3.1 Introduction

Selenisation is the process of incorporating elemental selenium into metallic layers to prepare binary or ternary selenides. Conventional technique involves annealing the required metallic layer in an atmosphere of hydrogen selenide or selenium vapour, which are extremely toxic gases. This requires highly sophisticated arrangements for complete safety and protection, which makes the set up much expensive. Moreover, this will become a problem in large-scale production. When one considers cost effectiveness as well as avoiding toxic gases, CBD is the best option for selenisation.

In the present investigation, we adopted CBD for the preparation of selenium (a-Se) in the form of thin films. Structural analysis of the films showed that the films are amorphous in nature.

3.2 A brief review on a-Se thin films

Selenium is the 34th element in the periodic table with two unsatisfied bonds in its outer orbital structure. It can exist in crystalline form but the amorphous form (a-Se) is of interest for different technological applications. Density of a-Se is 4.2 g/cc and it is believed to be an inorganic polymer consisting of covalently bonded chains. Although it is not a crystalline structure an effective band-gap of 2.2 eV can be ascribed to it. Resistivity of a-Se is exceedingly high (about $10^{16}$ ohm cm) making the material a very good insulator. However it is a photoconductor and if an electric field is present to separate the photogenerated electrons and holes, it can generate significant currents [1].

Amorphous selenium has been widely investigated over the decades because of the many scientific and technological interests. Earlier it was the xerographic material of choice for a long time, and is now being considered for
digital x-ray imaging [2]. Even though in the present work, we are not studying such applications, some of the recent research works on this material in this direction are reviewed here.

In a review report on amorphous semiconductors, David Adler described different suggestions made by many researchers on the structure of a-Se [3]. In that review, they proposed a combination of molecular Se₈ rings and polymeric chains to be consistent with all structural studies. Recently, Caprion et al showed that a-Se consists of interconnected chains and rings with a mean coordination number of 2.1 [4].

Structural changes from amorphous phase to crystalline phase (c-Se) are reported in recent studies. Laser induced crystallization is reported for a-Se films due to irradiation by linearly polarized He-Ne or Ti:Saphire (630 -750 nm) laser beams with sample temperature at and slightly above the glass transition temperature. They prepared a-Se thin films using thermal evaporation of gray selenium. After laser exposure, both β-monoclinic and hexagonal crystalline phases were detected [5].

Light-induced changes in a-Se films (prepared using pulsed laser evaporation) were investigated by Hansen et al. [6]. They explained this as light induced relaxation of void-filled short-chain selenium film into a denser equilibrium state of long polymer chain film which does not readily wet glass or silicon substrate. Peled et al reported photodeposition of a-Se films by continuous-wave argon ion lasers. When laser light was allowed to pass through a-Se colloid-Se ion solution. [7], they observed an increase in rate of redox reaction leading to the formation of Se⁰ from Se⁴⁺.

Dependence of crystallization of films on temperature and time of aging was investigated by Zienab et al. They calculated optical bandgap energies for different allotrops of selenium as 1.65 eV for black Se, 1.6 eV for monoclinic and 2.05 eV for amorphous Se [8]. Crystallization process was also found to depend on the deposition procedure. Parameters such as deposition rate, film thickness, substrate temperature and nature of substrate have marked effects on the structure.
of the film [9,10]. Fleury et al., used conductivity studies to analyse kinetics of structural change taking place in flash evaporated a-Se films [11].

In the applications of a-Se thin films, only a few important reports are listed here. In X-ray imaging, X-ray sensitivity of the film was investigated by Kasap et al., [12]. Holographic recording in ultra thin a-Se film was performed by Ballesteros et al. [13].

In the following sections, preparation of a-Se thin film using CBD and characterization of these samples using different techniques are described.

3.3 Preparation of a-Se using CBD

3.3.1 Principle

Principle of this technique is described in detail by Kitaev et al. [14]. They considered the formation of $\text{Na}_2\text{SeSO}_3$ by dissolving selenium in the aqueous solution of $\text{Na}_2\text{SO}_3$, which is represented as

$$\text{Se} + \text{Na}_2\text{SO}_3 \leftrightarrow \text{Na}_2\text{SeSO}_3 \quad (1)$$

or

$$\text{Se} + \text{SO}_3^{2-} \leftrightarrow \text{SeSO}_3^{2-} \quad (2)$$

Principle of selenium deposition is based on the fact that concentration of sulphites and hence solubility of selenium depends on pH of the solution. This could be explained as follows. For the reaction (2), equilibrium constant of this reaction is given by

$$K_{\text{SeSO}_3^{2-}} = \frac{[\text{SeSO}_3^{2-}]}{[\text{SO}_3^{2-}]} \quad (3)$$

where $[\text{SeSO}_3^{2-}]$ and $[\text{SO}_3^{2-}]$ are equilibrium concentration of the $\text{SeSO}_3^{2-}$ and $\text{SO}_3^{2-}$ respectively. Considering hydrolysis of sodium sulphite, the fractional concentration of $\text{SO}_3^{2-}$, $\alpha_{\text{SO}_3^{2-}}$ is given by

$$\alpha_{\text{SO}_3^{2-}} = \frac{[\text{SO}_3^{2-}]}{[\text{H}_2\text{SO}_3] + [\text{HSO}_3] + [\text{SO}_3^{2-}]} \quad (3)$$

$$\alpha_{\text{SO}_3^{2-}} = \frac{K_{\text{H}_2\text{SO}_3}}{[\text{H}^+] + K_1[\text{H}^+] + K_{\text{H}_2\text{SO}_3}} \quad (4)$$

where $K_1$ is the first dissociation constant of the reaction,
\[ \text{H}_2\text{SO}_3 \rightleftharpoons \text{HSO}_3^- + \text{H}^+ \text{ and is given by} \]
\[ K_1 = \frac{[\text{HSO}_3^-][\text{H}^+]}{[\text{H}_2\text{SO}_3]} \]

and \( K_{\text{H,SO}_3} \) is total dissociation constant given by
\[ K_{\text{H,SO}_3} = K_1 \times K_2 \] (5)

where, \( K_2 \) is the second dissociation constant of the reaction,
\[ \text{HSO}_3^- \rightleftharpoons \text{SO}_3^{2-} + \text{H}^+ \text{ and is given by} \]
\[ K_2 = \frac{[\text{SO}_3^{2-}][\text{H}^+]}{[\text{HSO}_3^-]} \]

From eq. (4) it is clear that as a result of hydrolysis of \( \text{Na}_2\text{SO}_3 \), concentration of \( [\text{SO}_3^{2-}] \) ions is defined not only by concentration of sodium sulphite salt in the solution but also the value of pH. Kitaev et al., determined the value of \( \alpha_{\text{SO}_3^{2-}} \) by substituting the value of \( K_1 = 1.3 \times 10^{-2} \) and \( K_{\text{H,SO}_3} = 8.2 \times 10^{-10} \) as given in the table below.

<table>
<thead>
<tr>
<th>PH</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha_{\text{SO}_3^{2-}} )</td>
<td>9.1 \times 10^{-7}</td>
<td>3.6 \times 10^{-6}</td>
<td>5.7 \times 10^{-5}</td>
<td>6.3 \times 10^{-4}</td>
<td>6.3 \times 10^{-3}</td>
</tr>
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<tr>
<th>PH</th>
<th>6</th>
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<tbody>
<tr>
<td>( \alpha_{\text{SO}_3^{2-}} )</td>
<td>5.9 \times 10^{-2}</td>
<td>0.33</td>
<td>0.87</td>
<td>0.98</td>
<td>.99</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Table 3.1: Fractional dissociation constant of \( \text{SO}_3^{2-} \) at different pH

As seen from the table 3.1, the concentration of \( \text{SO}_3^{2-} \) is equal to that of \( \text{Na}_2\text{SO}_3 \) in the solution, only at pH \( \geq 10 \). Hence, if pH of \( \text{Na}_2\text{SO}_3 \) solution is \( < 9 \), the concentration of \( \text{SO}_3^{2-} \) is,
\[ [\text{SO}_3^{2-}] = \alpha_{\text{SO}_3^{2-}} \times [\text{Na}_2\text{SO}_3] \] (6)

From the known amount of \( \text{Na}_2\text{SO}_3 \) the equilibrium constant of eq. (2), which expresses the precipitation of Se, becomes,
\[ K_{\text{SeSO}_3^{2-}} = \frac{[\text{SeSO}_3^{2-}]}{[\text{Na}_2\text{SO}_3] - [\text{SeSO}_3^{2-}]} \] (7)
From eq. (7) equilibrium concentration of $\text{SeSO}_3^{2-}$ can be calculated as,

$$[	ext{SeSO}_3^{2-}] = \frac{a_{\text{SO}_3^{2-}} \times K_{\text{SeSO}_3^{2-}}}{1 + a_{\text{SO}_3^{2-}} \times K_{\text{SeSO}_3^{2-}}} + [\text{Na}_2\text{SO}_3] \quad (8)$$

In the logarithmic form, this equation can be written as

$$p[	ext{SeSO}_3^{2-}] = p\frac{a_{\text{SO}_3^{2-}} \times K_{\text{SeSO}_3^{2-}}}{1 + a_{\text{SO}_3^{2-}} \times K_{\text{SeSO}_3^{2-}}} + p[\text{Na}_2\text{SO}_3] \quad (10)$$

where,

$$p[\text{SeSO}_3^{2-}] = -\log[\text{SeSO}_3^{2-}]$$

Eq. (8) describes the solubility of Se in $\text{Na}_2\text{SO}_3$ solution of the given concentration. This can be illustrated in the plot of $p[	ext{SeSO}_3^{2-}]$ vs. pH for $[\text{Na}_2\text{SO}_3]$ of 1 mole/l at 25 °C, as given in the figure 3.1. The graph reveals the solubility of Se in $\text{Na}_2\text{SO}_3$ increases with increase in the pH of the solution as $p[\text{SeSO}_3^{2-}]$ gives inverse of solubility.

![Figure 3.1: Variation of solubility of selenium in the $\text{Na}_2\text{SO}_3$ with pH of solution (conc. of $\text{Na}_2\text{SO}_3$ is 1 mole/l)](image)

Above mentioned calculations indicate the value of pH of the medium to be employed in the synthesis of $\text{Na}_2\text{SeSO}_3$ solution should be pH ≥ 10. Thus selenium can be precipitated by reducing the pH of selenosulphate solution to more acidic values.
In the present work, pH of Na$_2$SO$_3$ and Na$_2$SeSO$_3$ solutions were greater than 10. Rate of selenium precipitation is controlled by reducing pH of the selenosulphate solution to a value in the range 4.2-4.5, so as to form thin films. Effect of temperature and morality of the solution was also studied experimentally.

3.3.2 Experiment

A stock solution of 0.2 M sodium selenosulphate (Na$_2$SeSO$_3$) was prepared by dissolving selenium powder of weight equivalent to 0.2 M (99.99% pure) in aqueous solution of excess sodium sulphite kept at 363 K, subjected to constant stirring as described in sec. 2.2. pH of as-prepared Na$_2$SeSO$_3$ solution was ~ 10.5.

Well-cleaned glass slides of dimension 2.5×4.5×0.2 cm$^3$ with and without SnO$_2$ coating were used as substrate for the deposition process. Cleaning process of the slides was described in sec. 2.2. Preparation of SnO$_2$ coated glass substrates was also cited in the same section. In the case of glass substrates, these were heated to 673 K over which ethanol was sprayed and cooled down to room temperature. After cooling, these substrates were well-cleaned using soap solution and then in distilled water followed by drying in heater at 373 K.

Deposition was carried out in a 25 ml beaker to minimize the consumption and wastage of solution, even during initial trials. Three substrates were dipped vertically in the beaker so that three samples of area 5.5 cm$^2$ could be prepared at a time. Film deposited on the substrate surface facing the wall of the beaker was chosen as good film as mentioned in chapter 1.

As-prepared 0.2 M Na$_2$SeSO$_3$ solution (pH ≈ 10.5) was stable. However, acidification of the above solution resulted in selenium precipitation as described in the theory. In order to obtain selenium in the form of thin film, the precipitation was controlled by varying molarity, pH and temperature of the bath containing Na$_2$SeSO$_3$ solution. Volume of the solution was kept constant as 20 ml, the maximum volume that could be conveniently handled in a 25 ml beaker.
3.3.3 Parameters affecting the deposition

Growth of the selenium film depends on the rate of precipitation of selenium from the Na₂SeSO₃ solution, which in turn, depends on various factors such as pH, molarity, temperature of the bath and nature of the substrate as mentioned in introductory chapter. Here, experimental observations during growth process and nature of the films obtained at different conditions are described in the following paragraph.

i. Molarity

Initially, the deposition was carried out at different concentrations of Na₂SeSO₃ solution. For that, different molar solutions were prepared by dilution of the 0.2 M stock solution. The made up solutions were 0.006 M, 0.0125 M, 0.025 M, 0.05 M and 0.075 M, for trials. pH of all the solutions were adjusted to 4.5 (an arbitrary value) with 50% dilute acetic acid, keeping the bath at room temperature (300 K). Uniform films were obtained for 0.006 M solution after 3 hrs of deposition. Time of deposition was chosen on the basis the reaction rate. When molarity is increased from 0.006 M, immediate precipitation (colloidal), red in colour, was observed. Thus, for further trials, concentration was selected at 0.006 M Na₂SeSO₃.

ii. pH value

In order to study the effect of pH value, this parameter (of the 0.006 M solution) was varied from 3.00 to 7.2 at room temperature. Then it was seen that at lower pH values (3, 3.2, 3.5 etc.) precipitation was fast and hence no film was deposited. When it was in the range 4.2-4.7, uniform films were obtained. As pH value was made higher than this range, precipitation became slower and films were deposited in the form of 'patches'. When the pH of the solution was neutral or alkaline, there was no visible change for the solution, since it is stable according to the theory. Thus the pH was always kept at 4.5 for the deposition of Se films.

iii. Temperature

Furthermore, the deposition process was carried out at various temperatures using (0.006 M solution) (pH 4.5) viz at 278 K (keeping in the ice bath), 300 K, 323 K, 333 K and 343 K (keeping in hot air oven). At temperatures, higher than 300 K, the precipitation was fast and colour of the precipitate was gray. It was found that at 278 K, deposition time was 8 hrs to obtain uniform film of enough
Chapter 3

thickness. At 300 K, uniform films were formed as described earlier. So the optimum temperature for the film formation was found to be 300 K.

iv. Nature of the substrate

It was found that the uniformity of the films strongly depends on nature of surface of glass substrates. Three types of differently treated glass substrates were used for the deposition process. One type was bare glass slides. Second type was alcohol sprayed glass slides as mentioned earlier. SnO$_2$ coated glass slides were the third type. Films deposited on SnO$_2$ coated glass substrates and alcohol sprayed glass substrates, were found to be more adhesive than those formed on untreated glass substrates.

From the above discussion, the best samples were those prepared at 300 K from 0.006 M Na$_2$SeSO$_3$ solution at pH value 4.5 and therefore further analyses were done on this type of samples. The film was annealed to improve the structural, optical and electrical properties at different temperatures viz., 308 K, 323 K, 343 K and 373 K in high vacuum for 1h.

3.4 Characterization

After the preliminary visual observation of physical appearance of the films, morphological, structural, compositional, optical and electrical properties were analysed using different techniques. Morphology was analysed using SEM. Crystallinity was studied using XRD. XPS and SIMS were used for the depth-wise elemental analysis. The XPS spectra were recorded for 500 cycles for which each cycle corresponds to Argon ion sputtering for 1 min. ICP was used for bulk elemental analysis and. Optical properties were studied from optical absorption spectrum. Electrical characterization was done using I-V characteristics measured by SMU.

3.4.1 Visual observations

The as-prepared films were orange red in colour, uniform and smooth. It was found that due to aging, it was converted to gray form. The gray films were not uniform, but it was powdery. The conversion was relatively faster when the films were kept in open air rather than in dried conditions in desiccator. Also, films prepared on bare glass slides were less stable than that on alcohol sprayed or SnO$_2$
coated glass substrates. The film after annealing appeared as thinner, non-uniform and gray in colour. Damage during annealing occurs even at 313 K.

3.4.2 Thickness

Thickness of films was measured by stylus profilometer. Figure 3.2 shows the profile of the measurement. Thickness of the triple dipped films was measured as 5000 Å.

3.4.3 SEM

Surface nature of the films was studied using Scanning Electron Micrograph. Fig. 3.3(a) and fig 3.3(b) shows the morphology of selenium film deposited on glass and SnO₂ coated glass substrate respectively. This indicates the effect of substrate on the morphology of the films. On glass continuous lateral growth is observed while on SnO₂ coated glass, growth is granular type. This type of growth nature was reported by Kitaev et al., for amorphous selenium films [13].

3.4.4 XRD

Structural analysis of the films was carried out using XRD. The scan rate was 2 °/min in the range 2θ between 14 and 50 °. Figure 3.4 shows the pattern of Se film deposited on glass. The figure clearly shows amorphous nature of the films. When the film was annealed, no improvement in crystallinity was observed as the film was damaged.

3.4.5 XPS

XPS spectra of samples gave the composition of the films. Depth profile of the films deposited on SnO₂ coated glass substrate is shown in fig. 3.5. This reveals presence of selenium with binding energy at 55.5-56 eV [15], which corresponds to the elemental state. Traces of oxygen and tin are also detected at the front surface, which are diffused from the tin oxide coated glass substrate to selenium film. Oxide formation is ruled out as the binding energy of SeO₂ is 58.85 eV [16]. Presence of Na is also checked since there is a possibility of incorporation of Na from the Na₂SeSO₃ solution. The depth profile shows Na signal only in the region of glass substrate.
Fig. 3.2: Thickness of selenium thin film
Figure 3.3: Scanning electron micrograph of a-Se films on (a) glass substrate (b) SnO$_2$ glass substrate
3.4.6 SIMS

Depth-wise elemental analysis was confirmed by SIMS analysis as illustrated in figure 3.6. At the surface selenium and traces of sodium are present. Even though oxygen or sulphur was not observed in the spectrum, Na was detected in this analysis throughout the depth up to SnO₂-Glass interface. Towards the region of SnO₂-Glass amount of Na is more compared to that on the surface.

3.4.7 ICP

In this technique, film was dissolved in concentrated HNO₃ and very diluted solution of which is sprayed into plasma state. Emission line intensity corresponding to the ions was measured, which in turn proportional to the amount of element present in the solution. It was found that emission line consists of only selenium. Sodium or tin was not detected in the flame.
Figure 3.5: XPS profile montage of a-Se deposited on SnO$_2$ coated glass substrate
3.4.8 Optical properties

Wavelength dependence of optical absorption of the film in the range 450-700 nm is shown in fig. 3.7. The spectral dependence of absorption shows that the film has direct band gap (Eg). The Eg value is determined from the plot of \((\alpha h\nu)^2\) vs. \(h\nu\) as given in fig. 3.8. The value obtained is 2.1 eV as indicated in the plot and is in agreement with the reported value for amorphous selenium [8].
Figure 3.7: Wavelength dependence of optical absorption of a-Se film

Figure 3.8: $(\alpha \nu)^2$ Vs $\nu$ plot for a-Se film
3.4.9 Electrical characterization

Resistance of the film was evaluated from the I-V characteristic given in fig. 3.8. Measurements were taken across two magnamine wire leads pasted on two terminals coated on the surface of the film with separation of 5mm. Electrodes were Au layer evaporated on the film. The resistance evaluated from the graph is $1.2 \times 10^{10}$ ohm. It shows the film is electrically an insulator. Under illumination no change in resistance was observed.

![I-V characteristic graph](image)

Figure 3.9: I-V characteristics of a-Se at room temperature

3.5 Results and discussions

a-Se thin films were prepared by lowering pH value of Na$_2$SeSO$_3$ solution to $\sim$ 4.5. Morphological studies (fig.3.3(a) and (b)) of the films show that surface of the film has spreading of liquid drop like appearance, which is characteristics of amorphous material. Due to aging the red coloured film was converted to gray form and was found that in the open air, conversion was more effective. Also, less adhesive films were easily undergoing transformation. Hansen et al [6] described these structural changes as due to the presence of voids and dangling bonds in the films. Due to illumination or annealing, these atoms become more mobile and fill
the voids and attain a low energy configuration. They also observed formation of mottled films under room temperature storage for several days. In the present case, XRD could not identify the crystalline nature of gray form.

Both the as-prepared and gray coloured films are dipped in CS$_2$. The gray form was found to be insoluble and this shows it is the hexagonal form of selenium [6]. It is well known that CS$_2$ dissolves amorphous selenium while not affecting crystalline selenium. Since our aim was not in the detailed study of selenium thin films, further studies on conversion process were not carried out.

The presence of selenium film on the top of SnO$_2$ was confirmed using SIMS (fig. 3.6), XPS (fig. 3.5) and ICP. In SIMS analysis the Na level in the film and SnO$_2$ layer is more or less same and increases to more than one order at the glass face. This Na may be from the soda lime glass substrate, which contains 15% Na$_2$O as it is very clear from the XPS analysis [17]. Traces of Na from the glass may be ejected due to sputtering and detected during depth profiling, as SIMS is highly sensitive to sodium (10$^{14}$ atoms/cc). High sensitivity of Na to this technique is due to its low ionization potential and extremely high ionization cross-section of the element [18].

However, ICP analysis could not detect sodium in the film. If Na detected in SIMS analysis is from the film, it should have been detected in ICP analysis also, which is more sensitive than SIMS (10$^{13}$ atoms/cc). Hence the only possibility of detecting sodium (from SIMS) is from the substrate.

From the studies optical absorption, a-Se was found to possess a direct band gap of 2.1 eV. Electrically a-Se is found to be an insulator.

3.6 Conclusion

Amorphous selenium films could be deposited using CBD from sodium selenosulphate solution by adjusting the pH at 4.5, at room temperature. Thickness of triple-dipped films was 5000 Å. Morphological studies were performed by SEM. Structural and elemental analyses were done using XRD, XPS and SIMS. These studies reveal that the films obtained were pure amorphous selenium. Thus deposition of an element in the form of thin film could be achieved using CBD, the simple and low cost process. Optical band gap evaluated from the spectral
dependence of absorbance was 2.1 eV. Very high value of resistance revealed that the film was nearly electrically insulator.

Selenium, which is extremely toxic in its vapour state, is available in the non-toxic form and can be used for preparation of binary and ternary selenides. In the proceeding chapters, selenisation process using this selenium film is described.
References


