) (from XRD)
CdS	26.68	0.3340	(002)	2.379	5
$Zn_{0.5}Cd_{0.5}S$	26.68	0.3321	(002)	1.840	3
$Zn_{0.5}Cd_{0.5}S$ / CdS	26.68	0.3251	(002)	1.301	7

3. 2 ATOMIC FORCE MICROSCOPY (AFM) ANALYSIS

Figure 2 shows two-dimensional and three-dimensional AFM images of the prepared nanocrystalline thin films. Clearly, the substrate surface is well covered with grains are uniformly distributed over the surface. The image shows well defined particle like features with granular morphology and indicates the presence of small crystalline grains. Nanocrystalline $Zn_{0.5}Cd_{0.5}S$ deposited on CdS thin film presented a slight increase on the surface roughness. The Root Mean Square (RMS) roughness which is defined as the standard deviation of the surface height profile from the average height, is the most commonly reported measurement of surface roughness [14]. The root mean square, the average roughness and maximum height of the prepared nanocrystalline thin films were listed as shown in Table (3).

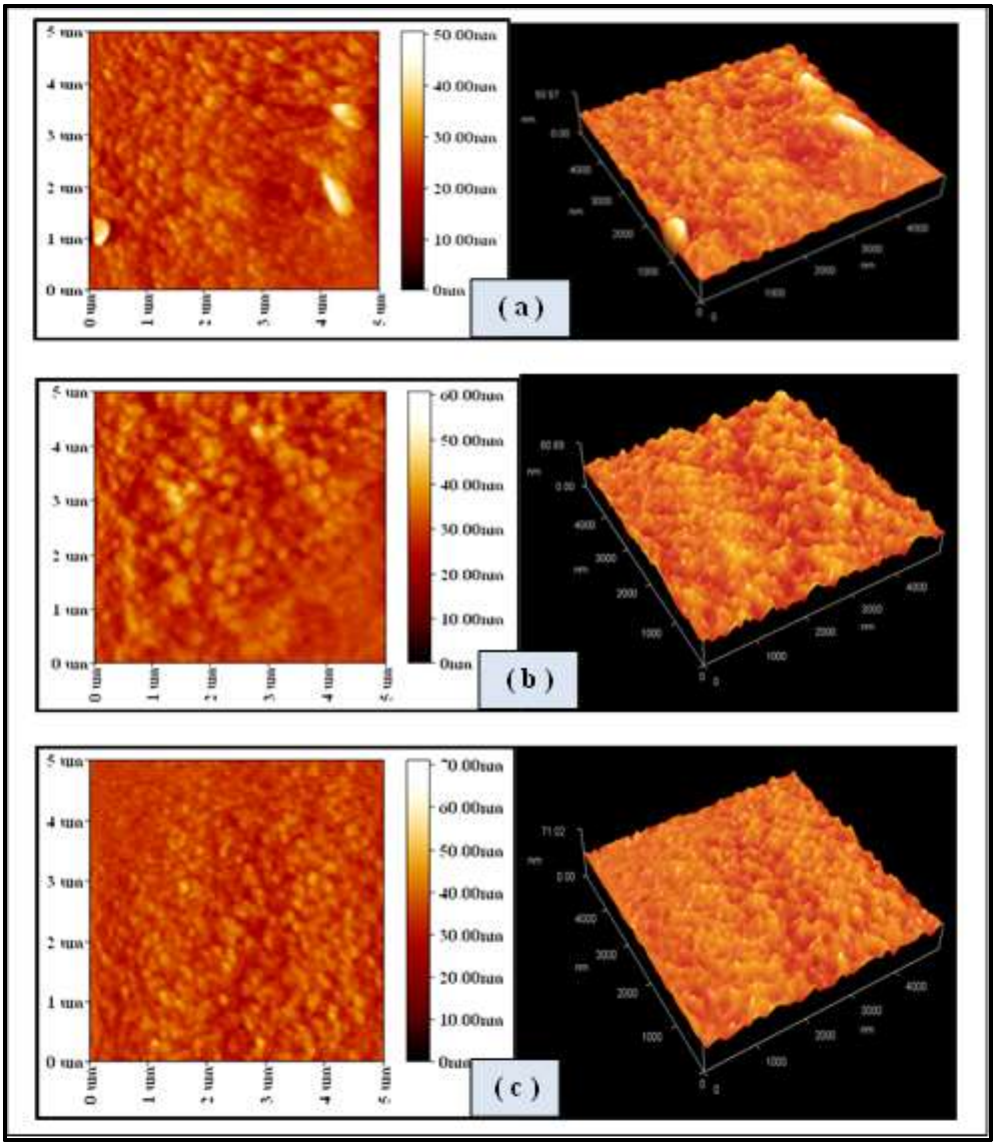

Figure 2: AFM images of nanocrystalline thin films with 2 dimension and 3 dimension. (a)- $Zn_{0.5}Cd_{0.5}S$, (b)- CdS and (c) - $Zn_{0.5}Cd_{0.5}S$ / CdS

Table 3: The surface texture properties of the prepared nanocrystalline thin films.

Sample	Roughness average (nm)	Root mean square (nm)	Ten point height (nm)	Average grain size (nm)
$Zn_{0.5}Cd_{0.5}S$	2.32	3.27	44.5	5
CdS	2.74	3.55	26.8	7
$Zn_{0.5}Cd_{0.5}S$ / CdS	2.5	3.21	29.1	11

3. 3 OPTICAL PROPERTIES

Figure 3 shows the optical transmission spectra of $Zn_{0.5}Cd_{0.5}S$, CdS and $Zn_{0.5}Cd_{0.5}S$ / CdS nanocrystalline thin films as a function of wavelength in the wavelength range 300–1100 nm. The difference in the transmission values as a result of different thickness of the prepared films. The spectra of these films show an average transmission of above 70 %. Also the optical transmission curves of $Zn_{0.5}Cd_{0.5}S$ / CdS and CdS thin films are observed to be slightly shifted towards the longer wavelengths in comparison with $Zn_{0.5}Cd_{0.5}S$ thin film, this effect is due to an increase in thickness of each the structure $Zn_{0.5}Cd_{0.5}S$ / CdS and CdS thin films. The absorption coefficient were calculated using the lamberts law:

$$\alpha = (2.303A)/t \qquad \text{……….}(13)$$

Where t is the film thickness and A is the absorbance of the material. The fundamental absorption, which corresponds to electron excitation from the valence band to conduction band [15], can be used to determine the nature and value of the optical energy band gap. The relationship between the fundamental absorption coefficient (α) and incident photon energy (hυ) can be written as [16,17]:

$$(ah\upsilon)^{1/n} = A\,(h\upsilon - Eg) \qquad \text{……….}\ (14)$$

where A is a constant, h is the planck's constant and n is also a constant, which depends on the type of transition. For direct allowed transition n = 2, for indirect allowed transition n=½. To determine the possible transitions, $(ah\upsilon)^{1/n}$ versus (hυ) was plotted. The corresponding band gap energies were obtained from extrapolating the straight portion of the graphs on the $h\upsilon$ axis at $(ah\upsilon)^{1/n} = 0$, [18]. Figure 4 shows the variation in the absorption coefficient as a function of wavelength. In general, the value of α increases with decreasing wavelength of the prepared films show high coefficient of absorption ($\alpha > 10^5\ cm^{-1}$ for $\lambda < 450$ nm and $10^4\ cm^{-1}$ for $\lambda > 450$ nm). It is clear that the value of the absorption coefficient (α) of nanocrystalline $Zn_{0.5}Cd_{0.5}S$ / CdS thin film structure increases as comparing with CdS and $Zn_{0.5}Cd_{0.5}S$ thin films. Figure 5 illustrated the optical band gap of the prepared nanocrystalline thin films. The band gap values are found to be 3.93, 3.8 and 3.7 eV for the nanocrystalline $Zn_{0.5}Cd_{0.5}S$, CdS and $Zn_{0.5}Cd_{0.5}S$ / CdS thin films respectively. It is clear that the band gap decreases when deposited $Zn_{0.5}Cd_{0.5}S$ on CdS thin film, this is attributed to increase in the thickness which leads to enhancement in crystallinity of the nano-size structure of $Zn_{0.5}Cd_{0.5}S$ / CdS thin films. The calculated optical band gap values are larger than the typical value of the bulk $Zn_xCd_{1-x}S$ (3.6 eV) and CdS (2.4 eV), this is attribute to the quantum size effect as expected from the nanocrystalline nature of the prepared thin films.

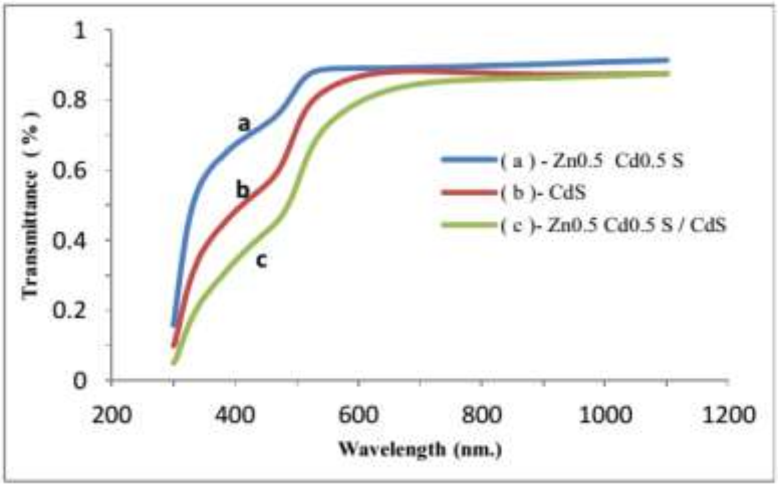

Figure 3: Transmittance spectra of nanocrystalline thin films versus wavelength(a)- $Zn_{0.5}Cd_{0.5}S$, (b)- CdS and (c) - $Zn_{0.5}Cd_{0.5}S$ / CdS

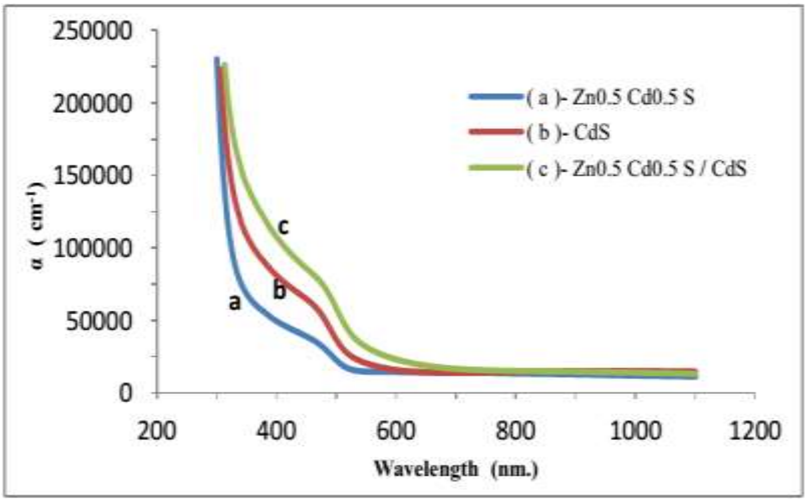

Figure 4: Absorption coefficient of nanocrystalline thin films versus wavelength(a)- $Zn_{0.5}Cd_{0.5}S$, (b)- CdS and (c)- $Zn_{0.5}Cd_{0.5}S$ / CdS

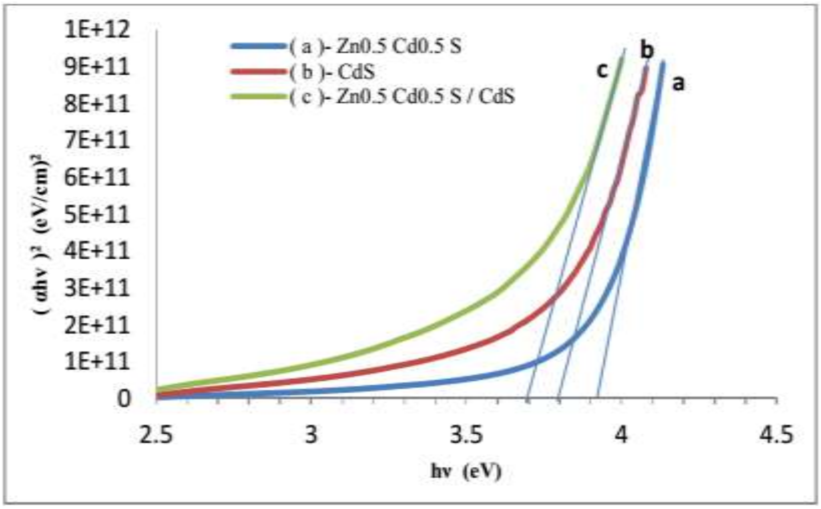

Figure 5: Optical energy gap of nanocrystalline thin films (a)- $Zn_{0.5}Cd_{0.5}S$, (b)- CdS and (c) - $Zn_{0.5}Cd_{0.5}S$ / CdS

3.4 ELECTRICAL MEASUREMENTS

The electrical behavior of prepared films, was analyzed by measuring their resistivity, Conductivity, mobility, carrier concentration and average Hall coefficient. Table 4 summarizes the obtained Hall measurements which were made by high quality instrument type (HMS-

3000). The resistivity is observed to increase from CdS (i. e. x=0), to $Zn_{0.5}Cd_{0.5}S$, this attributed to zinc incorporation which increases the resistivity. The mobility is observed to show an opposite behavior. The negative sign in Hall coefficient and carrier concentration indicates that the as-deposited thin films have n-type conductivity. The decreases in resistivity of $Zn_{0.5}Cd_{0.5}S$ / CdS may be ascribed to increases in thickness of $Zn_{0.5}Cd_{0.5}S$ / CdS. A wide bandgap combined with low resistivity is the crucial requirement of window material in solar cells.

Table 2: Electrical properties of the prepared nanaocrystalline thin films.

Sample	**Resistivity (Ω cm)**	**Conductivity $(\Omega\ cm)^{-1}$**	**Mobility (cm^2/Vs)**	**Carrier concentration $(cm)^{-3}$**	**Ava. Hall coefficient (m^2/C)**
CdS	3.50×10^{2}	2.85×10^{-3}	4.28×10^{4}	-4.15×10^{11}	-1.50×10^{7}
$Zn_{0.5}Cd_{0.5}S$	3.43×10^{3}	2.91×10^{-4}	4.37×10^{2}	-4.15×10^{12}	-1.50×10^{6}
$Zn_{0.5}Cd_{0.5}S$ / CdS	3.18×10^{2}	3.13×10^{-3}	4.75×10^{3}	-4.11×10^{12}	-1.51×10^{6}

4. CONCLUSIONS

Nanocrystalline $Zn_xCd_{1-x}S$, CdS and $Zn_xCd_{1-x}S$ / CdS thin films have been synthesis on a glass as substrate, the structural studies confirm that the films have polcrystalline structure with (002) orientation, while AFM images show that the films have uniform and homogenous surfaces without crack. From the optical properties results, the transmittance nearly more than 70 % with wide band gap as a result of quantum size effect. The resistivity of CdS, $Zn_{0.5}Cd_{0.5}S$ and $Zn_{0.5}$ $Cd_{0.5}S$ / CdS were (3.50×10^{2}, 3.43×10^{3} and 3.18×10^{2} Ω cm) respectively. From our results, the prepared nanocrystalline thin films are good candidate in order to be used in solar cells or photodetector.

REFERENCES

[1] A. S. Gorer, Albu-Yaron, and G. Hodes. "Quantum Size Effects in Chemicallydeposited, Nanocrystalline Lead Selenide Films" J. Phys. Chem.Vol.99, pp.16442 (1995).

[2] M. Thambidurai, N. Murugan, N. Muthukumarasamy, S. Agilan, S. Vasantha and R. Balasundaraprabhu. "Influence of the Cd/S Molar Ratio on the Optical and Structural Properties of Nanocrystalline CdS Thin Films" J. Mater. Sci. Technol. Vol.26, pp.193-199, (2010).

[3] G. B. Yacobi, "Semiconductor Materials an Introduction to Basic Principles", Vol. 107, pp. 154-157, (2004).

[4] R. S. Dubey, D. K. Gautam," Structural and optical properties of light emittingnanocrystalline porous silicon layers", Optoelectronic and Advanced Materials – Rapid Communications Vol. 3, No. 9, September, pp. 869 – 873, (2009).

[5] S. Adachi, "Properties of Semiconductor Alloys: Group-IV, III-V, and II-VI Semiconductors", pp. 4-5. (2009).

[6] M. Balkanski and R. F. Wallis, "Semiconductor Physics and Applications", Oxford University Press. Oxford. pp.1-69 (2000).

[7] A. Khare. "Effects of the Zn Concentration on Electro-Optical Properties Of $Zn_xCd_{1-x}S$ Films" Chalcogenide Letters Vol. 6, No. 12, pp. 661-671, (2009).

[8] D. Ompong. "Investigating The Optical Properties Of $Cd_{1-X}Zn_XS$ Thin Films Deposited by The DIP Technique"M.Sc. thesis.Kwame Nkrumah University of Science and Technology, (2010).

[9] R. Chandran , G.Suresh, "A Comparative Study of Physical and Optical Properties of CdZnS and CdNiS Nanocrystalline Films Deposited by Chemical Bath Method", Chalcogenide Letters Vol. 8, No. 11 , pp. 689 – 694 (2011).

[10] T. P. Kumar and K. Sankaranarayanan, " Tunability of Structure, Surface Texture, Compositional and Optical Properties of CdZnS Thin Films by Photo Assisted-Chemical Bath Deposition Tequnique. Chalcogenide Letters Vol. 6, No. 11, pp. 617-622, (2009).

[11] S. D. Chavhan, S. Senthilarasu, Soo-Hyoung Lee," Annealing effect on the structural and optical properties of a $Cd_{1-X}Zn_XS$ thin film for

photovoltaic applications", Applied Surface Science 254, pp.4539–4545 (2008).

[12] Xiangdong Zhou, Ziheng LI, Zhiyou LI, Shuang XU. ,"Preparation and formation mechanism of CdS nano-films via chemical bath deposition", Front Chem. China. 3(1), pp.1263–1268, (2008).

[13] J.J. Valenzuela-Jauregui, R. Ramrez-Bon, A. Mendoza-Galvan, and M. Sotelo-Lerma. Thin Solid Films, 441, (2003).

[14] T. Jiang, , N. Hall, A. Ho and S. Morin," Quantitative analysis of electrodeposited tin film morphologies by atomic force microscopy", Thin Solid Films, 417, pp. 76-85, (2005).

[15] P. K. Gosh, M. K. Miltra and K. K. Chattopadhyay," ZnS nanobelts grown in a polymer matrix by chemical bath deposition", Nanotechnology, Vlo. 16, Issue 1, pp. 107-112 (2005).

[16] P. K. Gosh, S. Jana, U.N. Maity and K.K. Chattopadhyay," Effect of partical size and inter-electrode distance on the field emission properties of nanocrystalline CdS thin films grown in a polymer matrix by chemical bath deposition", Physica E. 35, pp. 178-182 (2006).

[17] F. I. Ezema, A.B.C. Ekwealor and R.U. Osuji," Effect of thermal annealing on the band gap and optical properties of chemical bath deposition ZnSe thin films", Turkish journal of physics, 30, pp. 157-163 (2006).

[18] DDO Eya ," Influence of thermal annealing on the structural and optical properties of lead oxide thin films prepared by chemical bath deposition technique ", Pacific Journal of Science and Technology., 7(2), (2006).