CHAPTER-III

Synthesis of Binary and Ternary Mixed Transition Metal Dichalcogenide (TMDC) Thin Films

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3. A.1. Introduction

Synthesis of MoSe₂ thin films requires the detailed theoretical background of VI^B-VI^A group transition metal dichalcogenides. Molybdenum is a typical transition metal situated in VI^B group and 5\(^{th}\) period of the periodic table, possessing five unpaired electrons in d-orbitals, which accounts for its high melting point, strength and modulus elasticity. It has atomic mass 95.94 a.m.u. Swedish Chemist Carl Welhelm Scheel has discovered molybdenum in 1778. Primarily it was found in the ore ‘molybdenite’ (MoS\(_2\)). Its compounds have low toxicity. It is essential to life in trace amounts. It has role in nitrogen fixation and some enzymes. Its primary source MoS\(_2\) contains 60% of Molybdenum. Like MoS\(_2\), MoSe\(_2\) also resembles graphite in appearance and having excellent lubricating properties, hence it is used as a lubricant additive and as a solid lubricant, however MoSe\(_2\) is not found in nature. It is grey black compound with covalent character [1]. The VI^B-VI^A group metal dichalcogenides are crystalline with layered structure. Their single crystals attract the attention of researchers because of their potential electrochemical applications. However, only few experiments have been made on sputtered MoSe\(_2\) films and these have dealt with the lubrication properties of the material[2,3].Bichsel et al. have studied to determine the chemical composition of sputtered MoSe\(_2\) films as a function of processes conditions using electron spectroscopy for chemical analysis (ESCA) combined with x-ray photoelectron spectroscopy (XPS). Krishana C.et al. synthesized Semiconducting MoSe\(_2\) thin film chemically and characterized by various Physical methods [4]. Among the various methods used for the preparation of metal chalcogenide thin films, described in chapter II, the most convenient arrested precipitation technique was selected and employed for the preparation of MoSe\(_2\) thin films. This section of the chapter describes the
experimental set up and optimization of experimental conditions for the preparation of MoSe₂ thin films by an arrested precipitation technique (APT).

This chapter describes the desired fabrication of experimental set up used for the synthesis of transition metal dichalcogenide thin films. Section-A is devoted to chemosynthesis of binary molybdenum diselenide (MoSe₂), section B describes electrosynthesis of binary tungsten diselenide (WSe₂) thin films and Section-C of this chapter is devoted to the synthesis of MoₓW₁₋ₓSe₂ thin films by a hybrid process which consist of combination of electro synthesis followed chemosynthesis by arrested precipitation technique (APT). The procedural details and technical knowhow in the deposition of pure binary MoSe₂, WSe₂ and ternary MoₓW₁₋ₓSe₂ mixed transition metal dichalcogenide thin films are presented in this chapter.

3. A.2. Thin Film Deposition Technique

Several techniques have been employed for the deposition of transition metal dichalcogenide thin films as the film properties are extremely sensitive to the method of preparation. However, no single technique can deposit the films covering all the desired aspects, such as cost of equipment, reproducibility, economy of chemicals, deposition conditions and nature of deposit etc. Methods used for thin film deposition are discussed in Chapter 2A. Section 2.A.3.

- Arrested Precipitation Technique

For the deposition of MoSe₂ thin films, the Chemical Deposition technique was reported in literature [5], however the modified technique, the Arrested Precipitation Technique is found most suitable for deposition [6]. In order to make the chemical deposition technique more sophisticated to have the controllability of the film growth and fine quality of the resulting materials, one should consider a process for the active control, which is usually missing in the ordinary chemical deposition processes. The strategy for the active control varies depending on the mechanism of the film growth. The Arrested Precipitation Technique used for the deposition of Molybdenum diselenide thin films involves the controlled dissociation of arrested metal ion by organic complexing agents such as triethanolamine, EDTA, thioacetamide, tartaric acid, citric
acid etc. Then the thin film formation involves creation of a nucleation centres at the substrate surface followed by growth of metal chalcogenides by the ion-by-ion condensation of appropriate ions from the solution. After certain time, this results in saturation of film growth known as terminal growth phase of thin film deposition. As the metal ion present in organic atmosphere most of the impurities remain in the solution because dissociation constant of every metal complex depends on specific pH value [7,8]. The Arrrested Precipitation Technique is ideally suited for large area thin film depositions. It is simple, inexpensive and does not require sophisticated instrumentation. Dissociation rate of organometallic complex to release free metal ions for reaction is well controlled by maintaining the pH of reacting solution. In this electrical conductivity of the substrate material is not an important criterion. Hence APT is the suitable process for the deposition of transition metal dichalcogenide thin films.

- **Experimental Set up for Deposition of MoSe$_2$ Thin Films**

  a. Thin film Deposition Chamber and Assembly:

  This section deals with fabrication of the thin film deposition technique and associated accessories. A thin film deposition chamber was designed and fabricated in our laboratory having dimensions 1.8 x 0.8 x 1 m$^3$ to maintain clean ambient atmosphere necessary for the deposition and to protect the deposition system from the physical hazards. Fig. 3.1 shows photograph of thin film deposition chamber and deposition assembly, while Fig. 3.2 shows the cross sectional view of deposition assembly. It consists of an exhaust fan at the top of deposition chamber to remove toxic gases, constant speed motor, metallic stand, substrate holder, temperature controller with sensor, reaction container, constant temperature bath etc.

  b. Constant Speed Motor:

  This is a single–phase A. C. gear motor type [Remi Make Universal RU-56-24.1/8 HP (1.1 Amp)]. The motor is fitted to a sturdy metallic stand. A metallic rotating shaft having length 15 cm and cross sectional diameter 0.5 cm was attached to the motor. One end of the rod was attached to a constant speed A. C. gear motor while other end was fitted to a substrate holder as shown in Fig. 3.1 & 3.2. A dimmer stat cum
regulator was also provided to control speed of motor. The speed of motor can be varied from 30 rpm to 150 rpm with the help of regulator

c. Substrate Holder:

Geometry of substrate holder plays an important role in quality and uniformness of the thin film prepared by arrested precipitation technique. The substrate holder was designed and fabricated in our laboratory. Fig. 3.3A shows design of the substrate holder while cross sectional view of substrate holder is shown in Fig. 3.3B.

It is a circular disc made from Bakelite material having diameter 5 cm and thickness 1 cm with four slots which are perpendicular to each other. The substrates to be deposited were fitted in these slots with the help of screws in such a way that rotating substrates do not touch the wall of the solution container. The disc was grooved and attached to a shaft of the constant speed gear motor.

Fig. 3.1 Thin film deposition chamber and deposition assembly
Fig. 3.2. *Cross sectional view of the thin film deposition assembly.*

Fig. 3.3.A. *Design of the substrate holder.*  

Fig. 3.3.B. *Cross sectional view of substrate holder.*
d. Constant Temperature Assembly:

Reacting solutions were taken in glass container having capacity 150 cm$^3$. The reaction container was kept in cylindrical water pot of 10 cm in height and 20 cm in diameter. It was provided with controlled heater to heat the water. A 0.1°C thermometer was used to measure the temperature of the bath. A magnetic stirrer was used to stir the water to achieve uniform temperature throughout the water bath.

3. A.3. Experimental Details:

a. Nature and Cleaning of the Substrate:

Glass slides of dimensions 75 mm x 25 mm x1.35 mm were used as substrates, in order to get good adhesion between the chemically deposited films and the substrates, a special attention was paid to the pretreatment of the substrates. So in chemical deposition, substrate cleaning plays an important role because the cleanliness is a measure of sticking of the film to the substrate support. Cleanliness is the process of breaking the bonds between substrates and contaminants (e.g. grease, air borne dust, adsorbed water and oil particles) without damaging the substrates. The glass substrate and fluorine doped tin oxide (F: SnO$_2$) coated glass substrates were used.

The glass substrate and fluorine doped tin oxide (F:SnO$_2$) coated glass substrates were cleaned using following procedure:

I. The glass substrate and the fluorine doped tin oxide (F:SnO$_2$) coated glass substrates were washed with detergent solution and then with double distilled water.

II. The both type of substrates were boiled in chromic acid for 20 minutes and rinsed with double distilled water.

III. At last substrates were cleaned with Acetone and dried.

IV. Thoroughly cleaned glass substrates were mounted on a substrate holder.

b. Chemicals:

All the chemicals used were analytical reagent grade. These chemicals were Molybdenum trioxide [MoO$_3$], Selenium Metal Powder, Triethanolamine
c. Preparation of Precursor Solutions:

i) Mo-TEA Complex Solution:

3.6 gm MoO₃ triturated (crushed) with 30 ml triethanolamine for four hours then four drops of ammonium hydroxide added to it and the resulting solution was diluted to 100 mL with double distilled water.

\[
\text{MoO}_3 + 2\text{N(\text{CH}_2\text{-CH}_2\text{-OH})_3}+2\text{NH}_4\text{OH} \xrightarrow{\text{pH 9.6}} (\text{NH}_4)_2(\text{Mo (N (\text{CH}_2\text{-CH}_2\text{O})_3)})_2 + 3\text{H}_2\text{O}+2\text{OH}^- \]

ii) 6.0 gm of Selenium metal powder and 30 gm of Sodium sulphite (anhydrous) taken in 1 litre round bottom flask along with 250 mL double distilled water and refluxed for nine hours at 60 °C. Then the refluxed solution further diluted to 250 mL with double distilled water.

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

iii) 20 gm of Na₂S₂O₄ dissolved in 100 mL of double distilled water.

3. A.4. Deposition of MoSe₂ Thin Films:

As mentioned above the technique of film deposition is greatly influencing properties of resulting thin film. There are number of deposition techniques reported in literature [9-13]. Every process has its own advantages and disadvantages and of course, no single technique can deposit the films, covering all the desired aspects, such as cost, deposition conditions and nature of the substrate etc. The arrested precipitation technique was found to be most suitable for expected type, quality and properties of the thin film.

3. A.4.1. Preparative Parameters:

a) Bath Composition:

The deposition bath was prepared in 150 mL beaker by the addition of 20 mL of 0.25 M Mo-TEA complex, 10 mL of 10% solution of ammonium acetate, 5 mL of 2 M acetic acid, 10 mL of 25% solution of ammonium hydroxide, 10 mL of 20% solution of sodium dithionite, 20 mL of 0.25 M solution of sodium selenosulphite, and rest of the distilled
water was added to make the total volume 100 mL. The final pH of the reaction mixture was made 9.6 by adding ammonia. Thoroughly cleaned glass/fluorine doped tin oxide (F: SnO$_2$) coated glass substrates were mounted on a specially designed substrate holder. The substrate holder was attached to constant speed gear motor and rotated at a speed of 50±2 rpm. The temperature of the bath was maintained at 60°C. After deposition period of 55 minutes, samples were taken out, washed with distilled water and kept in desiccators.

b) Complexing Agent:

In arrested precipitation technique, a complexing agent is used to bind the metallic ions to avoid the immediate precipitation of the corresponding compound. The formation of complex ion is essential to control the rate of reaction and to avoid the immediate precipitation of the compound in the solution. The metal complex hydrolyses slowly to generate the positive ions in the solution. Triethanolamine was used as a complexing agent.

**Probable structure of Mo-TEA complex**

![Probable structure of Mo-TEA complex](image)

**Fig. 3.4 A. Mo-TEA complex**

c) pH:

In arrested precipitation technique to release slowly the metal ions from metal ion complex and the chemical reaction to takes place properly, a suitable pH must be
maintained throughout the deposition process. In order to select the essential pH for the deposition processes, pH of the reaction mixture was varied. The thickness of deposition and quality of the film was compared and finally the suitable pH 9.6 was selected as a characteristic pH of the process. The effect of change in pH on the deposition was studied by weight difference method. Was therefore kept constant throughout the further studies.

d) Temperature:

The preparation parameter temperature is also playing an important role, in proper slow decomposition of metal ion complex, as well as the deposition process. Number of experimental deposition sets were set up with varied temperature to find out the specific temperature. Temperature 60°C ±2 was selected as characteristic temperature for this process. The effect of temperature on the deposition was studied by weight difference method. The deposition temperature 60°C ±2 was therefore kept constant throughout the further studies.

e) Time:

The growth rate was also studied for various deposition durations. Initially Mo⁶⁺ ions were complexed with triethanolamine (TEA) to slow down the rate of release of Mo⁴⁺ ion at pH 9.6 therefore, growth of thin film is time dependent. Hence the deposition time of the film was varied from 20 to 120 minutes and film thickness was measured. It is obvious that growth rate is initially almost linear and then it becomes quasilinear and saturates there after a deposition period of about 55 min. The deposition time of 55 min. was therefore kept constant throughout the further studies.

f) Speed of the Substrate Rotation:

The deposition of the metal dichalcogenide thin films on substrate material is greatly influenced by speed of the substrate rotation. The impingement of ionic species from reaction container over the substrate surface is necessary for better adhesion and growth of metal dichalcogenides. At lower speed (<30rpm) thick porous and less adherent films were obtained, while at higher speed (>70rpm) very thin adherent films and reflecting films were get deposited over substrate support. Therefore, speed of the
substrate rotation was kept at an optimum value of 50 ±2 rpm so as to form highly reflecting, uniform, stoichiometric and adherent thin films on the substrate surface.

**Table-3.1 Preparative Parameters, Bath Composition for the Molybdenum Diselenide Thin Films along with their Film Thickness.**

<table>
<thead>
<tr>
<th>Film Composition</th>
<th>Bath Composition</th>
<th>Preparative Parameters</th>
<th>Thickness in nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoSe₂</td>
<td>20ML 0.25M Mo-TEA Complex+10mL20% Ammonium acetate+5mL 2M Acetic acid+10 mL 25% Ammonia solution + 10 mL 20% Sodium dithionate solution + 20 ML 0.25 M. Sodiumselenosulphite solution</td>
<td>pH: 9.6 Temp: 60 °C ±2 Deposition Time: 55 min. Speed of Substrate Rotation: 50 ±2 rpm</td>
<td>900</td>
</tr>
</tbody>
</table>

3. A.5. Growth Mechanism

Molybdenum diselenide thin films were deposited from an aqueous alkaline medium containing Mo-TEA complex and Se²⁻ ions.

The deposition process based on simple ion by ion mechanism it involves three steps

I) Dissociation of complex to free Mo⁴⁺ ions

ii) Formation of Se²⁻ ions

iii) MoSe₂ formation by ionic reaction

In this in the beginning, the Mo-TEA complex dissociates and release Mo⁴⁺ ions.

\[(NH₄)₂\left[Mo(N(CH₂—CH₂—O)₃)₂\right] + 6H₂O → Mo₄⁺ + 2NH₄OH + 2N (CH₂—CH₂—OH)₃ + 4OH⁻ \ldots \ldots 3.3a\]

Similarly the Sodium Selenosulphite hydrolyses and forms Se²⁻ ions. It followed by the formation of MoSe₂, it occurs by condensation on ion by ion basis on the glass substrate. The formation of MoSe₂ is possible when the ionic product of Mo⁴⁺ and S²⁻ ions exceeds the solubility product of MoSe₂. In the present investigation, the formation
of MoSe$_2$ involves hydrolysis of sodium selenosulphite which releases the selenium ions into the reaction bath. In an aqueous alkaline medium sodium selenosulphite hydrolysed to give Se$^{2-}$ ions as

$$\text{Na}_2\text{SeSO}_3 + \text{OH}^- \leftrightarrow \text{Na}_2\text{SO}_4 + \text{HSe}^- \tag{3.3b}$$

$$\text{HSe}^- + \text{OH}^- \leftrightarrow \text{Se}^{2-} + \text{H}_2\text{O} \tag{3.4}$$

It is clear from these reactions that the equilibrium constant of HSe$^-$ is predominant in the solution. The concentration of Se$^{-}$ ions can be increased by addition of the excessive hydroxide ions to facilitate forward reaction. The reaction 3.3 and 3.4 reveal that Mo$^{4+}$ and Se$^{2-}$ ions will condense ion by ion on the glass substrate as

$$\text{Mo}^{4+}_{(aq)} + 2\text{Na}_2\text{SeSO}_3 + 4 \text{OH}^- \xrightarrow{\text{pH}9.6} \text{MoSe}_2 + 2\text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O} \tag{3.5}$$

$$\text{60}^\circ\text{C} \pm 2$$
Part-B

Electrosynthesis of Tungsten Diselenide (WSe$_2$) Binary TMDC Thin Films.

3. B.1 Introduction

Peter woulfe deduced the existence of new element Wolfram (Tungsten) in 1779 while studying an ore wolframite, further Fausto and Juan Jose de Elhuyar had isolated it in 1783. It is situated in VI$^B$ group and third transition series. It is a very hard, dense, silvery white, lustrous metal that tarnishes in air, used for electric bulb filament, and its alloys are as a high speed cutting tools etc., It is low toxic and found in living systems also. It is having considerable affinity for chalcogens and form stable dichalcogenides. WSe$_2$ was reported by L.H. Brixner as a semiconducting material [14]. It was extensively studied by Hicks [15] and found WSe$_2$ the semiconducting material showing lower electrical conductivity, then there was considerable interest developed for this compound due to its semiconductor properties. The transition metal dichalcogenide compounds become much popular since their potential applications in various fields of science and technology becomes known [16]. The extensive research is going on in the search of photoelectrochemical (PEC) solar cells for low cost energy conversion where the use of tungsten diselenide as a photoanode is desired, since tungsten diselenide belongs to the group, VI$^B$ transition metal dichalcogenide and is semiconducting with layered structure.

The electronic properties of WSe$_2$ have been reviewed and found to be crystallized in hexagonal MoS$_2$ type layered structure with space group P6$_3$/mmc by Brixner [17, 18]. Photoelectrochemical study of Tungsten dichalcogenide reported by G. Prasad et al. [19]. Skyllus kazacos et al. studied n-WSe$_2$ photoelectrode for their temperature dependence. Hansen [20] has reported that there were neither higher nor lower compound of W and Se was known. Investigations concerning the stoichiometry of WSe$_2$ have indicated that the homogeneity range of this compound must be extremely narrow. Its structure is like that of the tungsten disulphide, whith the metal trigonal prismatically surrounded by selenium [21]. Unlike WS$_2$ the only known modification of WSe$_2$ is the 2H-type and that no rhombohedral diselenide exists. Silverman’s high pressure, high temperature experiments (covering a very wide
pressure-tempure profile, up to 70 kbr and 2400°C) gave only the Hexagonal form. Wildervanck’s work [22] and studies of Al-Hilli et al.[23], Kershaw et al. [24], Revolinsky et al.[25] report the preparations of the polycrystalline substance by direct reactions

**Experimental Setup for Deposition of WSe$_2$ Thin Films:**

The schematic diagram of experimental setup for electrodeposition technique is shown in Fig. 3.5. It consists of conventional three-electrode system, i.e. working electrode (cathode), counter electrode (anode) and reference electrode, bakelite holder, cylindrical glass container and heater with temperature controller. The working electrode is metallic or FTO coated glass substrate of dimensions 1 x 4 cm$^2$. The counter electrode is a polished inert graphite plate of dimensions 1.5 x 4 cm$^2$. The reference electrode is a saturated calomel electrode (SCE). The distance between counter electrode and working electrode is 0.4 cm. These three electrodes are fitted in the bakelitie holder having thickness 1 cm and diameter 3.5 cm and fixed in cylindrical corning glass cell with capacity 30 cc. Electrochemical studies and film deposition were made by using a potentiostat, Princeton Perkin Elmer, Applied Research Versastat-II, Model 250/270 Fig. 3.6 in the three electrode configuration for potentiostatic mode of operation.

![Fig 3.5 Experimental setup for electrodeposition technique](image-url)
3. B.2. Experimental Details:

a. Nature and Cleaning of Substrates:

WSe$_2$ thin films were electrodeposited on to the stainless steel and F:SnO$_2$ coated glass substrates. The substrates were cleaned chemo-mechanically. The cleaning of substrate was carried out as earlier described in 3.A.3.1. Usually, conducting substrates like stainless steel, ITO, titanium, copper, and fluorine doped tin oxide (F:SnO$_2$) coated glass substrates were used.

In present study the stain less steel substrates and fluorine doped tin oxide (F:SnO$_2$) coated glass substrates were used.

The metallic substrates were cleaned in following manner.

I. Using fine grade polish paper substrates were mechanically polished to mirror surface.

II. The substrate were washed with liquid detergent and then degreased by acetone.
III. Then substrate were etched with 3 % HCl and further cleaned ultrasonically.

IV. At last substrates were cleaned with double distilled water followed by distilled acetone and dried.

V. The pretreatments were performed just before the substrates were immersed into the solution to begin electrodeposition or cyclic voltammetry measurements.

b. Chemicals:

All the chemicals used were analytical reagent grade. These chemicals were Tungstic acid [H$_2$WO$_4$] and Selenium dioxide [SeO$_2$] etc.

c. Preparation of Precursor Solutions:

For the deposition of tungsten diselenide (WSe$_2$) thin films, all the solutions were prepared in double distilled water. Precursors used to prepare WSe$_2$ thin films were as follows;

I. Analytical Grade extra pure tungstic acid H$_2$WO$_4$ was used to prepare 0.25 M H$_2$WO$_4$ solution.

II. Analytical Grade extra pure selenium dioxide (SeO$_2$) was used to prepare 0.1 M H$_2$SeO$_3$ solution.

d. Cyclic Voltammetry (CV):

The Cyclic Voltammogram of electrolytic bath containing a. Tungstic acid, b. Selenium dioxide and mixture of tungstic acid and selenium dioxide at pH 9.6 were run on potentiostat (Princeton Perkin Elmer, Applied Research Versatat-II, Model 250/270) in three electrode configuration to define the potential region in which the reaction occurs. The voltammograms are shown in following fig.3.7 a and b. The deposition potential was found -0.8625 mV. for reaction mixture bath.
Fig.3.7 Cyclic Voltammogram of solution containing a) 0.25 M $\text{H}_2\text{WO}_4$

b) 0.1 M $\text{H}_2\text{SeO}_3$

3. B.3. Deposition of WSe$_2$ Thin Films:

Tungsten diselenide (WSe$_2$) electrodeposition was carried out in electrolytic bath consisting of a three electrode system under a galvanostatic mode. A graphite plate was used as an anode, fluorine-doped tin oxide (FTO) coated conducting glass substrates and stainless steel substrates were used as cathode and saturated calomel electrode (SCE) was used as a reference electrode. The electrolytic bath was prepared by mixing 18 mL 0.25 M $\text{H}_2\text{WO}_4$ and 12 mL 0.1 M $\text{H}_2\text{SeO}_3$ solution. The final pH of the electrolytic bath containing 0.2 M $\text{H}_2\text{WO}_4$ and 0.1 M $\text{H}_2\text{SeO}_3$ solution was 9.6. During the deposition the distance between working electrode (stainless steel (ss) and FTO coated glass substrate) and counter electrode (graphite plate) was kept constant as 0.4 cm. The electrodeposited WSe2 thin films were found to be pin hole free, uniform and well adherent to substrate support for deposition period of about 35 minute at 60$^\circ$C.

The solution concentration, pH of the bath and deposition time was optimized by using photoelectrochemical (PEC) characterization technique. PEC solar cell was fabricated using a two electrode configuration, comprising n-WSe$_2$ thin film as a photoanode, graphite as a counter electrode and SCE as a reference electrode. The redox electrolyte was 0.1M sulphide/ polysulphide ($\text{Na}_2\text{S-S}_x\text{NaOH}$). The cell was
illuminated with 500 W xenon filament lamp for the measurement of short circuit current (Isc) and open circuit voltage (Voc). The film shows the higher short circuit current (Isc) 1.49 (Ma/cm$^2$) and open circuit voltage (Voc) 284.2 (mV) for condition mentioned above.

Thickness of n-WSe2 thin film was measured by the gravimetric weight difference method using the relation

$$t = \frac{M \cdot A}{\rho} \quad \text{------------------------3.6}$$

$$M = m_1 - m_2 \quad \text{------------------------3.7}$$

where ‘t’ is film thickness, ‘M’ is mass of the film material, ‘A’ is area of the film, $m_1$ is mass of the substrate with film, $m_2$ is mass of the substrate without film and ‘$\rho$’ is density of the deposited material.

The density of the deposited material is assumed to be the same as that of the bulk material. The maximum thickness of the film was 1.50 $\mu$m attained after the deposition for 35 minutes. As the further deposition time was increased above 35 min, the film was peeled out from the substrate in the form of flakes. This can be attributed to the tensile stress that tends to cause delamination, when the film becomes thick.

- **Preparative Parameters:**
  
  **a. Bath Composition:**
  
  The electrolytic bath was prepared by mixing 18 mL 0.25 M H$_2$WO$_4$ and 12 mL 0.1 M H$_2$SeO$_3$ solution.
  
  **b. pH of the Bath Solution:**
  
  The final pH of the electrolytic bath containing 0.2 M H$_2$WO$_4$ and 0.1 M H$_2$SeO$_3$ solution was 9.6.
  
  **c. Deposition Time:**
  
  For the uniform, homogeneous and adherent deposition of the film deposition time was kept 35 minutes.
3. B.4. The Growth Mechanism:

The aqueous deposition mixture an electrolyte, consists of tungstic acid and selenium dioxide in alkaline medium. The induced co-deposition mechanism of WSe$_2$ film formation took place as follows.

\[ \text{H}_2\text{WO}_4 + \text{NH}_4\text{OH} \leftrightarrow (\text{NH}_4)_2\text{WO}_4 + 2\text{H}_2\text{O} \]  \hspace{1cm} \text{(3.8)}

\[ (\text{NH}_4)_2\text{WO}_4 \leftrightarrow 2 (\text{NH}_4)^+ + \text{WO}_4^{2-} \]  \hspace{1cm} \text{(3.9)}

\[ \text{WO}_4^{2-} + (6-n) \text{e}^- = \text{W}^{n+} \text{ oxide/hydroxide} \]  \hspace{1cm} \text{(3.10)}

\[ \text{SeO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HSeO}_2^+ + \text{OH}^- \]  \hspace{1cm} \text{(3.11)}

\[ \text{HSeO}_2 + 2\text{e}^- \leftrightarrow \text{Se}_{(s)} + \text{O}_2 + \frac{1}{2}\text{H}_2 \]  \hspace{1cm} \text{(3.12)}

\[ \text{Se}_{(s)} + 2\text{H}_2\text{O} \leftrightarrow \text{HSeO}_2^+ + 3\text{H}^+ + 4\text{e}^- \]  \hspace{1cm} \text{(3.13)}

\[ \text{H}^+ + \text{e} (\text{ySe}) \leftrightarrow \text{H} (\text{ySe}) \]  \hspace{1cm} \text{(3.14)}

\[ \text{W}^{n+} \text{ oxide/hydroxide} + n \text{H} (\text{ySe}) = \text{W}_x \text{Se}_y \]  \hspace{1cm} \text{(3.15)}
Chapter-III
Part-C
Hybridsynthesis of $\text{Mo}_x\text{W}_{(1-x)}\text{Se}_2$ TMDC Thin Films

3. C.1. Introduction:

The binary TMDC thin films MoSe$_2$ and WSe$_2$ are having semiconducting behaviour and posses the other related characteristics. The Chemicaly deposited (APT) MoSe$_2$ thin films were having comparatively higher band gap than WSe$_2$. So for having more precise and most efficient semiconductor material it was proposed to synthesize a mixed transition metal dichalcogenide material. In literature the solid solution formation, information can be found in reports from Brixner [17], Brixner and teufer [18], Hicks [10] and Revolinsky and Beernsten [25]. Brixener [17] prepared the solid solutions by having the constituent elements, W, Ta and Se in evacuated sealed quartz ampoules for 10-15 hours at 600-700$^\circ$C after which the black looking reaction products were remixed inside the tube by shaking. Revolinsky and Beernsten [25] prepared polycrystalline samples of the MoSe$_2$-WSe$_2$ and the MoTe$_2$-WTe$_2$ systems, by heating the powdered elements weighted in the proper proportions to 700-800$^\circ$C for a period of 72 hours followed by air quenching. It also reports that the complete solid solubility was observed between WSe$_2$ and MoSe$_2$, the small difference in their cell parameter results in a linear variations of the crystallographic parameters of the ternary compound. W.K. Hofmann et al. have reported synthesis of single crystal of Mo$_x$W$_{(1-x)}$Se$_2$ by CVT method and studied photoactivity[26].

3. C.2. Experimental Set up for Deposition of Mo$_x$W$_{(1-x)}$Se$_2$ Thin Films:

The deposition of Mo$_x$W$_{(1-x)}$Se$_2$ was tried several times by arrested precipitation technique (APT) as well as chemical bath deposition technique (CBD), however the attempts were not met with success. This is because though Mo and W, both the elements belongs to the same VI$^B$ group of periodic table, there is very much difference in their reactivity. As can be seen from the potential diagrams of some of the oxidation states of Mo and W, for pH = 0 and 14, they are reactive metals, however as the reactivity increase with increasing atomic number and pH value in VI and V group of
periodic table, this does not applied to all the oxidation states of the W [27]. Hence first time the new hybrid synthesis technique was used for the synthesis of Mo$_x$W$_{(1-x)}$Se$_2$ ternary mixed transition metal dichalcogenide thin films.

For the deposition of ternary mixed transition metal dichalcogenide thin films, the experimental set up was made by combining the processes of the deposition of WSe$_2$, and MoSe$_2$ successively. All chemicals used were of A.R. reagent grade manufactured by BDH & E,Merck. The arrested precipitation technique arrangement was as described in sections 3.B.2. and 3.A.2.respetively.

3. C.3. Deposition of Mo$_x$W$_{(1-x)}$Se$_2$ Mixed Transition Metal Dichalcogenide Thin Films: The synthesis of Mo$_x$W$_{(1-x)}$Se$_2$ is carried out by Hybrid process. The preparative parameters for synthesis were maintained very much precisely and accurately it has great influence over the composition of resulting product. The complete process is devided in three stages.

   i. The electrosynthesis of WSe$_2$
   ii. The chemosynthesis of MoSe$_2$
   iii. Post deposition treatment to films.

i. The Electrosynthesis of WSe$_2$:
For this in an electrolytic bath a mixture of 18 mL 0.25M tungstic acid solution ,12mL of 0.1 M selenium dioxide solution was taken and by using ammonia its pH was maintained to 9.6 , then a conventional three electrode system was set up in electrolytic bath .FTO coated glass substrate as a working electrode (cathode),graphite plate as a counter electrode (anode)and standard calomel electrode was used as reference electrode. The electrolytic bath was kept in constant temperature thermostat bath .The electrodes attached with potantiostat and a voltage of 5 mV was passed through it for precisely controlled time of 20 minutes.

   As per the preparative parameters set up in section 3B, temp was kept constant at 60 °C By cyclic Voltammogram the deposition potential of mixture of tungstic acid and selenium dioxide was deduced, it was -0.8625 mV hence a slight higher potential
than this i.e. -0.97Mv was kept constant, for good quality uniform, adherent, and pin
hole free films. The terminal thickness of the film was obtained at 35 minutes. However
for final effective composition of ternary mixed metal TMDC film, time variation was
carried out and finally 20 minute time was found specific. The deposition process was
run for 20 minutes and as deposited films were taken out from the electrolytic bath, then
washed with distilled water and dried in air.

ii. Chemosynthesis of MoSe$_2$ Thin Films:
The above electrodeposited WSe$_2$ thin films after washing and drying in air without any
further treatment mount on substrate holder. On which chemosynthetic deposition of
MoSe$_2$ by APT process can be carried out.
The composition of the deposition bath for APT. process was made as described in
section 3.A.5.It consists of 20 mL of 0.25 M Mo-TEA complex, 10 mL of 20%
ammonium acetate, 5.ml of 2 M acetic acid,10 mL of 25% ammonia solution,10 ML of
20% sodium dithionate solution and 20 mL of 0.25 M sodium selenosulphite solution.
The final pH of the reaction mixture was made 9.6, temperature of the thermostat bath
was kept constant at 60 $\pm 0$C and speed of the substrate rotation was kept constant at
50 $\pm$ rpm. For this deposition the time period for terminal thickness is 55 minutes
however for desired composition of the ternary mixed TMDC, time variation study was
carried out and 35 minutes was found specific. Hence the deposition was run for 35
minutes. Thin films are taken out from deposition bath and washed with distilled water
and kept in decicator.

iii. Post Deposition Treatment:
The as deposited films were further post treated. The films then annealed at
250$^0$C in muffle furnace for three hours. Due to the annealing the both types of films
deposited one over other get diffused in one another and uniform films with thickness in
the range of 900 nm to 1.5 $\mu$m. in gray black colour were obtained. These films further
checked for different characterizations. The ternary mixed TMDC thin films synthesized
by hybrid synthesis process by maintaining specific time have fixed composition $\text{Mo}_{0.5} \text{W}_{0.5} \text{Se}_2$ the process was showing repeated considerable reproducibility.
3. C.4. Growth Mechanism:

Growth mechanism took place here, as described in sections 3B and 3A of this chapter, further after the as deposited thin films were obtained, the post deposition treatment given to the films. In which the diffusion of both the films and their atoms took place and gray-black coloured, uniform and adherent ternary mixed transition metal dichalcogenide thin films were obtained.

\[ W^{n+} \text{ oxide/hydroxide} + n \text{ H (ySe)} = W_x \text{ Se}_y \]  \hspace{1cm} -------3.16

\[ \text{Mo}^{4+} (\text{aq}) + 2\text{Na}_2\text{SeSO}_3 + 4 \text{ OH}^- \xrightarrow{\text{pH 9.6}} \text{MoSe}_2 + 2 \text{ Na}_2\text{SO}_4 + 2\text{H}_2\text{O} \]  \hspace{1cm} -------3.17

\[ 60^\circ \text{C \pm 2} \]

\[ \text{Mo}^{4+} + W^{4+} + n\text{Se} \rightarrow \text{Mo}_x\text{W}_{(1-x)}\text{Se}_2 \]  \hspace{1cm} -------3.18

\[ \text{WSe}_2 + \text{MoSe}_2 \rightarrow \text{Mo}_x\text{W}_{(1-x)}\text{Se}_2 \]  \hspace{1cm} -------3.19

3. C.5. Optical Images of Thin Films:

Fig. 3.4. Optical image of as deposited a.\text{MoSe}_2 thin film, b.\text{wse}_2 thin film and c. \text{Mo}_x\text{W}_{(1-x)}\text{Se}_2 thin film.
3. A.B.C. Conclusions:

1. The arrested precipitation technique is found to be most convenient method for deposition of MoSe$_2$ thin films. The deposited films were compact, homogeneous, very adherent and with mirror aspect. The Molybdenum complexed with triethanolamine in an aqueous alkaline medium at lower pH, but at higher pH ($\approx 9.6$) Mo$^{4+}$ slowly releases ions to condense ion by ion to form MoSe$_2$ thin films, with almost negligible consumption of electrical power and basic material. The novelty of this process is the rotating substrate stir well automatically the reaction mixture leading to uniform and good quality deposit.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Deposition Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>9.6</td>
</tr>
<tr>
<td>Temperature</td>
<td>60 ±2$^0$C</td>
</tr>
<tr>
<td>Time</td>
<td>55 min</td>
</tr>
<tr>
<td>Speed of Substrate Rotation</td>
<td>50 ±2 rpm</td>
</tr>
</tbody>
</table>

2. Polycrystalline WSe$_2$ thin films were successfully deposited by electrodeposition technique on stainless steel and FTO coated conducting glass substrate from aqueous alkaline bath. The films were gray–black coloured, uniform, adherent and pin hole free.

3. By hybrid synthesis technique ternary Mo$_x$W$_{(1-x)}$Se$_2$ thin films were synthesized successfully. The successive deposition of WSe$_2$ by electrodeposition technique followed by deposition of MoSe$_2$ by APT on the same films was carried out and the post deposition treatment to the resulting films was given they were annealed in furnace at 250 °C for three hours. It results in to good quality ternary mixed TMDC thin films. The films were gray-black adherent, uniform and pin hole and crack free.
REFERENCES