Doping of near stoichiometric CGS films with different at.% of the fifth group element antimony is elaborated in this chapter. The change in conductivity and optical band gap on Sb doping are analyzed and presented here with structural, compositional and morphological characterizations.

6.1 Introduction

This chapter details the effect of antimony (Sb) doping in CGS, a V group element. Sb has been doped to attempt induction of n-type conductivity in CGS. But in agreement with earlier works where Sb has been reported to occupy Se site resulting in acceptor defect levels, here also Sb doped CGS has been found to have acceptor defects leading to p-type conduction. The variations in structural, morphological and optoelectronic properties of CGS with Sb doping of three different at.% is discussed in this chapter.

6.2 Preparation and Characterization Details

Sb doped CGS (CGS:Sb) thin films are prepared by reactive evaporation of the four elements Cu, Ga, Se and Sb in vacuum. For this 99.999% pure Cu and 99.99% Ga are evaporated from molybdenum boats and 99.99% Se from a glass crucible kept in a Mo basket. For the evaporation of the 99.999% pure Sb, another glass crucible kept in a Mo basket is used. The chamber containing the boats is evacuated to a pressure of $\sim 10^{-5}$ Torr and the substrate temperature is maintained at 523 K. The elements Cu, Ga
and Se are evaporated under the optimized conditions given in chapter 4 and the dopant is evaporated from the crucible simultaneously, so that the reaction takes place at the substrate to form films of proper composition.

The structural characterization of the thin films thus prepared is done by X-ray diffraction and the phase purity is further checked by Raman spectroscopy as in the case of CGS (Chapter 4). EDAX measurements for compositional analysis and SEM analysis for morphological studies are done. The optical absorbance, room temperature and high temperature conductivity and Hall data of the doped films are studied.

6.3 Results and Discussion

6.3.1 Structural, Compositional and Morphological Studies

The samples used for this study are nearly stoichiometric (Cu/Ga at.% ~ 1.00±0.05 and Se/Cu+Ga ~ 0.996±0.005) doped with three different Sb at.%. The doped samples are grouped into CGS:Sb A, CGS:Sb B and CGS:Sb C with Sb at.% ~ 4, 6 and 8 respectively. The EDAX spectra of the representative samples are shown in Fig. 6.1.

![EDAX spectra of Sb doped CGS films](image)

Fig. 6.1 EDAX spectra of Sb doped CGS films
XRD patterns of these representative samples are shown in Fig. 6.2. All the samples have the peak at ~ 27.7° as the intense peak, confirming their chalcopyrite structure. This peak results due to the reflections from the (112) plane of chalcopyrite structure [1,2]. The other planes of reflections such as (105) and (220/204) in the CGS structure are also present in these doped samples which again confirm this structure (JCPDS 65-5338). The lattice parameters ‘a’ and ‘c’ are calculated using equation (4.3) of chapter 4 from the distinct peaks of XRD and are in close match with the values for undoped CGS [3,4]. The grain size (t) of the polycrystalline samples are found by Scherrer’s formula (equation (4.2)). The strain in the lattice is also calculated, using equation (5.1). These values are given in Table 6.1.

![Fig. 6.2 (i) XRD patterns and (ii) Raman spectra of CGS:Sb the films](image)

Raman measurements on the samples show the characteristic peak of chalcopyrites at ~185 cm\(^{-1}\) as the most intense one in both the samples which support the phase purity of the structure [5]. This peak arises due to the vibration of Se atoms with the cations being at rest [5-7]. The peak ~ 261 cm\(^{-1}\) arising due to the E or B\(_2\) symmetry vibration is also due to the chalcopyrites by reports. The phase pure chalcopyrite structure is confirmed by the Raman spectra.
Table 6.1 Structural parameters of CGS:Sb films

<table>
<thead>
<tr>
<th>Sample</th>
<th>a(Å)</th>
<th>c(Å)</th>
<th>η</th>
<th>t(nm)</th>
<th>Strain(10³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CGS:Sb A</td>
<td>5.575</td>
<td>10.998</td>
<td>0.986</td>
<td>18</td>
<td>3.53</td>
</tr>
<tr>
<td>CGS:Sb B</td>
<td>5.617</td>
<td>10.981</td>
<td>0.973</td>
<td>10</td>
<td>6.51</td>
</tr>
<tr>
<td>CGS:Sb C</td>
<td>5.591</td>
<td>11.099</td>
<td>0.993</td>
<td>10</td>
<td>6.68</td>
</tr>
</tbody>
</table>

The surface morphology of the films are analyzed using SEM pictures given in Fig. 6.3. In Sb doped samples agglomerations seem to be uniformly formed when compared to those in Al doped samples. In sample A smaller uniform particles of size ~ 50 nm are seen along with agglomerated masses of size ranging from 100 nm - 200 nm. In sample B, smaller grains are seen with size in the range of 40 nm - 80 nm along with agglomerations of size 90 nm - 140 nm. Sample C has agglomerated grains all through the surface with a shape change in agglomerations to rather elongated structures. It is suggested that larger uniform grains improve the absorber properties to a great extent [8,9].

![Fig. 6.3 SEM pictures of CGS:Sb samples](image)

6.3.2 Electrical Studies

Conductivity (σ) changes from $10^{-1}$ to $10^{1}$ S cm$^{-1}$ as the Sb at.% vary from 4 to 8%. The increase in conductivity with Sb doping is in consistency with the variation in carrier concentration ($10^{18}$ cm$^{-3}$ to $10^{20}$ cm$^{-3}$) as obtained by Hall measurements. The retaining of p-type conductivity along with enhancement in σ values indicate acceptor defect level formations on Sb doping. This suggestion is in agreement with the reports where Sb is suggested to occupy Se vacancies, resulting in acceptor levels [10]. The probability of such a defect is admissible here since the compositional analysis indicates Se vacancies in the samples. Though Sb samples show
increase in carrier concentration, no significant change in carrier mobility is observed. The mobility of the samples is $\sim 10^{-1} \text{cm}^2/\text{Vs}$.

Conductivity measurements are done on the samples from room temperature (303 K) upto 423 K. The samples A and B with 4-6 at.% Sb are semiconducting in the entire temperature range whereas sample C shows non degenerate nature at temperatures above 413 K. This may be due to the high carrier concentration of $10^{20} \text{cm}^{-3}$. Sample A has an activation energy of $\sim 185 \text{meV}$ while the ln $\sigma$ vs. 1000/T graphs of Samples B and C do not have appropriate linear regions for the determination of activation energy.

**6.3.3 Optical Studies**

Sb doped samples have good absorption coefficient $\sim 10^6 \text{m}^{-1}$. The absorbance and Tauc’s plots are shown in Fig. 6.5. The band gap of the Sb doped samples show an increase from that of undoped CGS. Also, there is small decrease in the Eg value from 1.78 eV to 1.72 eV with Sb at.% varying as 4, 6 and 8 respectively. This indicates that tuning of band gap is possible by Sb doping.
6.4 Conclusion

Near stoichiometric CGS samples are doped with different at.% Sb. Light doping ~ 4 at.% Sb does not introduce any appreciable conductivity change in these samples when compared with the stoichiometric CGS. But on increasing the Sb at.%, conductivity changes by two orders of magnitude. The band gap of all samples show an increase from 1.68 eV in undoped CGS to ~ 1.72 eV - 1.78 eV in doped samples. Doping of ~ 8 at.% Sb introduces degeneracy at higher temperatures.
References


