SYNTHESIS, CHARACTERIZATION AND STUDY OF CADMIUM SULPHIDE (CdS) FILMS FABRICATED USING CHEMICAL BATH DEPOSITION METHOD

[1]Mahesh Kamble, [2]Bharat Bade, [3]Sachin Rondiya, [4]Subhash Pandharkar, [5]Adinath Funde, [6]Sandesh Jadkar*

[1]Assistant professor, [2]Research Scholar, [3] Research Scholar, [4] Research Scholar, [5] Assistant professor, [6] Professor

[1]Department of Physics,
[1]PDEA'S Anantrao Pawar Collge, Pirangut, Pune, India
[2-5]School of Energy Studies,
[2-5]Savitribai Phule Pune University, Pune, India
[6]Department of Physics,
[6]Savitribai Phule Pune University, Pune, India

Abstract: In the present manuscript we report synthesis and characterization of CdS thin films deposited on soda lime glass at low temperature using chemical bath deposition technique (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 deposition time on the structural and optical properties of CdS films were investigated. The CdS films were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and UV-VIS spectroscopy for the analysis of structural, bonding configuration and optical properties. The XRD patterns of the films deposited reveals the presence of nanocrystalline CdS is in the hexagonal structure. The formation of CdS is confirmed from FTIR and Raman spectroscopy. The optical bandgap of the CdS films were estimated from transmittance and reflectance spectra recorded using UV-Visible spectroscopic technique and it was observed to be nearly 2.2 eV.

Index Terms **– CdS by chemical bath deposition, Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy.**

I. INTRODUCTION

Cadmium sulfide (CdS) films is a chalcogenide n-type semiconductor especially attractive because of excellent optoelectronic properties such as direct optical energy band gap (2.28 eV - 2.45 eV) (A. Kariper et al. 2011), high absorption coefficient, high photoconductivity, high electron affinity, easy ohmic contact and low resistivity etc.(S. Yılmaz et al. 2017). These properties offer CdS a great technological potential for electronic and optoelectronic device application. There are several deposition techniques established for device quality fabrication of CdS films, which include sol-gel (Zhang H et al. 2016), hydrothermal (Chen, R. et al. 2016), Solvo-thermal (Ren, B. et al. 2016), co-precipitation (Elavarthi, P. et al. 2016), photochemical, polyol (Darwish, M. et al. 2016) pulsed laser deposition (PLD) (X. Yang et al 2016), direct current magnetron sputtering (DCMS) (F. Lisco et al 2015), spray pyrolysis (A.A. Yadav and E.U. Masumdar, 2011), Chemical Bath deposition (CBD) (A. Mondal et al. 1983) etc. The development of economical and effective deposition method to fabricate solar cell is important for cost reduction. The CdS films deposited by Chemical Bath deposition have been widely studied because of excellent chemical stability and nearly stoichiometric behavior. The highest laboratory efficiency of CZTS based solar cell is 12.7 % reported by Jeehwan Kim et al. (Jeehwan Kim et al. 2014) in this case too, the CdS films were synthesized by using chemical bath deposition (CBD) technique. Thus CBD appears to be a promising technique for depositing CdS in high efficiency CZTS based solar cells. The CBD process is attractive because of simplicity in comparison with other techniques, and is inexpensive and low temperature deposition method. In this manuscript, we investigated the effect of deposition time on structural and optical properties of CdS film grown by CBD.

II. Experimental detail

All chemicals used in this work were analytical grade and used without further purification. To prepare appropriate CdS Complex solution, 0.1.molar cadmium chloride monohydrate [$CdCl_2.2H_2O$] was mixed with double distilled water in 200 ml beaker. The bath was placed over a heater cum magnetic stirrer and was set at room temperature under constant stirring. The pH of the solution was increased up to 10.5 by drop wise addition of ammonia (NH_3) which makes the solution as milky precipitate. Then 0.1 molar thiourea [$NH_2.SC.NH_2$] was added in this bath which turned the milky precipitate to yellow colored solution. After 30 min of constant stirring at 80 ^oC temperature, a brownish yellow colored solution was obtained.

The commercially available soda lime glass substrates were initially washed with distilled water. Further these substrates were kept in ethanol solution for 15 min and ultrasonically washed and cleaned in acetone and doubled distilled water. Finally it is dried by using dry nitrogen blow before kept in the chemical bath. The dimensions of the substrates used for the deposition of CdS films were 2 cm X 4 cm. The cleaned glass substrates then were immersed vertically in chemical bath. After a suitable deposition time, the substrate was removed from the solution, rinsed with double-distilled water to remove any residue and dried at room temperature without any further treatment. The prepared films showed stable, homogeneous, compact and good adherence to the substrates. The set of depositions were carried out for 50, 60 and 70 minutes of deposition times.

III. Film characterization

The nature of chemical bonding was studied by Fourier Transform Infrared (FTIR) Spectroscopy (JASCO, 6100-type A) in the transmission mode between 400 and 4000 cm^{-1}. From this spectrum we are able to detect Cd-S peaks in the IR spectra. The

optical bandgap was calculated from transmittance and reflectance spectra of the films deposited on soda lime glass, which were recorded using a JASCO, V-670 UV-Visible spectrophotometer in the range 250–1100 nm. The band gap was estimated using the procedure followed by Tauc (J. Taucet al. 1972). Raman spectra were recorded with micro-Raman spectroscopy (Jobin Yvon Horibra LABRAM-HR) in the range100–1200 cm^{-1}. The excitation source was 532.8 nm line of He–Ne laser. The power of the Raman laser was kept less than 1 mW to avoid laser induced crystallization in the samples. Low angle X-ray diffraction pattern was obtained by X-ray diffractometer (Bruker D8 Advance, Germany) using Cu Kα line (λ =1.54 ˚A) at a grazing angle of 1^0.

IV. Results and discussion

Low Angle XRD Analysis

Low angle XRD measurements were carried out to investigate the film's crystal structure and to calculate average crystalline size. Films deposited on soda lime glass were used for the XRD measurements. Figure 1 displays the XRD pattern of the films deposited at different deposition times. As seen from the XRD patterns, the films deposited at 50 minutes, 60 minutes and 70 minutes shows an intense peak located around 2θ ~ 26.60^0 and weaker diffraction peak around 2θ ~ $43.90^0$and 52.10^0 corresponding to the (002), (110) and (112) planes of the hexagonal CdS structure respectively. The XRD patterns were well matched with JCPDS reference data of hexagonal CdS (JCPDS file code # 41-1049). XRD spectra shows the preferred crystalline orientation of the CdS crystallites along the (002) direction. Hexagonal structure of CdS has a higher transmission and good electrical conductivity in solar cells relative to the cubic phase; the hexagonal CdS thin films are more suitable to be n-type window layer for CdTe solar cell (Y.E.H. Chin-Yu et al. 1992).

The average crystalline size of CdS is calculated by measuring FWHM in radian corresponding to (002) peaks by using scherrer equation $d_{x-ray} = \frac{0.9\,\lambda}{\beta\cos(\theta)}$ where, λ is the wavelength of diffracted radiation, θ is the Bragg angle and β is the line width (FWHM) in radians. The average crystalline size has increase from 11.5 nm to 18.5 nm as deposition time increased from 50 minutes to 60 minutes further increasing deposition time crystalline size reduces and looks like amorphous behavior because of saturation of sulphur ions and peeling of materials from the substrate. From the XRD study we conclude that deposition time significantly influenced the crystalline size of CdS thin film and maximum crystalline size of CdS particle is 18.5 nm observed.

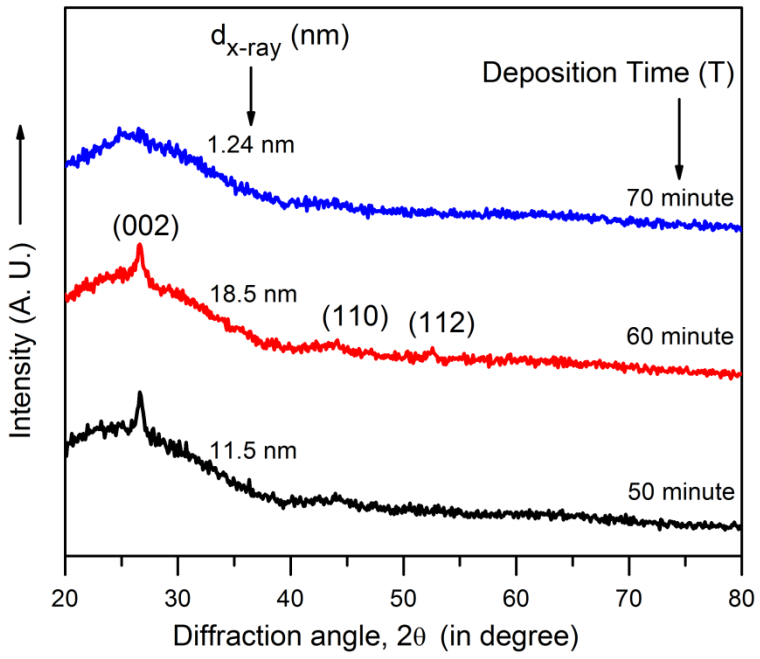

Figure 1: Low angle x-ray diffraction pattern of CdS films deposited at different deposition time

Fourier Transform Infrared (FTIR) Spectroscopy Analysis

Fourier transform infrared (FTIR) spectroscopic examination gives strongest evidence of formation of CdS. Figure 2 is FTIR transmission spectra of CdS films grown at different deposition time by CBD technique. For clarity, the spectra have been broken horizontally into two parts, namely, between 500–2100 cm^{-1} and 3100–4000 cm^{-1}. As seen from the figure, all the films shows strong absorption band centered at ~ 670 cm^{-1} corresponding to vibrations of Cd-S stretching mode (E. C. Dela Cruz Terrazas et al. 2015). Thus formation of CdS is confirmed from FTIR. As seen from the FTIR spectra intensity of CdS peak for the film deposited at 60 minutes is maximum as compare to other two films, shows that the bond density of Cd-S is maximum, further increasing deposition time bond density decreases because of peeling of film from the substrate. Thus from FTIR spectra we conclude that 60 minutes deposition time is favorable for the deposition of good quality CdS films using CBD.

In addition, the spectrum also exhibits a weak absorption bands centered at ~800-950 cm^{-1}, ~1200 cm^{-1} and ~ 1376 -1460 cm^{-1} which is corresponding to the C-C stretching Band (Feroz A. Mira et al.2015), C-CH bending (V. Krylova et al. 2019) and sulphate group S=O respectively. (Aneeqa Sabah et al 2010). The medium strong absorption bands observed at 1512 cm^{-1} and 1543 cm^{-1} correspond to N-H bending vibrations (Y. Li and G. Yang 2004). The absorption peak located at ~1713 cm^{-1} represents stretching vibrations of C=O bound to the CdS particles. (Aslam Khan 2012). In the second parts of the spectrum all the films shows absorption band nearly at 3618 and 3740 cm^{-1} correspond to O-H stretching (A. K. Verma et al. 2017).

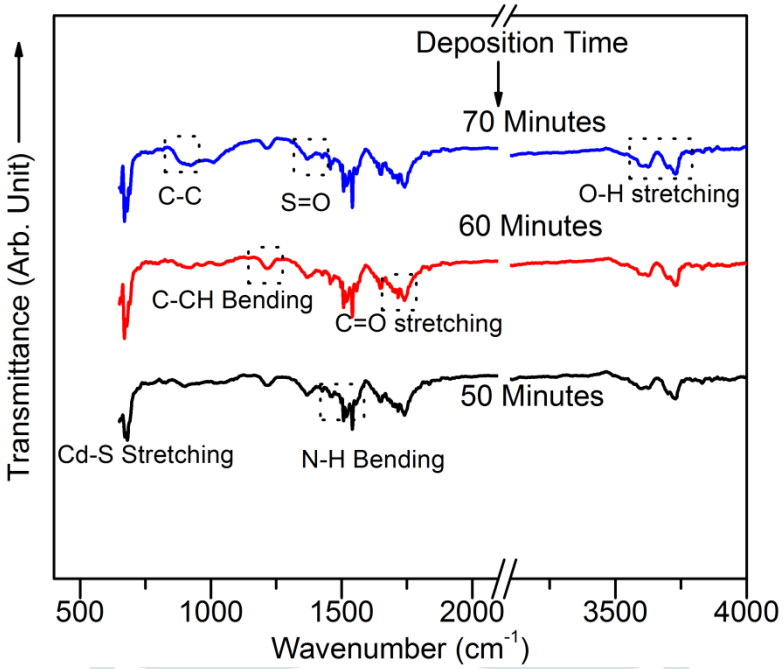

Figure 2: FTIR spectrum of CdS thin films grown at various deposition times

Raman spectroscopy analysis

The Raman spectra of CdS films grown by CBD on soda lime glass are shown in figure 3. Two distinct active Raman modes were observed at ~303 and 605 cm^{-1} in the spectrums, which correspond to the first order longitudinal optical (1LO) and second-order longitudinal optical (2LO) phonon modes of CdS. The first order longitudinal optical (1LO) phonon modes of single crystal CdS is at 305 cm^{-1}.(O. De Mello et al.1994), in present case (1LO) phonon mode is observed at 302 cm^{-1}, 303 cm^{-1}, 302 cm^{-1} for the films deposited at 50 minute, 60 minute and 70 minute respectively. According to Oladeji I.O. et al, less shift in (1LO) indicate that film has better structure (I.O. Oladejia et al.2000). Thus from Raman analysis we confirm the formation of CdS and film deposited at 60 minutes deposition time shows the better structured as compared to other. Thus the Raman results are consistence with the XRD results.

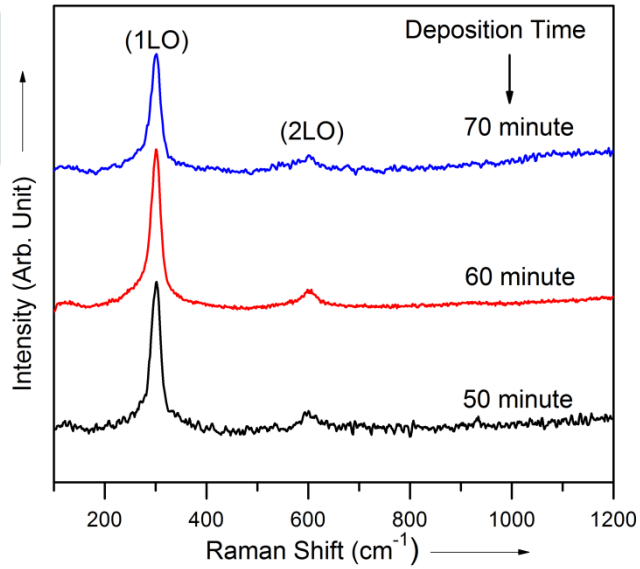

Figure 3: Raman spectra of CdS films deposited by CBD at various deposition time

UV-Visible Spectroscopy Analysis

Optical properties of CdS films grown by CBD on soda lime glass were investigated from UV-Visible spectroscopy. The optical band gap of the film calculated from the dependence of the absorption coefficient (α) on the photon energy (hν) using Taucs relation $(\alpha h\nu) = B(h\nu - E_g)^n$ (Tauc, T. and Abeies, F. et al. 1970), Where B is Tauc's constant which is characteristic parameter independent of photon energy, α is the absorption coefficient, h is the Planck's constant, υ is photon frequency, and E_g is the bandgap of the material. The exponent n depends on type of transition; n takes values 1/2, 2, 3/2 and 3 corresponding to allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively. As Cadmium sulphate have direct allowed transitions we choose n = 1/2. The optical band energy of CdS films was determined by extrapolating the straight line portion of the graph plotted $(\alpha h\upsilon)^2$ against energy (hυ). The intercept of the extrapolated line on the energy (hυ) axis give the band gap value of the material. The optical band gap of all the films deposited at different deposition time was found nearly 2.20 eV which is lower than band gap of bulk CdS (2.42 eV). The main factors affecting on the bandgap are crystalline quality, sulphur content and defects like vacancies, dislocations interstitials etc. Figure 4 shows the absorbance vs wavelength and the Tauc's plot

for the film deposited at 60 minutes deposition time. The film deposited at 60 minute deposition time shows the blue shift in the absorbance edge it means that band gap is higher as compare to the other two films deposited at 50 and 70 minutes deposition time. Based on the literatures, the decrease of the band gap energy is due to an increase in the structural disorder. This indicates that there are fewer defects and impurity energy levels in the CdS film deposited at 60 minute deposition time (H. Metin and R. Esen 2003).

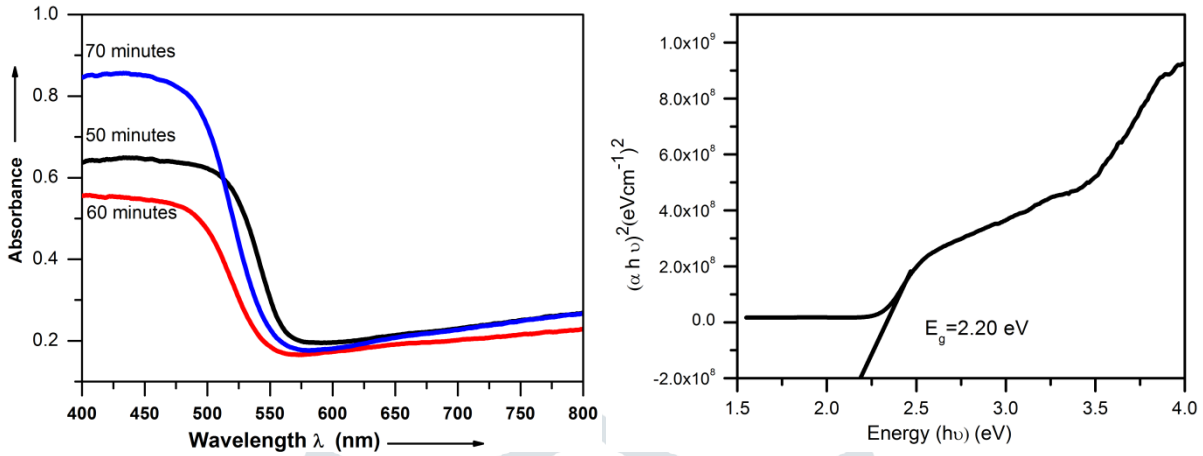

Figure 4: The variation of optical absorbance with wavelength for CdS films and Tauc's plot for the film deposited at 60 minutes deposition time

Conclusion:

The good structural and optical quality CdS films have been successfully synthesized using chemical bath deposition on soda lime glass substrate. The influence of deposition time on structural and optical properties of CdS films has been investigated in detail. The deposition time was varied from 50 to 70 minutes. Formation of CdS films has been confirmed from XRD, FTIR and Raman analysis. The detailed study of XRD spectra shows that CdS is in the hexagonal structure. The nanocrystals size was observed in the range of 1.24–18.5 nm. The UV–VIS spectra analysis shows the CdS films showed a blue shift in absorption edge compared with bulk CdS. Finally, it has been concluded that the method used in the present study is simple, cost-effective and easy method to grow device quality CdS thin films**.**

Acknowledgments

The authors wish to thank gratefully the School of Energy Studies, Savitribai Phule Pune University, Pune for the use of some of the experimental facilities and technical assistance.

REFERENCES

[1] A. Kariper, E. Guneri, F. Gode, C. Gumus, T. Ozpozan. 2011. The structural, electrical and optical properties of CdS thin films as a function of pH. Mater. Chem. Phys., 129: 183–188.

[2] S. Yılmaz, S. B. Töreli, İ. Polat, M. A. Olgar, M. Tomakin, and E. Bacaksız. 2017. Enhancement in the optical and electrical properties of CdS thin films through Ga and K co-doping. Materials Science in Semiconductor Processing, 60: 45–52.

[3] Zhang H.2016. Effects of post-annealing treatment on the structure and photoluminescence properties of CdS/PS nanocomposites prepared by sol-gel method. Optoelectron Lett., 12: 81–84.

[4] Chen, R., Han, B., Yang, L., Yang, Y., Xu, Y., Mai, Y.2016. Controllable synthesis and characterization of CdS quantum dots by a microemulsion-mediated hydrothermal method. J. Lumin., 172: 197–200.

[5] Ren, B., Cao, M., Zhang, Q., Huang, J., Zhao, Z., Jin, X., Li, C., Shen, Y., Wang L.2016. Controllable synthesis of CdS nanowire by a facile solvo thermal method and its temperature dependent photoluminescent property, J. Alloys Compd., 659: 74–81.

[6] Elavarthi, P., Kumar, A.A., Murali, G., Reddy, D.A., Gunasekhar, K.R.2016. Room temperature ferromagnetism and white light emissiveCdS:Cr nanoparticles synthesized by chemical co-precipitation method. J. Alloys Compd., 656: 510–517

[7] Darwish, M., Mohammadi, A., Assi, N.2016. Microwave-assisted polyol synthesis and characterization of pvp-capped CdS nanoparticles for the photocatalytic degradation of tartrazine. Mater. Res.Bull., 74: 387–396.

[8] X. Yang, Z. Bao, R. Luo, B. Liu, P. Tang, B. Li, J. Zhang, W. Li, L. Wu, L. 2016. Preparation and characterization of pulsed laser deposited CdS/CdSe bi-layer filmsfor CdTe solar cell application, Mater. Sci. Semicond. Process, 48: 27–32.

[9] F. Lisco, P.M. Kaminski, A. Abbas, K. Bass, J.W. Bowers, G. Claudio, M. Losurdo, J.M. Walls.2015. The structural properties of CdS deposited by chemical bath deposition and pulsed direct current magnetron sputtering, Thin Solid Films 582: 323–327.

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

[11]A. Mondal, T.K. Chaudhuri, P. Pramanik.1983. Deposition of cadmium chalcogenide thin films by a solution growth technique using triethanolamine as a complexing agent, Sol. Energy Mater., 7: 431–438.

[12] Jeehwan Kim , Homare Hiroi , Teodor K. Todorov , Oki Gunawan , Masaru Kuwahara , Tayfun Gokmen , Dhruv Nair , Marinus Hopstaken , Byungha Shin , Yun Seog Lee , Wei Wang , Hiroki Sugimoto , and David B. Mitzi.2014. High Effi ciency $Cu_2ZnSn(S,Se)_4$ Solar Cells by Applying a Double In_2S_3 /CdS Emitter. Adv. Mater.,26(44): 7437–7431.

[13] J. Tauc, in: F. Abeles (Ed.). 1972. Optical Properties of Solids, North Holland Publications,Amsterdam, 1034.

[14] Y.E.H. Chin-Yu,Z.W.Lu,S.Froyen.1992.Phys.Rev.B, 46:10086–10097

[15] E. C. Delacruz Terrazas, R. C. Ambrosio,M.L. Mota González,, P.A. Luque, S. J. Castillo,A. Carrillo-Castillo.2015. Chalcogenide Letters, 12(4): 147 – 153.

[16] Feroz A. Mira, Indrajit Chattarjeeb, Aijaz A. Darc, K. Asokand, G.M. Bhat.2015.Preparation and characterizations of cadmium sulfide nanoparticles. Optik. 126: 1240–1244.
[17] V. Krylova, N. Dukstiene.2019. The structure of PA-Se-S-Cd composite materials probed with FTIR spectroscopy. Applied Surface Science, 470: 462–471.
[18] 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
[19] Y. Li, G. Yang.2004. Studies on molecular composites of polyamide 6/polyamide 66, Macromol. Rapid. Commun. 25 (19): 1714–1718.
[20] Aslam Khan.2012. CdS Nanoparticles with a Thermoresponsive Polymer:Synthesis and Properties. Hindawi Publishing Corporation Journal of Nanomaterials, 2012:1- 8.
[21]Arvind Kumar Verma, Pramesh Chandra, Anchal Srivastava and Shukla R. K. 2017. Optoelectronic Studies of Commercially and Lab Prepared Cadmium sulfide Chalcogenide. Research & Reviews: Journal of Material Sciences RRJOMS, 5(2): 28–34.
[22] O. De Mello, L. Hernandez, O. Zeleya-Angel, R. Lozada-Morales, M. Becerril, E. Vasco.1994. Low resistivity cubic phase CdS films by chemical bath deposition technique. Appl. Phys. Lett., 65: 1278–1280.
[23] I.O. Oladejia, L. Chowa, J.R. Liub, W.K. Chub, A.N.P. Bustamantec, C. Fredricksena, A.F. Schultea.2000. Comparative study of CdS thin flms deposited by single, continuous, and multiple dip chemical processes. Thin Solid Films, 359:154-159.
[24] H. Metin, R. Esen.2003. Annealing studies on CBD grown CdS thin films, J. Cryst.Growth 258: 141–148.