International Journal of Thin Films Science and Technology

http://dx.doi.org/10.12785/ijtfst/040202

Synthesis and Characterization of CdSe Nanocrystalline Thin Film by Chemical Bath Deposition Technique

Fekadu Gashaw Hone[*], *Francis Kofi Ampong, Tizazu Abza, Isaac Nkrumah, Robert Kwame Nkum* and *Francis Boakye.*

Kwame Nkrumah University of Science and Technology, Department of Physics, Ghana

Received: 20 Aug. 2014, Revised: 30 Mar. 2015, Accepted: 31 Mar. 2015.

Abstract: A well adherent nanocrystalline thin film of cadmium selenide (CdSe) has been successfully deposited from chemical bath containing cadmium acetate, tartaric acid, ammonia and sodium selenosulphate, at a bath temperature of 85 ^{0}C and a pH of 9.5. The films were characterized using a variety of techniques. Powder X-ray diffraction revealed a cubic phase of CdSe nanocrystalline thin film with preferred orientation along the (111) plane. The SEM micrographs showed the film surface was composed of spherically shaped grains over the entire glass substrate. The elemental composition of the thin film was confirmed by energy dispersive X-ray spectroscopy. The optical band gap energy was found to be 1.86 eV.

Keywords: Nanocrystalline, Cadmium selenide thin film, Chemical bath deposition, Characterization

1 Introduction

Within the last two decades, extensive research has been devoted to study the fabrication and characterization of chalcogenide compounds in the form of thin films [1]. Among these compounds, cadmium selenide is one of the group II-VI semiconductors considered as a promising material for the development of many interesting applications such as nanosensors, biomedical imaging device, photoelectrochemical, solar cells, optoelectronic devices, electron-beam pumped lasers, light emitting diodes, electroluminescent devices, etc [2-5]. CdSe is an n-type semiconductor material [6] with a direct band gap of 1.74 eV and a dielectric constant of 10.2 at 300 K. It has high efficiency of radioactive recombination, high absorption coefficient, high photosensitivity, and direct band gap corresponding to a wide spectrum of wavelengths from ultraviolet to infrared regions [7, 8] and quantum size effects [9].

There are three main documented structures of CdSe; a hexagonal wurtzite structure, a cubic zinc blende (sphalerite) structure and the rock salt. Only the wurtzite and the sphalerite exist at atmospheric pressures. The band gap of CdSe varies among its various structures and the rock salt has the least recording band gap of 0.6 eV at 3 GPa. Usually the cubic modification exists in thin layers, while the bulk CdSe has the hexagonal structure [10]. Semiconductor devices based on CdSe thin films strongly depend on the structural and optical properties of the films obtained from various experimental conditions [11]. There exists a wide variety of techniques available for the deposition of CdSe thin films such as thermal evaporation [12], successive ionic layer adsorption and reaction (SILAR) [13], Physical vapor deposition [14], Electrochemical [15], Photochemical [16], Metal oxide chemical vapor deposition (MOCVD) [17], Photoelectrochemical [18], Electron beam evaporation [19] and Chemical bath deposition (CBD) [20, 21]. Among these techniques, Chemical bath deposition (CBD) is becoming an important deposition technique for thin films of compound materials like chalcogenides [22]. The process is sensitive to precursor concentrations, bath pH and to the substrate used [23]. Highlights of CBD include low cost, operation at low temperature and atmospheric pressure, and scalability to large area substrates [7]. The characteristics of chemical bath deposited CdSe thin films depend strongly on the growth conditions; by changing the deposition key parameters, one can control thickness, size of the nanoparticles, and the energy band gap of the obtained thin films [24].

A survey of available literature on chemical bath deposited CdSe thin films shows that, most researchers use complexing agents such as; ammonia, triethylamine, sodium hydroxide, trisodium citrate, among others. There are very few reports on the use of tartaric acid as a complexing agent for the deposition of CdSe thin films. Among few available reports [25] indicates that deposition was carried out at room temperature and at a pH of 12.1. In this paper we present the synthesis and characterization of nanocrystalline CdSe thin films from chemical bath containing cadmium acetate, tartaric acid, ammonia and sodium selenosulphate, at a bath temperature of 85 ^{0}C and a pH of 9.5. To the best of our knowledge, this is the first time cadmium acetate is being

---

[*] Corresponding author e-mail: fekeye@gmail.com

used as the source of cadmium ions in combination with tartaric acid as complexing agent for the deposition of CdSe thin film.

2 Materials and Methods

2.1 Substrate Preparation

The preparation of substrates is a critical aspect that can contribute to film adherence. Commercially available glass slides with a size of 75 mm × 25 mm × 2 mm were used as substrates for the deposition of CdSe thin films. The microscope glass slides were degreased in nitric acid overnight and subsequently kept in ethanol for about 30 minutes, then ultrasonically cleaned with distilled water and dried under ambient conditions before being used for the deposition.

2.2 Deposition of the thin film

The starting chemicals used were cadmium acetate dihydrate [Cd (CH3COO)$_2$. 2H$_2$O], as the source of cadmium ions, sodium selenosulphate [Na_2SeSO_3] which provided selenium ions, and tartaric acid [(CHOH·COOH)$_2$] as a complexing agent. Ammonia (NH_3) was used to adjust the pH of the aqueous solutions. The Sodium selenosulphate was prepared by refluxing about 9 gm of selenium powder with approximately 15 gm of anhydrous sodium sulphate (Na_2SO_3) in 250 ml of distilled water for 6 hours at 80 °C. All the chemicals used were of analytical grade.

The mixture for the bath was prepared by mixing the appropriate amount of cadmium acetate and tartaric acid in a 100 ml beaker. The pH of the solution was adjusted to 9.5 by addition of ammonia. After which 10 ml of sodium selenosulphate [Na_2SeSO_3] and some distilled water was added to obtain a final volume of 65 ml. The reaction mixture was stirred and maintained at a temperature of 85 °C for deposition. The coated substrates were removed after one and a half hours, washed with distilled water and allowed to dry under ambient conditions before film characterization. The as-deposited films were red in color and well adherent.

The reaction process for the formation of CdSe thin films may be described by the following steps: In the anionic precursor solution, the hydrolysis of sodium selenosulphate releases selenide ions as [13, 25].

$$Na_2SeSO_3 + OH^- \leftrightarrow Na_2SO_4 + HSe^- \qquad (1)$$

$$HSe^- + OH^- \leftrightarrow H_2O + Se^{2-} \qquad (2)$$

The cationic precursor solution releases Cd^{2+} ions from complexed $[Cd(\text{tartaric acid})]^{2+}$as:

$$[Cd(\text{tartaric acid})]^{2+} \rightarrow Cd^{2+} + \text{tartaric acid} \qquad (3)$$

$$Cd^{2+} + Se^{2-} \rightarrow CdSe + \text{tartaric acid} \qquad (4)$$

3 Characterization of the thin film

The crystallographic structure of the film was analyzed with a PANalytical Empyrean Series 2 powder X-ray diffractometer with a Cu-K_α radiation ($\lambda_{\alpha 1}$ = 1.5406 Å) source. The machine was operated at 40 mA and 45 kV. Scanning electron microscopy (SEM) measurements were conducted using a Zeiss 1550 VP (SEM) operating at an accelerating voltage of 20 kV and a working distance of 6.7 mm. The elemental composition of the samples were determined using an energy dispersive X-ray analysis (EDX) attached to the scanning electron microscope. Optical properties were measured at room temperature by using a Shimadzu UV/VIS mini-1240 Spectrophotometer within the wavelength range of 200 nm – 1100 nm.

4 Results and Discussion

4.1 X-ray diffraction analysis

Figure 1 shows the X-ray diffraction pattern of the as-deposited CdSe thin film analyzed over the diffraction angle 2θ between 5^O and 80^O.

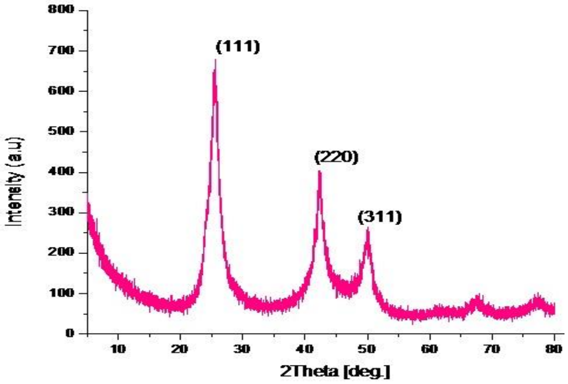

Figure 1: XRD pattern of as-deposited CdSe thin film

From Fig. 1, the XRD pattern shows three well defined peaks at position 2θ values of 25.46^0, 42.33^0 and 49.77^0 which can be indexed as reflections from the (111), (220) and (311) planes of the cubic structure CdSe compound. The diffraction pattern was well matched with standard JCPDS data file number 00-019-0191. The intensity of the peak at position 25.46^0 indicates that the grains have a preferred orientation along the (111) plane. The XRD results are well agreed with earlier report by [26]. Lattice constant (a_{hkl}) for the cubic structure was calculated using Eq. (5) and the results are presented in Table 1.

$$a_{hkl} = d_{hkl}\sqrt{h^2 + k^2 + l^2} \qquad (5)$$

The average crystallite size (D) was obtained from the X-ray diffraction pattern, using the Scherrer (1918), formula which is given as:

$$D = \frac{K\,\lambda}{\beta_{2\theta}\,Cos\theta} \qquad (6)$$

where, θ is the diffraction angle, β is the full width at half maximum measured in radians, K is the constant known as the shape factor, taken as 0.94 by assuming the crystallites to be spherical in shape [9] and λ is the wave length of the X-ray radiation. The average grain size was estimated to be 4 nm.

Table 1: Comparison of crystallographic parameters of CdSe thin film obtained from XRD analysis with standard JCPDS data file number 00-019-0191.

d-space in Å standard	observed	Cell parameter (a) in Å standard	calculated	Crystalline size (D_{hkl}) (nm)	Average Crystalline size D (nm)
3.510	3.4956	6.077	6.053	4.37	4.02
2.149	2.1330			3.82	
1.833	1.8304			3.86	

From table 1, the calculated lattice constant deviates from the standard bulk value. This shows that the crystallites may be under some strain [27] . If the size and strain broadening are present simultaneously then the crystallite size and strain can be obtained from the Williamson-Hall (W–H) plot using the following mathematical relation [28]:

$$\beta_{hkl} \cos\theta = \frac{K\lambda}{D} + 4\varepsilon \sin\theta \qquad (7)$$

Where K, λ, θ and D are defined in equation 6, and ε is the lattice strain for nanocrystalline CdSe thin film. A plot of cosθ versus 4sinθ for CdSe thin film is shown in Fig. 2. The slope of the plot gives the amount of lattice strain, which turns out to be 2×10^{-3} for CdSe thin film. The reciprocal of intercept on the βcosθ axis gives the average crystallite size which is 4.83 nm. The average crystallite size estimated shows close agreement with the value obtained from Debye-Scherrer's formula.

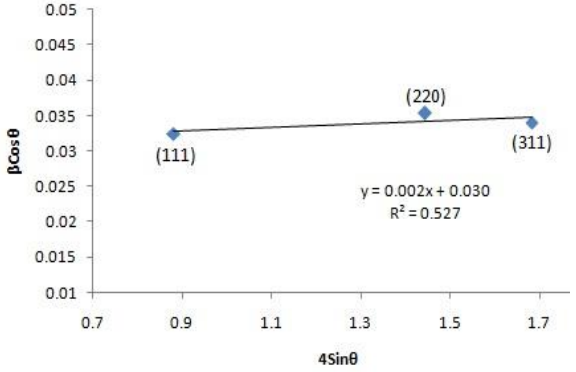

Fig. 2: Williamson–Hall plot for as-deposited CdSe thin film

4.2 Elemental analysis and morphological studies

Elemental analysis for the as-deposited CdSe thin film was carried out using EDX attached to the SEM.

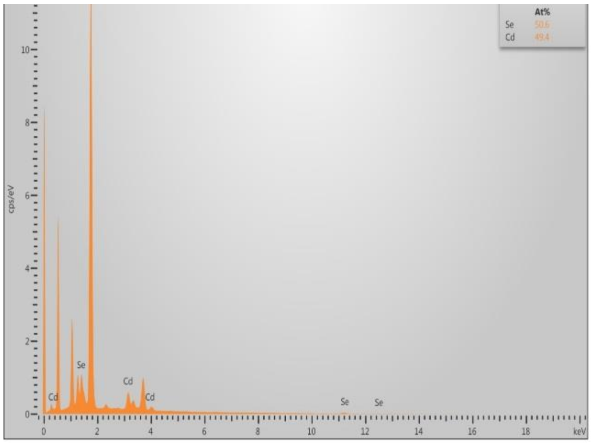

Fig. 3: EDX spectrum of the as-deposited CdSe thin film.

Figure 3 shows the EDX spectrum of the as-deposited CdSe thin film, which is consistent with the formation of the binary compound. The atomic percentage of Cd:Se is 49.4:50.6, which is very close to 1:1 indicating that the thin film had the desired stoichiometric ratio. This is comparable to results reported by [9, 29].

Figure 4a, 4b and 4c shows the SEM micrographs of the as-deposited CdSe thin films taken at different magnifications. The surface morphology is composed largely of spherically shaped grains with different sizes and uniformly distributed over a smooth homogenous background without visible defects such as, cracks, peeling or pinholes. Some of the micrographs also show the presence of pockets of clusters of spherically shaped grains. Similar observations were reported by [2, 30].

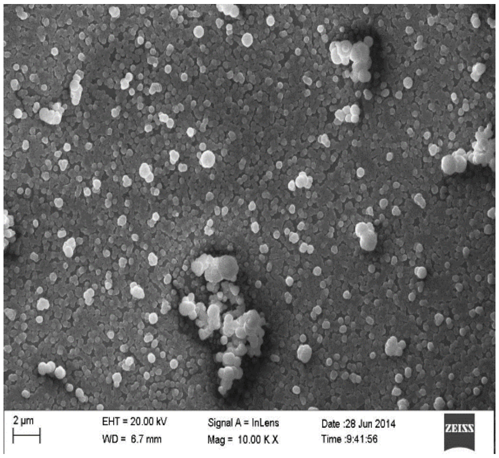

Fig. 4 (a): The SEM micrograph of as-deposited CdSe thin film (magnification 10 KX)

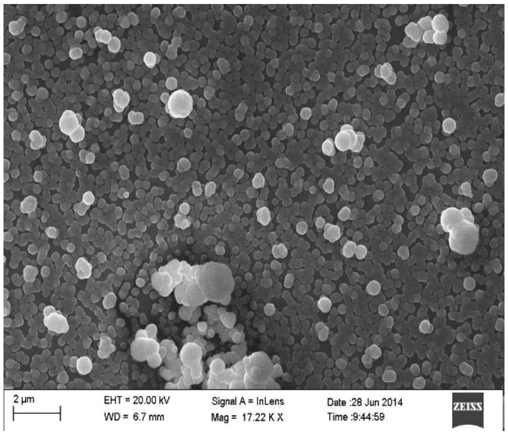

Fig. 4 (b): The SEM micrograph of as-deposited CdSe thin film (magnification 17.22 KX)

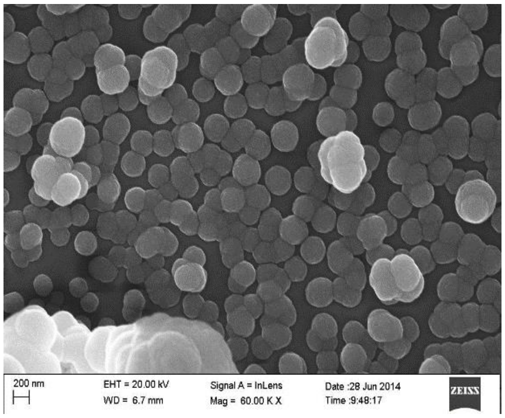

Fig. 4 (c): The SEM micrograph of as-deposited CdSe thin film (magnification 60 KX)

4.3 Determination of the Optical Band gap

The energy band gap and transition type was determined from mathematical treatment of data obtained from optical absorbance versus wavelength with the Stern (1963), relationship of near-edge absorption which is given as [31].

$$A = \frac{[k\left(h\upsilon - E_g\right)]^{n/2}}{h\upsilon} \tag{8}$$

Where v is the frequency, h is the Planck's constant, k is a constant while n carries the value of either 1 for direct transition or 4 for indirect transition. CdSe is a direct band gap material, thus n is taken as 1. The band gap energy is obtained by extrapolating the linear portion of $(Ahv)^2$ versus hv to the energy axis at $(Ahv)^2 = 0$. The optical band gap for CdSe thin film was estimated 1.86 eV, which is in good agreement with earlier reports [29, 32]. The plot of $(Ahv)^2$ versus hv shown in Fig. 5 is linear at the absorption edge which indicates the presence of direct transition [20].

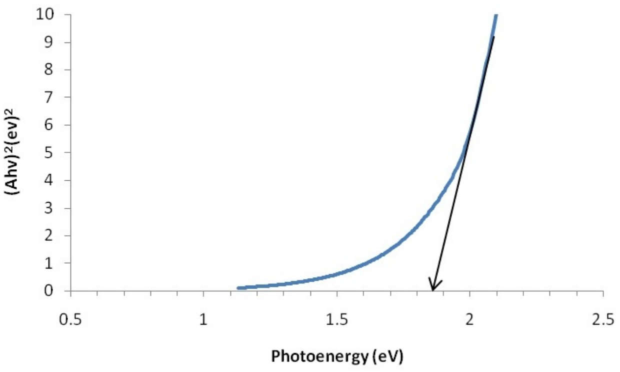

Fig. 5: A graph of $(Ahv)^2$ plotted as a function of the photon energy($h\upsilon$) for as-deposited CdSe thin film

The value of the band gap determined for the CdSe thin film shown in Fig. 5 is slightly higher when compared to the reported bulk value of 1.74 eV [33]. It is known that such blue shift to higher optical band gaps arises from very small grain sizes and the resulting quantum confinement of electronic states in the thin film [34]. For example, in chemically deposited CdSe films with grain sizes less than 5 nm, optical band gap of up to 0.7 eV higher than the bulk value of 1.74 eV has been reported by [35]. In our sample the average grain size estimated from XRD measurements was 4 nm, and this explains the slightly larger band gap when compared to the bulk value.

5 Conclusion

A well adherent cadmium selenide nanocrystalline thin film has been successfully deposited on glass substrate by using chemical bath deposition technique. X-ray diffraction study revealed that a cubic phase of CdSe nanocrystalline thin film. The average crystallite size of CdSe thin film was obtained using the Debye-Scherrer equation and found to be 4 nm. The SEM micrographs show the surface morphology is composed of spherically shaped grains. Energy dispersive X-ray spectroscopy confirmed that the as-deposited thin films had the desired stoichiometric ratio. The optical band gap, determined from optical absorption spectroscopy, was found to be 1.86 eV with direct transition. It is concluded that the reactants, bath temperature, pH and deposition time used for this work, provide another set of deposition conditions for the growth of quality CdSe thin films by CBD technique. The effect of annealing on the morphology, structural and optical properties are under investigation and would be reported in subsequent publications.

Acknowledgement:

One of the authors Fekadu Gashawe Hone would like to acknowledge Intra-ACP academic mobility scheme for financial support for the research work.

References:

[1] W. Cyrus, A.P. Alivisatos, D.M. Kammen, Materials availability expands the opportunity for large-scale photovoltaics deployment, Environ. Sci. Technol., 43 (2009) 2072-2077.

[2] K.S. Ajaya, S.R. Deo, G.S. Thool, R.S. Singh, Y.R. Katre, A. Gupta, Synthesis and Characterization of Chemically Deposited Nanocrystalline CdSe Thin Film, Synth. React. Inorg. Met.Org. Chem., 41 (2011) 1346 -1350.

[3] Y.R. Toda, K.S. Chaudhari, A.B. Jain, D.N. Gujarathi, Structural and Optical Properties of CdSe Thine Films Deposted by Chemical bath deposition Technique, Asian J. Chem. and Envi. Res., 4 (2011) 40-43.

[4] V.T. Patil, V.P. Joshi, D.A. Tayade, J.V. Dhanvij, D.N. Gujarathi, Surface morphological and optical properties of CdSe thin films by closed space sublimation technique Chalcogenide Letters, 10 (2013) 239-247.

[5] H.L. Mansour, K.A. Mishjil, N.F. Habubi, S.S. Chiad, Structural and Optical Properties of $Cd_{0.4} Se_{0.6}$ Thin Films Prepared by CBD, Int. J.Thin Films Sci. Tec., 3 (2014) 57-60.

[6] S. Velumani, X. Mathew, P.J. Sebastian, S.K. Narayandass, D. Mangalaraj, Structural and optical properties of hot wall deposited CdSe thin films, Solar energy materials and solar cells, 76 (2003) 347-358.

[7] R.C. Kanithla, D.K. Pandya, K.L. Chopra, Photo-Electronic Properties of Solution-Grown CdSe Films, Solid-State Electronics, 25 (1982) 73-76.

[8] D.S. Sutrave, G.S. Shahane, V.B. Patil, L.P. Deshmukh, Micro-crystallographic and optical studies on Cd< sub> $_{1-x}$</sub> Zn< sub> $_{x}$</sub> Se thin films, Materials chemistry and physics, 65 (2000) 298-305.

[9] M.P. Deshpande, N. Garg, S.V. Bhatt, P. Sakariya, S.H. Chaki, Characterization of CdSe thin films deposited by chemical bath solutions containing triethanolamine, Materials Sciencein Semiconductor Processing, 16 (2013) 915-922.

[10] O. Zakharov, A. Rubio, M.L. Cohen, Calculated structural and electronic properties of CdSe under pressure, Physical Review B, 51 (1995) 4926-4930.

[11] K. Sarmah, R. Sarma, H.L. Das, Correlative assessment of structural and photoelectrical properties of thermally evaporated CdSe thin films, Journal of Non-Oxide Glasses, 1 (2009) 143-156.

[12] U. Pal, M.H. Zaldivar, R. Sathyamoorthy, V. Manjuladevi, P. Sudhagar, S.C. Mohan, S. Senthilarasu, Nanocrystalline CdSe Thin Films of Different Morphologies in Thermal Evaporation Process, Journal of Nanoscince Nanotechnology 8(2008) 1-7.

[13] H.M. Pathan, B.R. Sankapal, J.D. Desai, C.D. Lokhande, Preparation and characterization of nanocrystalline CdSe thin films deposited by SILAR method, Materials Chemistry and Physics, 78 (2002) 11-14.

[14] M.K. David, S. Devadason, A Comparative Study on the Optical Properties of Multilayer CdSe / CdTe Thin Film with Single Layer CdTe and CdSe Films, Jounal of Nano-and Electronic Physics, 5 (2013) 1-4.

[15] R.I. Chowdhury, M.S. Islam, F. Sabeth, G. Mustafa, S.F.U. Farhad, D.K. Saha, F.A. Chowdhury, S.H. and, A.B.M.O. Islam, Characterization of Electrodeposited Cadmium Selenide Thin Films, Dhaka Univ. J. Sci., 60 (2012) 137-140.

[16] M. Ichimura, R. Kumaresan, N. Sato, E. Arai, Photochemical deposition and Elrctrochemical deposition of semiconductors for solar cell, in: 4th International Conference on Mechanical Engineering, Dhaka, Bangladesh, 2001, pp. 1-4.

[17] D.Y. Chae, K.W. Seo, S.S. Lee, S.H. Yoon, W. Shim, CdSe Thin Films Grown by MOCVD Method Using New Single-source Precursors, Bull. Korean Chem. Soc, 27 (2006) 762-764.

[18] A.V. Moholkar, S.M. Pawar, K.Y. Rajpure, C.H. Bhosale, Electrosynthesis and characterization of CdSe thin films: Optimization of preparative parameters by photoelectrochemical technique, Journal of Physics and Chemistry of Solids, 67 (2006) 2386-2391.

[19] N.J.S. Kissinger, J. Suthagar, B.S. Kumar, T. Balasubramaniam, K. Perumal, Effect of Substrate Temperature on the Structural and Optical Properties of Nanocrystalline Cadmium Selenide Thin Films Prepared by Electron Beam Evaporation Technique, Acta Physica Polonica A, 118 (2010).

[20] C.D. Lokhande, R.B. Kale, Band gap shift, structural characterization and phase transformation of CdSe thin films from nanocrystalline cubic to nanorod hexagonal on air annealing, Semicond. Sci. Technol. , 20 (2005) 1-9.

[21] O. Calzadilla, M. Zapata-Torres, L. Narvaez, S. Jiménez, F. Rábago, Effect of annealing temperature on the crystalline quality of chemically deposited CdSe films, Superficies y Vacío, 14 (2002) 35-37.

[22] G. Hodes, Chemical solution deposition of semiconductor films, Marcel Dekker, Inc., New York, 2002.

[23] S. Elisabetha, I. Zilbermann, E. Maimon, Y. Nahmani, H. Cohen, E. Adarc, D. Meyerstein, Radical catalyzed debromination of bromo-alkanes by formate in aqueous solutions via a hydrogen atom transfer mechanism, Tetrahedron Letters, 45 (2004) 989-992.

[24] N. Ghobadi, R. Moradian, Strong localization of the charge carriers in CdSe nanostructural films, International Nano Letters, 3 (2013) 1-5.

[25] P.P. Hankare, S.D. Delekar, M.R. Asabe, P.A. Chate, V.M. Bhuse, A.S. Khomane, K.M. Garadkar, B.D. Sarwade, Synthesis of Cadmium Selenide thin films at low-temperature by simple Chemical route and their Characterization, Journal of Physics and Chemistry of Solids, 67 (2006) 2506-2511.

[26] A.S. Khomanea, P.P. Hankare, Structural, optical and electrical characterization of chemically deposited CdSe thin films, Journal of Alloys and Compounds, 489 (2010) 605-608.

[27] N. Choudhury, B.K. Sarma, Structural analysis of chemically deposited nanocrystalline PbS films, Thin Solid Films, 519 (2011) 2132-2134.

[28] C. Mehta, J.M. Abbas, G.S.S. Saini, S.K. Tripathi, Effect of deposition parameters on the optical and electrical properties of nanocrystalline CdSe, Chalcogenide Letters, 4 (2007) 133-138.

[29] H.E. Esparza-Ponce, J. Hernández-Borja, A. Reyes-Rojas, M. Cervantes-Sánchez, Y.V. Vorobiev, R. Ramírez-Bon, J.F. Pérez-Robles, J. González-Hernández, Growth technology, X-ray and optical properties of CdSe thin films, Materials Chemistry and Physics, 113 (2009) 824-828.

[30] H. Metin, S. Erat, M. Ari, M. Bozoklu, Characterization of CdSe films prepared by chemical bath deposition method, Optoelectronics and Advanced Materials 2(2008) 92-98.

[31] K. Anuar, W.T. Tan, M. Jelas, S.M. Ho, S.Y. Gwee, Effects of Deposition Period on the Properties of FeS_2 Thin Films by Chemical Bath Deposition Method, Thammasat Int. J. Sc. Tech.,, 15 (2010) 62-69.

[32] Y. Zhao, Z. Yan, J. Liu, A. Wei, Synthesis and characterization of CdSe nanocrystalline thin films deposited by chemical bath deposition, Materials Sciencein Semiconductor Processing, 16 (2013) 1592-1598.

[33] A.A. Yaron, G. Hodes, F. Decker, P. Motisuke, Phys. Rev. B 36 (1987) 4215.

[34] S.S. Kale, C.D. Lokhande, Thickness-dependent properties of chemically deposited CdSe thin film, Materials Chemistry and Physics 62 (2000) 103-108.

[35] P.K. Nair, M.T.S. Nair, V.M. Garcıa, O. L.Arenas, Y. Pen, A. Castillo, I.T. Ayala, O. Gomezdaza, A. Sanchez, J. Campos, H. Hu, R. Suarez, M.E. Rinco, Semiconductor thin films by chemical bath deposition for solar energy related applications, Solar Energy Materials and solar cells 52 (1998) 313-344.