International Journal of Thin Film Science and Technology

Volume 5
Issue 3 *Sep. 2016*

Article 3

2016

Properties of Cadmium Selenide Thin Films Deposited by Dip Method

P. A.Chate
Dept. of Chemistry, J.S.M. College, Alibag. M.S. India, pachate04@rediffmail.com

V. D. Bhabad
JJT University, Jhunjhunu, Rajasthan, India.\\ Bhausaheb Nene College, Pen, (M.S.). India., pachate04@rediffmail.com

Recommended Citation

A.Chate, P. and D. Bhabad, V. (2016) "Properties of Cadmium Selenide Thin Films Deposited by Dip Method," *International Journal of Thin Film Science and Technology*: Vol. 5 : Iss. 3 , Article 3.
Available at: https://digitalcommons.aaru.edu.jo/ijtfst/vol5/iss3/3

International Journal of Thin Films Science and Technology

http://dx.doi.org/10.18576/ijtfst/050303

Properties of Cadmium Selenide Thin Films Deposited by Dip Method

P. A.Chate[1,] and V. D. Bhabad[2,3]*

[1] Dept. of Chemistry, J.S.M. College, Alibag. M.S. India
[2] JJT University, Jhunjhunu, Rajasthan, India.
[3] Bhausaheb Nene College, Pen, (M.S.). India.

Received: 21 Jul. 2016, Revised: 3 Aug. 2016, Accepted: 10 Aug. 2016.

Abstract: The cadmium selenide thin films have been deposited using dip technique. Cadmium sulphate and sodium selenosulphate were used as Cd^{+2} and Se^{-2} ion sources, respectively. Trichloroacetic acid is used as complexing agent. The preparative parameters such as concentration, pH have been optimized in order to deposit CdSe thin films. CdSe thin films are specularly reflective and red in colour. The films are characterized using structural, optical, morphological and electrical properties.

Keywords: Thin films; Semiconductors; Chemical synthesis; X-ray diffraction.

1 Introduction

Cadmium selenide (CdSe) is naturally grown as n-type and hexagonal, cubic or mixed crystal structure with direct band gap energy of 1.7 eV at room temperature [1]. This makes it interesting materials for various applications such as solar cells, photodetectors, light emitting diodes, and other optoelectronic devices [2-5]. It also shows bright luminescence in the visible range of optical spectra [6]. It has high absorption coefficient near the band edge, which allows its use in the thin film devices; it is especially interesting for application in solar hybrid system [7-8]. The CdSe thin films with different morphology, such as nanowires, nanotubes, nanorods and needle have been obtained [9-13].

Inorganic thin films with controlled morphology and properties can be fabricated using chemical method. Deposition of CdSe by chemical method has been carried out by many workers. The complexing agent plays an important role in the formation of CdSe thin film. Khomane [14] used formic acid as complexing agent to deposit CdSe thin film. Okereke et al [15] prepared CdSe thin films by using triethanolamine as complexing agent. Gopalkrishan et al [16] have used ethylene diammine tetra acetic acid as chelating agent for synthesis of CdSe thin film.

In this paper, CdSe thin films are deposited on glass substrates by using dip method. CdSe thin films have been synthesized first time using trichloroacetic acid as complexing agent. The thickness measurement technique, X-ray diffraction, scanning electron microscopy, EDAX, optical absorption and electrical measurement technique is used to characterize the films.

2 Experimental

2.1 Chemicals

All reagent employed in the works were analytical grade. Cadmium sulphate octahydrate, trichloroacetic acid, ammonia, selenium and sodium sulphite are used.

2.2 Preparation of sodium selenosulphate

Sodium selenosulphate (0.2 M) was used as a selenium source for the deposition of CdSe thin films. The solution was prepared by refluxing 5 g selenium powder with 15 g sodium sulfite in 200mL double distilled water for 9 h at 363 K. The solution was cooled, filtered to remove undissolved selenium and stored in an airtight bottle [17].

2.3 Preparation of CdSe thin films

In the synthesis of CdSe thin films, 10 mL of 0.2 M Cd^{+2} ions were taken in 100 mL beaker, and then it was complexed with trichloroacetic acid. 15 mL of 5N ammonia was added in the above reaction mixture. Then 10 mL of 0.2 M sodium selenosulphate was added in the above reaction mixture. The resulting solution was diluted up to 75 mL with distilled water. The pH of the reaction mixture

---

[*] Corresponding author E-mail: pachate04@rediffmail.com

was found to be 10.21. The temperature of the reaction mixture was maintained at 278 K using an ice bath. The solution was stirred vigorously before dipping glass substrates, which were kept vertically slightly tilted in the reactive bath. The temperature of the bath was then allowed to increase up to 298 K very slowly. After 4 h, the slides were removed and washed several times with double-distilled water. The deposited substrate was dried naturally, preserved in dark desiccators over anhydrous $CaCl_2$ and subjected to various characterizations.

3 Results and Discussion

3.1 Physical properties and thickness measurement

CdSe films were uniform, tightly adherent to the substrate, pinhole free. The as grown CdSe films were dark red in color. The terminal thickness of the films has been determined by weight difference density consideration method. The thickness was measured every 1 hour and plotted against time as shown in Fig. 1.From the figure, the thickness varies linearly with time, but above certain time the concentration of the reactive species decreases. Thickness remains the constant. The terminal thickness was found to be 0.54 μm.

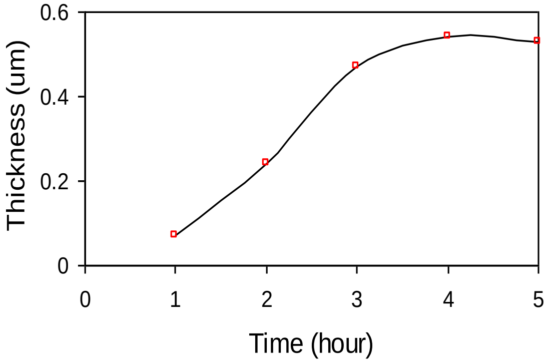

Fig 1. Effect of time on thickness of CdSe thin films.

3.2 Structural Analysis

The X-ray diffraction patterns of CdSe films deposited on glass substrates is shown in Fig. 2. The crystallographic phase, overall crystalline quality, cell parameters, micro strain, crystallite size and dislocation density of the CdSe thin films have been investigated using X-ray diffractrogram. On further analysis of data, it is found that CdSe films are polycrystalline nature with a hexagonal crystal structure [JCPDS-08-0459]. The diffused background is due to amorphous glass substrate and some amorphous phase material. The XRD spectrum shows peak at d = 3.720 Å, $2\theta = 23.90^0$ which corresponds to the (100) plane of the hexagonal (wurtzite) crystal structure. A similar crystallographic orientation is exhibited by CdSe thin film obtained by electrodeposition method [18]. Mixed cubic and hexagonal phases were not observed. Then, this dip method is suitable for the preparation of single phase hexagonal CdSe thin film.

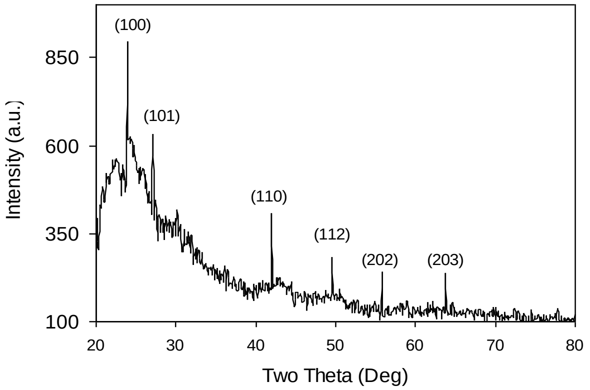

Fig. 2.X-ray diffraction pattern of CdSe thin films.

The lattice parameters of the hexagonal structure have been calculated from X-ray diffraction data by using following relation [19];

$$(1/d^2) = (4/3)\,(h^2+k^2+ l^2)/a^2) + (l^2/c^2)\text{-------------}(1)$$

Where h, k and l are the lattice planes and d is the interplanar spacing determined by using Bragg's equation. The obtained lattice constant "a" and "c" have been 4.296 and 7.064 Å, respectively. These values are in good agreement with the literature ones [20]. A technique which determines the magnitude of the favored orientation factor 'f' for a given plane comparative to other planes in substance was used [21]. According to this manner the prefer orientation factor 'f' (100) of the (100) plane for the CdSe samples has been calculate by evaluating the fraction of (100) plane intensity over the summation of intensities of every peaks has been determined for the films. f(100) = 0.3317, f(101) = 0.2349, f(110) = 0.1515, f(112) = 0.1045, f(202) = 0.0893, f(203) = 0.0878. The full width at half maximum (FWHM) of thin films equivalent to most intense reflections suggest that the films are having approximately the identical crystallite size. The average crystallite size (D) of the CdSe thin films was calculated using Debye Scherrer's formula [22];

$$D = (K\lambda/\beta\cos\theta)\text{------------------------}(2)$$

where, θ is the diffraction angle, β is the full width at half maximum, K is the constant known as the shape factor, taken as 0.9 by assuming the crystallites to be spherical in shape and λ is the wavelength of X-ray radiation (1.54056 Å). The average crystallite size was found to be 59.72nm. The microstrain developed in the thin film was calculated using formula [23];

$$\varepsilon = \beta\cos\theta/4\text{---------------------------}(3)$$

The observed value of microstrain was found to be 5.803×10^{-4}. Dislocation density is calculated using the relation [24];

$$\delta = n/D^2 \text{-------------------------------}(4)$$

where n is the factor which is equal to unity for minimum dislocation density. The value was found to be 2.98 x 10^{14} m^{-2}. Information of the strain and the particle size (D) are obtained from the FWHM of the diffraction peaks. Williamson Hall analysis is a simplified integral breadth method where both size-induced and strain-induced broadening is used by considering the peak width as a function of 2θ [25-26]. The FWHM can be expressed as a linear combination of the contributions from the strain and particle size through the following relation [27];

$$[\beta\cos\theta/\lambda = (K/D) + \varepsilon\sin\theta/\lambda] \text{-----------------}(5)$$

Fig 3 represents the plot of βcosθ/λ against sinθ/λ for CdSe thin film which is a straight line. The slope of the plot gives the amount of residual strain, which turns out to be -1.32 x 10^{-3} for CdSe thin films. The reciprocal of intercept on the y-axis gives the average particle size as 59.21nm. The negative value of residual strain for the film indicates the compressive strain. If the film is deposited free from impurities, the compressive strain is generated at the film substrates inferface, when the very small crystallites are bonded to substrates due to surface tension effect.

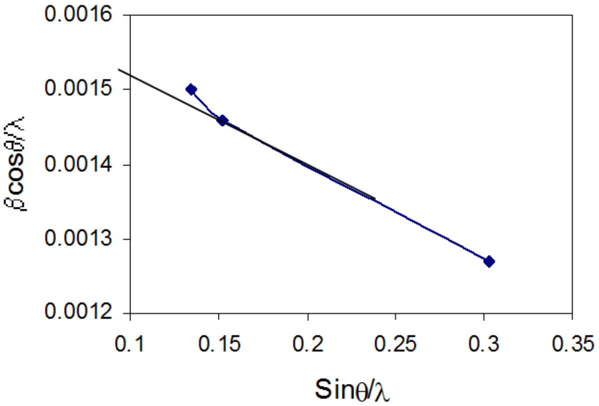

Fig. 3. Plot of sinθ/λ against βcosθ/λ for CdSe thin film.

3.3 Optical Analysis

Optical properties are studied by recording the transmission and absorption spectra of the films. Fig. 4 shows the transmission data of CdSe thin films deposited by dip method. The fall in transmission at about 700 nm corresponds to the onset of fundamental absorption edge indicating the photon energy required to excite an electron across the optical energy gap. The sample is non-absorbing at longer wavelength while most absorbing at 400-500 nm. Fig. 5 shows the absorption spectrum of the CdSe thin film. The absorption value increases steeply below 700 nm. The absorptivity is calculated by using relation;

$$\alpha = (A/t) \text{----------------------------}(6)$$

Fig. 6 indicates the variation of absorptivity against wavelength. The absorptivity decreases with increases in wavelength. At 400 nm the absorptivity was found to be 2.592 x 10^4 cm^{-1} while at 800 nm absorptivity was found to be 0.185 x 104 cm^{-1}. The band gap energy of the films was determined by plotting a graph between $(\alpha h\nu)^2$ and hν and shown in Fig. 7. Extrapolating the straight line portion of the plot $(\alpha h\nu)^2$ versus hν for zero absorption coefficient value gave the band energy. The band energy for CdSe thin

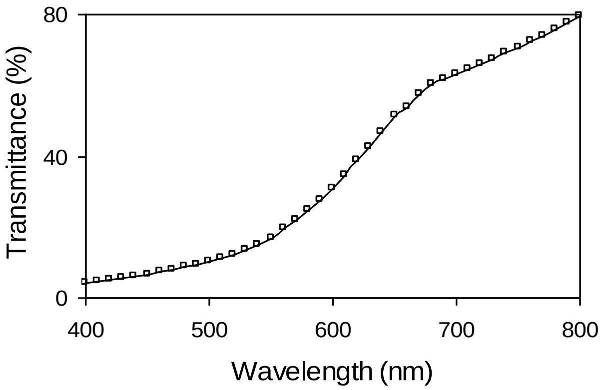

Fig.4. Transmittance spectrum of CdSe thin film.

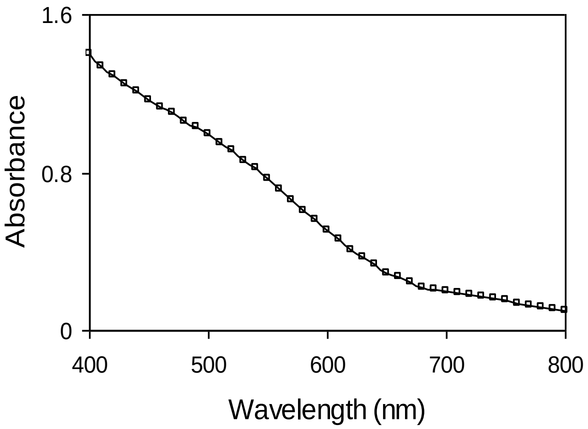

Fig. 5. Absorbance spectra of CdSe thin film.

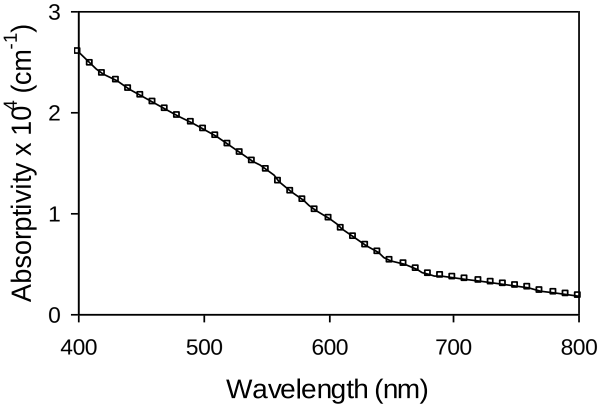

Fig. 6. Absorptivity of CdSe thin film.

film was found to 2.10 eV. It is compared to 1.74 eV reported for the band gap of CdSe [28], a blue shift of about 0.36 eV can be observed which is due to nanometer sized particles. The band gap value is influenced by various factors like thickness, crystallite size, structural parameters, carrier concentrations, presence of impurities, deviations from stoichiometry of the film and lattice strain [29-30]. The type of transition was confirming by plotting the graph of ln (hν-Eg) against ln (αhν). The slope of the graph was found to be 0.509 indicating direct type of transitions. The graph is represented in Fig. 8.

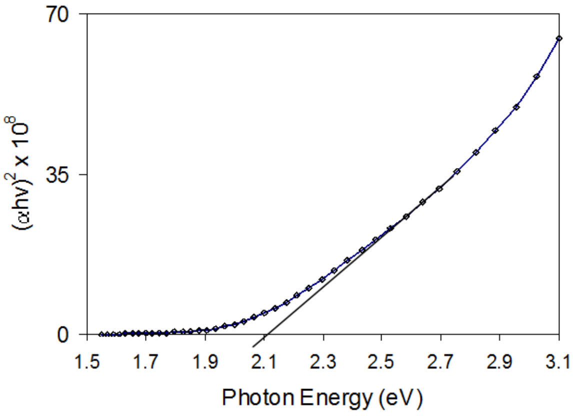

Fig.7. Determination of band gap energy for CdSe thin films.

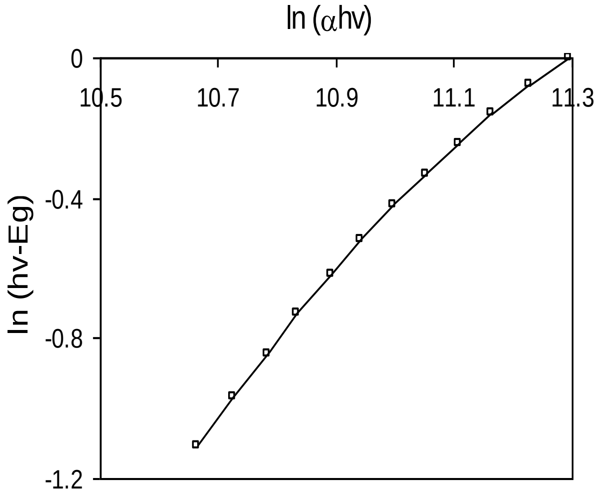

Fig.8. Determination of type of transition for CdSe thin film.

3.4 *Morphological Analysis*

In order to further elucidate the size and crystal structure of the films, scanning electron micrograph image was taken and is shown in Fig.9. An overview of image the film consist of spherical crystallites of about 65nm in diameter aggregated in the form of polydispersive clusters of spherical size and shape.

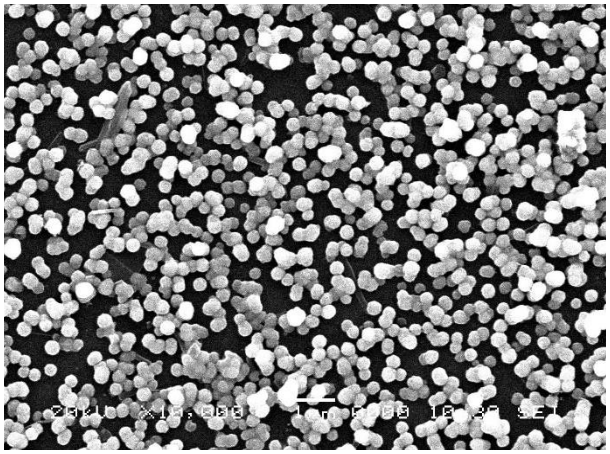

Fig. 9. Scanning electron micrograph of CdSe thin film.

3.5 *Electrical Analysis*

Fig. 10 shows the dependence of conductivity on inverse temperature for the films. These curves show a similar dependence to those of Khomane[31], who interpreted their results in term of Petritz [32] inter crystalline barrier model in which conductivity is thermally activated and follow the relation;

$$\sigma = \sigma_o \exp (Ea/kT) \text{ -----------------------}(7)$$

Where σ_o is a constant and the activation energy (Ea) may be obtained from the slope of the curves. In the present case, the activation energies were in the range of 0.11-0.30 eV. They are consistent with previously observed values [33]. Berger et al [34] obtained lower activation energies varying the range of 0.005-0.047 eV, which was identified by conductivity measurements. Since, the temperature activation energy represents a mean value of the inter-crystalline barrier height combining the effects of both carrier density and mobility. The general dependence of conductivity on temperature is clearly consistent, and indicates the existence of a well defined potential barrier between inter-crystallite grains, which may be overcome by thermal activation.

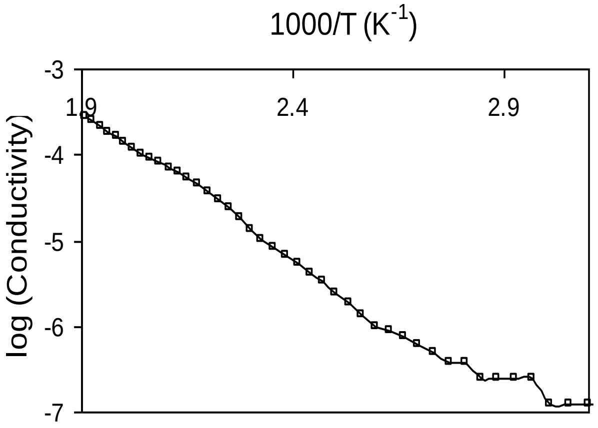

Fig. 10. Electrical conductivity of CdSe thin film.

4 Conclusions

The deposition of CdSe thin film on glass substrate was carried out using dip method. CdSe thin film was polycrystalline along with some amorphous phase present in it. From scanning electron micrograph studies, it was revealed that the CdSe thin film is uniform, homogenous and well coverage to the glass substrate. The optical analysis showed that the CdSe film has optical energy of 2.10 eV. The film is semiconducting with room temperature electrical conductivity of the order of 10^{-7} $(\Omega \text{ cm})^{-1}$.

References

[1] Y. Akaltum, M. A. Yildirim, A. Ates, M. Yildirim, *Opt. Comm.* 284 (2011) 2307.

[2] K. Sharma, A. Kabbi, G. Saini, S. Tripathi, Curr. *Appl. Phys.* 13 (2013) 964.

[3] J. Zheng, Z. Zheng, W. Gong, X. Hu, W. Gao, *Solid State Commun.* 147 (2008) 429.

[4] I. Gur, N. Fromer, M. Geier, A. Alivisator, *Science* 310 (2005) 462.

[5] S. Tripathi, *J. Mater. Sci*. 45 (2010) 5468.

[6] B. Bhattacharjee, C. Hsu, C. Lu, R. Ruaan, *Chalcogen. Lett.* 7 (2010) 71.

[7] K. Sharma, A. Kabbi, G. Saini, S. Tripathi, *J. Alloy Compd.*540 (2012) 198.

[8] J. Brandenburg, X. Jin, M. Kruszynska, J. Ohland, J. Kolny-Olesiak, I. Riedel, H. Borchert, J. Parisi, *J. Appl. Phys.* 110 (2011) 64509.

[9] Y. Zhao, Z. Yan, J. Liu, A. Wei, *Mater. Sci. Semi. Process.* 16 (2013) 1592.

[10] S. Kung, W. Xing, W. Veer, F. Yang, K. Donavan, M. Cheng, J. Hemminger, R. Penner, *Acs. Nano.* 5 (2011) 7627.

[11] J. Haremza, M. Hahn, T. Krauss, *Nano Lett.* 2 (2002) 1253.

[12] C. Shan, Z. Liu, S. Hark, *Appl. Phys. Lett.* 87 (2005) 163108.

[13] K. Leschkies, R. Divakar, J. Basu, *Nano Lett.* 7 (2007) 1793.

[14] A. Khomane, *Mater. Res. Bull.* 46 (2011) 1600.

[15] N. Okereke, A. Ekpunobi, *Chalcogen. Lett.* 8 (2011) 377.

[16] T. Shyju, S. Anandhi, R. Indirajith, R. Gopalkrishan, J. Alloy Compd. 506 (2010) 892.

[17] P. Hankare, P. Chate, S. Delekar, V.Bhuse, M. Asabe, B. Jadhav, K. Garadkar, *J. Crystal Growth* 291 (2006) 40.

[18] R. Henriquez, A. Badan, P. Grez, E. Munoz, J. Vera, E. Dalchiele, R. Marotti, H. Gomez, *Electroch. Acta*, 56 (2011) 4895.

[19] P. Hankare, B. Jadhav, P. Chate, D. Sathe, I. Mulla, *J. Alloys Compd.* 509 (2011) 2948.

[20] N Kissinger, J Suthagar, B Kumar, T. Balasubramaniam, K Perumal *Acta Physica Polonica A* 118 (2010) 623.

[21] P. Chate, S. Lakde *Int. J. Thin. Fil. Sci. Tec.* 4 (2015) 237.

[22] B. Cullity *Elements of X-ray diffraction, 2nd Ed., Addison Wesley*, 1978, P-102.

[23] P. Chate, D. Sathe, P. Hankare, U. Sankpal, *J. Mater. Sci.: Mater. Electron.* 24 (2013) 2000.

[24] 41. D. Richards, R. Angelis, M. Kramer, J. House, D. Cunard, D. Shea, *Adv. X-ray Anal.* 47 (2004) 354.

[25] C. Suryanarayana, M. Grant Norton, *X-ray Diffraction: A Practical Approach, Springer, New York,* 1998.

[26] M.P. Deshpande, Nitya Garg , SandipV.Bhatt, Pallavi Sakariya, S .H.Chaki *Mater. Sci. Semicond. Process.* 16 (2013) 915–922

[27] C. Mehta, J. Abbas, G. Saini, S. Tripathi *Chalcogen. Lett*. 4 (2007)133.

[28] U. Woggon, *Optical properties of semiconductor quantum dots, springer, Tracts in Modern Physics, Berlin,* 1997.

[29] R. Kale, C. Lokhande *Appl. Surf. Sci.* 223 (2004) 343.

[30] C. Lokhande, E. Lee, K. Jung, O. Joo *Mater. Chem. Phys.* 91 (2005) 200.

[31] A. Khomane *Mater. Res. Bull.* 46 (2011) 1600.

[32] R. Petriz *Phys. Rev.* 100 (1956) 1508.

[33] F. Shalleross *Trans. Met. Soc. AIME* 236 (1966) 309.

[34] H. Berger, G. Janiche, N. Grachovskay, *Phys. Stat. Sol.* 33 (1969) 417.