Annealing effect on structural and electrical properties of AgGaSe$_2$ thin films

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Structural, thermo-electrical and electrical properties of AgGaSe$_2$ (AGS) thin films prepared in vacuum onto glass substrates by stacked elemental layer (SEL) deposition technique have been studied. The films were annealed at 100 to 350°C for 15 min. The atomic composition of the films has been measured by energy dispersive analysis of X-ray (EDAX) method. The structural and thermo-electrical properties of the films have been ascertained by X-ray diffraction (XRD) and the hot-probe method, respectively. The electrical properties of the films are measured by standard dc method using a liquid nitrogen cryostat. The structural, thermo-electrical and electrical properties have been investigated as a function of different annealing temperature. The X-ray diffraction (XRD) reveals that the films were polycrystalline in nature. The lattice parameters, grain size, strain and dislocation densities of the films have been calculated. The thermoelectric power indicates the presence of $p$-type majority carriers. The electrical conductivity of the films has been found to vary from $1.40 \times 10^{-5}$ to $2.18 \times 10^{-2}$ (Ω-cm)$^{-1}$ as temperature varies between -173 and 100°C. The activation energies vary from 43.60 to 94.70 meV as annealing temperatures vary between 350 and 100°C. Probable identities of the origin of AGS films have been obtained by using these activation energies. The dominance of grain boundary effect has been ascertained by applying the Seto’s model.

Keywords: AgGaSe$_2$ thin films, Annealing temperature, Electrical conductivity, Activation energy

1 Introduction

In recent years, there has been considerable interest in thin film ternary semiconductors for their use in solar cells. Ternary compound of AgGaSe$_2$ (AGS) is a useful absorber material for the fabrication of thin film heterojunction solar cells$^{1-3}$. Electrical conductivity is a fundamental parameter of solar energy materials, which is optimized to apply on the materials in the preparation of solar cells. The conductivity is dependent on the number of charge carriers, in turn, is affected by various sources of scattering when they (carriers) move through the material. Hence, precise knowledge about the mode of transport of carriers in the material is very important for its application as an optical absorber in the preparation of solar cells. Many researchers$^{4-7}$ have already prepared AGS crystal and thin films by different techniques and studied their electrical properties. The utilization of ternary semiconductors in photovoltaic devices has been reported in the literature$^{8-11}$. In the present paper, some aspects of the structural and electrical measurements have been reported. The electrical conductivity of the films has been analyzed and some useful parameters have been deduced utilizing the conventional models.

2 Experimental Details

2.1 Growth of the films

The films of silver, gallium and selenium were deposited sequentially onto chemically and ultrasonically cleaned glass substrates by thermal evaporation of individual elemental layers to form a stack, in vacuum ($\approx 10^{-7}$ mbar) by using oil diffusion pump (E306A, Edwards, UK). The thickness of the films was 500 ± 50 nm. The growth, compositional and structural characteristics of AGS thin films have been described in earlier studies$^{12,13}$.

2.2 Thermo-electrical and electrical measurements

The type of electrical conduction was determined by the hot-probe method. A small heater is attached close to one end of the film to develop the temperature gradient. The electrical measurement technique of AGS thin films have been studied earlier$^{14}$. 


3 Results and Discussion

To check the compositional homogeneity of the films, EDAX data at several different locations for each film were noted. The variation of composition from one location to another did not exceed 2%, which ascertains the reasonable compositional homogeneity of the films. In our previous paper\textsuperscript{12}, the typical EDAX spectrum of AGS thin films having stoichiometry (elemental atomic composition of 25.52\%, 24.54\% and 49.94\% for Ag, Ga and Se, respectively) has been studied. In our observation, all films were found to be stoichiometric with different annealing temperature.

Figure 1 shows the X-ray diffraction patterns of stoichiometric AGS films annealed at different temperatures. The X-ray diffractogram revealed that the films were polycrystalline in nature. Expected peaks for AGS thin films are (112), (201), (211), (220), (204), (301), (312). But in our work, (110), (112), (211), (114), (220), (204), (310) peaks are present. The intensity and position of (112) peak are in good agreement with ASTM data for tetragonal silver gallium selenide (JCPDS card no. 05-0724, 75-0114). The (112) peak is prominent peak for AGS thin films and other researchers obtained (112) peak of higher intensity\textsuperscript{15}. In our case, the films annealed at 200, 250 and 350°C show low-intensity (112) peak. This peak is absent for the film annealed at 100°C.

![XRD spectra of AGS thin films having different annealing temperature](image)

The strain, ε was calculated by using the formula\textsuperscript{20}:

\[
\varepsilon = \frac{B \cos \theta}{4}
\]  

<table>
<thead>
<tr>
<th>Annealing temperature, $T_A$ (°C)</th>
<th>Lattice Parameters</th>
<th>Grain size (nm)</th>
<th>Strain, $\times 10^{-4}$ (line$^{-2}$ m$^{-4}$)</th>
<th>Dislocation density, $\delta \times 10^{14}$ (line/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>5.93 11.32 14.85</td>
<td>23.20</td>
<td>45.34</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>6.00 10.91 17.10</td>
<td>20.13</td>
<td>34.20</td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>5.99 10.89 34.20</td>
<td>10.11</td>
<td>8.64</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>6.01 10.93 41.04</td>
<td>8.38</td>
<td>5.93</td>
<td></td>
</tr>
<tr>
<td>350</td>
<td>5.99 10.89 45.90</td>
<td>7.50</td>
<td>4.74</td>
<td></td>
</tr>
</tbody>
</table>
The dislocation density, $\delta$, defined as the length of dislocation lines per unit volume of the crystal, was evaluated from the formula:

$$\delta = \frac{1}{(B_{\text{crystalline}})^2}$$  \hfil (4)

Strain and dislocation densities decrease as annealing temperature increases (Fig. 2). Since dislocation density and strain are the manifestation of dislocation network in the films, the decrease in dislocation density indicates the formation of high-quality films\textsuperscript{21}. The inhomogeneous strain component is localized at the sub grain and sub domain level near grain boundaries. Pertsev and Arlt\textsuperscript{22} introduced a fictitious dislocation density to model the inhomogeneous strain. The spontaneous strain in their model is analogous to the mechanical plastic deformation, for instance, in metals. This facilitates the analysis substantially because models developed for dislocations can be readily applied. They obtained two components of strain/stress fields: a homogeneous volume component extending over the whole grain volume and an inhomogeneous component concentrated near grain boundaries. We argue that dislocation effects are a real origin of inhomogeneous strains in AgGaSe\textsubscript{2} thin films and that large change in dislocation density and configuration may occur. This is possibly because of the fact that when the temperature is kept higher, the dislocation densities get more thermal energy and have a higher carrier concentration.

The thermoelectric power, also known as Seebeck coefficient, is a measure of the Seebeck effect. This effect consists on the open-circuit voltage, $\Delta V$, developed when a temperature difference, $\Delta T$, is applied along the films. The phenomenon arises because charge carriers at the highest temperature regions of the film diffuse into suitably available states of lower energy at the lowest temperature regions of the films. The accumulation of charge carriers at the cold end will set up an electric potential difference or electric field between the ends of the films. This electric field builds up until a state of dynamic equilibrium is established between the charge carriers with a natural tendency to diffuse down the temperature gradient and those that are forced up the temperature gradient by the electrostatic repulsion due to excess charge at the cold end.

The thermoelectric power, $S$, is defined by:

$$S = \lim_{\Delta T \to 0} \frac{\Delta V}{\Delta T}$$  \hfil (5)

Thermoelectric power is used to interpret the conduction mechanism in semiconductor materials. The measurement of thermoelectric power is simple and its sign gives vital information about the type of electrical conduction in semiconductors whether they are $n$-type or $p$-type. The type of electrical conduction of the grown films having different temperatures has been determined by hot-probe method. Figure 3 shows the variation of thermoelectric power with hot junction temperature for different annealing temperatures. The thermoelectric power was found to be positive in the range 0.026-0.113 mV/°C, which indicates the presence of $p$-type majority carriers\textsuperscript{23,24}.

![Fig. 2 — Dependence of strain and dislocation density of AGS thin films having different annealing temperatures](image1)

![Fig. 3 — Variation of thermoelectric power with hot junction temperature of AGS films having different annealing temperature](image2)
Figure 4 shows the variation of electrical conductivity with temperature of the AGS thin films having various post-deposition annealing temperatures in the range 100°C-350°C for 15 min. It is observed that the conductivity varies from 1.40×10^{-5} to 2.18×10^{-2} (Ω-cm)^{-1} as annealing temperatures vary from 100°C-350°C. Electrical conductivity is strongly dependent on annealing temperature. The conductivity increases as the annealing temperature increases which ascertains the semiconducting nature of the films.

The movement of charge carriers becomes easier if the number of grain boundary (GB) decreases and consequently the conductivity of the films increases. Hence, scattering at the GB may make substantial contribution to the electrical conductivity. The variation of logarithmic conductivity as a function of inverse of temperature is shown in Fig. 5.

The variation shows thermally activated process and dependence of conductivity $\sigma$ with temperature $T$, may be expressed by the equation:

$$\sigma = \sigma_0 \exp\left(-\frac{\Delta E}{kT}\right)$$  \hspace{1cm} ...(6)

where $\sigma_0$ is conductivity at infinite temperature, $\Delta E$ the thermal activation energy and $k$ is the Boltzmann’s constant. The straight-line nature of these plots suggests that GB limited conduction is the dominant conduction mechanism. The activation energy which is calculated from Fig. 5, varies between 43.60 and 94.70 meV as annealing temperature varies between 350 and 100°C as shown in Fig. 6. Each film has single activation energy.

It was found that the activation energy decreases continuously while the electrical conductivity is progressively increasing (Fig. 6). Considering the similarity between CuInSe$_2$ and AgGaSe$_2$, the identity of the origin of the acceptor levels may possibly be interpreted as follows:

The films annealed at 100 and 250°C have acceptor-like levels, which may be attributed to the Se-interstitials and Ag- and Ga-vacancies, respectively. The probable identity of the origin of acceptor levels for the films annealed at 200, 300 and 350°C is Ga-vacancy and Ag in Ga-sites.

The average grain dimensions of these films were small ≈40 nm. The effect of the grain boundaries is
dominant when the grain size is small. The atoms at grain boundaries are disordered. There are a large number of defects as a result of incomplete atomic bonding. These results in the formation of trapping states and charge carriers which are trapped and immobilized. The traps become electrically charged and give rise to potential barriers\(^27\). To verify if GB effect is dominant, a plot of \(\ln(\sigma T^{1/2})\) versus \(10^3/T\) (Seto’s model) is drawn in the temperature range \(-173-100^\circ C\) (Fig. 7). It is noticed that this plot is a straight line, which confirms the dominance of GB effect.

### 4 Conclusions

The films were reasonably homogeneous in composition and stoichiometric as evident from the EDAX data at various locations on the films. The films have been found to be polycrystalline in nature. The lattice parameters are independent of annealing temperature of the films. The grain size varies directly, whereas strain and dislocation density vary indirectly with temperature. The electrical conductivity of the films varies directly with annealing temperature that ascertains the semiconducting nature of the material. The variation shows thermally activated process. The probable identity of the origin of the films annealed at 100 and 350\(^\circ C\) has acceptor-like levels, which may be attributed to the Se-interstitials and Ag- and Ga-vacancies, respectively. The films annealed at 200, 250 and 300\(^\circ C\) showed Ga-vacancy and Ag in Ga-sites. The dominance of the GB effect has been ascertained by applying the Seto’s model.

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### References