CHAPTER IV

The Kinetic and growth Mechanism of Film Formation

4.1 Introduction

It is well known that the properties of thin films depend strongly on the technique of preparation used [1]. Therefore, to get good quality thin films of HgTe, ZnTe and Zn$_{1-x}$Hg$_x$Te, the preparation parameters such as temperature super-saturation, pH and composition of the reaction bath etc are most necessary to optimized. So far, among the different deposition techniques, the chemical bath deposition technique is considered to be the best method to grow II-VI kind of ionic compounds. This method requires low temperature, low cost, and soft method for the growth of not only thin films but also different types of alloys [2-4].

In this chapter the theoretical background of the chemical bath deposition and the growth profile of the thin film formation have been discussed. Thin films deposited by using this method are further characterized by means of compositional, structural, morphological, electrical and photoelectrical techniques.

4.2 Theoretical Background of Chemical Bath Deposition

The theoretical background of the thin film deposition includes ionic product, solubility and solubility product and super saturation which are discussed in this section;

4.2.1 Solubility, Ionic Product and Solubility Product

At a given temperature, the concentration of a solute in its saturated solution is known as solubility. Some ionic compounds are very slightly soluble in water. In a saturated solution of sparingly soluble salt (electrolyte), the product of molar concentration of ions raised to power equal to number of moles at constant temperature is called solubility product, $K_{sp}$. The product of molar concentration of ions in a solution of electrolyte is called ionic product. The solubility product of compound
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plays an important role in the deposition of thin films. Various properties like homogeneity, stoichiometry and adhesiveness are mainly depend upon the solubility.

When a sparingly soluble salt (electrolyte) like ‘BA’ is added to water, a saturated solution containing $B^+$ and $A^-$ ions along with undissociated solid BA is obtained and equilibrium is established between the solid phase and solution as;

$$\text{BA}_{\text{solid}} \rightleftharpoons \text{BA}_{\text{undissociated}} \rightleftharpoons B^+_{\text{(aq)}} + A^-_{\text{(aq)}} \quad \text{...(4.1)}$$

Applying the law of mass action to above equation, we get

$$K = \frac{[B^+] [A^-]}{[\text{BA}]} \quad \text{...(4.2)}$$

But at a given temperature, $[\text{BA}]_{\text{solid}}$ is constant say $(K_1^1)$ so we can write 4.2 as

$$:. \quad K = \frac{[B^+] [A^-]}{K_1^1} \quad \text{...(4.3)}$$

Where, $K_{sp}$ is solubility product and $[B^+] [A^-]$ are ionic product of sparingly soluble electrolyte BA.

In general, the solubility product of sparingly soluble electrolyte (salt) like $BxAy$ is given as

$$BxAy_{(s)} \rightleftharpoons xB^{y+} + yA^{x-}$$

$$K_{sp} = [B^{y+}]^x [A^{x-}]^y$$

By comparing the values of ionic product in the solution with its solubility product, it can be predicted that the precipitation takes place or not.

In a solution, following conditions are useful;
i) When ionic product is less than the solubility product (I.P. < $K_{sp}$) then solution is unsaturated and precipitation does not occur.

ii) When ionic product is equal to the solubility product (I.P. = $K_{sp}$) then the solution is just saturated and precipitation does not occur.

iii) When ionic product exceeds the solubility product (I.P. > $K_{sp}$) then the solution is super saturated and precipitation takes place. Thus precipitation is possible only when ionic product is greater than the solubility product.

### 4.2.2 Factors Affecting Solubility Product

The magnitude of solubility product mainly depends upon the factors like temperature, solvent used and particle size of solute [5-7]. Increase in temperature shifts the equilibrium towards right as more molecules are dissociated. The solubility of moderately insoluble substance in water is reduced by the addition of the solvent having lower dielectric constant (e.g. alcohol or any water soluble / miscible solvent), while it increases with decrease in particle size of solute.

Solubility constant can be determined by using different methods like calorimetric titration, cation exchange conductivity, ion exchange, polarography, thermodynamic data, rate of reaction, etc. As the solubility constant depends on the temperature, medium and method of measurements a difference of several orders of magnitude in $K_{sp}$ of a solute has been reported in the literature [8-9]. Recently, using thermodynamic data and incorporating a new free energy of formation for aqueous S$^{2-}$ in alkaline medium has shown that the solubility product of the insoluble metal sulphide salts are several orders of magnitudes smaller than previously considered [10]. The solubility constant data for the ZnTe and HgTe compounds are $10^{-31}$ and $10^{-59}$ respectively at 300K temperature in water.
4.2.3 Super Saturation and Relative Super Saturation

The major factor involved in the deposition of material by chemical bath deposition method is the super saturation with respect to an individual solution phase. The solubility depends upon the particle size. A super saturated solution is one that contains a greater concentration of solute than permitted by its solubility product. It is given by

\[
\text{Supersaturation} = Q - S \quad \ldots (4.4)
\]

Where Q is the molar concentration of the product formed momentarily in the solution at any instant and S is the molar equilibrium concentration in a saturated solution of the same solute.

The particle size of precipitate can be determined largely by the experimental conditions and relative supersaturation prevailing at the time of its formation. The relative super saturation is defined by equation

\[
Rs = (Q - S) / S \quad \ldots (4.5)
\]

The particle size varies inversely with average relative super saturation. A state of supersaturation may be achieved by lowering the temperature of an unsaturated solution of the solute. A process of precipitate formation depends upon several factors like temperature, rate of mixing of solution, concentration of reactants and the solubility product [11].

4.2.4 Mechanism of Precipitate Formation

The process of precipitation involves two steps:

i) Nucleation

ii) Growth of particles

i) Nucleation

Nucleation is the process of formation of nuclei in the precipitate (solution). For any type of precipitate, the minimum number of ions or molecules are required to produce a stable second phase in contact with a solution is called as ‘nucleus’. The rate of formation of nuclei in the
solution depends on the degree of supersaturation solution. The rate of nucleation increases exponentially in highly supersaturated solution,

\[ \text{Rate of nucleation} = K [Q - S]^x \]  

...(4.6)

Where, \( K \) and \( x \) are constants and \( x > 1 \).

**ii) Growth of Particles**

Second step in precipitate formation is the growth of particles which is already present in the solution. The growth of particle begins when nuclei or other seed particles are present or by mechanical means such as shaking and stirring. For ionic solids, the process involves deposition of cations and anions on the appropriate sites [11].

\[ (BA)_n + B^+ + A^- \rightarrow (BA)_{n+1} \]

\[ (BA)_{n+1} + B^+ + A^- \rightarrow (BA)_{n+2} \]  

...(4.7)

where, ‘n’ is the number of cations \( B^+ \) and anions \( A^- \) required for given stable phase \((BA)n\).

The rate of growth is directly proportional to the supersaturation;

\[ \text{Rate of growth} = K_0 \times a (Q-S) \]  

...(4.8)

Where,

‘a’ is the surface area of the exposed solid; \( K_0 \), is a constant, which is the characteristic of the given precipitate.

If the supersturation is maintained at low level throughout the precipitation process, the precipitation occurs instead of film formation. Due to this, a large number of nucleation centers are formed. As a result, none of the particle grows in large size and colloidal suspension consists of finally divided solid particles. Under the same circumstances, colloidal particles come together and adhere to one another. The resulting solid is called coagulation. Colloidal particles when coagulated have different properties from a crystalline solid since the particles are arranged irregularly.
4.2.5 Process of Thin Film Formation

For the deposition of most of the II-IV group elements and other semiconductor materials, a chemical bath deposition (CBD) method is used. This method is better than the other costly intensive methods [12-18]. In the present work, a modified low temperature chemical bath deposition method is used for deposition of ZnHgTe alloy thin films of various compositions. The chemical bath method is also called as solution growth, controlled precipitation, arrested precipitation, electroless deposition etc.

The formation of thin film on the surface of substrate by chemical bath method is a two step process [19-20]. First step is the nucleation on the surface of substrate and growth is the second step. An impurity already deposited on the substrate in contact with reaction mixture can acts as nucleation centers. Once a layer of material is formed, further growth takes place by adsorbing more and more ions from the solution giving a continuous film. The film growth takes place by either ion by ion condensation or by adsorption of colloidal particles on the surface of substrate [21-23]. However, concentration of ions decreases as deposition proceeds and growth rate is found to decrease. In case of metal chalcogenide the formation of film takes place when the ionic product of metal ion and chalcogen ion exceeds the solubility product.

4.3 Zn$_{1-x}$Hg$_x$Te Thin Film Formation

The growth of film usually occurs either by ion by ion combination or by adsorption of colloidal particles on the surface of substrate. In case of metal chalcogenide the formation of film / precipitation takes place when the ionic product of metal ion and chalcogen ion (Te$^2-$) exceeds the solubility product. The precipitation takes place only when ionic product is greater than the solubility product and the solution becomes supersaturated [24]. The metal ion ‘M’ and chalcogen ion ‘X’ combine to form the nuclei ‘MX’ on the substrate and in the solution. Once MX is formed, it acts a
catalyst for the further deposition of fresh portion of the MX preferentially. Impurities already present in the solution initiate the nucleation process and therefore the growth of MX particles. Though the exact role of these impurities is not known, but it is supported by the fact that in any precipitation system, there are many particles of different nucleation efficiencies. If the supersaturation is maintained at low level throughout the precipitation, relatively few nuclei will be formed and will grow in size to become large particles contributing the ion by ion growth of thin film [25-26]. The kinetics of growth mechanism depends on the various deposition parameters and the methods of precipitation also. The ion by ion growth results in thin, uniform and adherent films where as cluster by cluster growth yields thick powdery, diffusely reflecting films [27].

In our experimentation, initial temperature of reaction mixture was maintained at 313K. The reaction mixture was prepared by mixing mercury nitrate, zinc nitrate, sodium telluro sulphate complexed with aqueous ammonia solution as a complexing agent. It formed a clear solution and no precipitation occurred even when solution is kept for a long time at low temperature. Low temperature lowered the kinetic energy of ions and the metal ions were in the stable complexed state. The temperature of reaction mixture was then slowly allowed to increase up to 343K. This resulted in the release of metal ions from complexed state; this is a thermally activated process [28]. As the temperature increased slowly from 313K to 343K, the dissociation of metal complex was initiated to generate bare ions which combined to produce compounds or an alloy in the formation of thin film. The various reactions taking place during film formations are as under;

\[
M^{2+} + nA^2 \rightarrow [M \text{ (A)}_n \ [M = \text{Zn/ Hg } [A = \text{NH}_3 ] \ ...(4.9)
\]

\[
\text{Na}_2\text{SO}_3 + \text{Te} \rightarrow \text{Na}_2\text{TeSO}_3 \ ...(4.10)
\]

\[
[\text{Zn(NH}_3)_4]^2+ \rightarrow \text{Zn}^{++} + \text{NH}_3 \text{ (aq) } \ ...(4.11)
\]

\[
[\text{Hg(NH}_3)_4]^2+ \rightarrow \text{Hg}^{++} + \text{NH}_3 \text{ (aq) } \ ...(4.12)
\]
\[ \text{Na}_2\text{TeSO}_3 + 2 \text{OH}^- \rightarrow \text{Na}_2\text{SO}_4 + \text{HTe}^- + \text{H}_2\text{O} \quad \ldots(4.13) \]

\[ \text{HTe}^- + \text{OH}^+ \rightarrow \text{Te}^{2-} \quad \ldots (4.14) \]

\[(1-x)[\text{Zn(A)}_n + x[\text{Hg(A)}_n] + \text{Te}^{2-} \rightarrow \text{Zn}_{1-a}\text{Hg}_a\text{Te} + n\text{A} \quad \ldots(4.15)\]

Where, \( M^{2+} = \text{Zn}^{++}/\text{Hg}^{++} \). In this method the precipitation takes place only when ionic product is greater than the solubility product. The process involves the nucleation followed by the growth. The solubility product of \( \text{ZnTe} \) is greater (Ksp of \( \text{ZnTe} = 10^{-31} \)) than that of \( \text{HgTe} \) (Ksp of \( \text{HgTe} = 10^{-59} \)) at 300K.

An important criterion for synthesis of film via ion by ion combination method is the delayed precipitation. With this, sufficient time can be provided for nucleation on further growth, adhesion and structure depends. The space of nucleation is another important criterion which provides sufficient space for nucleation. Moderately stable precursors \( \text{Zn(NH}_3)_4 \), \( \text{Hg(NH}_3)_4 \) and \( \text{Na}_2\text{TeO}_3 \) decompose by slow increase in temperature, stirring etc. giving bare ions such as \( \text{Zn}^{2+} \), \( \text{Hg}^{2+} \) and \( \text{Te}^{2-} \). Initial room temperature helps to arrest the dissociation of ammonia complexes of \( \text{Zn}, \text{Hg} \) ions and \( \text{Na}_2\text{TeO}_3 \) to considerable extent and lower the kinetic energy of the existing bare ions. Some of these bare ions get combined on substrate to produce a group of nuclei constituting the solid phase (nucleation phase) which subsequently grow by congregation of cations and anions to give \( \text{ZnHgTe} \) thin film on substrate. A slow increase in temperature helped to dissociate the metastable complex compound provided the cations and anions required for the growth process. At room temperature it is difficult to obtain film because of instant precipitation. As the solubility product is low and depends on the temperature and which control over ion concentrations, therefore growth is feasible by controlling the deposition temperature and engaging bare ions in complex state.

The film formation takes place by co-precipitation, a phenomenon in which soluble substances are picked up from solution by the precipitate during the formation of \( \text{Zn}_{1-a}\text{Hg}_a\text{Te} \) thin film. On the basis of solubility...
criterion the Zn$^{2+}$ ions were picked up and substituted in place of Hg$^{2+}$ during the formation of Zn$_{1-x}$Hg$\textsubscript{x}$Te crystalline phase. As the nucleation is not observed within the first 45 minutes, hence an induction time is required for the nucleation. The present investigation indicates that homogeneous Zn$_{1-x}$Hg$\textsubscript{x}$Te thin film has been deposited at 180 minutes. The thickness of film was measured at every 30 minutes and plotted against time as shown in fig.4.1. From the figure, the thickness varies linearly with time but after 180 minutes the concentration of reactive species decreases which results in decrease in thickness. All the deposited films were homogeneous, well adherent to the substrate. Growth kinetics for the development of the typical Zn$_{0.5}$Hg$_{0.5}$Te films is shown in fig.4.2. The figure shows that, in early stages of growth the deposition varies linearly with deposition time and then decreases after typical time. At higher temperature the rate of release of M$^{2+}$ and Te$^{2-}$ ions is faster, so precipitation occurs instead of film formation.

The various parameters to get good quality films have been optimized as 0.25 M concentration of reactants initial temperature 313K, final temperature 343K, stirring rate 45±2 rpm and deposition time 180 minutes. The color of one of the typical Zn$_{0.5}$Hg$_{0.5}$Te film was found to be yellowish white. The color of the Zn$_{1-x}$Hg$_{x}$Te changes from yellowish white to whitish as the composition parameter (x) varies from 0 to 1.

4.4 Physical Properties

All the films obtained were uniform, well adherent to the substrate and pin hole free. The as grown ZnTe and HgTe films were yellowish white and whitish respectively. The color of the Zn$_{1-x}$Hg$_{x}$Te varies from yellowish white to whitish as composition parameter (x) varies from 0 to 1. The change in color is due to substitution of Zn$^{2+}$ ions in the lattice of HgTe. The terminal thickness of the films has been determined by weight difference density consideration method. Fig.4.3 shows the terminal thickness versus composition parameter (x) for whole range. It shows that
the terminal thickness is decreased linearly with the compositional parameter ‘x’. This is attributed to the difference in rates of deposition with respect to the formation of ZnTe and HgTe thin films. The deposition of HgTe is found to be faster than that of ZnTe material.

4.5 Compositional Analysis

The composition of zinc and mercury in thin films was determined by atomic absorption spectroscopy (AAS). From these studies the amount of zinc ions entered in to the lattice of HgTe was determined. The results were confirmed by EDAX analysis. The compositional study carried out by using EDAX analysis indicated that the ratio of Zn\(^{2+}\) and Hg\(^{2+}\) ions is similar to those of taken in bath in \(\pm 5\) % error limit. The amount of Zn\(^{2+}\) and Hg\(^{2+}\) taken bath and those obtained from AAS are displayed in table 4.1. The tellurium in the films was determined by employing a standard gravimetric method [11].
### Table 4.1 Compositional analysis of Zn$_{1-x}$Hg$_x$Te thin films

<table>
<thead>
<tr>
<th>Sr no</th>
<th>Composition</th>
<th>Bath content (in ppm) (calculated)</th>
<th>Ratio of [Hg]/[Zn] in bath ($\chi_{\text{bath}}$)</th>
<th>Film content by i) AAS ppm</th>
<th>Ratio of [Hg]/[Zn] in film ($\chi_{\text{film}}$)</th>
<th>Thickness of film in ( \mu m )</th>
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<tbody>
<tr>
<td></td>
<td></td>
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<td>---</td>
<td>135</td>
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<td>2</td>
<td>Zn$<em>{0.5}$Hg$</em>{0.1}$Te</td>
<td>16</td>
<td>495</td>
<td>198</td>
<td>30.94</td>
<td>4.0</td>
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<tr>
<td>3</td>
<td>Zn$<em>{0.8}$Hg$</em>{0.2}$Te</td>
<td>33</td>
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<td>198</td>
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<td>8.3</td>
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<tr>
<td>4</td>
<td>Zn$<em>{0.7}$Hg$</em>{0.3}$Te</td>
<td>49</td>
<td>385</td>
<td>198</td>
<td>7.85</td>
<td>12.2</td>
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<td>5</td>
<td>Zn$<em>{0.6}$Hg$</em>{0.4}$Te</td>
<td>65</td>
<td>330</td>
<td>198</td>
<td>5.08</td>
<td>16.23</td>
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<td>6</td>
<td>Zn$<em>{0.5}$Hg$</em>{0.5}$Te</td>
<td>82</td>
<td>275</td>
<td>198</td>
<td>3.35</td>
<td>20.5</td>
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<tr>
<td>7</td>
<td>Zn$<em>{0.4}$Hg$</em>{0.6}$Te</td>
<td>98</td>
<td>220</td>
<td>198</td>
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<td>24.5</td>
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<td>8</td>
<td>Zn$<em>{0.3}$Hg$</em>{0.7}$Te</td>
<td>114</td>
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<td>9</td>
<td>Zn$<em>{0.2}$Hg$</em>{0.8}$Te</td>
<td>131</td>
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<td>198</td>
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<td>10</td>
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