

Effect of Temperature on Morphological, Structural and Optical Properties of Cadmium Selenide (CdSe) Thin Films Deposited by Chemical Bath Deposition Method

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Abstract

In this work CdSe thin films were successfully deposited on glass substrates by using tartaric acid as complexing agents, sodium selenosulphite as source of Se^{2-} and cadmium acetate as sources of Cd^{2+} in basic medium. The thin films of the binary compound CdSe were also deposited at various temperature ranges and the effects of these deposition temperatures on the properties of the thin films were investigated. The as-deposited CdSe thin films were characterized by X-Ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive x-ray (EDX) and optical absorption spectroscopy. The XRD studies showed that all the CdSe samples had cubic crystal structure with space group F-43m. This is the XRD pattern of CdSe thin films at different deposition temperature. The diffracted peaks are indexed as the (111), (220) and (311) planes which are coincided with 26.001, 42.985 and 49.848 angle 2θ . XRD results showed that as the deposition temperature increased three peaks were appeared. This may be attributed with the enhancement of the crystal size with temperature. It is also noticed that the preferred orientation of the crystal was along the (111) plane for the two samples. The crystalline size of the CdSe thin films increases as the bath temperature increase. Conversely the interplanar distance between the lattice points were decreased. The SEM and EDX investigations revealed that, the CdSe thin films deposited at 60 °C and 80 °C were free from cracks and the deposited films were composed of the desired elements. The band gaps of the films were 1.78 eV, 1.75 eV and 1.70 eV for the deposition temperatures 60 °C, 70 °C and 80 °C respectively.

Keywords: Cadmium Selenide (CdSe), thin film

1. Introduction

Nano-crystalline semiconducting materials have been used in electronic, optoelectronic and solar energy conversion devices. II-VI compound semiconductors have the band gap between 1-3 eV in the visible region and these semiconducting materials are used worldwide in optoelectronic devices. Cadmium selenide (CdSe) is one of such popular semiconductor materials in this group and its physical properties have been constantly investigated during recent years for both fundamental and practical aims (R.I. Chowdhury et al., 2012). Structural properties of CdSe thin films were studied by X-ray diffraction. CdSe can form the hexagonal, wurtzite type structure or the cubic, zincblend-type structure (Y. G. Gudage et al., 2007).

CdSe is a direct band-gap semiconductor belongs to II-VI group, possesses excellent optoelectronic properties. CdSe has band gap of $E_g \approx 1.797$ eV in the wurtzite crystal phase and $E_g \approx 1.712$ eV in the zinc-blende phase such a wide band gap favors absorption over a wide range of the visible spectrum (M. L. Gaur et al., 2014). Normally, CdSe is an n-type semiconductor (S. Velumani et al., 2003) (N. Gopakumar et al., 2010).

Cadmium selenide (CdSe) thin films as II-VI group semiconductor are an important research field because of their wide application in various fields of optoelectronic devices (M.N. Zaher et al., 2010) (B. Alpers et al., 1999). This is due to their high transparency, wide and direct band gap width (1.74 eV), photoconductivity, high electron affinity and n-type conductivity. They can be crystallized in hexagonal, cubic or mixed (hexagonal cubic) forms (I.A. Kariper et al., 2014).

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 M. P. Deshpande et al., (2013) indicates that deposition was carried out at room temperature and the pH of value was kept constant around 10.50 ± 0.10 .

In this paper we present the effect of temperature on morphological, structural and optical properties of cadmium selenide (CdSe) thin films deposited from chemical bath containing cadmium acetate, tartaric acid ammonia and sodium selenosulphate, at a bath temperature at 60 °C, 70 °C and 80 °C and a pH of 9.5.

To the best of our knowledge, this is the first time cadmium acetate is being used as the source of cadmium ions in combination with tartaric acid as complexing agent for the deposition of CdSe thin film at a bath temperature at 60 °C, 70 °C and 80 °C and a pH of 9.5.

2 Materials and Methods

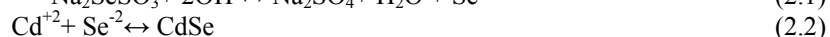
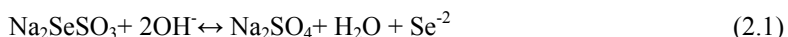
2.1 Substrate Preparation

The preparation of substrates is a critical aspect that can contribute to film adherence. 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.

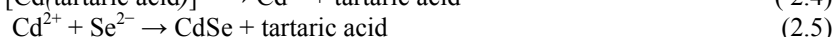
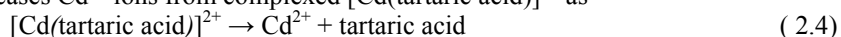
2.2 Deposition of Cadmium selenide Thin Films

For deposition of CdSe thin films, a chemical bath was prepared by mixing 13 ml (0.2M) cadmium acetate [Cd(CH₃COO)₂ · 2H₂O] acts as a source of Cd²⁺, 5 ml (1 M) tartaric acid [(CHOH·COOH)₂] acts as complex agent, in a 75 ml beaker. To this 5 ml (0.5 M) sodium selenosulphate (Na₂SeSO₃) acts as a source Se²⁻ was added at room temperature and the final volume was made to 65 ml by adding double distilled water. The pH of the reactive mixture was adjusted around 9.5 by adding some drops of ammonium hydroxide (NH₄OH). The beaker was then kept in water bath. The cleaned glass slides were inserted vertically on a special designed substrate holder that prepared in our lab, were a magneto-stirrer rotates at a constant rate per minute (rpm). Three systems were made and were kept at 60 °C, 70 °C and 80 °C bath temperature for 100 minute without disturbing. The CdSe thin film deposited on clean glass plate were taken out after 100 minute and allowed to dry in air. Similar observation has been reported by (Paresh Saha *et al.*, 2017).

Deposition of cadmium selenide (CdSe) thin film involves controlled release of cadmium ions from the cadmium tartaric acid complex and its reaction with Se²⁻ ions of Na₂SeSO₃ present in the reaction bath. The formation of CdSe involves the following steps: in the anionic precursor solution, the hydrolysis of sodium selenosulphite releases selenide ions reported by (Kariper, 2016). CdSe thin films are still produced using them, especially sodium selenosulphite.



The cationic precursor solution releases Cd²⁺ ions from complexed [Cd(tartaric acid)]²⁺ as



Tartaric acid was used to limit the hydrolysis of the metal ion and impart some stability to the bath (Hone *et al.*, 2015).

3. Samples Characterization

Sample characterization is an integrated process with thin film deposition. Different techniques were used for the characterization of the thin films. Structural characterization of the CdSe thin films was carried out by using a Bruker D8 x-ray diffractometer operating at 45 kV and 40 mA with Cu K α monochromatic radiation ($\lambda=0.15406$ nm) in the Bragg-Brentano geometry. Optical properties were studied by measuring the absorbance of the thin films at room temperature using Perkin Elmer Lambda 950 UV/VIS/NIR Spectrometer.

4. Characterizations CdSe Thin Films

4.1 Optical analysis

During this investigation the optical absorption measurement was carried out in the wavelength range from 300 nm to 800 nm by using a Perkin Elmer Lambda 950 UV/VIS/NIR spectrophotometer at room temperature. From equation (4.16), the band gap energy (E_g) can be obtained by taking the linear portion of the curve towards zero absorption (Ahv)² ≈ 0. As shown in the Figure 5.1, the estimated band gap values of the films deposited at 60^o C, 70^o C and 80^o C are 1.78 eV, 1.75 eV and 1.70 eV, respectively. The sharp rise in the absorption suggests that it is direct band gap semiconductor (N. Gopakumar *et al.*, 2010).

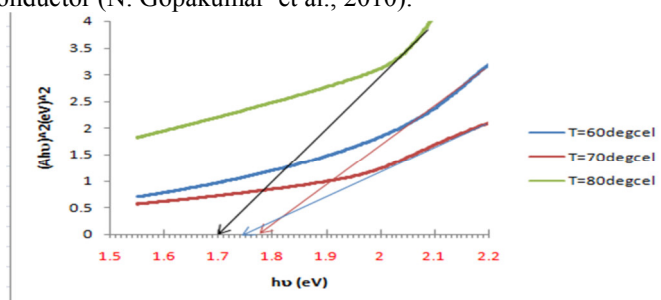


Figure 1 shows UV-Vis absorbance of the CdSe thin films grown from a chemical bath at different deposition temperatures, at T=60 °C, T=70 °C and T=80 °C.

According to this experimental result, the CdSe band gaps decreased from 1.78 eV to 1.70 eV as the bath temperature was increased from 60 °C to 80 °C, which was in good agreement with earlier reports (E. Gholami Hatam and Ghobadi, 2016). This may be due to the improvement of the crystal size with deposition temperature.

4.2 Surface Morphological Study

The surface morphology and elemental composition analysis of the thin films were investigated using a scanning electron microscopy (SEM). Figure 2 show the surface morphology of the CdSe thin films produced at three different bath temperatures by having magnification power (X2500).

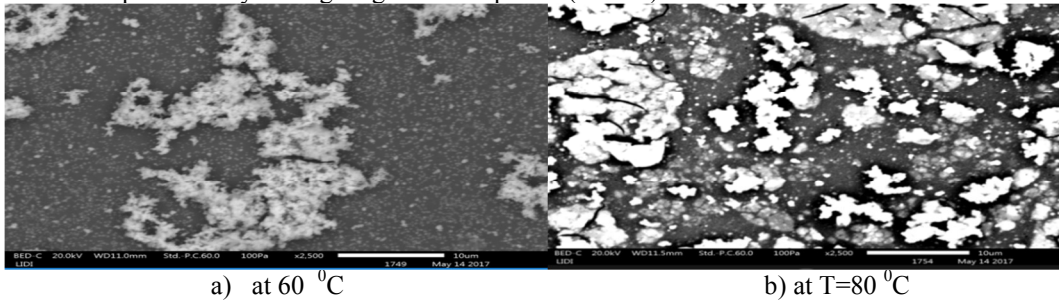


Figure 2 SEM micrographs of CdSe thin films deposited at 60 °C and 80 °C within (X2500) magnifications power.

The SEM image in figure 2 (a), and (b) indicates that glass substrate is over coated by CdSe uniformly. In addition to this there is substance which just like cotton that cover over CdSe thin films in some parts of the surface. As the bath temperature increased from 60 °C to 80 °C, the cotton like substance becomes increased its distribution. This may be due to the agglomeration of some nanoparticles to a bigger cluster.

4.3 Compositional Analysis

The elemental analysis of CdSe thin films deposited on glass substrate was performed using EDX analyses are presented in Fig.3

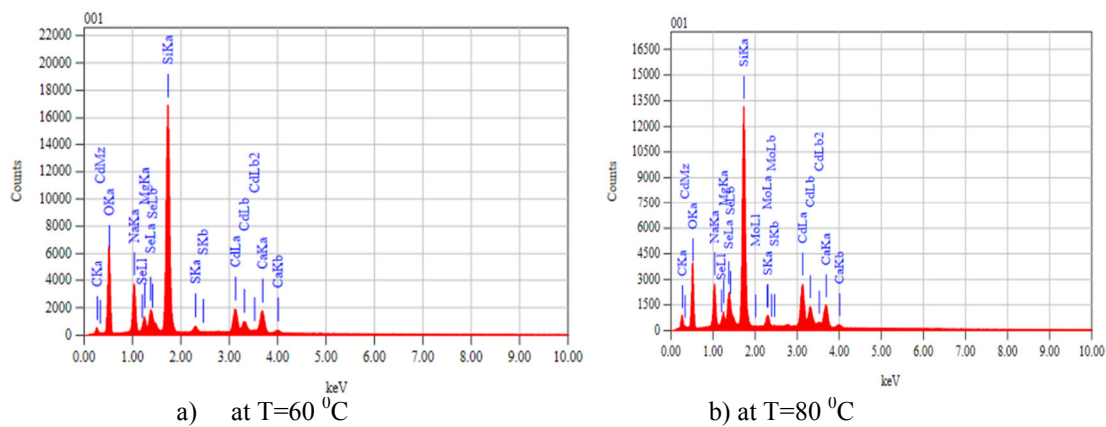


Fig.3 EDX pattern of CdSe films on glass substrate surface at different bath temperatures.

The elemental analysis of CdSe thin films deposited on glass substrate was performed using EDX analyses are presented in Fig.3. As the ranges of bath temperature increasing from 60 °C to 80 °C then the amount of Cd and Se concentration deposited on the glass substrate were increased since as the temperature increases the rate chemical reaction is increase until the equilibrium reaction was takes place. It is noted that there are some oxygen, carbon and other contamination of the films that can be attributed to contamination of the surface of the film from the atmosphere (Chowdhury *et al.*, 2012). In addition these impurities may be due to the silica glass substrate. The calculated Cd to Se atomic ratios of the thin films deposited at 60 °C, and 80 °C were 1.57:1, and 1.83:1, respectively. As the temperature increases the concentration Cd in the film increased.

4.4 Structural Analysis

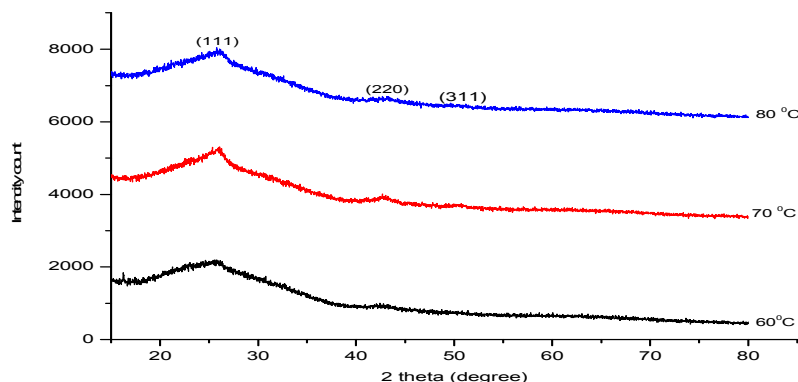


Fig.4. X-ray diffraction patterns for CdSe thin films grown with three different bath temperatures deposited for 100 minute.

The CdSe thin film deposited at 60 °C is almost amorphous. However, the films deposited at 70 °C and 80 °C show three very small peaks but, the third peak not visible in detail. The diffracted peaks are indexed as the (111), (220) and (311) planes which are coincided with 26.001, 42.985 and 49.848 angle 2θ. The diffracted planes are well matched with JCPDS card No: 01-073-6987 of cubic crystal structure. The above XRD results showed that as the deposition temperature increased three peaks were appeared. This may be attributed with the enhancement of the crystal size with temperature. It is also noticed that the preferred orientation of the crystal was along the (111) plane for the samples. The XRD results are well agreed with earlier report by (A.S. Khomanea, *et al.*, 2010). The average crystalline size (D) was obtained from the X-ray diffraction pattern, using the Scherrer (1918), formula which is given as:

$$D = \frac{K\lambda}{\beta_{2\theta} \cos\theta} \quad (5.1)$$

And also from Bragg's law we can obtain $d = n\lambda/2\sin\theta$, where $n = 1, 2, 3, \dots$. And K is shape factor.

The crystalline parameters had been calculated from XRD pattern as shown in the following table 1 below.

Table1. The crystalline parameters obtained from XRD pattern for CdSe thin films deposited on glass substrate at three different bath temperatures.

Temperature(°C)	(hkl)	FWHM[β(2θ)]	d-space in(A ⁰)		Position of peak (2θ)	Average crystalline size D(A ⁰)
			Standard	observed		
60	Unknown	Unknown	Unknown	unknown	Unknown	Unknown
70	111	6.5514	3.493	3.424	26.001	12.6711
80	111	6.201	3.493	3.420	26.027	13.3229
	220	Unknown	2.139	2.102	42.985	Unknown

As we have seen from this table, as the bath temperature increases from 70 °C to 80 °C the average crystallites size were increased while the interplanar distance between lattice points is decrease.

5. Conclusion

In this work, the CdSe nanocrystalline thin films were successfully deposited by CBD method on the glass substrate at three different bath temperatures. Using the various characterization techniques it was concluded that the deposition temperature has a characteristic role for synthesis of the thin layers. The optical band gap studies for deposited CdSe thin films after 100 minutes indicated that the optical band gap decreases from 1.78 eV to 1.70 eV as temperature increases from 60 °C to 80 °C. Therefore, the deposition temperature and band gap energy have inversely proportional to each other. XDR showed the deposited CdSe thin films had simple cubic crystal structure with the (111) plane preferred orientation. The crystalline size of the CdSe thin films increases as the bath temperature increase. Conversely the interplanar distance between the lattice points were decreased. SEM micrograph indicated the surface morphology deposited CdSe thin films were more compact irregular shapes. EDX spectroscopy indicated that the deposited films were composed of the desired elements.

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