

THE EFFECT OF ZN COMPOSITION ON STRUCTURAL AND OPTICAL PROPERTIES OF $Zn_xCd_{1-x}S$ THIN FILMS

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ABSTRACT: Zinc Cadmium Sulphide ($Zn_xCd_{1-x}S$) thin films were deposited on glass substrate with different Zn composition ($x = 0, 0.2, 0.4, 0.6, 0.8, 1$) by using vacuum thermal evaporation method. Optical bandgap of $Zn_xCd_{1-x}S$ thin films were determined by using the UV-Visible spectrophotometer. It reveals that the optical bandgap can be tailor by controlling the Zn content. Value of bandgap varies from 2.4 eV to 3.5 eV as the Zn ($0 \leq x \leq 1$) content increases. Composition of thin films was confirmed by using the energy dispersive analysis of x-ray (EDX). The structural properties of thin films were examined by making use of x-ray diffractometer (XRD). The XRD sketches show that both the binary compounds ZnS and CdS have been entirely modified to $Zn_xCd_{1-x}S$ ternary alloy. The preferential orientation of the thin films is (002) for the Zn concentration up to $x=0.8$ and contain the hexagonal (wurtzite) crystal structure, but at $x=1$ the pure ZnS has orientation alongside (111) and contains the cubic crystal structure.

Keywords: Vacuum Thermal Evaporation; $Zn_xCd_{1-x}S$; Optical Bandgap;

INTRODUCTION

Currently many efforts are going on by researchers to increase the efficiency of solar cells. The semiconductors are the dominant materials for window layer and absorber layer of the solar cells. Among the various semiconductor materials, the II-VI wide bandgap materials have been used most abundantly for the prospective applications in various fields namely optoelectronic devices [1], non-linear optical devices [2], predominantly their tunable optical properties [3,4]. Semiconductor alloying is the common technique used for the bandgap tailoring, optical and electronic properties [5]. Mostly in semiconductor alloys, the lattice parameters which alter linearly and tailoring of bandgap follows the Vegard's law [6].

In recent times, the II-VI ternary semiconductor alloys have captivated more attention than the II-VI binary composites due to the enhanced physical properties, particularly their tunable optical properties controlled by the ingredient mole fraction, morphology and particle size. Amongst the various II-VI ternary semiconductors, the zinc cadmium sulphide ($Zn_xCd_{1-x}S$) alloys have been extensively used as a broad bandgap material in the photo-conductive devices [7] and heterojunction solar cells [8]. The $Zn_xCd_{1-x}S$ is the best material for the window layer in the fabrication of p-n junction solar cells without lattice mismatch in the devices based on quaternary materials like $CuIn_xGa_{1-x}Se_2$ [9].

Interest in the $Zn_xCd_{1-x}S$ thin films has developed because it gives the better photovoltaic solar cell performance rather than currently used cadmium sulphide. It has tunable bandgap ranging from 2.42 eV to 3.54 eV. $Zn_xCd_{1-x}S$ ($0 \leq x \leq 1$) compound is a combination of ZnS and CdS. This compound is also called the ternary alloy and it belongs to the II-VI group. The zinc cadmium sulphide is most promising material for the photovoltaic applications [10, 11]. The bandgap of $Zn_xCd_{1-x}S$ ($0 \leq x \leq 1$) can be controlled by varying the composition of CdS and ZnS. In the past few years, the $Zn_xCd_{1-x}S$ made from CdS and ZnS have become much attractive for the PV applications. There are various

similar chemical properties in ZnS and CdS. The cadmium sulphide (CdS) is replaced with the ternary alloy zinc cadmium sulphide ($Zn_xCd_{1-x}S$) of high energy bandgap in the thin film CdS/CdTe solar cell due to which window absorption losses decrease and short circuit current increase [11]. The aim of this work is to study effect of Zn on optical and structural properties of $Zn_xCd_{1-x}S$ ($0 \leq x \leq 1$) thin films for solar cell applications.

Literature Survey

Currently many efforts are going on by researchers to increase the efficiency of solar cells. They are studying the different parameters of solar cells, developing new materials and experimenting with different techniques to obtain the desired results. Amongst all, Zinc Cadmium Sulphide is the most promising material other than the conventional materials for the photovoltaic applications due to its large variable bandgap. $Zn_xCd_{1-x}S$ thin films with variable Zn concentrations are used in the heterojunction photovoltaic solar cells.

Hyeong Lee et al. [12] prepared the $Zn_xCd_{1-x}S$ thin films from ZnS and CdS using the thermal evaporator method at very low pressure. Tungsten boats were used as a source due to high melting points. The thicknesses of thin films were one micron. During the evaporation, the glass substrate was used at 150°C. The XRD pattern of the thin films shows the good crystallinity. The optical bandgap of the $Zn_xCd_{1-x}S$ films varies continuously from 2.4-3.6 eV as the Zn concentration varies from $x=0$ to 1.

Ngamnit et al. [13] fabricated the thin films of $Zn_xCd_{1-x}S$ ($x=0$ to 1) by using thermal evaporation method under the vacuum 5×10^{-5} mbar using various precursors. Firstly, the $Zn_xCd_{1-x}S$ compound was prepared from the highly pure (99.999%) CdS and ZnS. Secondly, this compound was obtained from the solution in chemical bath reaction. The ZnS and CdS materials were mixed mechanically and pellets were formed under 6 GPa pressure. These pellets were placed in crucible for the direct sublimation under vacuum 5×10^{-5} mbar. The thin films were deposited on glass substrates at the room temperature. The $Zn_xCd_{1-x}S$ films were adherent, uniform

and bright yellow which changes to light yellow as the Zn concentration increases. The pure ZnS film was white and transparent in color. The optical, electrical and structural properties were studied of both type thin films. The XRD pattern of thin films shows the good crystallinity in both cases. The $Zn_xCd_{1-x}S$ films bandgap has direct relation with the Zn concentration. The optical bandgap varies from 2.31 to 3.47 eV by increasing the Zn concentration from $x=0$ to 1.

D. Patidar et al. [14] fabricate the thin films of $Zn_xCd_{1-x}S$ ($x=0$ to 1) by thermal vacuum evaporation method. In this experiment, the different Zn concentrations effect was studied on structural, electrical and optical properties. The $Zn_xCd_{1-x}S$ ($x=0$ to 1) was prepared by using mechanical mixing method (pestle and mortar) for 6 hours. The thin films were prepared at the room temperature under vacuum 2×10^{-5} torr. Simple glass slides were used as a substrate and Mo boat was used as a source. These thin films were heated for the 10 minutes ($75^\circ C$) under same vacuum to remove the defects on surface and for the better adhesion. The XRD peaks show that the $Zn_xCd_{1-x}S$ thin films have polycrystalline nature. All the samples have hexagonal structure and preferred orientation (002) along the plane. The peaks intensity decreases as the Zn concentration increases. So, the pure ZnS thin film has no major peaks. The optical bandgap increase linearly as the Zn concentration increases. The optical bandgap varies from 2.40-3.16 eV as the Zn concentration varies from $x=0$ to 1. By increasing the Zn concentration the resistivity also increases which is due to decrease in grain size.

T. D. Dzharfarov *et al.* [15] studied the Zn layer diffusion properties in CdS layer. Zn has melting point $418^\circ C$. If the CdS layer deposited on the substrate and the Zn layer deposited on the CdS layer. By diffusion the Zn in CdS, different $Zn_xCd_{1-x}S$ ($x=0$ to 1) thin films were obtained. The bandgap of these thin films vary from 2.43-3.67 eV as the Zn concentration vary from $x=0$ to 1. These non-crystalline wide bandgap thin films are used in solar cells and optoelectronic devices.

S. Riaz *et al.* [16] perform the experiment to prepare the thin films of $Zn_xCd_{1-x}S$ ($x=0$ to 1) using the CdS (99.999% pure) and ZnS (99.999%). The evaporation technique was used to deposit the thin films under the vacuum 10^{-6} torr and source current 50-65 ampere. The rate of deposition was about 0.25 nm/ sec and the whole process was done at the room temperature. The deposited thin films were uniform and stable in the air atmospheric state. Then the annealing process was done at the $300^\circ C$ temperature and $400^\circ C$ temperature. The $Zn_xCd_{1-x}S$ thin films have thickness range from $0.2\mu m$ to $0.6\mu m$. The pure CdS thin film was bright yellow and yellowness decreases by increasing the Zn content. The pure ZnS film was white and transparent in color. The XRD pattern reveals that the crystallinity gets better by increasing the Zn composition. By annealing, the non-linearity can be observed in the lattice parameter as the Zn content increases. The transmission spectrum of $Zn_xCd_{1-x}S$ shows that the material has direct bandgap and the bandgap was measured in the range 2.59 eV to 3.55 eV.

M. A. Mahdi [17] deposited the $Zn_xCd_{1-x}S$ thin films on glass substrates (Mo) which are thoroughly cleaned. The thermal evaporation method was used to deposit the thin films under

the vacuum 5×10^{-5} torr. Both the constituent material ZnS and CdS were 99.999% pure. The temperature of glass substrate was determined by using the thermocouple which is directly connected to substrate holder. The substrate temperature was kept 350 K during the deposition process. The rate of deposition was adjusted to 40-45 nm/ sec. The thickness of thin films was about 400 nm. The optical bandgap was measured by using the transmission spectrum of thin films. In this case the bandgap (E_g) value of $Zn_xCd_{1-x}S$ films vary from 2.40-3.50 eV as the Zn content vary from $x=0$ to 1.

Experimental Details

The $Zn_xCd_{1-x}S$ ($0 \leq x \leq 1$) thin films were prepared by simple, easy and cost-effective method for different Zn compositions. The Zn composition varies in the range of 0-1.0. The source material $Zn_xCd_{1-x}S$ was put together by mixing CdS and ZnS powders of high purity (99.995%). The $Zn_xCd_{1-x}S$ alloy was prepared by the method of mechanical mixing with pestle and mortar about 90 min for each composition of Zn to get uniformly mixed powder. Then the weights for each composition were measured by using the below relation

$$\text{Weight of CdS} = 144.48(1 - x) \text{ g} \quad (2.1)$$

$$\text{Weight of ZnS} = 97.474(x) \text{ g} \quad (2.2)$$

Where 144.48 is the molecular weight of CdS and 97.474 is the molecular weight of ZnS. As these calculated weights were large so we reduce them by equal fraction [18]. The glass slides were used as a substrate (1x3 inch) for the thin films. These substrates were cleaned through detergent cleaning about 15 min, ultrasonically cleaned in the acetone bath for 30 min go after the isopropanol for about 30 min and lastly dried using the nitrogen. In this work, vacuum thermal evaporation method was used to deposit the $Zn_xCd_{1-x}S$ thin films. The deposition was made under the vacuum 10^{-6} torr. The tantalum (Ta) boat was used as a source and its temperature was kept between $550-600^\circ C$. The growth rate was 0.50nm/sec and thickness of all the thin films was kept about 500 nm. All the thin films were prepared under the same experimental conditions. Finally, the thin films obtained were stable in the atmospheric pressure.

The optical properties of $Zn_xCd_{1-x}S$ thin films were studied by using the spectrophotometer (Model UV-240), the structural properties were studied by using an x-ray diffractometer (XRD) and the elemental analysis of thin films were carried out by energy dispersive x-ray (EDX).

RESULTS AND DISCUSSIONS

Thin film samples were characterized by using various techniques which are discussed below in detail.

UV-Visible Spectroscopy

The spectrophotometer was used to record the percentage transmittance as a wavelength function of the sample [19].

To calculate the optical bandgap energy, first of all we convert the wavelength into m from nm. Then the absorbance (A) was calculated from the percentage transmittance (%T) by using the relation given in equation (3.1).

$$A = \log(100/\%T) \quad (3.1)$$

The bandgap energy of the films was calculated by using tauc's relation [20]

$$\alpha hv = A(E_g - hv)^m \tag{3.2}$$

Where A is a constant and m is 1/2 for direct bandgap materials. E_g is a bandgap energy, h is a plank’s constant and v is the incident radiation frequency.

The absorption coefficient (α) measured from the absorbance (A) and thin film thickness (t) is given in the equation (3.3). The thicknesses of all the $Zn_xCd_{1-x}S$ thin films were kept just about 0.5 μm . The thin film thickness was measured by using the crystal attached to the substrate holder [21].

$$\alpha = (1/t) \ln (100/\%T) \tag{3.3}$$

Then the factor $(\alpha hv)^2$ was calculated. Finally, the graph was drawn between E (eV) on x-axis and $(\alpha hv)^2$ on y-axis to measure the bandgap energy. The bandgap value varies in each graph continuously. The bandgap increases as we increase the Zn concentration from x=0 to 1. The comparison of all these graphs is given in the figure (3.1) which shows the variation in bandgap values of the $Zn_xCd_{1-x}S$ thin films.

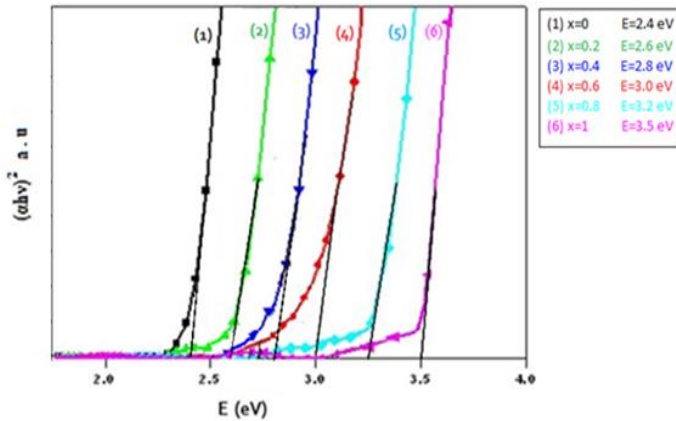


Figure 3.1: $(\alpha hv)^2$ versus E (eV) for the bandgap measurement

The linear portions of the graphs show that the $Zn_xCd_{1-x}S$ is a direct bandgap semiconductor material. The bandgap of each sample was measured by drawing the line from the maximum linear portion of graph to the energy axis (x-axis) which is shown in the figure (3.1) by blackish straight lines. The bandgap value of pure CdS (x=0) is 2.4 eV and pure ZnS (x=1) is 3.5 eV. Hence the bandgap values alter from 2.4 eV to 3.5 eV as we increase the Zn concentration from x=0 to 1. The bandgap of all the direct bandgap materials increases as we increase the value of x in $Zn_xCd_{1-x}S$ thin films [22, 23].

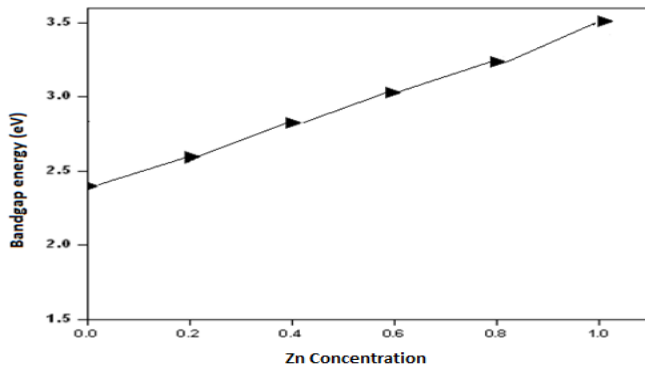


Figure : Bandgap energy versus Zn concentration

The bandgap energy increases as we increase the Zn concentration in $Zn_xCd_{1-x}S$ thin films which is clearly shown

in the figure (3.2). As the ionic radius of Zn is smaller than the Cd. So, the lattice constant and grain size was reduced. There occurred a blue shift due to the grain size reduction and therefore the $Zn_xCd_{1-x}S$ bandgap increases.

X-ray Diffractometry (XRD)

XRD is used to examine the composition, crystal structure and phase of $Zn_xCd_{1-x}S$ (x=0, 0.2, 0.4, 0.6, 0.8, 1) thin films as shown in the fig (3.3). Polycrystalline nature of the $Zn_xCd_{1-x}S$ thin films is confirmed from the sharp peaks of XRD pattern. The preferential orientation of the thin films is H(002) plan for the Zn concentration up to x=0.8 and contain the hexagonal (wurtzite) crystal structure, but at x=1 the pure ZnS has orientation alongside C(111) plan and contains the cubic crystal structure. The angle 2θ and corresponding plans are also shown in the figure (3.3). The x-ray patterns authenticate that the binary compounds are completely transferred into the ternary alloy and the thin film of single phase is formed. Qualitatively these patterns reveal that $Zn_xCd_{1-x}S$ thin films composition is similar like that of the initial material. The XRD patterns clearly show that the diffraction angle peak move in the direction of higher angle as we increase the Zn concentration in the $Zn_xCd_{1-x}S$ thin films. This happened because of the substitution of Cd atoms (large ionic radii) with the Zn atoms (small ionic radii) and for that reasons the lattice constant reduces. The XRD results have great conformity with reported outcomes [24, 25].

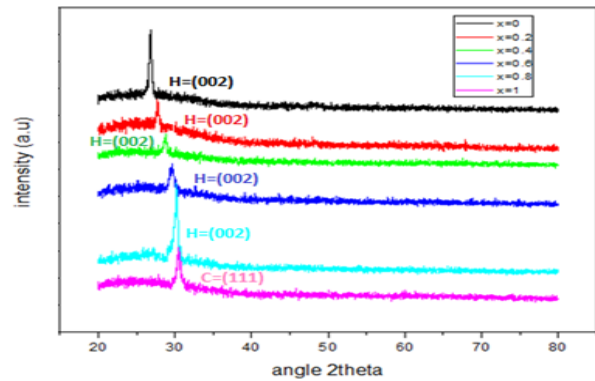


Figure 3.3: XRD pattern of $Zn_xCd_{1-x}S$ thin films

Energy Dispersive X-rays (EDX)

The energy dispersive x-ray (EDX) technique uses the SEM for the chemical micro analysis. The $Zn_xCd_{1-x}S$ thin film analysis was carried out by using the spectrometer which is attached to the SEM. One of the samples ($x=0$) was examined whose spectrum is given in the figure (3.4).

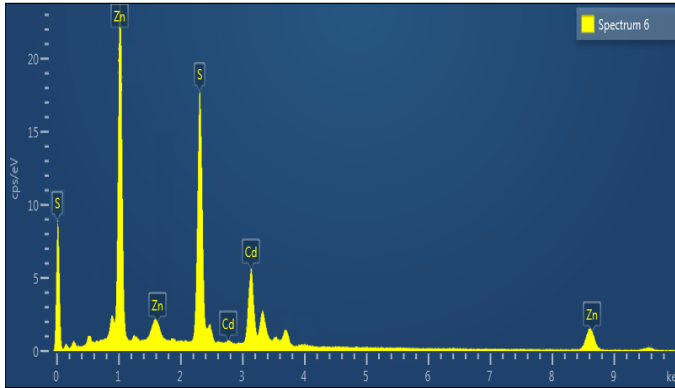


Figure 3.4: EDX image of $Zn_xCd_{1-x}S$ thin film at $x=0.8$

The resulted composition of the sample ($x=0.8$) shows that they are nearly equal to the quantity as used for the $Zn_xCd_{1-x}S$ thin film preparation.

CONCLUSION & FUTURE WORK

The $Zn_xCd_{1-x}S$ thin films were deposited by thermal evaporation method on simple glass substrate from mechanically mixed ZnS and CdS powder. The XRD patterns reveal that all the $Zn_xCd_{1-x}S$ thin films are hexagonal (wurtzite) excluding pure ZnS thin film which is a cubic in phase. The UV-Visible results show that the optical bandgap values increases as the Zn content increases. Thin film compositions were confirmed by using the energy dispersive analysis of x-ray (EDX). $Zn_xCd_{1-x}S$ thin films have different applications in the field of photovoltaic technology. In future, it can be used in electro-optical modulators and water splitting.

REFERENCES:

[1] K. Nagamani et al., "Physical Properties of $Zn_xCd_{1-x}S$ Nano crystalline Layers Synthesized by Solution Growth Method," *International Journal of Optoelectronic Engineering*, **2**(2): 1-4, (2012).

[2] Coe S., Woo W. K., Bulovic M., and Bulovic V., "Electroluminescence from single monolayer's of nanocrystals in molecular organic devices", *Nature*, **420**, 800-803, (2002).

[3] Jang E. J., Jun S., and Pu L. S., "High quality CdSeS nanocrystals synthesized by facile single injection process and their electroluminescence", *Chem. Commun.*, **48** (24), 2964-2965 (2003).

[4] Bailey R. E., and Nie S. J., "Alloyed semiconductor quantum dots: Tuning the optical properties without changing the particle size", *J. American Chem. Soc.*, **125** (23), 7100-7106 (2003).

[5] Romeo N., Sberveglieri G., and Tarricone L., "Low-resistivity ZnCdS films for use as windows in hetero-junction solar cells", *Appl. Phys. Lett.* **32** (12), 807-809, (1978).

[6] Upadhyaya H. M., and Chandra S., "Chemical bath deposition of band gap tailored $Cd_xPb_{1-x}S$ films", *J. Mater. Sci.*, **29** (2), 2734-2740, (1994).

[7] Torres J., and Gordillo G., Photoconductors based on $Zn_xCd_{1-x}S$ thin films, "Thin Solid Films, 207 (1-2), 231-235 (1992).

[8] Ramakrishna. Reddy K. T., and Jayarama Reddy P., "Studies of $Zn_xCd_{1-x}S$ films and $Zn_xCd_{1-x}S/CuGaSe_2$ hetero-junction solar cells", *J. Phys. D: Appl. Phys.*, **25** (9), 1345-1348 (1992).

[9] Yamaguchi T., Matsufusa J., and Yoshida A., "Optical transitions in RF sputtered $CuIn_xGa_{1-x}Se_2$ thin films", *Jpn. J. Appl. Phys.*, **31** (6A), L703-705 (1992).

[10] Kumar. V, Singh. V, Sharma. S. K, Sharma. T. P, "Band gap determination in thick films from reflectance measurements", *Optical Materials*, **11**, (1998), 29.

[11] Yamaguchi. T, Yamamoto. Y, Tanaka. T, Demizu. Y, and Yoshida. A, "Influence of precursor structure on the properties of $Cu(In, Ga)Se_2$ thin films by thermal crystallization", *Thin Solid Films*, **281/282**, 375 (1996).

[12] Jae-Hyeong Lee, Woo-Chang Song, Jun-Sin Yi, Kea-Joon Yang, Wun-Dong Han, Joon Hwang, "Growth and properties of the CdZnS thin films for solar cell Applications", *Thin Solid Films* **431-432** (2003) 349-353.

[13] Ngamnit Wongcharoen and Thitinai Gaewdang, "Comparative Studies of Thermally Evaporated $Cd_{1-x}Zn_xS$ Thin Films Prepared by Using Different precursors", E-Mail address: kgthitin@kmitl.ac.th

[14] D. Patidar, N. S. Saxena and T. P. Sharma, "Structural, optical and electrical properties of CdZnS thin films", *Journal of Modern Optics* **Vol. 55**, No. 1, 10 January (2008), 79-88.

[15] T. D. Dzhabarov, F. Ongul and I. Karabay, "Formation of CdZnS thin films by Zn diffusion", *J. Phys. D: Appl. Phys.* **39** (2006) 3221-3225.

[16] S. Riaz, S. Ali, M. A. Jamil and S. Naseem, "Optical and Structural Properties of Evaporated $Zn_xCd_{1-x}S$ ($0 \leq x \leq 1$) Thin Films", *J. American scientific publishers (ASP)*, (2011).

[17] Mazin A. Mahdi, "Optical Properties of $Zn_xCd_{1-x}S$ Thin Films", *J. Basrah Researches (Sciences)* **Vol. 32**. Part. 3. 44-50 (2006).

[18] Arshad mahmood et al. "Ellipsometric analysis of $Cd_{1-x}Zn_xSe$ thin films prepared by a thermal evaporation technique," *Phys. Scr.* **83** (7pp), 065706, (2011).

[19] A Schamadzu Recording spectrophotometer UV-240 Manual.

[20] J. Tauc, *Amorphous & Liquid Semiconductors* (Plenum, New York, 1974), p. 159.

[21] J. N. Hodgson, "Optical Absorption and Dispersion in Solids," London: Chapman and Hall taken from *J. of Optoelectronics and Advanced Materials*, **7**, 2085 (2005).

[22] P. Kumar, A. Misra, D. Kumar, N. Dhama, T. P. Sharma, P. N. Dixit, "Optical materials", **Vol. 27**, P. 261-264 (2004).

[23] M. Bedir, R. Kayali and M. Oztas, *J. phys.* **Vol. 26** P. 121, Turk (2002).

[24] Prem Kumar T., Saravanakumara S., Sankaranarayan K., "Effect of annealing on the surface and band gap alignment of CdZnS thin films, *Applied Surface Science*, **257** (6), 1923-1927 (2011).

[25] Xia W., Welt J. A., Lin H., Wu H. N., Ho M. H., and Tang C. W., "Fabrication of $Cd_{1-x}Zn_xS$ Films with controllable zinc doping using a vapor zinc chloride treatment, *Solar Energy Materials & Solar Cells*, **94** (12), 2113-2118 (2010).