CHAPTER-3

Characterisation of copper selenide thin films

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Reference
3.1 Introduction

Preparation and characterisation of any material are two equally important aspects like the two sides of a coin. In the case of thin films, appropriate characterisation often widens the scope of applications. However characterising thin films with precision is a challenging job.

This thesis work includes:

i) Morphological characterisation by visual appearance, thickness measurement using Tolansky method and Stylus method and surface morphological studies using SEM (Scanning Electron Microscope).

ii) Structural characterisation using XRD (X-Ray Diffraction) analysis.

iii) Optical characterisation using absorption and transmission spectral studies.

iv) Compositional analysis using XPS (X-ray Photoelectron Spectroscopy), ICP (Inductively Coupled Plasma) and XRD analysis.

v) Electrical characterisation using Hall measurements

3.2 Morphological characterisation

Microstructure and thickness have profound influence on the properties of thin films. For instance, when copper selenide finds application as an absorber layer in the field of photovoltaics, two major requirements are large grain size and a film thickness around 2\mu m [1]. Moreover, in solar cells where Cu$_{2-x}$Se is used as window material, the poor cell efficiency was attributed to non-uniformity and presence of pinholes in the Cu$_{2-x}$Se film [2].

3.2.1 Visual appearance

Thin films of Cu$_{2-x}$Se prepared from Bath 1:1, Bath 2:1, Bath 3:1 and Bath 5:1 were reddish brown in colour [2] and uniform in appearance. Bath 1:1 Na and Bath 1:2 resulted in Cu$_{3}$Se$_{2}$ films with a bluish green colour. The group of cuprous selenides, which includes Cu$_{3}$Se$_{2}$, is known to have a similar colour [3]. When observed with naked eye the film from Bath 1:1 Na was more uniform than that from Bath 1:2. In short, Cu$_{2-x}$Se phase has a reddish colour, while Cu$_{3}$Se$_{2}$ is bluish green. Hence preliminary differentiation of the two phases was very easy.
3.2.2 Thickness measurement

Thickness of as-prepared films was measured using Tolansky technique. For this method, it is necessary to have a sharp and well defined straight edge of the film. Usually CBD films have a curved hazy edge, as the solution bath forms a meniscus curved downwards due to capillary rise. In order to get a sharp edge, glass slides were masked with tightly wound teflon tapes before dipping in the reaction bath. After the final stage of drying the films, teflon tapes were removed carefully.

In the case of Cu$_{2x}$Se film, thickness of one-dip was found to be around 0.2 $\mu$m. As two-dip and three-dip films were thicker than the measurable range of this technique, they were analysed using gravimetric method. The thickness was estimated to be around 1 $\mu$m 1.2 $\mu$m. For Cu$_3$Se$_2$ film the thickness of two-dip was near 1.2 $\mu$m.

In order to counter check the accuracy of this method, Stylus profiling was also done on few of the samples and the results were found to agree with the Tolansky method. Stylus profiler makes use of a diamond probe, which moves over the film surface. When this probe encounters the step formed by the thin film edge, a corresponding electrical signal is generated from which thickness of the film can be calculated.

3.2.3 Surface morphology

Scanning electron microscope (SEM) was used for studying surface morphology and micro structural features of the as-prepared copper selenide thin films. In this technique, secondary electrons are emitted from the surface layer of the film and hence the micrograph obtained will be a faithful reproduction of the surface features.

SEM equipment of Hitachi Co. (model: S 2400) was used for the present study. As copper selenide films were low resistive, no additional conducting coating was given to the film surface. 15 K magnification was chosen as most suitable for observing grains in the as-prepared thin films. From this morphology study, it was possible to understand the effect of varying the relative concentration of copper in the reaction mixture, the effect of substrate and temperature of deposition on the grain size and also to differentiate Cu$_{2x}$Se phase from Cu$_{3}$Se$_{2}$ phase.

Micrographs of Cu$_{2x}$Se film prepared from Bath 1:1 and Bath 2:1 are shown in Fig.(3.1) and Fig.(3.2) respectively. Both have more or less same appearance and
Fig (3.1) SEM micrograph of Cu$_{2-x}$Se film from Bath 1:1

Fig (3.2) SEM micrograph of Cu$_{2-x}$Se film from Bath 2:1
average grain size around 0.2 μm. Grain boundaries are well defined even in the as-prepared form. Detailed examination reveals that film from Bath 1:1 is slightly more uniform than the film from Bath 2:1. The micrographs of film prepared from Bath 3:1 and Bath 5:1 [Fig.(3.3) and Fig.(3.4)] show that the grain boundaries become more diffused when the relative concentration of copper is increased beyond a Cu:Se ratio of 2:1. In films from Bath 5:1, the granularity of the phase is almost lost. In the present work, due to the most uniform surface morphology, the films from Bath 1:1 are chosen as the representative sample of the Cu$_{2-x}$Se phase (referred as sample No: 1).

All the above mentioned films were deposited on glass substrate. However Fig.(3.5) shows the film deposited from Bath 1:1 on SnO$_2$ substrate. Average grain size in this case is found to be 0.3 μm. This reveals the effect of substrate on grain size of Cu$_{2-x}$Se phase, i.e. bigger grain size is obtained on SnO$_2$ substrates than on glass substrates.

Comparison of SEM micrograph of film from Bath 1:1 LT [Fig.(3.6)] with Fig.(3.1) reveals the effect of temperature of deposition on the surface morphology. It can be observed that surface of the film deposited at low temperature is not uniform as the grains have a tendency to grow as clusters. Moreover the grain boundaries are not well defined.

Fig.(3.7) shows the micrograph of Cu$_{3}$Se$_2$ phase deposited from Bath 1:1 Na. Here average grain size is around 0.4 μm. When compared with standard Cu$_{2-x}$Se phase (Fig.(3.1)), surface of Cu$_{3}$Se$_2$ film shows ups and downs along with cluster formation. The grain size of Cu$_{3}$Se$_2$ phase is almost double that of Cu$_{2-x}$Se phase. Hence the general conclusions are:

i) Cu$_{2-x}$Se film from Bath 1:1 is very uniform with distinct grains of average size 0.2 μm.
ii) The gradual increase in concentration of copper in the reaction bath leads to poor film morphology.
iii) Deposition at low temperature is found to result in grain growth in the form of clusters.
iv) When compared with Cu$_{2-x}$Se phase, Cu$_{3}$Se$_2$ phase grows in clusters with less defined grain boundaries, but with a larger grain size of the range 0.4 μm.
Fig (3.3)  SEM micrograph of Cu$_{2-x}$Se film from Bath 3:1

Fig (3.4)  SEM micrograph of Cu$_{2-x}$Se film from Bath 5:1
Fig (3.5) SEM micrograph of Cu$_{2-x}$Se film from Bath 1:1 SnO$_2$

Fig (3.6) SEM micrograph of Cu$_{2-x}$Se film from Bath 1:1 LT
This study on grain size and surface nature is significant when these thin films find applications in optoelectronics and photovoltaics.

3.3 Structural characterisation

3.3.1 XRD analysis

X-ray diffraction is the most convenient tool for crystallographic structural analysis. In the present work this was used as a major analytical technique for differentiating various phases of the as-prepared copper selenide thin films. This analysis was done using Rigaku (D.Max.C) X-ray diffractometer, which makes use of Cu Kα (λ=1.5405 Å) radiation. After preliminary trials, the scan range for 2θ was fixed between 20° and 55° for these thin films.

a) Cu$_{2-x}$Se phase

XRD pattern of the film from Bath 1:1 is shown in Fig.(3.8). On comparing the d values of this spectrum with the standard JCPDS data index 6-0680, the structure was identified as cubic phase of Cu$_{2-x}$Se. In the standard data the highest intensity is attributed to (022) plane, while in the present case peak corresponding to (111) plane has maximum intensity. Due to the amorphous nature of the glass substrate the background intensity is very high in the spectrum. The d values and the relative intensities after background correction are shown in Table (3.1).

<table>
<thead>
<tr>
<th>d (Å) experimentally observed</th>
<th>d (Å) as per JCPDS file 6-0680</th>
<th>hkl</th>
<th>I/I₀ (Observed)</th>
<th>I/I₀ (Standard)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.323</td>
<td>3.330</td>
<td>111</td>
<td>100</td>
<td>90</td>
</tr>
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<td>2.030</td>
<td>2.030</td>
<td>022</td>
<td>71</td>
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</tr>
<tr>
<td>1.729</td>
<td>1.729</td>
<td>113</td>
<td>18</td>
<td>80</td>
</tr>
</tbody>
</table>

Table (3.1) X-ray diffraction parameters of cubic Cu$_{2-x}$Se film

The cubic phase of Cu$_{2-x}$Se is usually known as the high temperature phase [4-9]. However depending on the extent of non-stoichiometry in the copper selenide
Fig (3.7) SEM micrograph of Cu$_3$Se$_2$ film from Bath 1:1 Na.

Fig (3.8) XRD spectrum of Cu$_{2-x}$Se film from Bath 1:1
phase, the cubic phase can occur even at room temperature. The phase diagram shown in Fig.(3.9), as reported by Tonejc et al. [10], depicts this situation clearly. It suggests that the low temperature phase exists as the single phase only if the composition is around Cu$_{1.997}$Se. At this composition when the temperature is increased to 130°C, the high temperature phase begins to appear and at a temperature above 140°C the sample completely gets converted to the high temperature phase. The low temperature to high temperature transition always occurs through a stage of mixed phase. But when 1.97 $\leq$ (2-x) $\leq$ 1.84, the low temperature phase is highly unstable in air and it gets converted to high temperature phase, at temperatures lower than 130°C. From the figure it is clear that at composition x $\geq$ 0.2 the high temperature phase can occur as a single phase at temperatures above 30°C. In the present case, the composition was analysed to be x $\geq$ 0.2 (refer section 3.5) and it justifies the cubic phase at room temperature. Similar results are reported in other publications also [1,2,11-13].

\textit{b) Cu$_{3}$Se$_{2}$ phase}

XRD pattern of the films deposited from Bath 1:1 Na and Bath 1:2 were similar. However as the samples from Bath 1:1 Na were more uniform, they were chosen as the standard film of Cu$_{3}$Se$_{2}$ phase (referred to as Sample No.2). The XRD spectrum of this is shown in Fig.(3.10) and the d values coincide with the JCPDS data index 47-1745 for tetragonal Cu$_{3}$Se$_{2}$ phase. All the major diffraction peaks in the standard file were repeatedly reproduced in the sample. As only a thin layer of this material could be deposited on a plane glass substrate, the intensities of the diffraction peaks were very small. Hence Cu$_{3}$Se$_{2}$ films were preferably deposited on SnO$_{2}$ coated glass. XRD spectrum of Cu$_{3}$Se$_{2}$ on glass and on SnO$_{2}$ coated glass were the same except for the difference in peak intensities, background intensities and the presence of peaks from SnO$_{2}$. Table (3.2) shows the XRD parameters of the Cu$_{3}$Se$_{2}$ film (the relative intensities being calculated after background correction).
Fig. (3.9) Phase diagram of low temperature (L.T) and high temperature (H.T) phase of Cu$_2$X in relation to stoichiometry and temperature

Fig (3.10) XRD spectrum of Cu$_3$Se$_2$ film from Bath 1:1 Na
Table (3.2) X-ray diffraction parameters of tetragonal Cu$_3$Se$_2$ film

<table>
<thead>
<tr>
<th>d (Å) experimentally observed</th>
<th>d (Å) as per JCPDS file 47-1745</th>
<th>hkl</th>
<th>I/I$_0$ (Observed)</th>
<th>I/I$_0$ (Standard)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.575</td>
<td>3.557</td>
<td>101</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>3.214</td>
<td>3.202</td>
<td>200</td>
<td>44</td>
<td>55</td>
</tr>
<tr>
<td>3.126</td>
<td>3.111</td>
<td>111</td>
<td>56</td>
<td>61</td>
</tr>
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<td>2.874</td>
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<td>19</td>
</tr>
<tr>
<td>2.563</td>
<td>2.563</td>
<td>201</td>
<td>16</td>
<td>20</td>
</tr>
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<td>2.264</td>
<td>220</td>
<td>35</td>
<td>51</td>
</tr>
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<td>2.143</td>
<td>2.139</td>
<td>002</td>
<td>16</td>
<td>19</td>
</tr>
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<td>2.029</td>
<td>2.024</td>
<td>310</td>
<td>19</td>
<td>30</td>
</tr>
<tr>
<td>2.008</td>
<td>2.001</td>
<td>221</td>
<td>11</td>
<td>21</td>
</tr>
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<td>1.910</td>
<td>301</td>
<td>24</td>
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<td>1.833</td>
<td>1.830</td>
<td>311</td>
<td>46</td>
<td>63</td>
</tr>
<tr>
<td>1.781</td>
<td>1.778</td>
<td>202</td>
<td>31</td>
<td>47</td>
</tr>
</tbody>
</table>

c) Effect of increase in film thickness of Cu$_{2-x}$Se phase

Fig. (3.11) shows the XRD spectrum of Cu$_{2-x}$Se films after one dip, two dip and three dip respectively. The peak heights were found to increase considerably with thickness. Values of FWHM (full width at half maximum) of the peak corresponding to the characteristic (022) plane in these three cases are tabulated in Table (3.3) along with the maximum peak intensity. Decrease in FWHM of the peak with increase in the number of dippings shows improvement in crystallinity of the Cu$_{2-x}$Se film with increase in thickness.

<table>
<thead>
<tr>
<th>No: of dippings</th>
<th>FWHM</th>
<th>Maximum intensity (counts/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 dip</td>
<td>2.226</td>
<td>112</td>
</tr>
<tr>
<td>2 dip</td>
<td>0.949</td>
<td>181</td>
</tr>
<tr>
<td>3 dip</td>
<td>0.541</td>
<td>485</td>
</tr>
</tbody>
</table>

Table (3.3) Variation in FWHM and maximum intensity of XRD peak with increase in film thickness
Fig. (3.11) Variation in XRD spectrum of Cu$_{2-x}$Se film with thickness
d) Effect of increase in the relative concentration of copper in the reaction bath

Fig.(3.12) shows the XRD spectrum of films from Bath 1:1, Bath 2:1, Bath 3:1 and Bath 5:1 in succession. This reveals the influence of gradual increase in relative concentration of copper for a fixed concentration of selenium in the reaction bath. Peak intensity and FWHM of (022) plane for this series of $\text{Cu}_2\text{Se}$ film are tabulated in Table (3.4).

<table>
<thead>
<tr>
<th>Bath conditions</th>
<th>FWHM</th>
<th>Maximum intensity (c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bath 1:1</td>
<td>0.589</td>
<td>181</td>
</tr>
<tr>
<td>Bath 2:1</td>
<td>0.949</td>
<td>209</td>
</tr>
<tr>
<td>Bath 3:1</td>
<td>1.495</td>
<td>170</td>
</tr>
<tr>
<td>Bath 5:1</td>
<td>1.548</td>
<td>158</td>
</tr>
</tbody>
</table>

Table (3.4) Variation in FWHM and maximum intensity of the XRD peak with increase in copper concentration in the reaction bath

The highest intensity of (022) peak is for films from Bath 2:1 and it suggests maximum thickness. Further decrease in peak intensity for films from Bath 1:3 and Bath 1:5 shows decrease in film thickness. This is obvious with naked eye also. When the relative concentration of copper in the reaction bath is increased, the rate of reaction increases, leading to faster precipitation and thereby resulting in thinner films. Here the gradual increase in FWHM hinds to the gradual decrease in grain size of the $\text{Cu}_2\text{Se}$ film. SEM micrograph also supports this result.

3.4 Optical characterisation

Optical properties are very significant as far as applications in any optoelectronic devices are concerned. Optical band gap and absorption coefficient are two important parameters of a solar cell material.

In the present study, optical characterisation was done to the determination of nature of absorption and transmission spectra and energy bandgap of copper selenide. These properties have dependence on grain size and chemical composition of the thin films. Therefore it is logical to study the optical properties in correlation with the above mentioned factors.
Fig. (3.12) Variation in XRD spectrum of Cu$_{2-x}$Se film with relative concentration of Cu in the reaction bath.
3.4.1 Optical absorption

UV-VIS-NIR spectrophotometer (U-3410 model of Hitachi group) was used for the optical studies. Studies were mainly conducted in the range 340 nm to 2000 nm. Band edge calculated from the absorption spectrum was used as a tool to differentiate the formation of the two different phases of copper selenide.

Determination of optical band gap is based on the photon induced electronic transition between conduction band and valance band. At the absorption edge, absorption coefficient $\alpha$ can be expressed as

$$\alpha = (hv-Eg)^{\gamma}$$  [14].

This was used to find out the nature of transition in the thin film material. Here $hv$ stands for photon energy, $Eg$ for band gap and $\gamma$ is a constant which is equal to $\frac{1}{2}$ for allowed direct transition, $\frac{3}{2}$ for forbidden direct transition and 2 for allowed indirect transition.

For both Cu$_{2-x}$Se and Cu$_3$Se$_2$ thin films, the plot of $(\alpha thv)^2$ versus photon energy was found to be linear as shown in Fig.(3.13) and Fig.(3.14) ($t$ stands for the film thickness). The graphs suggest a direct bandgap for both the materials. Extrapolation of these curves to zero absorption coefficient showed the optical energy gap of the Cu$_{2-x}$Se phase as 2.20 eV and Cu$_3$Se$_2$ phase as 2.83 eV. This band gap of Cu$_{2-x}$Se phase is comparable with that reported earlier by Garcia et al. and others [1,12,15]. To the best of our knowledge this is the first report on the band gap of Cu$_3$Se$_2$ phase and hence no comparison is possible [16,17].

Band edge calculated for one dip, double dip and triple dip of the Cu$_{2-x}$Se film showed a shift towards lower values in succession, Fig.(3.15). The results are tabulated in Table (3.5). This is due to the effect of increase in average grain size with gradual increase in the number of dips. High value of band gap for the one-dip film suggests the very small size of the crystals. This blue shift of the optical spectra is a usual phenomenon in the case of chemically deposited thin films [18,19]. In the present case, the results are also supported by XRD analysis (refer section 3.3.1.c).

<table>
<thead>
<tr>
<th>No: of dippings</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I dip</td>
<td>2.31</td>
</tr>
<tr>
<td>II dip</td>
<td>2.20</td>
</tr>
<tr>
<td>III dip</td>
<td>2.05</td>
</tr>
</tbody>
</table>

Table (3.5) Variation in absorption edge of the Cu$_{2-x}$Se film with thickness
Fig. (3.13) $\alpha hv$ vs. hv graph of Cu$_2$Se film

$E_g = 2.2$ eV

Fig. (3.14) $(\alpha hv)^2$ vs. hv graph of Cu$_2$Se film

$E_g = 2.83$ eV
Absorption spectrum is also found to vary slightly with increase in relative concentration of copper in the reaction mixture. The absorption edge calculated for films from the Bath 1:1, Bath 2:1, Bath 3:1 and Bath 5:1 (Fig (3.16)) are tabulated in Table (3.6). The slight increase in the band edge with increase in relative concentration of copper may be the result of decrease in grain size (as suggested in section 3.3.1.d), decrease in film thickness and decrease in the non-stoichiometric index (as mentioned in section 3.5.3).

<table>
<thead>
<tr>
<th>Bath condition</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bath 1:1</td>
<td>2.20</td>
</tr>
<tr>
<td>Bath 2:1</td>
<td>2.31</td>
</tr>
<tr>
<td>Bath 3:1</td>
<td>2.32</td>
</tr>
<tr>
<td>Bath 5:1</td>
<td>2.34</td>
</tr>
</tbody>
</table>

Table (3.6) Variation in absorption edge with increase in relative concentration of Cu in the reaction bath

3.4.2 Optical transmission

Fig.(3.17) shows the transmittance spectra of the Cu_{2-x}Se film deposited from Bath 1:1 and the Cu_{3}Se_{2} film deposited from Bath 1:1 Na respectively. The peak value of transmittance is around 780 nm for the Cu_{2-x}Se film while it is around 580 nm for Cu_{3}Se_{2} films. A substantial decrease in transmittance is observed throughout the IR region for both the phases. This is the result of free carrier absorption in this degenerate semiconductor films [1]. This transmittance spectrum of Cu_{2-x}Se suggests a potential application of these films as microwave (IR) shielding coating or selective solar control coating [12,13]. Such effects have been reported for all copper selenides in general [20].

3.5 Compositional analysis

Characterisation by optical or electrical methods can be thought of as indirect way of analyzing a material, for these properties in turn depend on the primary quality of chemical composition or stoichiometry. Often the lack of repeatability and discrepancy between the expected behaviour and experimental observation, are due to lack of proper analysis and documentation of the composition of the material.
Fig. (3.15) Variation in absorption edge of Cu$_{2\alpha}$Se film with thickness

Fig. (3.16) Variation in absorption edge of Cu$_{2\alpha}$Se film with relative concentration of Cu in the reaction bath
Fig. (3.17) Transmission spectra of (a) Cu$_2$Se film (b) Cu$_3$Se$_2$ film
X-ray photoelectron spectroscopy (XPS) is considered as one of the most powerful tool, for characterising the chemical composition of thin films [21]. In the present work this technique was used for elemental analysis. Inductively coupled plasma (ICP) analysis was also done as a bulk analytical technique to confirm the stoichiometry as suggested by XPS analysis. Indirect interpretation of composition from XRD analysis is also included in this section.

3.5.1 XPS analysis

In XPS analysis it is possible to predict the chemical environment of various elements and to evaluate the percentage composition. It is also possible to have depth profile of the required region by sputtering the surface layers of the sample with heavy ions. Chemical environment of each element is interpreted by comparing the calculated value of binding energy from the XPS spectrum with the standard value for high purity elements and compounds.

Here this technique was used to analyse the uniformity of composition and also the atomic concentration along the depth of the copper selenide thin film. But as little reference is available on the XPS study of various phases of copper selenide, a comparative study of this material was not possible.

A ULVAC-PHI unit (model 5600) employing argon ion sputtering was used for the present XPS analysis. Here Al K$_\alpha$ X-ray (1486.6 eV) with a beam diameter of 0.8 mm and a power of 400 W was used as the incident beam. An argon ion gun with 3 kV voltage was employed for etching.

Fig.(3.18) shows the XPS depth profile of the as-prepared Cu$_{2-x}$Se thin film. This sample was deposited on SnO$_2$ substrate. Hence the elements analysed by this technique included tin, oxygen and silicon (Sn, O, and Si) apart from copper and selenium (Cu and Se). In this figure, the two peaks of Cu refer to 2p$_{1/2}$ and 2p$_{3/2}$, one peak of Se refers to 3d$_{5/2}$ and one peak of O refers to 1s electronic spectrum (referred in succession from left to right in the figure). The bottom layer of this figure refers to the surface of the film while the top portion corresponds to the substrate region. The substrate region can also be identified from the presence of Sn and O signal corresponding to SnO$_2$. This picture reveals the slight diffusion of copper and selenium into the SnO$_2$ substrate. Each horizontal line of the spectrum refers to signal collected after etching the surface for 1 minute in succession. This Cu$_{2-x}$Se sample
Fig. 3.18 XPS depth profile of as-prepared Cu$_{2-x}$Se film
was etched for 100 cycles and hence there are 100 horizontal lines for each element in
the spectrum.

The constant peak height of Cu and Se spectrum from the top surface to the
bottom layer of the film shows that the composition of the film is uniform across its
thickness. In the first two cycles on the surface of the film presence of oxygen is
obvious. The binding energy of this O 1s spectrum is around 531 eV, which
corresponds to chemisorbed water or hydroxide [22,23]. This contamination is
unavoidable for any surface prepared under ambient conditions. Oxygen signal is
absent in the bulk of the film, revealing the absence of any oxide impurity phase.
Fig.(3.19) shows the total XPS survey i.e. N(E)/E versus binding energy in the wide
range of 0 eV to 1400 eV taken after the fifth cycle of etching. Absence of binding
energy corresponding to oxygen confirms the absence of oxides. This result is of
importance as copper oxide impurity has often been a concern for copper selenide
films prepared in an aqueous medium [24]. The depth profile of the Cu$_2$Se$_2$ thin film
has more or less the same appearance and is shown in Fig.(3.20).

This depth profile spectrum was insufficient to trace the exact binding energy
of Cu and Se in the Cu$_{2-x}$Se phase and Cu$_3$Se$_2$ phase. Hence the enlarged spectrum of
these signals, after the fifth cycle of etching was taken. Fig.(3.21) shows the Cu
spectrum while Fig(3.22) shows the Se spectrum for both the phases. The peak
positions of Cu 2p and Cu 2p$_{3/2}$ are more or less the same for Cu$_{2-x}$Se and Cu$_3$Se$_2$, and
they are positioned at binding energies of 952.1 eV and 931.1 eV respectively. The Se
3d$_{5/2}$ spectrum shows a very small shift of 0.2 eV between the two phases. For Cu$_2$
Se film it is seen at 53.9 eV while for Cu$_3$Se$_2$ phase it is at 53.7 eV. A shift of 0.2 eV
being within the error limit, no useful interpretations can be made. The only reference
available for the binding energy of this material is for the CuSe phase and its energy
values are 952 eV for Cu 2p$_{3/2}$, 932.5 eV for Cu 2p$_{3/2}$ and 55 eV for Se 3d$_{5/2}$ [20].
Kasmerski et al. [25] have reported the binding energies for Cu$_x$Se phase in general
and the values are included in Table (3.7) for comparison.

Atomic concentration of Cu and Se could also be measured by this analysis.
But as the response of the instrument was relatively less for Se when compared to Cu,
a correction factor had to be evaluated using a standard sample. Standard CuSe
powder (Soekawa Chemical) was analysed and the figurative results are tabulated
along with the data from the atomic concentration spectra of the present Cu$_{2-x}$Se and
Cu$_3$Se$_2$ films, Table (3.8). Fig.(3.23) shows the percentage composition of Cu$_{2-x}$Se
Fig.(3.19) Total XPS survey of as-prepared Cu$_{2-x}$Se film.
Fig. (3.20) XPS depth profile of as prepared Cu$_3$Se$_2$ film
Fig (3.21)  XPS spectrum of copper after the 5\textsuperscript{th} cycle of etching of (a) $\text{Cu}_{2-x}\text{Se}$ and (b) $\text{Cu}_3\text{Se}_2$ phases.
Fig (3.22) XPS spectrum of selenium of (a) Cu$_{2-x}$Se and (b) Cu$_3$Se$_2$ phases after the 5$^{th}$ cycle of etching.
Fig. (3.23) Percentage composition graph of Cu$_{2-x}$Se thin film
phase before applying the correction. From the table it can be seen that the estimated stoichiometry of Cu$_{2x}$Se is Cu$_{1.82}$Se where x = 0.18. Similarly for Cu$_3$Se$_2$ phase, the Cu:Se value is estimated to be 1.58:1. This is very close to the expected value of 1:5:1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Element</th>
<th>Area cts -eV/s</th>
<th>Sensitivity factor</th>
<th>Concentration (%)</th>
<th>Uncorrected Cu/Se</th>
<th>Corrected Cu/Se</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSe standard</td>
<td>Se 3d</td>
<td>3386</td>
<td>14.570</td>
<td>40.62</td>
<td>1.46</td>
<td>1.00</td>
</tr>
<tr>
<td>CuSe standard</td>
<td>Cu 2p3</td>
<td>20432</td>
<td>60.150</td>
<td>59.38</td>
<td>1.46</td>
<td>1.00</td>
</tr>
<tr>
<td>Cu$_2$Se (from present work)</td>
<td>Se 3d</td>
<td>3659</td>
<td>14.570</td>
<td>27.28</td>
<td>2.66</td>
<td>1.82</td>
</tr>
<tr>
<td>Cu$_2$Se (from present work)</td>
<td>Cu 2p3</td>
<td>40273</td>
<td>60.150</td>
<td>72.72</td>
<td>2.66</td>
<td>1.82</td>
</tr>
<tr>
<td>Cu$_3$Se$_2$ (from present work)</td>
<td>Se 3d</td>
<td>4053</td>
<td>14.570</td>
<td>30.24</td>
<td>2.31</td>
<td>1.58</td>
</tr>
<tr>
<td>Cu$_3$Se$_2$ (from present work)</td>
<td>Cu 2p3</td>
<td>38603</td>
<td>60.150</td>
<td>69.76</td>
<td>2.31</td>
<td>1.58</td>
</tr>
</tbody>
</table>

Table (3.8) Cu/Se ratio as calculated from XPS analysis

### 3.5.2 ICP analysis

Inductively coupled plasma (ICP) analysis was performed on copper selenide samples to confirm the stoichiometry. The thin film samples were completely dissolved in conc. HNO$_3$ for this analysis. The resulting solution was diluted to a very low concentration and it was sprayed as a fine jet into an evacuated high temperature space where it gets converted to plasma state. Then the emission line intensity of each element was quantitatively measured and was fitted on to a standard graph. The
standard graph is drawn separately for Cu and Se by measuring the emission counts of a solution containing known concentration of these elements at various dilution. In the present case standard solutions of CuSO₄ and Na₂SeSO₃ were used. Making use of this standard graph, copper to selenium ratio in the sample solution was calculated depending on the corresponding emission intensity.

Cu₂xSe thin films showed Cu:Se ratio to be around 1.80:1, while for Cu₃Se₂ film this ratio was around 1.54:1. These values support the expected proportion of Cu and Se in the two as-prepared phases. This is in agreement with the XPS results.

### 3.5.3 XRD analysis

The inter planar spacing (d) of the (022) plane of the cubic phase of copper selenide has a linear dependence on the stoichiometry of this compound as shown in Fig.(3.24). This inter dependence has been used by many researchers to evaluate the value of non-stoichiometric index ‘x’ in the Cu₂ₓSe phase [10, 26].

In the present study also, this linear dependence of d value on ‘x’ has been used to understand the effect of variation in the relative concentration of Cu in the thin film deposition bath. XRD spectrum of films from Bath 1:1, Bath 2:1, Bath 3:1 and Bath 5:1 were taken with special emphasis on the 2θ region 42° to 47°. Corresponding to the peak position of the (022) plane, d values were noted from the spectrum. Fig.(3.25) shows the selected area view of graph in Fig.(3.24) where the experimental d values fit in.

Table (3.9) shows these experimental d values tabulated against Cu/Se ratio as obtained from Fig.(3.25). Corresponding to the slight increase in d value from Bath 1:1 to Bath 5:1 in succession, there is a slight increase in the Cu/Se value there by resulting in corresponding decrease in the ‘x’ value of the Cu₂ₓSe phase. The corresponding ‘x’ value and resulting chemical formula is also included in the table. Though these results vary slightly from the XPS and ICP analysis, the general trend shown by this indirect method of compositional analysis can be accepted.

An important inference from these results is that, it is possible to influence the stoichiometry of Cu₂ₓSe phase to a small extent by changing the relative concentration of Cu and Se in the reaction bath.
Table (3.9) Variation of stoichiometry of Cu$_{2-x}$Se film with relative concentration of Cu in the reaction bath as obtained from Fig. (3.25)

To understand the influence of temperature of deposition on stoichiometry, the $d$ values of the film from Bath 1:1 and Bath 1:1 LT were compared by fitting into the standard graph of Fig (3.24) as in the above case. Fig.(3.26) shows the experimental $d$ values fitted on to the standard graph. The results are tabulated in Table (3.10).

Table (3.10) Variation of stoichiometry of Cu$_{2-x}$Se film with temperature of deposition as obtained from Fig. (3.26)

From this observation it can be inferred that if the copper selenide deposition is carried out at low temperature, the incorporation of selenium into the deposited thin film can be enhanced. In the present case, the deposited phase shifts from the chemical formula Cu$_{1.71}$Se to Cu$_{1.65}$Se. This forms the first report of a novel and simple method to improve the selenium content in selenide films deposited using CBD technique.

3.6 Electrical characterisation

3.6.1 Hall measurements

Hall measurements along with resistivity measurements were done on Cu$_{2-x}$Se and Cu$_{3}$Se$_{2}$ films and the present work forms the first detailed report of the kind. This study helped to understand the conduction mechanism of copper selenides to a great extent. Variation in resistivity with temperature could be understood in terms of carrier density and mobility. The influence of variation in copper concentration in the
Fig. (3.24) Linear dependence of interplanar spacing (d) of the XRD peak of (022) plane on the stoichiometry of Cu$_2$Se phase.

Fig. (3.25) Variation in the stoichiometry of Cu$_2$Se phase with relative Cu in the reaction bath.

Fig. (3.26) Variation in the stoichiometry of Cu$_2$Se phase with temp of deposition.
reaction bath on the resistivity of the as-prepared films was noted from this study. The
effect of temperature of deposition on the carrier density and mobility was also
studied.

After loading the sample of 1sq.cm area on the sample holder with thermal
grease and then evacuating the enclosure, linearity check was done to confirm the
uniformity and ohmic behaviour of the contact. Resistivity of the sample was
measured by Vander Pauw method. Hall effect measurements were carried out to
determine the mobility, density of carriers, Hall coefficient and type of carriers.

For analysing the Hall measurement data in detail, here the following points
are considered:
1. Copper selenide is a defect semiconductor showing extrinsic behaviour in the
temperature range -192°C to 700°C depending on the extent of non-stoichiometry
[27]. Here copper vacancies act as acceptors [28]. Hence all forms of copper selenide
have p-type conductivity where the concentration of holes depends on the copper
deficiency [29].
2. Effect of copper vacancy should be understood in relation to superlattice crystal
structure of cubic Cu$_{2-x}$Se phase [30]. A model of this is shown in Fig.(3.28). This
consists of an immobile sub lattice of cubic cage structure (constituted by four Se ions
and four Cu ions) and a disordered mobile cation subsystem formed by the remaining
Cu ions statistically distributed over the cage interstitial sites.
3. Copper vacancy scattering is the major factor that determines the mobility and
hence resistivity of the material.
4. Carrier scattering by grain boundaries in the film will only cause relatively little
reduction in mobility when compared to the decrease in mobility due to copper
vacancy scattering [28].
5. The carrier concentration of copper selenide phase is always in the order of $10^{20}$
$- 10^{22}$ cm$^{-3}$. Such high values make this material a degenerate semiconductor, or in other
words this is equivalent to a highly doped semiconductor. Hence mobility is generally
found to have inverse proportionality with carrier concentration.
Fig. (3.27) Structure of Cu$_{2-x}$Se
Stacking sequence of the planes along the b super lattice axis ([111]$_{fcc}$ direction).
Immobile planes are a and c (a – Se cage plane and c – Cu cage plane). Mobile
planes of Cu are b and d (b – terahedrally coordinated d – octahedrally
coordinated). Here the arrows indicate pairing between tetrahedral vacancy and
octahedral ions.

a) **Comparison of as-prepared Cu$_{2-x}$Se and Cu$_3$Se$_2$ phases:** [Table (3.11)]

Holes are the majority carriers in both Cu$_{2-x}$Se and Cu$_3$Se$_2$ phases. As-prepared
Cu$_{2-x}$Se film is found to be low resistive. Resistivity is around $8 \times 10^{-4} \Omega$ cm and it
agrees with the earlier reported values [4, 31]. Cubic phase of Cu$_{2-x}$Se is usually
reported as a superionic conductor where ionic conductivity varies with the non­
ostiometry index ‘x’, Fig (3.28) [32]. In the present case as the ‘x’ value is
evaluated to be around 0.18 [section 3.5.1], the contribution from ionic conductivity
will be very low. According to the above reference, for $x \sim 0.18$ the contribution of
ionic conductivity at room temperature will be only around $1 \times 10^{-2} \Omega^{-1}$ cm$^{-1}$, while the
net observed conductivity in the present case is in the order of $1 \times 10^{3} \Omega^{-1}$ cm$^{-1}$. This
indicates that the ionic contribution to the conductivity of the as-prepared phase is
negligible [27].

The resistivity of the as-prepared Cu$_{2-x}$Se film is found to be less by an order
when compared to that of Cu$_3$Se$_2$ film which is around $6 \times 10^{-3} \Omega$ cm. The carrier
concentration is found to be $\sim 5 \times 10^{20}$ cm$^{-3}$ in both the phases at room temperature but
there is difference in resistivity. The increase in resistivity of Cu$_3$Se$_2$ is the result of
very low carrier mobility. Hall coefficient of both phases is in the order of 
\(1 \times 10^{-2} \text{ cm}^3 \text{C}^{-1}\).

<table>
<thead>
<tr>
<th></th>
<th>(\text{Cu}_{2-x}\text{Se})</th>
<th>(\text{Cu}_x\text{Se}_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistivity ((\Omega\cdot\text{cm}))</td>
<td>(8.0 \times 10^{-4})</td>
<td>(6.6 \times 10^{-3})</td>
</tr>
<tr>
<td>Mobility ((\text{cm}^2/\text{Vs}))</td>
<td>(1.5 \times 10^1)</td>
<td>(1.7)</td>
</tr>
<tr>
<td>Carrier density ((\text{cm}^{-3}))</td>
<td>(5.2 \times 10^{20})</td>
<td>(5.6 \times 10^{20})</td>
</tr>
<tr>
<td>Hall coefficient ((\Omega/\text{cm}^2))</td>
<td>(1.2 \times 10^{-2})</td>
<td>(1.1 \times 10^{-2})</td>
</tr>
<tr>
<td>Sheet resistance ((\Omega/\text{cm}^2))</td>
<td>(8)</td>
<td>(6.6 \times 10^1)</td>
</tr>
<tr>
<td>Type of carriers</td>
<td>Hole</td>
<td>Hole</td>
</tr>
</tbody>
</table>

Table (3.11) Comparison of Hall parameters of \(\text{Cu}_{2-x}\text{Se}\) and \(\text{Cu}_x\text{Se}_2\) phases

**b) Effect of variation in copper concentration in the reaction bath:** [Table (3.12)]

In order to understand the role of relative concentration of Cu and Se in the reaction bath, Hall measurements were done on films prepared at various concentrations of Cu for a fixed concentration of 0.2 M Se. The results of films from Bath 1:1, Bath 2:1, Bath 3:1 and Bath 5:1 are tabulated in Table (3.12).

Bath 1:1 film is found to have very low resistance when compared to the rest. This may be due to the fact that there can be large deviation for this film from the stoichiometric form \(\text{Cu}_2\text{Se}\). The decrease in resistivity with increase in the value of \(x\) has been reported by other researchers also, Fig.(3.29) [28, 33]. In films from Bath 2:1, Bath 3:1 and Bath 5:1, it is seen that the resistivity is higher by an order when compared with Bath 1:1 films. But the order of resistivity of films from Bath 2:1, Bath 3:1 and Bath 5:1 is almost same. This depicts the saturation of \(\text{x}\) at a stable value with the increase in concentration of the copper in reaction mixture.

XRD studies of section (3.3.1) and SEM studies of section (3.2.3) have revealed the decrease in grain size of the \(\text{Cu}_{2-x}\text{Se}\) film with the increase in copper concentration in the reaction bath. Diffused grain boundaries and smaller grain size increases the grain boundary scattering of the majority carriers. This may also contribute to the decrease in the mobility and increase in resistivity with increase in copper ion concentration in the reaction bath of \(\text{Cu}_{2-x}\text{Se}\) film.
Fig.(3.28) Ionic conductivity of Cu$_{2-x}$Se phase at 150°C as a function of non-stoichiometric index ‘x’

Fig.(3.29) Graph showing decrease in resistivity of Cu$_{2-x}$Se phase with increase in the non-stoichiometric index ‘x’.
Table (3.12) Effect of variation of copper concentration in the reaction mixture on the Hall parameters of Cu$_{2-x}$Se film

<table>
<thead>
<tr>
<th>Table (3.12) Effect of variation of copper concentration in the reaction mixture on the Hall parameters of Cu$_{2-x}$Se film</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bath 1:1</td>
</tr>
<tr>
<td>----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Resistivity ($\Omega$-cm)</td>
</tr>
<tr>
<td>Mobility (cm$^2$/Vs)</td>
</tr>
<tr>
<td>Carrier density (cm$^{-3}$)</td>
</tr>
<tr>
<td>Hall coefficient (cm$^2$/C)</td>
</tr>
<tr>
<td>Sheet resistance ($\Omega$/cm$^2$)</td>
</tr>
<tr>
<td>Type of carriers</td>
</tr>
</tbody>
</table>

c) Effect of temperature (300 K - 400 K) on Cu$_{2-x}$Se film: [Table (3.13)]

In order to understand the effect of temperature on electrical properties of Cu$_{2-x}$Se phase, Hall measurements were conducted in the temperature range 300 K - 400 K. To confirm the results, this study was carried out in films from Bath 1:1, Bath 2:1 and Bath 3:1. All of them showed the same trend with regard to resistivity and related parameters. Resistivity is found to increase slightly with temperature, unexpected of ordinary semiconductors. This is due to the decrease in mobility, which predominates the effect of increase in carrier density as observed from the table. This effect is more pronounced in films prepared from Bath 1:1. This may be due to the large deviation from the stoichiometric form of Cu$_{2}$Se.

This metallic behaviour of decrease in mobility with increase in temperature can be explained as follows: When temperature increases more and more copper ions diffuse from the immobile cage structure into the mobile sublattice. The resulting increase in copper vacancy in the immobile subsystem leads to the decrease in mobility of holes.

For the same range of temperature, Hall coefficient is found to vary from $10^{-2}$ to $10^4$ cm$^3$/C in Bath 1:1 films and from $10^{-2}$ to $10^3$ cm$^3$/C in Bath 2:1 films. In the case of Bath 5:1 films, this variation is less pronounced. From these observations, it can be inferred that the influence of temperature on carrier density is less pronounced in film having better stoichiometry. All these films invariably show p-type conduction in this temperature range.
### Table (3.13) Effect of temperature on Hall parameters of Cu\textsubscript{2-x}Se films

<table>
<thead>
<tr>
<th>Bath 1:1</th>
<th>300 K</th>
<th>350 K</th>
<th>400 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistivity (Ω-cm)</td>
<td>8x10\textsuperscript{-4}</td>
<td>9.1x10\textsuperscript{-4}</td>
<td>9.9x10\textsuperscript{-4}</td>
</tr>
<tr>
<td>Mobility (cm\textsuperscript{2}/Vs)</td>
<td>1.5x10\textsuperscript{1}</td>
<td>1.3</td>
<td>9.7x10\textsuperscript{-1}</td>
</tr>
<tr>
<td>Carrier density (cm\textsuperscript{-3})</td>
<td>5.2x10\textsuperscript{20}</td>
<td>5.3x10\textsuperscript{21}</td>
<td>6.5x10\textsuperscript{21}</td>
</tr>
<tr>
<td>Hall coefficient (cm\textsuperscript{3}/C)</td>
<td>1.2x10\textsuperscript{-2}</td>
<td>1.2x10\textsuperscript{-3}</td>
<td>9.6x10\textsuperscript{-4}</td>
</tr>
<tr>
<td>Sheet resistance (Ω/cm\textsuperscript{2})</td>
<td>8</td>
<td>9.1</td>
<td>9.9</td>
</tr>
<tr>
<td>Type of carriers</td>
<td>Hole</td>
<td>Hole</td>
<td>Hole</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bath 2:1</th>
<th>300 K</th>
<th>350 K</th>
<th>400 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistivity (Ω-cm)</td>
<td>1.6x10\textsuperscript{-3}</td>
<td>2.1x10\textsuperscript{-3}</td>
<td>2.3x10\textsuperscript{-3}</td>
</tr>
<tr>
<td>Mobility (cm\textsuperscript{2}/Vs)</td>
<td>6.1</td>
<td>2.7</td>
<td>2.3</td>
</tr>
<tr>
<td>Carrier density (cm\textsuperscript{-3})</td>
<td>6.4x10\textsuperscript{20}</td>
<td>1.1x10\textsuperscript{21}</td>
<td>1.2x10\textsuperscript{21}</td>
</tr>
<tr>
<td>Hall coefficient (cm\textsuperscript{3}/C)</td>
<td>9.7x10\textsuperscript{-3}</td>
<td>5.6x10\textsuperscript{-3}</td>
<td>5.2x10\textsuperscript{-3}</td>
</tr>
<tr>
<td>Sheet resistance (Ω/cm\textsuperscript{2})</td>
<td>1.6x10\textsuperscript{1}</td>
<td>2.1x10\textsuperscript{1}</td>
<td>2.3x10\textsuperscript{1}</td>
</tr>
<tr>
<td>Type of carriers</td>
<td>Hole</td>
<td>Hole</td>
<td>Hole</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bath 3:1</th>
<th>300 K</th>
<th>350 K</th>
<th>400 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistivity (Ω-cm)</td>
<td>1.7x10\textsuperscript{-3}</td>
<td>1.8x10\textsuperscript{-3}</td>
<td>1.9x10\textsuperscript{-3}</td>
</tr>
<tr>
<td>Mobility (cm\textsuperscript{2}/Vs)</td>
<td>5</td>
<td>3.9</td>
<td>1.4</td>
</tr>
<tr>
<td>Carrier density (cm\textsuperscript{-3})</td>
<td>7.2x10\textsuperscript{20}</td>
<td>8.8x10\textsuperscript{20}</td>
<td>2.3x10\textsuperscript{21}</td>
</tr>
<tr>
<td>Hall coefficient (cm\textsuperscript{3}/C)</td>
<td>8.7x10\textsuperscript{-3}</td>
<td>7.1x10\textsuperscript{-3}</td>
<td>2.7x10\textsuperscript{-3}</td>
</tr>
<tr>
<td>Sheet resistance (Ω/cm\textsuperscript{2})</td>
<td>1.7x10\textsuperscript{1}</td>
<td>1.8x10\textsuperscript{1}</td>
<td>1.9x10\textsuperscript{1}</td>
</tr>
<tr>
<td>Type of carriers</td>
<td>Hole</td>
<td>Hole</td>
<td>Hole</td>
</tr>
</tbody>
</table>

**4) Effect of temperature on the deposition of Cu\textsubscript{2-x}Se film:** [Table (3.14)]

Hall parameters of film deposited at low temperature (Bath 1:1 LT) was compared with the film deposited at room temperature (Bath 1:1). This revealed the
influence of deposition temperature on electrical properties of the film. It is found that resistivity becomes almost half when deposition is carried out at low temperature. This is due to the fact that at low temperature, film deposition proceeds in a more ordered manner resulting in better crystallinity and improved mobility. Hence due to increase in mobility, sheet resistance is seen to decrease from $8 \, \Omega \text{cm}^2$ to $4.5 \, \Omega \text{cm}^2$.

<table>
<thead>
<tr>
<th></th>
<th>Room temperature</th>
<th>Low temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistivity ($\Omega \cdot \text{cm}$)</td>
<td>$8.0 \times 10^{-4}$</td>
<td>$4.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>Mobility (cm$^2$/Vs)</td>
<td>$1.5 \times 10^1$</td>
<td>$4.3 \times 10^1$</td>
</tr>
<tr>
<td>Carrier density (cm$^{-3}$)</td>
<td>$5.2 \times 10^{20}$</td>
<td>$3.2 \times 10^{20}$</td>
</tr>
<tr>
<td>Hall coefficient (cm$^3$/C)</td>
<td>$1.2 \times 10^2$</td>
<td>$1.9 \times 10^2$</td>
</tr>
<tr>
<td>Sheet resistance ($\Omega / \text{cm}$)</td>
<td>8</td>
<td>4.5</td>
</tr>
<tr>
<td>Type of carriers</td>
<td>Hole</td>
<td>Hole</td>
</tr>
</tbody>
</table>

Table: (3.14) Effect of temperature of deposition on the Hall parameters of Cu$_{2-x}$Se film

e) Effect of temperature (300 K- 400 K) on Cu$_3$Se$_2$ films: - [Table (3.15)]

In the range of temperature 300 K to 400 K Cu$_3$Se$_2$ films are found to behave in a different manner when compared to Cu$_{2-x}$Se films. Resistivity of Cu$_3$Se$_2$ phase is found to decrease with temperature, similar to the general behaviour of semiconductors.

On heating Cu$_3$Se$_2$ phase disproportionates into Cu$_{2-x}$ Se and Se (refer section 4.2.2.2). A cation vacancy or an anion presence can contribute to hole concentration and so the presence of Se is equivalent to two holes [27]. Hence carrier concentration increases as observed in Table (3.15). Here inspite of increase in carrier concentration an increase in mobility is observed. The sheet resistance is found to decrease from 66 $\Omega \text{cm}^2$ to 9.5 $\Omega \text{cm}^2$ in the temperature range 300 K to 400 K. Corresponding to the increase in carrier density the Hall coefficient is found to decrease from $10^{-2}$ to $10^{-3}$ order.
<table>
<thead>
<tr>
<th></th>
<th>300 K</th>
<th>350 K</th>
<th>400 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistivity (Ω-cm)</td>
<td>6.6×10^{-3}</td>
<td></td>
<td>9.5×10^{-4}</td>
</tr>
<tr>
<td>Mobility (cm²/Vs)</td>
<td>1.7</td>
<td>5.5</td>
<td>6</td>
</tr>
<tr>
<td>Carrier density (cm⁻³)</td>
<td>5.6×10^{20}</td>
<td>7.4×10^{20}</td>
<td>1.1×10^{21}</td>
</tr>
<tr>
<td>Hall coefficient (cm²/C)</td>
<td>1.1×10^{-2}</td>
<td>8.4×10^{-3}</td>
<td>5.6×10^{-3}</td>
</tr>
<tr>
<td>Sheet resistance (Ω/ cm²)</td>
<td>6.6×10^1</td>
<td>1.5×10^1</td>
<td>9.5</td>
</tr>
<tr>
<td>Type of carriers</td>
<td>Hole</td>
<td>Hole</td>
<td>Hole</td>
</tr>
</tbody>
</table>

Table (3.15) Effect of temperature on Hall parameters of Cu₂Se₂ film

### 3.7 Conclusion

Cu₂₋ₓSe films deposited from Bath 1:1 were found to be most uniform and it was considered as the representative sample of this phase. Cu₃Se₂ films deposited from Bath 1:1 Na were chosen as the representative sample of this phase. Cu₂₋ₓSe phase had a reddish brown colour while Cu₃Se₂ had a bluish green colour.

SEM analysis helped to understand the film morphology of these films. XRD analysis confirmed the formation of the two different phases of copper selenide. Optical absorption studies showed the band gap of Cu₂₋ₓSe phase and Cu₃Se₂ phase to be 2.2 eV and 2.8 eV respectively. Variation in band edge with the increase in thickness of the film was also studied.

XPS analysis helped to evaluate the percentage composition. The chemical formula suggested for the two phases was Cu₁₈Se and Cu₃₁Se₂. ICP analysis supported these results. Hall measurement studies showed both the phases to be of low resistance. Cu₃Se₂ phase was found to be comparatively more resistive than Cu₂₋ₓSe phase. The carrier density was generally high and the carrier mobility low for both the phases. With increase in copper ion concentration in the reaction bath of Cu₂₋ₓSe phase, decrease in mobility of the carriers and hence increase in resistivity was observed. In the case of Cu₂₋ₓSe, resistivity increased with temperature while in the case of Cu₃Se₂ resistivity decreased with temperature. Carrier mobility was found to increase in the Cu₂₋ₓSe film when the deposition was carried out at low temperatures.
Reference


