

Influence of Synthesizing Temperatures on the Crystallinity, Morphology and Band Gap of CdSe Thin Films

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Abstract—CdSe thin films were deposited using Chemical Bath Deposition (CBD) by maintaining the bath at 20 °C, 40 °C, 60 °C and 80 °C temperatures. The thin films were deposited on ordinary glass substrates then characterized for their crystallinity, morphological and optical properties. From the X-ray Diffraction (XRD) analysis; it was revealed that there was a significant difference in crystallinity and the UV-vis spectroscopy enhanced the study of the energy band gaps which showed a drastic shifting. The study performed on the surface morphologies of the CdSe thin films exhibited a double layer of deposition; but did not show considerable difference from each other for different temperatures. The EDS pattern helped in determining the stoichiometric ratio.

Keywords— CdSe, Chemical Bath Deposition, Temperature Effect, Crystallinity, Energy Band Gap, Surface Morphology and EDS.

I. INTRODUCTION

The physical properties of the metal chalcogenide semiconducting thin films have been mainly governed by the method of preparation and their preparative conditions that comprises precursors type and their relative concentrations of metal and chalcogenide ions, substrate temperature, solution pH, nature of complex reagent, reaction time etc. It also critically depends on relative elemental composition of metal and chalcogenide, crystallinity of deposited film, structural phase and various types of defects originated during growth of thin films [1-6]. Many methods are prevalent until date; but the CBD routine has stood superior compare to most of the methods [1]. Narayana Swamy T N [2] et al have performed work on CdSe thin film. Research has also been performed on the applications of CdSe thin films [7].

II. MATERIALS & PROCEDURE

0.25 M Cadmium acetate and freshly prepared 0.25 M sodium selenosulphate were used as the precursors of CdSe. Narayan Swami T. N. [2] has explained the growth reaction mechanism of the CdSe thin films. The

preparation of cadmium selenide thin films were carried out by making use of the CBD by means of an aqueous ammonia 30% solution. All chemicals used were A. R. grade supplied by s. d. fine chem. Ltd. Mumbai. The films of cadmium selenide were developed on glass substrates from an aqueous alkaline bath (PH > 12). The chemical reaction has been mention by C. A. Vanderhyde et al [8] in their article.

In order to study regarding the influence of deposition temperature; CdSe films are deposited at different temperature at 20 °C, 40 °C, 60 °C and 80 °C for optimized duration.

2.1 Chemical Bath Deposition of CdSe Thin Films at Different Temperature:

The deposition of CdSe thin film is actually based on the slow release of Cd²⁺ and Se²⁻ ions in the solution that condense onto the substrate. For this, Cadmium acetate along with ammonia 30% had been used as complexing agent to release Cd²⁺ ion source and sodium selenosulphate to release Se²⁻ ion source into the solution.

2.2 Growth and Reaction Mechanism for the Formation of Thin Films:

The growth of thin films strongly depends on growth conditions, such as duration of deposition, composition and temperature and pH of the solution, and topographical and chemical nature of the substrate. The film formation in CBD involves two steps, nucleation and particle growth. Froment and Lincot [9] had proposed that the nucleation is associated with the agglomeration of colloids formed in solution by the homogeneous reaction. It is called as 'cluster by cluster' growth that results into formation of films. The latter is a growth mechanism involving the reaction of atomic species at the substrate surface; also called an 'ion by ion' process.

Table. 1 Optimized parameters for CdSe thin films at different temperature

Deposition conditions			
Ion Sources	Deposition Temp. (°C)	Deposition Time (hrs)	Thickness (μm)
Cadmium acetate, Sodium selenosulfate, liquid NH ₃	20	96	0.600
Same as above	40	15	0.582
Same as above	60	8	0.594
Same as above	80	3.5	0.606

The dominance of one given mechanism is governed by the classical laws of homogeneous versus heterogeneous nucleation on a solid surface, involving the super saturation ratio in the solution and the catalytic activity of the substrate [10]; in short, the growth mechanism depends on the experimental conditions. The deposition temperature affects the rate of release of chalcogenide ions and dissociation of metal ions from the complex reagent. From our experiment it is important to note that CdSe film formation takes place at a wide range of temperatures.

III. CHARACTERIZATIONS

The film thickness had been measured using weight difference method by using a sensitive digital microbalance. X-ray diffraction (XRD) patterns of the deposited thin films were recorded using a Rigaku miniflex tabletop X-ray Diffractometer with CuKα

radiation. The XRD data was collected with a scan rate of 2 ° per minute. The shape, size and distribution of nanostructures were observed with scanning electron microscope (SEM) model JEOL JSM-6010 and Tescan depending on the availability, attached to an energy dispersive X-ray analyzer (EDXA), Oxford Instruments, to measure the elemental composition. To study the optical properties, the optical absorption spectra were recorded with UV-Visible spectrophotometer (Shimadzu UV 1800).

3.1 X-ray Diffraction (XRD) Results & Discussion:

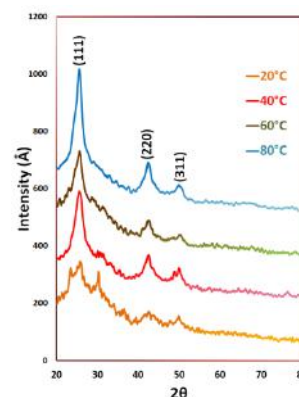


Fig. 1 XRD of CdSe thin films at different temperatures

As already stated cadmium selenide thin films can grow with metastable sphalerite cubic (zinc blende type) or stable hexagonal (wurtzite type) structure [11]. In order to determine the crystal structure of CdSe thin films, the XRD patterns of the deposited thin films were analyzed. The XRD patterns of CdSe thin films deposited at different temperature are shown in Fig. 1. The observed XRD data was compared with standard JCPDS data files [12]. The XRD pattern depicts that the film deposited at a temperature lower than room temperature (20 °C) is of poor crystalline nature. The peaks over a broad hump could be assigned to (111), (220) and (311) planes that corresponds to sphalerite (cubic phase) of CdSe [13]. The low intensity peaks shows that the CdSe film deposited at 20°C is composed of coarsely fine crystallites or nanocrystalline. It may be due to slow release of Se²⁻ ions from relatively stable Na₂SeSO₃ precursor at lower temperatures. Also the film prepared at 20°C gives one additional unwanted peak nearly at 31° (2θ). It is possibly due to the presence of either Cd(OH)₂, [13], due to scarcity or delay in release of Se²⁻ ions at low temperature. Since, at a lower temperature Se²⁻ ions possibly releases slowly from the Na₂SeSO₃ precursor. Fig. 1 also depicts the XRD patterns of the films deposited at higher temperature. The relative intensities of the peaks are in good agreement with standard data [12]. However, the

positions of peaks were slightly shifted to lower 2θ values, due to induced tensile strain in CdSe. This could be possible because of the early nucleation taking place in accordance with higher deposition temperatures. The XRD patterns showed that with increase in temperature of deposited films, the diffraction peaks became sharper with a decrease in the full width at half-maximum (FWHM). It clearly indicates that there is improvement in crystallinity of deposited CdSe thin films at a higher temperature. It is worthwhile to note that the XRD graphical patterns did not show any of the unwanted peaks corresponding to $\text{Cd}(\text{OH})_2$, CdO or SeO_2 at any stage of higher temperature, indicating the high purity of the deposited film, etc. The sharpness of the peaks determined the degree crystallinity of the films that were deposited at different temperatures. It was perceived that the crystallinity was very poorly developed at a lower temperature and was found to significantly increase at higher temperatures, indicating the dependence of the crystallinity in accordance with the temperature of the bath solution. Previous reports on the chemically synthesized CdSe thin films exhibited films forming either cubic (zinc blende) or hexagonal (wurtzite) type structure depending on growth conditions. Pawar et al [14] reported nanocrystalline cubic phase of CdSe thin films developed at 70 °C for 8h. Esparza-Ponce et al [15] reported that the CdSe thin films developed at 80 °C grown with cubic phase. Gopakumar et al [16] reported hexagonal crystal structure of CdSe thin films developed by the CBD at temperatures of 90 °C. Purohit et al [17] obtained cubic structure for the CBD deposited thin films. It clearly illustrates that the grown crystal structure of CdSe thin films deposited by CBD method was mainly governed by the their preparative conditions such as type of precursors (metal and chalcogenide ions) and their relative concentrations, pH of resultant solution, nature of complex reagent, reaction time and temperature etc. The temperature played a vital role on the crystallinity of thin films.

3.2 Elemental Composition Analysis:

As a representative EDS pattern of CdSe thin films at deposited 40 °C are revealed in Fig. 2. The average ratio of atomic percentage of Cd:Se was 52.00:48.00, showing that the samples are in good stoichiometric ratio, with slightly excess in Cd atoms.

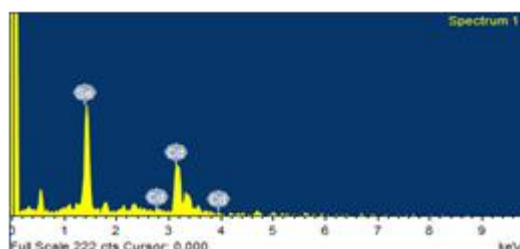


Fig. 2 EDS of CdSe thin film at 40 °C

3.3 Surface Morphology Results and Discussion:

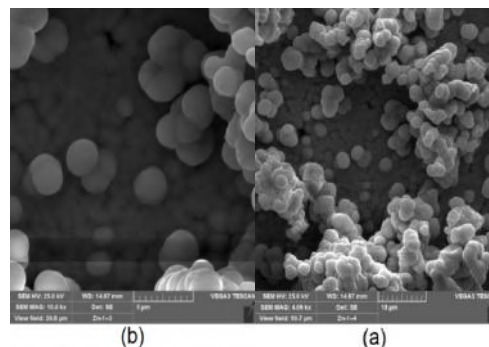


Fig. 3(A) SEM of CdSe thin films deposited at 20 °C for (a) 4 KX and (b) 10 KX

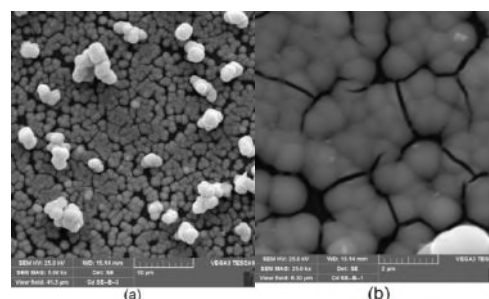


Fig. 3(B) SEM of CdSe thin films deposited at 40 °C for (a) 5 KX and (b) 25 KX

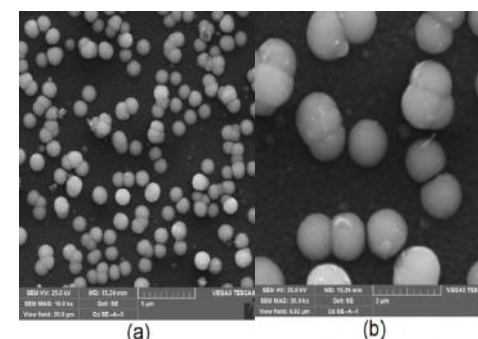
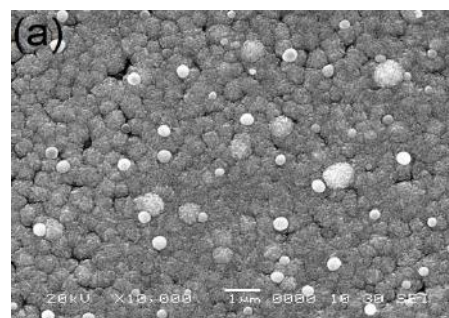


Fig. 3(C) SEM of CdSe thin films deposited at 60 °C for (a) 5 KX and (b) 25 KX



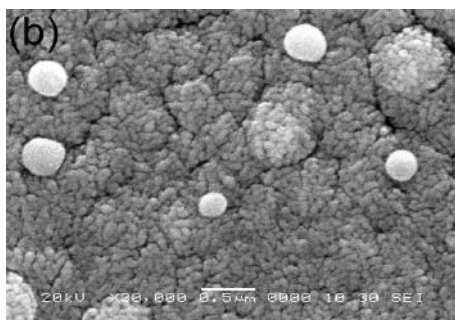


Fig. 3(D) SEM of CdSe thin films deposited at 80 °C for (a) 5 KX and (b) 25 KX

Fig. 3(A), 3(B), 3(C) and 3(D) shows scanning electron microscope (SEM) images of CdSe thin films deposited at different temperature. The SEM images revealed that the CdSe thin films deposited at different temperatures are uniform and homogeneous, and well covered the substrate thoroughly. Extreme minute examination further revealed a bi-layer growth of CdSe over the substrate surface. The somewhat smooth CdSe particles were uniformly deposited on the substrate surface that forms an initial layer. The initially formed layer was covered by a latter with three dimensional (3D) micron-sized spherically shaped CdSe grains. These microspheres were heavily packed with the primarily formed layer and were closely connected with each other. The microspheres were composed of tiny CdSe nucleates or nanodots, which is more clearly visible in the SEM micrographs of the CdSe thin films deposited at higher temperature. As a result, micro-spherical grains are bigger than the individual crystallites. The observed morphology probably explained by a two stage growth mechanism. The first stage is attributed to instantaneous nucleation and 2D lateral growth that covers the surface of substrate, while the second stage was due to 3D nucleation and growth at random sites on top of the first layer [18]. The SEM image of the film deposited at 80 °C clearly shows that the microstructures consisted with minute nanocrystallites that are engaged with each other to form the resultant morphology.

IV. OPTICAL ABSORPTION RESULTS & DISCUSSION

According to Y.G. Gadage et al the energy band gap 'E_g' by using absorption data and applying Tauc's relation [19]. Fig. 4 shows the graphs of $(\alpha h\nu)^2$ against $h\nu$ for CdSe thin films deposited at different temperatures (20 °C, 40 °C, 60 °C, 80 °C). The 'E_g' value of CdSe thin film prepared at a lower temperature (20 °C) is 2.1 eV, which is much higher than the standard bulk 'E_g' value of CdSe. The values of

'E_g' for thin films prepared at 40 °C, 60 °C and 80 °C was 1.96 eV, 1.87 eV and 1.8 eV respectively. These values are greater than the standard 'E_g' value of bulk CdSe (1.72 eV), such high values of 'E_g' is due to a size quantization effect that was commonly observed in nanocrystalline metal chalcogenide semiconductors.

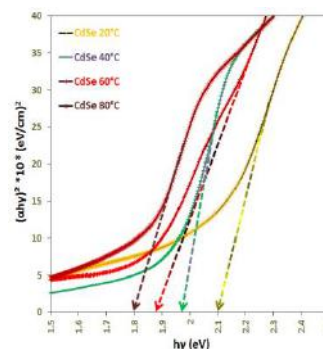


Fig.4. Plot of $(\alpha h\nu)^2$ vs. $h\nu$ of CdSe thin films deposited at different temperatures

V. DISCUSSION

The XRD patterns (Fig 1) of CdSe thin films deposited at various temperatures also revealed the nanocrystalline nature of CdSe thin films. As the deposition temperature was increased the diffraction peaks becomes sharper with decreasing full width of half maximum that shows improvement in crystallinity and increase in crystallite size. Hence increase or improvement in crystallite size with increasing deposition temperature reduces the 'E_g' value of deposited CdSe thin film and consequently approaches towards bulk value of CdSe material [14, 19-21].

VI. CONCLUSION

From the above studies, it is concluded that the CdSe films, can be deposited at different temperatures ranging from 20-80°C. The above study concludes that the growth of the film at various temperatures is mainly governed by ion-by-ion process. The film grown at 20 °C with was poorly crystallized with cubic phase along with presence of hydroxide and/or oxide content which resulted in a band that was too wide compare to the bulk band gap. The increase in deposition temperature improves the crystallinity of the CdSe thin films deposited and also decreases the band value. The films were grown with a pure cubic phase and it is worth to mention that in the present work, no evidence has been observed for the growth of hexagonal phase of CdSe thin films in the range of the deposited temperatures. The band gaps of the CdSe thin films were found to decrease with increasing

deposition temperature and consequently approached towards bulk band value.

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REFERENCES

- [1] D. Mugle, M. Barote, G. Jadhav, (2018), Study on Photoelectrochemical Properties of Ternary Doped Cd_{1-x}Zn_xS thin Film Deposited by Chemical Bath Deposition, IJASE, 6(2): 87-95.
- [2] Narayana Swamy T N, Pushpalatha H L, Ganesh R, (2017), Synthesis of CdSe Thin Film by Chemical Bath Deposition and Characterization, IJESIT, Vol.6, Iss.1: 41-49
- [3] G. Hodes, (2003), Chemical Solution Deposition of Semiconductor Films, Marcel Dekker, Inc., New York.
- [4] R. S. Mane, C. D. Lokhande, (2000), Chemical deposition method for metal chalcogenide thin films, Mater. Chem. Phys. 65: 1-31.
- [5] O. Masala, R. Seshadri, (2004), Synthesis Routes for Large Volumes of Nanoparticles, Annual Review of Materials Research, 34(1): 41-81.
- [6] S. M. Pawar, B. S. Pawar, J. H. Kim, Oh-Shim Joo, C. D. Lokhande, (2011), Recent status of chemical bath deposited metal chalcogenide and metal oxide thin films, Current Appl. Phys.11(2): 117-161.
- [7] O. I. Olusola, O. K. Echendu, I. M. Dharmadasa (2015), Development of CdSe thin films for application in electronic devices, J. Mater. Sci.: Mater. Electron., 26: 1066–1076.
- [8] C. A. Vanderhyde, S.D. Sartale, Jayant M. Patil, Karuna P. Ghoderao, Jitendra P. Sawant, Rohidas B. Kale (2015), Room temperature chemical bath deposition of cadmium selenide, cadmium sulfide and cadmium sulfoselenide thin films with novel Nanostructures, Solid State Sci. 48: 186-192.
- [9] M. Froment, D. Lincot, (1995), Phase formation processes in solution at the atomic level: Metal chalcogenide semiconductors, Electrochimica. Acta 40: 1293-1303.
- [10] VON A. E. NIELSEN, (1964), KINETICS OF PRECIPITATION, PERGAMON PRESS, OXFORD.
- [11] P. P. Hankare, V. M. Bhuse, K. M. Garadkar, A. D. Jadhav, (2001), A novel method to grow polycrystalline HgSe thin films, Mater. Chem. Phys., 71: 53-57.
- [12] JCPDS File No. 19-0191
- [13] JCPDS File No. 73-2207
- [14] S. A. Pawar, R. S. Devan, D. S. Patil, A. V. Moholkar, M. G. Gang, Y. R. Ma, J. H. Kim, P. S. Patil, (2013), Improved solar cell performance of chemosynthesized cadmium selenide pebbles, Electrochimica. Acta 98: 244-254.
- [15] H. E. ESPARZA-PONCE, J. H. BORJA, A. R. ROJAS, M. C. SÁNCHEZ, Y. V. VOROBIEV, R. R. BON, J. E. PÉREZ-ROBLES, J. G. HERNÁNDEZ, (2009), GROWTH TECHNOLOGY, X-RAY AND OPTICAL PROPERTIES OF CdSe THIN FILMS, MATER. CHEM. PHYS. 113: 824-828.
- [16] N. Gopakumar, P. S. Anjana, P. K. Vidyadharan Pillai, (2010), Chemical bath deposition and characterization of CdSe thin films for optoelectronic applications, J Mater Sci 45: 6653-6656.
- [17] A. PUROHIT, S. CHANDER, S. P. NEHRA, C. LAL, M. S. DHAKA, (2015), EFFECT OF THICKNESS ON STRUCTURAL, OPTICAL, ELECTRICAL AND MORPHOLOGICAL PROPERTIES OF NANOCRYSTALLINE CdSe THIN FILMS FOR OPTOELECTRONIC APPLICATIONS, OPT. MATER., 47: 345-353.
- [18] G. Hodes, (2002), Chemical Solution Deposition of Semiconductor Films, CRC Press
- [19] Y. G. Gudage, N. G. Deshpande, A. A. Sagade, R. P. Sharma, S. M. Pawar, C. H. Bhosale, (2007), Photoelectrochemical (PEC) studies on CdSe thin films electrodeposited from non-aqueous bath on different substrates, Bull. Mater. Sci., Vol. 30, No. 4: 321–327.
- [20] E. Lifshitz, I. Dag, I. Litvin, G. Hodes, S. Gorer, R. Reisfeld, M. Zelner, H. Minti, (1998), Optical properties of CdSe nanoparticle films prepared by chemical deposition and sol gel methods, Chem. Phys. Lett. 288: 188-196.
- [21] K. R. Murali, P. Sasindran, (2004), Structural and optical properties of sonoelectrochemically deposited CdSe films, J. Mater Sci. 39: 6347-6348