Review Article

Review on Effect of Deposition Parameters and Annealing on Structural Properties of Nanocrystalline MSe Thin Films by Chemical bath Deposition

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Abstract: Chemical bath deposition technique has been used to synthesize metal selenide (MSe) thin films. MSe(M= Sn, Zn, Pb, Cd and Cu) thin films are deposited on glass substrates in an aqueous alkaline medium using sodium selenosulphate as Se\(^{2-}\) ion source. The quality and the crystalline size of the MSe thin films has been calculated by X-ray diffraction (XRD). Information of the strain and the particle size has been obtained from the full widths at half maximum (FWHM) of the diffraction peaks. Solar selective coatings, solar control, photoconductors, solid state and photoelectrochemical solar cells, optical imaging, hologram recording, optical mass memories etc. are some of the applications of metal selenide thin films. In the present review paper we have discussed in detail, how the particle size varies by changing the deposition parameters like substrate temperature and deposition time and also describe the effect of annealing.

Keywords: MSe, thin films, structural, substrate temperature, deposition time, annealing, chemical bath deposition

INTRODUCTION

There has been an increasing demand of binary and ternary semiconducting chalcogenide thin films during the last few decades, because of the widespread applications in various fields of science and technology [1-6]. Chalcogenide films are the chains of random lengths and random orientations formed by bonding of chalcogen elements sulphur (S), selenium (Se) and tellurium (Te) and alloys containing these chalcogen as the major constituents [7]. These have low phonon energy, high photosensitivity, easy fabrication and processing leads to various photonic applications such as ultrafast optical switches, frequency converters, optical amplifiers, optical recording devices, integrated optics, infrared lasers and infrared transmitting optical fibers [8-10]. Among the many chalcogenide semiconductors, CdSe, ZnSe, SnSe and PbSe have received more attention because these materials possess the following criteria, that make them potential candidate in PEC solar cells: (i) the band gap is between solar energy spectrum making them capable of absorbing a major portion of solar energy (ii) they are chemically and electrochemically stable in either acid or alkaline condition and the constituent elements are abundantly available and cheap. These semiconductors form an interesting and important class of isomorphous materials, which are in many ways intermediate between two-dimensional systems and three-dimensional crystals [11]. These semiconductor MSe films, chosen for study, are direct wide band gap semiconductors. These materials show significant quantum confinement effects. In materials, emission of a photon must also conserve the wavevector-allowed only in case of direct-gap semiconductors. The main advantage of these semiconductors is that, they make up the group of direct wide band gap semiconductors which are very important for both emissive as well as photovoltaic applications. These semiconducting nanoparticles are desired for the next generation of optoelectronic communication systems, light sensors, optical recording devices and blue diode laser. MSe films are highly photosensitive so they are very useful in solar energy devices. Selenium based materials are very important for study as: (i) Se is highly photosensitive materials, (ii) It has a wide optical response from X-rays to NIR, and (iii) it can be prepared in amorphous, polycrystalline or crystalline forms.

MATERIALS AND METHODS

Chemical bath deposition (CBD) offers a simple and inexpensive route to deposit semiconductor nanostructures and thin films. CBD is traditionally performed in a beaker, requiring only a substrate to be immersed in a supersaturated solution of aqueous precursors such as metal salts, complexing agents, and
pH buffers. The advantages of CBD methods include low cost, operation at low temperature, solution (almost always aqueous) technique and scalability to large area substrates. The size of the crystals formed in CBD is also very small.

In CBD, MSe thin films were deposited onto cleaned, spectroscopic grade glass substrates. For preparing substrate the microscope glass slides can be cut into any size and shape; These slides are cleaned first by boiling in chromic acid, then rinsed in acetone and finally cleaned thoroughly with double distilled water prior to the deposition. All chemicals used in the reactions were of AR Grade.

Formation of the chalcogenide ion source (Selenide anion)

To prepare sodium selenosulphate solution, 15 g of sodium sulfite in 200 ml water was refluxed with 5 g of selenium for almost 10 hours at 75°C. The mixture remained under constant stirring throughout the reflux process. Selenosulphate is produced according to the following reaction:

\[ \text{Na}_2\text{SO}_3 + \text{Se} \rightarrow \text{Na}_2\text{SeSO}_3 \]  

(1)

Unreacted selenium is filtered off and selenosulphate solution is placed in air tight bottle. It is recommended to make small volumes of selenosulphate stock solution to be used within 3–4 days.

Preparation of PbSe thin films

To prepare thin films of PbSe, 0.5 M Pb(CH\textsubscript{3}COO)\textsubscript{2} solution was prepared. To this 1 M tri sodium citrate solution is added, and then the pH of the solution was adjusted to 10.8 by drop-wise addition of KOH. Finally, Na\textsubscript{2}SeSO\textsubscript{3} was added and the pH of the final deposition bath was adjusted to 11. The glass substrates were vertically immersed in the deposition bath at the desired temperature. After a deposition period of 2.5 h, the substrates were taken out, rinsed in distilled water and dried. The as-deposited films were uniform, continuous, and pinhole free. These were specularly reflective, and extremely adherent to the substrates. The bath temperature is almost 325K.

Preparation of CdSe thin films

Sodium selenosulphate has been used as precursor of Se\textsuperscript{2-} ions. The deposition solution is obtained as follows: 10ml of 0.35M of cadmium acetate is dissolved in 10ml of 0.15M of trisodium citrate (complexing agent). The solution will become milky turbid (due to precipitates of Cd(OH)\textsubscript{2}). To this mixture, 10 ml of Na\textsubscript{2}SeSO\textsubscript{3} solution is added slowly with constant stirring. The colour of the solution starts changing from white to light yellow on the addition of Na\textsubscript{2}SeSO\textsubscript{3} The deposition solution is kept at ~303K. The final pH of the chemical bath is 8.0.

Preparation of ZnSe thin films

The deposition solution is obtained by mixing an appropriate amount of 1 M zinc acetate with 2 M NaOH and with 80% hydrazine hydrate in a beaker. To this mixture, approx. 20 ml of 1 M sodium selenosulphate is added slowly with constant stirring. The final pH of the chemical bath comes out to be 13.00. The solution is stirred for few seconds and then transferred to another beaker containing substrates. Then the reactant vessel is kept in a constant temperature water bath maintained at 50°C which provides the external heat energy for ZnSe formation. The film formation does not take place at room temperature. This is because, at low temperatures, most of Zn\textsuperscript{2+} ions are in a bound state due to strong Zn–amine complex formation [12]. The deposition time is almost 2.5 hrs.

Preparation of SnSe thin Films

To deposit SnSe, sodium hydroxide (1 M) solution in deionized water is prepared. This solution is used to maintain alkaline media of pH at about 11.4. In a beaker sodium hydroxide is added drop wise to 0.95 g of tin chloride dissolved in 10 ml water to obtain an alkaline media of pH 11.4. Then 10 ml of sodium selenosulphate solution is introduced into the beaker and glass substrates are mounted vertically in the bath. The film growth was carried out at 50°C. A dark brown precipitate gradually fills the bath and turns black after 15min. During deposition period the beaker was kept undisturbed for a time period of 2.5 hours. Then the SnSe nanocrystalline films obtained are uniform, well adherent to the substrate and yellowish–brown in colour.

Preparation of CuSe thin films

The deposition solution is obtained as follows: 10 ml of 0.5 M CuSO\textsubscript{4}·5H\textsubscript{2}O, 1.5 ml of 30% NH\textsubscript{3(aq)} (15 M), 30 ml of a freshly prepared solution of 0.20 M Na\textsubscript{2}SeSO\textsubscript{3} and the rest distilled water to make the

![Fig. 1: Experimental set up of chemical bath deposition.](image)
volume to 100 ml. The substrates were placed vertically immersed in the deposition baths against the wall of the beaker. The deposition was allowed to proceed at room temperature, 30°C, for duration, 2h.

RESULT AND DISCUSSION

From the XRD patterns it is possible to evaluate the average grain size (D) of the CdSe thin films by using the well known Debye-Scherer’s formula [13],

\[ D = \frac{K\lambda}{\beta \cos\theta} \]

(2)

Where, \( K \) is a constant of the order of unity, \( \lambda \) is the wavelength of X-rays, \( \theta \) is the Bragg's angle and \( \beta \) is the full width at half maximum.

Effect of substrate temperature

\( \text{PbSe thin films} \)

Anayara Begum et al. [14] have reported that the average crystallite size of PbSe thin films prepared at different temperatures calculated using Scherrer’s formula was found to increase from 23 to 33 nm with an increase of temperature from 303 to 343 K.

\( \text{CdSe thin film} \)

J. R. Aguilar-Hernández et al. [19] also reported that there is change of the crystalline structure as the bath temperature increases going from the wurzite to the zincblende one and also there occur increase of the grain size, which causes a red shift of the band gap.

Oscar Portillo Moreno et al. [20] explained in their paper that for the CdSe, average grain size (GS) increased monotonic with deposition temperature reaching saturation of 343K.

\( \text{ZnSe thin films} \)

Charita Mehta et al. [21] have reported that the temperature of the deposition bath is a significant factor for CBD method and found an increase in particle size as the temperature increases from 318 K to 353 K. They explained that the change in temperature affects the rate of release of Se²⁻ ions from hydrolysis of sodium selenosulphate and the dissociation of metal ions from the complexant [22]. As the temperature is increased, the kinetic energy increases, as a result the dissociation increases resulting in higher concentration of Zn²⁺ and Se²⁻ ions in the solution bath. This will increase the reaction rate and hence the deposition rate. So, increase in temperature increases the crystal size of nanoparticles.

M. R. A. Bhuiyan et al. [23] have also given that the particle size increases with increase in substrate temperature.

\( \text{SnSe thin Film} \)

Asha Bhardwaj et al. [15] have also varied the temperature of the bath and observed that the grain size increases with increase of the temperature. The grain size varies from 25nm to 45 nm when temperature of bath varies from 343K to 363K.

Anuar Kassim et al. [16] have also explained as the bath temperature was increased, the surface of the films starts to grow thicker. The films deposited at higher bath temperature show low appearance of grains over the films surface. The grains sizes of these films were much bigger (5-40μm) and were distributed randomly over the surface of substrate. The number of PbSe peaks and grain size both were increased as the bath temperature was increased from 313K to 353K according to XRD and SEM results.

T.S. Shyju et al. [17] have also reported that the crystalline nature of the films from the XRD patterns of thermally evaporated PbSe films at different substrate temperatures varying from 423K to 723K. There occurs increase in crystallite size (D) of the predominant peak (200) with increasing substrate temperature.

<table>
<thead>
<tr>
<th>MSe thin film</th>
<th>S. No</th>
<th>Variation of temperature</th>
<th>Size Variation</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbSe thin Film</td>
<td>1.</td>
<td>303-343K</td>
<td>Increases (23 to 33nm)</td>
<td>Begum et al. [14]</td>
</tr>
<tr>
<td>2.</td>
<td>343-363K, Increases (25nm to 45 nm)</td>
<td>Bhardwaj et al. [15]</td>
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<td>3.</td>
<td>313-353K, Increases (5-40μm)</td>
<td>Kassim et al. [16]</td>
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<tr>
<td>4.</td>
<td>423-723K, Increases</td>
<td>Shyju et al. [17]</td>
<td></td>
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<tr>
<td>CdSe thin film</td>
<td>1.</td>
<td>320-350K, Increases</td>
<td>Muskhan A. Mohammad et al. [18]</td>
<td></td>
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<tr>
<td>2.</td>
<td>273-353K, Increases</td>
<td>Hermández et al. [19]</td>
<td></td>
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<tr>
<td>3.</td>
<td>343K, Increases</td>
<td>Moreno et al. [20]</td>
<td></td>
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<tr>
<td>ZnSe Thin film</td>
<td>1.</td>
<td>318-353K, increases (6.2 to 9.3 nm)</td>
<td>Mehta et al. [21]</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>373-473K, Increases</td>
<td>Bhuiyan et al. [23]</td>
<td></td>
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<tr>
<td>SnSe thin Film</td>
<td>1.</td>
<td>318-353K, 14.47 to 54.76nm</td>
<td>Shikha et al. [24]</td>
<td></td>
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</table>

\( \text{CdSe thin films} \)

Mudhafar A. Mohammad et al. [18] have shown that the grain size of CdSe film changes with the change of the deposition temperature and given the effect of deposition temperature from 320K to 350K.

J. R. Aguilar-Hernández et al. [19] also reported that there is change of the crystalline structure as the bath temperature increases going from the wurzite to the zincblende one and also there occur increase of the grain size, which causes a red shift of the band gap.

Oscar Portillo Moreno et al. [20] explained in their paper that for the CdSe, average grain size (GS) increased monotonic with deposition temperature reaching saturation of 343K.
SnSe thin film

Deep Shikha et al. [24] have presented that as we increase the deposition temperature of the film from 318K to 353K, the grain size increases from 14.47 to 54.76nm.

Effect of deposition time

PbSe thin films

Barote Maqbul et al. [25] varied the deposition time between 30 min. to 90 min and show the variation of film thickness with deposition time. Initially, PbSe film thickness was increased linearly up to 70 min. and slightly decreased for further deposition time. The maximum thickness of the PbSe film was found to be 335 nm and further film thickness decreased due to dissolution of film in the solution. The thickness of the film is increased by retreating the samples, each time to fresh quantities of the solutions. The authors showed in their paper as thickness of the sample increases from 335nm to 638nm with deposition time and the grain size also increases from 10nm to 18nm.

CdSe Thin films

P. Aggrawal et al. [22] have shown that the grain size of the CdSe film has increased from 4.4nm to 5.9nm as the deposition times are increased from 60min to 150 min.. The dominant mechanism in present study is cluster mechanism which is supported by the increase in size of crystallites.

Pavlo Shapoval et al. [26] have also given that the thickness of CdSe film increases linearly with the number of deposition cycles or deposition time.

P.K.Nair et al. [27] also have reported the thickness increases with increase of deposition period and explained it by plotting the graph in their paper. As the thickness of the film increases, the grain size increases.

ZnSe thin films

R.B. Kale et al. [28] have varied the deposition time between 3 and 15 h. After 2 h, clear solution was changed into faint red color, indicating initiation of the reaction. Initially, CdSe film thickness was increased linearly up to 12 h, and slighter decreased for further deposition time. This has been due to formation of outer porous layer [26]. The maximum thickness of the CdSe film was found to be 0.23 nm.

SnSe thin films

Z.C. Lokhande et al. [29] reported that initially, the ZnSe film thickness increases at a rate of 50 Å/min. with time and after about 30 min of deposition time, a film of 0.16µm is obtained. Further deposition time only yields a small increase in film thickness.

P.K.Nair et al. [27] have also observed that film thickness increases with increase of deposition period and explained it by plotting the graph.

César A. Estrada et al. [30] have explained the variation of thickness with deposition time. Films of 0.1 to 0.3 µm in thickness of ZnSe are obtained in 2 to 10 h depositions at 50°C.

SnSe thin films

Z. Zainal et al. [31] have reported that at a temperature of 318K, the film growth sets in after an initial nucleation period of about 1 h. The growth slows down after 2 h. Durations of deposition longer than 2 h results in less material formation on the substrate. This can be observed also from the XRD data indicating low intensity of SnSe peaks for films at 3 h of deposition. The intensity of the [2 0 1] peak shows a significant decrease indicating poor crystallinity as the deposition time was increased to 3 h. The author has also described that the film thickness decrease at deposition time was increased to 3h from 2h.

Table 2: Effect of time on MSe thin films

<table>
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<th>Table2: Effect of time on MSe thin films</th>
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<tbody>
<tr>
<td>MSe thin film</td>
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<tr>
<td>PbSe thin film</td>
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<tr>
<td>CdSe thin film</td>
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<td>ZnSe thin film</td>
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<tr>
<td>SnSe thin film</td>
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<tr>
<td>CuSe thin Film</td>
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</table>
CuSe thin films

V.M. Garcia et al. [32] have observed the film thickness against duration of deposition of the films. In all cases the film growth sets in after an initial nucleation period of about 1–2 h. The growth slows down after 4–8 h. The maximum thickness increased is 0.24 μm at 24 h duration.

César A. Estrada et al. [30] have shown the variation of thickness with deposition time. Films of 0.1 to 0.3 μm in thickness of CuSe are obtained in 2 to 10 h depositions at 50°C.

Effect of annealing

PbSe thin films

Sasha Gorer et al. [33] have reported that there occur a increase in the crystal size when the PbSe film is annealed. The film was annealed at 150°C, 300°C and 400°C.

CdSe thin films

R.B. Kale et al. [12] have given the variation of crystalline size with the annealing temperature. The size of the crystal is 40A° for as deposited film and increases up to 180A° with increasing annealing temperatures.

T.S. Shyju et al. [17] also have reported that the annealing of the film increases the crystallite size. The deposited CdSe thin films are annealed in the air atmosphere for 3 h at 350°C. Annealing the film at 350°C, the structure changes from cubic to hexagonal system with a high intense peak in (1 0 0) plane as preferred orientation [34]. Such a phase transition from cubic to hexagonal may occur due to change in atomic configuration, since smaller crystallite size and larger surface area appear to favor the phase transformation.

Gary Hodes et al. [35] also have explained that the increase in crystal size with annealing depends on temperature and time of annealing as well as on the material annealed and on the annealing atmosphere. For CdSe, which are usually annealed in air or sometimes in an inert atmosphere, as a rule of thumb, increase in crystal size is slow up to a temperature of ca. 300°C and increases greatly at a temperature somewhere between 300 and 400°C (with further growth at higher temperatures), together with a phase transformation (if the original film is sphalerite, as it tends to be in CBD films) to wurtzite structure.

ZnSe thin films

P.P. Hankare et al. [36] have calculated the average crystallite size by resolving the highest intensity peak i.e. (111) plane. It is found that crystallite size increases from 128 to 158 A° as the annealing temperature increases. The films were annealed at 348, 423 and 473 K for 3 h.

R.B. Kale et al. [12] have also reported that air annealing was found to increase crystallinity of the ZnSe films along with recrystalization process that changed nanocrystalline to metastable cubic to stable hexagonal phase with partial conversion of ZnSe into ZnO phase at higher (673 K) annealing temperature. Actually, the average crystallite size of as-deposited ZnSe thin film is found to be 65 A° that increased to 95 A° after annealing at 673 K.

SnSe thin films

Zulkarnain Zainal et al. [37] have shown the effect of annealing on the structural properties of SnSe thin films. The intensity of the (1 1 1) plane decreased gradually with increase in the annealing temperature and annealing at 150°C improved the crystallinity of the films.

Ana Cláudia Bernardes-Silva et al. [38] have also reported there occur a drastic increase in the particle size when the SnSe film is annealed. The film is annealed for 2 hrs at 300°C and 600°C the particle size become 592A° and 719A° from 74A°.

Biljana Pejova et al. [39] have reported that an average crystal size of 14.8 nm was estimated for as-deposited SnSe quantum dots using the Debye–Scherrer approach which increases to 23.3 nm upon annealing. Average crystal size increase upon thermal treatment is accompanied by slight enlargement of the unit cell parameters.

Sasha Gorer et al. [33] have also shown that there occur a increase in the crystal size when the PbSe film is annealed. The film was annealed at 423K, 573K and 673K.

CuSe thin film

V.M. Garcia et al. [32] have observed the XRD patterns of the as prepared and annealed samples of the films. The patterns show well-defined peaks suggesting that the films are crystalline and calculated the crystallite grain size in the films using the Scherrer formula. This paper reported that the grain size increases when the film is annealed.
Table 3: Effect of annealing temperature on MSe thin films

<table>
<thead>
<tr>
<th>MSe thin film</th>
<th>S.No</th>
<th>Annealing Temperature</th>
<th>Size Variation</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbSe thin film</td>
<td>1.</td>
<td>323-673K</td>
<td>Increases</td>
<td>Gorer et al. [33]</td>
</tr>
<tr>
<td></td>
<td>2.</td>
<td>673K</td>
<td>Increases (4nm to 18 nm)</td>
<td>Kale et al. [28]</td>
</tr>
<tr>
<td>CdSe thin film</td>
<td>1.</td>
<td>673K</td>
<td>increases</td>
<td>Shyju et al. [17]</td>
</tr>
<tr>
<td></td>
<td>2.</td>
<td>573-673K</td>
<td>increases</td>
<td>Hodes et al. [35]</td>
</tr>
<tr>
<td>ZnSe thin film</td>
<td>1.</td>
<td>348, 423 and 473K</td>
<td>Increases(12.8 to 15.8K)</td>
<td>Hankare et al. [36]</td>
</tr>
<tr>
<td></td>
<td>2.</td>
<td>673K</td>
<td>increases</td>
<td>Kale et al.[28]</td>
</tr>
<tr>
<td></td>
<td>3.</td>
<td>623K</td>
<td>increases</td>
<td>Shyju et al. [17]</td>
</tr>
<tr>
<td></td>
<td>4.</td>
<td>573-673K</td>
<td>increases</td>
<td>Hodes et al. [35]</td>
</tr>
<tr>
<td>SnSe thin film</td>
<td>1.</td>
<td>423K</td>
<td>increases</td>
<td>Zainal et al. [37]</td>
</tr>
<tr>
<td></td>
<td>2.</td>
<td>573K and 873K</td>
<td>Increases(7.4 to 71.9nm)</td>
<td>Bernardes-Silva et al. [38]</td>
</tr>
<tr>
<td>CuSe thin film</td>
<td>1.</td>
<td>300K and 400K</td>
<td>Increases</td>
<td>Garcia et al. [32]</td>
</tr>
</tbody>
</table>

CONCLUSION

In all the references for the effect of deposition temperature on MSe thin films given above we have seen that the grain size increases with increase of deposition temperature because at higher temperature, the rate of the deposition reaction increases and the crystallites grow faster resulting in a larger size.

The variation of the thickness of the MSe thin films with deposition time follow the given criteria as given in graph 1 in all the above mentioned references. Initially, the film thickness increases with time and then slightly decreased for further deposition time (as shown in graph 1). At large deposition time period the film became powdery and film thickness decreased due to dissolution of film in the solution and generally the grain size also varies as the thickness of the film with deposition time.

Graph 1: Variation of thickness with deposition time.

The grain become larger as the annealing temperature of the MSe films increases explained in all the above references. The nanometer size grains possess large overall surface area which means that their total surface energy is also high. However, the energy can be minimized when the annealing process was carried out, thus allowing the grains to agglomerate. Further increasing the annealing temperature reduced the surface energy of the grains and thus allowed to become more agglomerate

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