Effect of Deposition Temperature and Time on the Structural, Optical and Morphological Properties of Nanocrystalline CdSe Thin Films Deposited by Chemical Bath Deposition

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Abstract
Nanocrystalline thin CdSe films were prepared by Chemical Bath Deposition (CBD) method using potassium nitrilotriacetic acid cadmium complex and sodium selenosulphite. The as deposited films were red in colour, uniform and well adherent to the glass substrate. These films were strongly dependent on the deposition parameters such as bath composition, deposition temperature and time. Films were annealed at 350°C for four hours. The morphological, structural and optical properties were studied using X-ray diffraction (XRD), UV-VIS spectrophotometer measurements, scanning electron microscopy and atomic force microscopy. The XRD analysis confirmed that films are predominantly in hexagonal phase. The crystallite size increased from 4.4 nm to 5.9 nm with increase in deposition time. The optical band gap decreased from 2.12 eV to 1.72 eV with increase in deposition time. Scanning electron micrograph shows that the grains are uniformly spread all over the film and each grain contains many nanocrystals of size 4.4 nm to 5.9 nm.

Keywords
Chemical Bath Deposition, Nanocrystalline, Morphological, Optical Properties, Structural Properties

I. Introduction

Cadmium Selenide (CdSe) is one of the most important among all chalcogenides. CdSe is a very good absorber of electromagnetic radiations hence CdSe films are used as a photoelectrode for conversion of light energy into electric energy. This has led to its widespread use in electronic and optoelectronic devices [1]. Due to their unique physical and chemical properties nanomaterials have been studied widely. Their fundamental properties like optical and electrical can be varied by controlling the size, structure and surface states [2]. CdSe thin films can be deposited using various techniques like thermal evaporation, sol-gel, spin coating, pulsed laser deposition, ultrasonic spray pyrolysis, screen printing, chemical bath deposition and successive ionic layer adsorption reaction (SILAR) [3-7]. Chemical bath deposition is preferred over other methods because it is a simple, very low cost technique that produces homogenous, uniform, good quality thin films [8].
In this work, CdSe thin films are deposited by CBD method. The results on morphological, optical and structural properties are discussed.

II. Experimental Details

A. Deposition of the Films

Nanocrystalline CdSe thin films have been deposited by using potassium nitrilotriacetic acid (K_3NTA) as a complexing agent. In the deposition of films cadmium sulphate and sodium selenosulphite were used as a source of Cd^{+2} and Se^{-2} ions respectively. The Cd^{+2} ions are complexed with potassium nitrilotriacetic acid. The complex slowly releases Cd^{+2} ions, which are used for slow and homogenous deposition of CdSe thin films. The films were deposited on commercially available glass substrates. These substrates were washed with hot chromic acid and then cleaned ultrasonically prior to the deposition.
Na_2SeSO_3 is prepared by stirring 0.2M Se with 0.5M Na_2SO_3 at 60°C for several hours. The deposition solution was prepared by diluting 0.5M $CdSO_4$ solution with water and then 0.7M K_3NTA was added. The pH of the solution was adjusted to 8.5 by adding KOH. The two solutions were added and their pH was finally adjusted to 10 by adding KOH solution [8-9]. Three samples were prepared for 60 min., 120 min. and 150 min. at 50°C. The films were taken out of the bath and rinsed with deionized water. The films were found to be homogenous and well adherent to the substrate and are red in color. The films were annealed at 350°C for 4 hrs.

B. Characterization of Films

X-Ray Diffractometer Bruker D8 focus with CuKα radiation (1.5406A°) was used for crystallographic analysis of the film in the 2θ range 20° to 80°. Surface morphology studies were done using scanning electron microscope (ZEISS SUPRA 55) and atomic force microscope (PARK SYSTEM XE 70). The optical properties of the CdSe thin films were studied using UV-VIS spectrophotometer (SHIMADZU UV-1700) at room temperature in the wavelength range 200nm.-1100nm.

III. Results and Discussions

A. Structural Analysis

The crystallite size and phase of nanocrystalline CdSe thin films have been determined using X-ray diffraction measurements. CdSe films exist in either cubic or hexagonal phase. Sometimes a mixture of the two phases is also reported [10]. Fig. 1 shows the XRD patterns of the annealed CdSe films deposited for 60 min. (sample a), 120 min. (sample b) and 150 min. (sample c) respectively at 50°C. The analysis of the observed diffraction data was done using the JCPDS data [11]. The films are in hexagonal phase. There are three dominant diffraction peaks (002) (101) and (110). The (002) peak is the preferred orientation. Structural parameters are shown in Table 1. The average crystallite size was determined from peaks at 2θ=25.35° using the Debye Scherer formula

$$D = \frac{0.94\,\lambda}{\beta \cos\theta}$$

Where β is FWHM in radians, λ is wavelength of x-ray used. With increase in deposition time the crystallite size increased from 4.4 nm. to 5.9 nm. The crystallite size and FWHM are shown in Table 2.

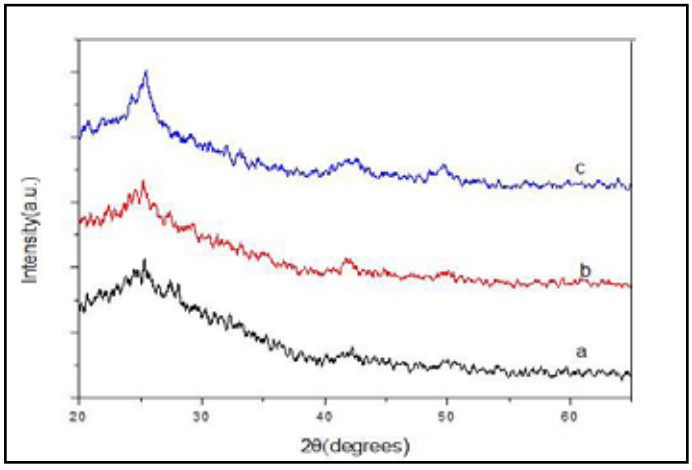


Fig. 1: XRD Patterns of Sample a, b and c

Table 1: Structural Parameters Calculated from XRD Patterns

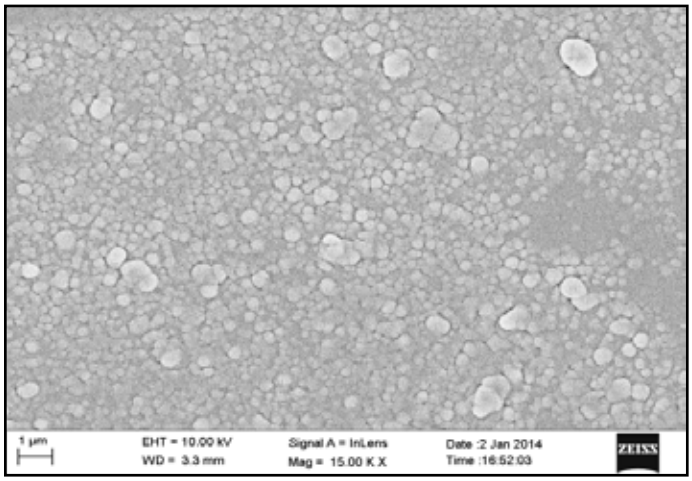
d_{st} (Å) JCPDS	d_{obs} (Å) sample a	d_{obs} (Å) sample b	d_{obs} (Å) sample c	(hkl)
3.51	3.49	3.51	3.49	$(002)_H$
3.29	3.25	3.25	3.20	$(101)_H$
2.15	2.14	2.15	2.15	$(110)_H$

Table 2: FWHM, Average Crystallite size Calculated from XRD Pattern and Optical Band Gap Calculated From UV-VIS Data

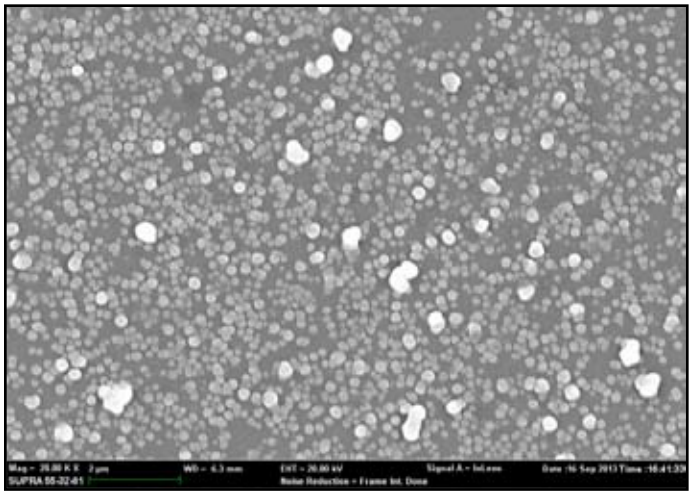
sample no.	FWHM (radians)	Average crystallite size(nm)	Band Gap(Eg) (eV)
a	0.0322	4.4	2.129
b	0.0251	5.6	1.755
c	0.0241	5.9	1.727

B. SEM Analysis

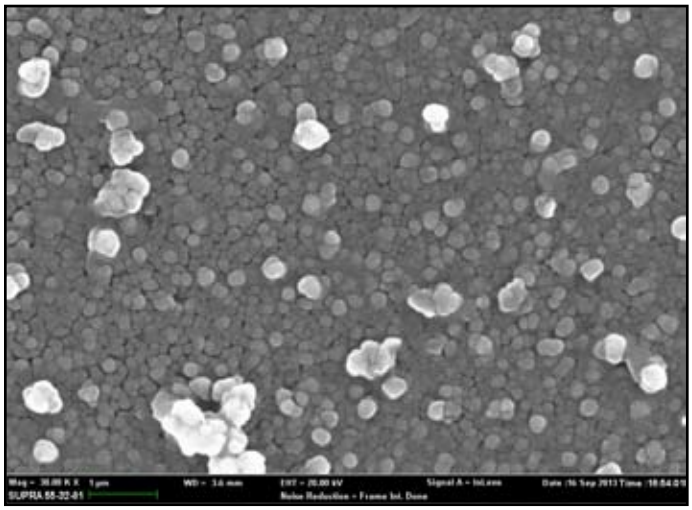
SEM is a convenient technique for studying morphology of the film. The SEM images of nanocrystalline thin CdSe films for samples 'a', 'b' and 'c' are shown in fig. 2a, 2b and 2c respectively. Images show large number of uniform grains spread all over the substrate. The average diameter of grains by and large increases with increase in deposition time. The average size of grain is 260 nm., 190 nm. and 270 nm. for films deposited for sample 'a', 'b' and 'c' respectively. The density of grains was found to be largest for sample 'c' and smallest for sample 'b'.



2(a)



2(b)



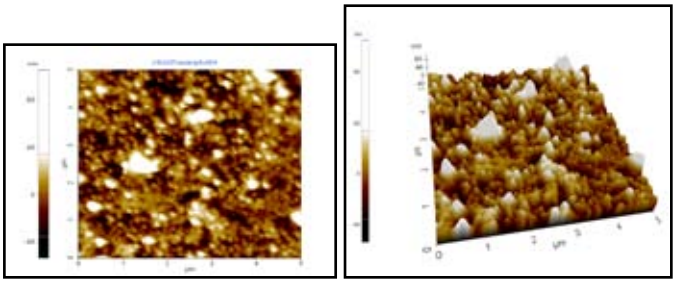
2(c)

Fig. 2: The SEM Micrographs of CdSe Films Annealed at 350°C. The Deposition Times of 2(a), 2(b) and 2(c) are 60, 120 and 150 Minutes Respectively.

C. Atomic Force Microscope Studies

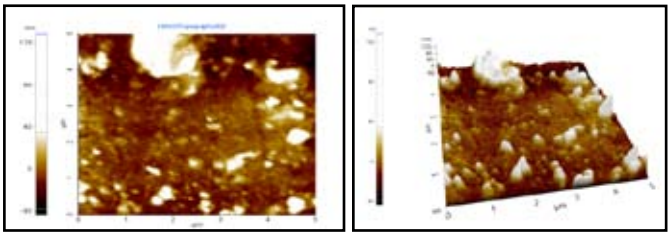
The morphology of the film is influenced by the deposition parameter. To have a deeper insight into the structural features of CdSe thin films atomic force microscopy has been performed. This method provides information about the grain size, surface roughness and structure of thin films. The 2D images of samples 'a', 'b' and 'c' are shown in fig. 3(a), 4(a) and 5(a) respectively.

The 3D images are shown in fig. 3(b), 4(b) and 5(b) respectively. From 3D images it is clear that there is particle agglomeration, which led to the formation of islands of different sizes. They have elongated morphology. The average grain size and roughness are shown in Table 3. The average roughness for samples 'a' and 'c' is nearly the same where as for sample 'b' the roughness is nearly three times of other samples. This can be clearly seen from the 3D images, the islands are very dense for samples 'a' and 'c' in comparison to sample 'b', which is the cause of large roughness. The average grain size by and large increase with increase in deposition time.



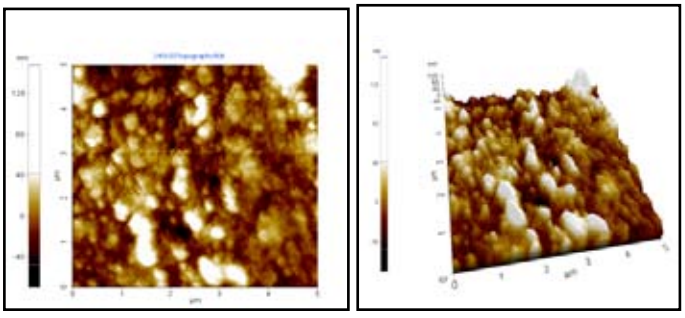
3(a) 3(b)

Fig. 3: 2D and 3D AFM Images of CdSe Films Deposited for 60 Minute



4(a) 4(b)

Fig. 4: 2D and 3D AFM images of CdSe films deposited for 120 minute.



5(a) 5(b)

Fig. 5: 2D and 3D AFM images of CdSe films deposited for 150 minute.

Table 3: Roughness and average grain size measured using atomic force microscopy.

Sample no.	Roughness (nm)	Average grain size (nm)
a	15.826	290
b	44.354	481
c	16.729	394

D. Optical Studies

The fundamental absorption which corresponds to the transition from valence band to conduction band, can be used to determine the band gap of the material [13]. The absorbances of all the film samples were measured in the wavelength range 200nm-1100nm. The relation between 'α' and the incident photon energy 'hν' is

$$\alpha = \frac{A(h\nu - E_g)^n}{h\nu}$$

where A is constant, Eg is optical band gap, n is a constant =1/2 for direct band gap semiconductor [8]. The optical band gap is obtained by extrapolating the straight line portion of $(\alpha h\nu)^2$ vs hν, fig. 5. The optical band gap increase from 1.727 eV to 2.129 eV as the particle size decreased from 5.9 nm to 4.4 nm.Table 2. The observed values of Eg for nanocrystalline CdSe thin films is higher than that of the bulk sample (1.74 eV) due to quantum confinement of carriers in the semiconductor nanocrystals [13]. This increase of band gap is called blue shift. The results agree well with earlier investigator results [12].

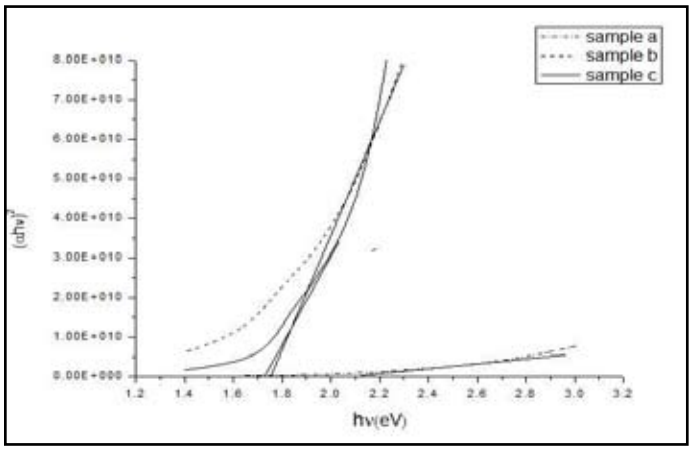


Fig. 5: A Plot of $(\alpha h\nu)^2$ vs hν for CdSe Films

IV. Conclusion

CdSe thin films have been deposited successfully using chemical bath deposition. XRD characterization of CdSe thin films confirmed that the films are nanocrystalline in nature and hexagonal in phase with (002) preferred orientation. With the increase in deposition time the average crystallite size increased whereas optical band gap decreased. Thus there is decrease in size quantization. The SEM and AFM results confirmed that each grain contains many nanocrystals. From AFM results particle agglomeration was confirmed.

References

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