THE EFFECT OF THIOUREA QUANTITY VARIATION ON STRUCTURAL AND OPTICAL PROPERTIES OF CdS FILMS DEPOSITED USING CBD TECHNIQUE

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Abstract: The semiconductor CdS films show a great potential due to their unique optoelectronic properties with high chemical stability. This makes CdS material as a suitable candidate for various opto-electronic device applications. In this work we have successfully grown stable, homogeneous, compact and good adherence CdS films on the soda lime glass substrate by means of chemical bath deposition (CBD). The bath composition included cadmium chloride monohydrate [$CdCl_2.2H_2O$], thiourea [$NH_2.SC.NH_2$] and ammonia (NH_3) solution. The effects of thiourea concentrations on the structural, morphological, and optical properties of CdS films were investigated. The material thus formed was characterized using different techniques and carefully analyzed. The X-ray diffraction pattern shows the formation of hexagonal CdS nanocrystals in all the films. The formation of CdS is again confirmed from FTIR and Raman spectroscopy. The optical properties were investigated from UV-Visible spectroscopy. The morphological study shows that films formed by CBD on soda lime glass substrate are without pinholes or cracks.

Index Terms **– CdS films, optical and morphological properties, CBD technique, molar concentration.**

I. INTRODUCTION

Cadmium Sulphide (CdS) is an inorganic compound with the chemical formula (CdS) and belongs to the group II–VI family of semiconducting materials. It is receiving a great interest because of numerous excellent optoelectronic properties and applications. CdS thin film has been extensively studied for the application of heterojunction solar cells (H.R. Motinho et. Al. 2003), light emitting diodes (C. Bozkaplan et al. 2017), large screen liquid crystal devices (A. Zeho et al. 2001), gas sensors (J. Levinson et al. 1982) and field effect transistors (J.H. Schon et al.2017). The direct wide band gap (~2.42 eV) of CdS make it is a key element for solar cell applications. Many physical and chemical techniques are used to grow CdS films on different substrate that includes successive ionic layer adsorption and reaction (SILAR) (Dhawale D.S. 2011), Sputtering (Tsai C.et al.1996), spray deposition (Yadav A. A, 1993) etc. These methods are either expensive or energy consuming. The Chemical bath deposition method is an inexpensive, simple and convenient method for large area preparation of films at low temperatures ranging from 20 to 95 ^oC. The film deposited by CBD is stable, homogeneous, compact and have good adherence to the substrates.

In the present study CdS thin films have been deposited on commercially available soda lime glass at different thiourea concentration using chemical bath deposition method. The structural, morphological and optical properties of CdS films have been studied.

II. Experimental detail

Cadmium sulphide (CdS) thin films were deposited on soda lime glass substrates by using chemical bath deposition (CBD) technique. The substrates were 2 cm × 4 cm glasses. The surfaces of glass Substrates were initially cleaned with distilled water. Further these substrates are kept in ethanol solution for 15 min and ultrasonically washed and cleaned in acetone and subsequently in double distilled water. Finally it was dried using a dry nitrogen blow before keeping it in the chemical bath. The bath composition included 0.2.molar of cadmium chloride monohydrate [$CdCl_2.2H_2O$], 0.1 to 0.4 molar thiourea [$NH_2.SC.NH_2$] and ammonia (NH_3) solution. Ammonia solution was used to adjust the solution pH in the range 10 to 10.5. The chemicals used for synthesis of CdS films were of analytical grade and were used without purification.

After the solution was prepared, cleaned soda lime glasses were dipped into the solution. The bath temperature was kept at 80 °C and the deposition time was kept to be 60 minutes. After CdS films deposition on soda lime glasses, the samples were then taken out from the solution. The films were given wash in double distilled water to remove loosely adhered CdS particles on the surface and finally dried in air at a temperature of 50 ^oC. The prepared films showed stable, homogeneous, compact nature and a good adherence to the substrates.

Table 1: Deposition parameters applied for the synthesis of CdS films

Deposition Parameters	Values
Deposition Time (minute)	60
Thiourea [SC $(NH_2)_2$]	**0.1 M to 0.3 M**
Cadmium Chloride ($CdCl_2$)	0.1 M
pH of the bath	10.5
Deposition Temperature (°C)	80 °C

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III. FILM CHARACTERIZATION

FTIR spectra were recorded in transmission mode by using FTIR spectrophotometer (JASCO, 6100-type A) in the range of 400–4000 cm^{-1}. The optical bandgap of the CdS films was deduced from transmittance and reflectance spectra of the films deposited on soda lime glass substrates and were measured using a JASCO, V-670 UV–visible spectrophotometer in the range of 200–900 nm. Raman spectra were recorded with Raman spectroscopy (Jobin Yvon Horibra LABRAM-HR) in the range of 200–1200 cm^{-1}. The spectrometer had backscattering geometry for detection of Raman spectrum with a resolution of 1 cm^{-1}. The excitation source was 532·8 nm line of He–Ne laser. The power of the Raman laser was kept at < 1 mW to avoid laser induced crystallization in the films. Low angle X-ray diffraction spectra were obtained by X-ray diffractometer (Bruker D8 Advance, Germany) using CuKα line (λ = 1·54 Å) at a grazing angle of 1°.

IV. RESULTS AND DISCUSSION

Low Angle XRD Analysis

The X-ray diffraction pattern was used to determine the crystalline size and crystal structure of CdS films deposited on soda lime glass substrate. The CdS exists in the cubic structure, hexagonal structure or sometimes a mixture of both phases. Figure 1 shows the low angle XRD patterns of CdS films grown by Chemical bath deposition at different thiourea concentrations from 0.1 to 0.3 molar. As seen from the figure diffraction peak located at around 2θ ~ 26.6°, 43.9° and 52.1° corresponding to the (002), (110) and (112) planes of the hexagonal CdS structure respectively and are in good agreement with standard JCPDS data of hexagonal CdS (JCPDS file code # 41-1049). As seen from the XRD patterns, the film deposited at 0.1 molar thiourea concentrations shows the three dominant peaks corresponding to the (002), (110) and (112) planes. As the thiourea concentration increases the (002) peak intensity decreases simultaneously there is increase in line width, it means that crystallinity in the film decreases. In CBD techniques it is well known that the correct selection of the initial reactants composition determines the development of the growth mechanism (Dona JM , 1997). The increase of thiourea concentration enhances excess amount of sulphur ions in the bath which leads to form the defective states in the films. As a result, the crystallinity gets hampered with the thiourea concentrations increase. Thus thiourea concentration plays an important role to induce and enhancement of crystallinity in the films. The average crystalline size of CdS films is calculated by using Scherrer formula. The calculated average crystalline size of the film deposited at 0.1 molar thiourea concentration corresponding to the (002) is 15.8 nm.

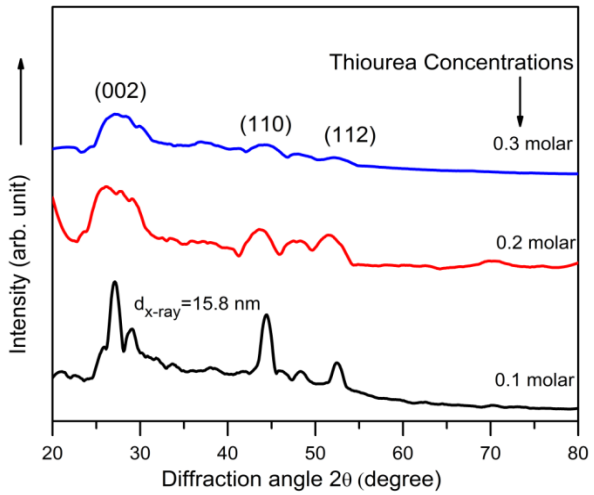

Figure 1: Low angle x-ray diffraction pattern of CdS films deposited at different thiourea concentration

Fourier Transform Infrared (FTIR) Spectroscopy Analysis

To investigate the different bonding configuration and confirmation of CdS formation in the films, Fourier transform infrared (FTIR) spectroscopy was used. Figure 2 shows the FTIR transmission spectra of CdS films deposited by CBD techniques at different thiourea concentration. Each absorption band in an infrared spectrum is assigned to bending and stretching mode for a particular bond. From figure it is observed that all the films deposited at various thiourea concentration shows the strong absorption peak located at ~ 408 cm^{-1} which is corresponding to the Cd-S stretching vibration mode (Singh and Chauhan, 2009, J.R.L. Fernandez, 2007) . The intensity of 408 cm^{-1} peak decreases with increasing thiourea concentration means Cd-S bond density decrease. The decrease in Cd-S bond density is due to the saturation effect of sulphur ions in the films. Thus thiourea

concentration thus plays an important role in the growth of stoichiometric CdS films. The absorption peak observed at ~780 cm^{-1} and 1650 cm^{-1} corresponds to the N-H stretching mode (C. Malarkodi et al. 2014 and Aslam Khan 2012). The traces of SO^{4-} ion impurity absorption band is observed in the range of 1090 cm^{-1} to 1150 cm^{-1} films (Aneeqa Sabah et al.2010). Very weak absorption band is observed ~ 1117.11 cm^{-1} corresponds to S-O bond (R.Hepzi Pramila Devamani 2017).

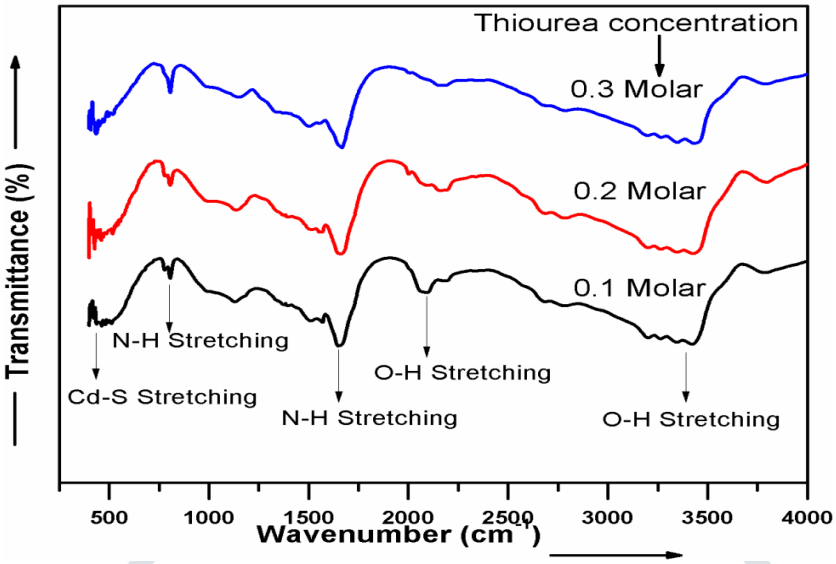

Figure 2: FTIR spectrum of CdS films deposited at different thiourea concentration

The strong absorption band ~ 2087 cm^{-1} and 3427 cm^{-1} are assigned to O-H stretching vibrations of adsorbed water on the surface of the film (P. Settu , 2018 and G. G. Ramteke, 2018).

Raman spectroscopy analysis

Raman spectroscopy is the versatile and sensitive technique used to get information of phase transition of material and to understand the local bonding configurations of materials. The Raman spectrum in the range 200-1000 cm^{-1} is practically the same for all the films deposited at various thiourea concentrations. Fig. 3 shows the Raman spectra of CdS flms grown by CBD at 0.1 molar thiourea concentrations. Each spectrum shows the two peaks corresponding to the Raman shift ~304 cm^{-1} and 605 cm^{-1}, which is attributed to the first order longitudinal optical (1LO) and second-order longitudinal optical (2LO) phonon modes of CdS. Similar lines Raman active modes were observed in other research group. (Rajeev R Prabhu and M Abdul Khadar 2008 **,** Sachin Rondiya et al.2017, Chuu D. et al.1991).Thus the formation of CdS is confirmed from Raman study.

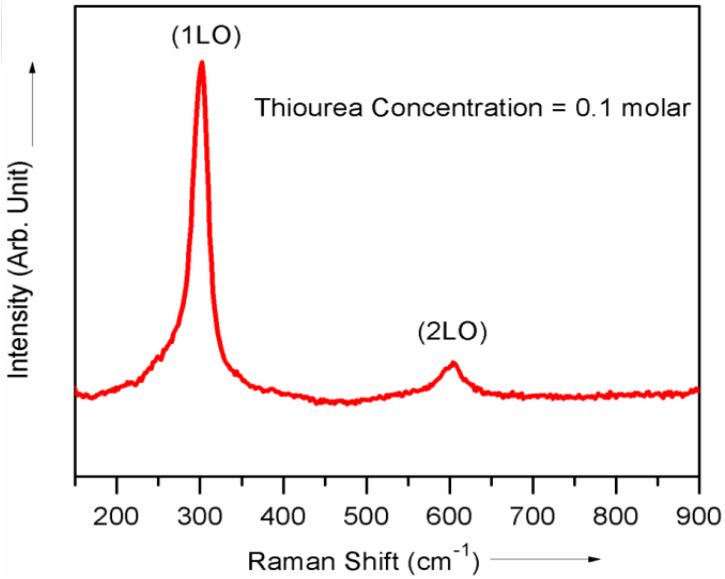

Figure 3: Raman spectra of CdS films deposited at different thiourea concentration

Surface morphology study:

The surface morphology of the CdS films deposited at 0.1 molar thiourea concentration obtained by SEM is shown in Fig. 4. The morphology shows that the film deposited at 0.1 molar thiourea concentrations have good adherence on the substrates without pinholes or cracks.

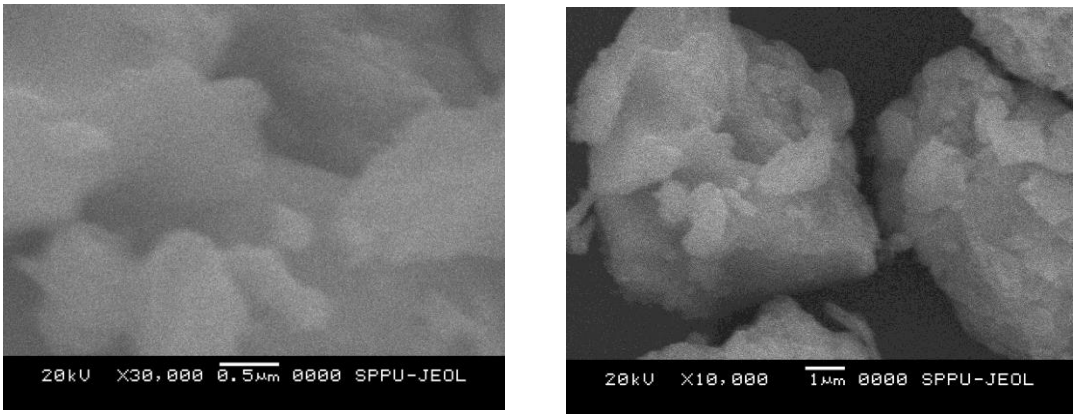

Figure 4: SEM image of CdS thin films deposited at 0.1 molar thiourea concentration

UV-Visible Spectroscopy Analysis:

The optical properties such as band gap (E_{opt}) and absorbance of the CBD grown CdS films at various thiourea concentrations were investigated from UV-visible spectroscopy. For direct allowed transition of CdS, absorption coefficient (α) and band gap can be expressed as (Tauc T. 1970)

$$(\alpha h\nu) = B(h\nu - E_g)^{1/2}$$

Where, B is Tauc's constant, α is the absorption coefficient, h is the Planck's constant, υ is photon frequency, and E_g is the optical band gap energy of the material. To determine the band gap, $(\alpha h\upsilon)^{1/2}$ is plotted against energy E(hυ). A straight line is fitted through the data points. A straight line fitting program was developed to fit the data in a straight line. The line is then extrapolated and the intercept of the extrapolated line on the energy axis gives the band gap.

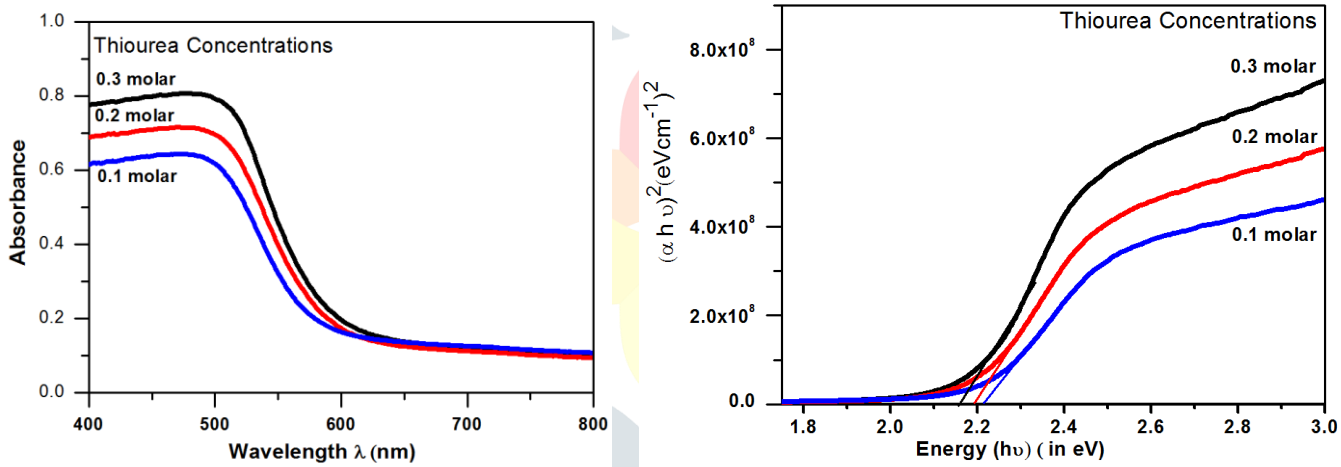

Figure 5: absorbance and Tauc's plots of CdS films deposited at different thiourea concentration

As shown from the absorption spectra of the CdS films deposited at various thiourea shows that as the concentration of thiourea increases, the absorption edge shifted toward blue. The blue shift may be attributed due to absorbance of CdS nanocrystals. (Abdullah M.A. 2012). Based on the literatures, the blue shift in the absorption edge indicates that there are fewer defects and impurity energy levels in the CdS film. (H. Metin et al.2003). The bandgap of the CdS films deposited by CBD is observed nearly 2.2 eV. As seen from figure band gap decreases with thiourea concentration increases from 1.0 molar to 0.3 molar. The decrease of the band gap energy is may be due to increase in the structural disorder induced by the sulphur. Thus FTIR results support the sulphur impurities are incorporated in the films with increases thiourea concentrations.

Conclusion

In summary, we have successfully grown stable, homogeneous, compact and good adherence to substrate CdS films on the soda lime glass by means of chemical bath deposition (CBD) with cadmium chloride monohydrate [$CdCl_2.2H_2O$] as Cd ion and thiourea [$NH_2.SC.NH_2$] as S ion sources. The experimental study investigate that the thiourea concentration i.e. sulphur ion plays an important role in the formation of stoichiometric films using CBD. X-ray diffraction patterns signifies that the thiourea concentration plays an important role to induce and enhancement of crystallinity in the film. The average crystallite size was estimated to be 15.8 nm at 0.1 molar thiourea concentrations. The formation of CdS is confirmed from the FTIR and Raman spectra. The film deposited at lower thiourea concentration shows blue shift of absorption edge.

References

[1] H.R. Motinho, D. Albin, Y. Yaan, R.G. Dheo, X. Li, C. Perkis, C.S. Jiang. 2003. Deposition and properties of CBD and CSS CdS thin films for solar cell application. Thin Solid Films, 436: 175-180

[2]C. Bozkaplan, A. Tombak, M. F. Genişel, Y. S. Ocak, and K. Akkilic.2017. The influence of substrate temperature on RF

sputtered CdS thin films and CdS/p-Si heterojunctions. Materials Science in Semiconductor Processing, 58: 34–38

[3] A. Zeho, J. G. Vazquez Luna. 2001. Magnetic field influenced growth kinetics in chemical CdS thin-film depositionSol. Energ. Mater. Sol,. C 68: 217-226

[4] J. Levinson, F.R. Shepherd, P.J. Scanlon, W.D. Westwood, G. Este, M. Rider. 1982. Conductivity behavior in polycrystalline semiconductor thin film transistors. J. Appl. Phys. 53, 1193-1202

[5] J.H. Schon, O. Schenker, B. Batlogg. 2017. RETRACTED: Solution processed CdS thin film transistors. Thin Solid Films 385, 271 -274

[6] Dhawale D.S., Dubal D.P., Phadatare M.R., Patil J.S., Lokhande C.D. 2011.synthesis and characterizations of CdS nanorods by SILAR method. Journal of Materials Science, 46:5009–5015.

[7] Tsai C., Chuu D., Chen G., and S. Yang. 1996.Studies of grain size effects in RF sputtered CdS thin films. J. Appl. Phys. 79(12): 9105-9109

[8] Yadav A. A., Masumdar E. U. 2011. Photoelectrochemical investigations of cadmium sulphide (CdS) thin film electrodes prepared by spray pyrolysis. Journal of Alloys and Compounds, 509 (17) 5394-5399

[9] Hoffmann P.h., Horn K., Bradshaw A.M., Johson R.L., Fuchs D. Cardona M. 1993. Dielectric function of cubic and hexagonal CdS in the vacuum ultraviolet region. Phys. Rev., 47: 1639-1642.

[10]Dona JM, Herrero 1997 J. Chemical Bath Deposition of CdS Thin Films: an approach to the chemical mechanism through study of the film microstructure. J Electrochem Soc, 144: 4081–90.

[11]V. Singh, P. Chauhan. 2009. Structural and optical characterization of CdS nanoparticles prepared by chemical precipitation method. J. Phys. Chem. Solids 7(7): 1074-1079.

[12]J.R.L. Fernandez, M. De Souza-Parise, P.C. Morais. 2007. Optical investigation of the red band emission of US nanoparticles .Surf. Sci. 601(18): 3805-3808

[13] C. Malarkodi, S. Rajeshkumar, K. Paulkumar, M. Vanaja, G. Gnanajobitha, and G. Annadurai .2014. Biosynthesis and Antimicrobial Activity of Semiconductor Nanoparticles against Oral Pathogens. Hindawi Publishing Corporation Bioinorganic Chemistry and Applications,2004:1- 10.

[14] Aslam Khan. 2012 CdS Nanoparticles with a Thermoresponsive Polymer:Synthesis and Properties Hindawi Publishing Corporation Journal of Nanomaterials,2012:1- 8 .

[15] Aneeqa Sabah, Saadat Anwar Siddiqi, Salamat Ali. 2010. Fabrication and Characterization of CdS Nanoparticles Annealed by using Different Radiations International Scholarly and Scientific Research & Innovation 4(9) 532-539

[16] R.Hepzi Pramila Devamani, R.Kiruthika, P.Mahadevi and S.Sagithapriya, 2017. Synthesis and Characterization of Cadmium Sulfide Nanoparticles IJISET - International Journal of Innovative Science, Engineering & Technology, 4 (1) 181-185.

[17] P. Settu, G. Gopi, P.Baskaran, K. Manikandan, 2018. Topological, Morphalogical, Structural and optical properties of CdS thin film with complex agents TEA /Ammonia mixer. International Journal of ChemTech Research 11 (2) 399-417,

[18] G. G. Ramteke, A. S. Lanje, D. M. Pimpalshende, 2018. Analysis of the Influence of Mn2+ Incorporation on Structural and Spectroscopic Features of CdS Nanoparticles. International Journal of Current Engineering and Scientific Research (IJCESR) 5, (5) 11-17

[19]Rajeev R Prabhu and M Abdul Khadar, 2008. Study of optical phonon modes of CdS nanoparticles using Raman spectroscopyull. Mater. Sci., 31 (3) 511–515.

[20]Sachin Rondiya, Avinash Rokade, Bharat Gabhale, Subhash Pandharkar, Madhavi Chaudhari, Abhijit Date, Minakshi Chaudhary, Habib Pathan, Sandesh Jadkar, 2017. Effect of bath temperature on optical and morphology properties of CdS thin films grown by chemical bath deposition Energy Procedia 110: 202 – 209.

[21] Chuu D, Dai C, Hsieh W, Tsai C. 1991. Raman investigations of the surface modes of the crystallites in CdS thin films grown by pulsed laser andthermal evaporation. J Appl Phys 69: 8402-8404.

[22] Tauc, T., Abeies, F., 1970. Optical Properties of solids. IOP Publishing Ltd, North Holland, Amsterdam, 903.

[23] Abdullah M.A. Al-Hussam , Salah Abdul-Jabbar Jassim, 2012. Synthesis, structure, and optical properties of CdS thin films nanoparticles prepared by chemical bath technique Journal of the Association of Arab Universities for Basic and Applied Sciences 11: 27–31

[24] H. Metin, R. Esen, 2003. Annealing studies on CBD grown CdS thin films, J. Cryst.Growth 258: 141–148.