Effect of Sb in Electrical Properties of Amorphous Sb$_x$Se$_{1-x}$ (x=40, 50, 60) Thin Films

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Citation

Abstract
Temperature dependence of the DC conductivity ($\sigma$) of amorphous Sb$_x$Se$_{1-x}$ (x=40, 50, 60) thin films, that prepared by physical thermal evaporation technique have been studied. The distribution of Sb atoms in Se matrix content leads to an increase of electrical conductivity with increase in Sb content and decrease the thermal activation energy in the temperature range between (150-400 K), we found two temperature regions (two activation energies) divided at approximately high ranges and low ranges temperatures in all samples. The thickness of thin films (~0.400nm), we have found that the incorporation of Sb atoms in Se matrix leads to an increase in carrier concentration. Its value for a-Sb$_2$Se$_3$ is 1.3x10$^{10}$ cm$^{-3}$ and increases to 3.7x10$^{14}$ cm$^{-3}$ for thin film of a-Sb$_3$Se$_2$ thin film. On the other hand, we have found the nature of the charge carriers change from p-type to n-type for Sb$_x$Se$_{1-x}$ at x=0.6. DC electrical conductivity of SbSe thin films, in the ranges of temperature between 150-400K, ($\sigma$) will increases with increase in concentration of Sb metal. The electrical conductivity for a-Sb$_2$Se$_3$ is 1x10$^{-8}$ (Ω.cm)$^{-1}$ increases to9.2x10$^{-4}$ (Ω.cm)$^{-1}$ for annealed a-Sb$_3$Se$_2$ at 300K. Therefore the thermal activation energy $E_a$ decreases from 0.64eV to 0.67 eV for conduction in extended state and from 0.074eV to 0.076eV for conduction in localized sites for a-SbSe and a-Sb$_3$Se$_2$ thin films respectively.

1. Introduction

In past years, a most deal of interest has been focused on semiconducting III-VI layered compounds material. SbSe is a typical layer structure compound that consists of two Sb and two Se sub-layers in the sequence of Se-Sb-Se, where the Se-Se and Sb-Sb layers are covalent in the layers and the Se-Se bond between adjacent four atomic layers is due to van der Walls forces [1]. Investigations on the physical properties like structural, electrical and optical properties of SbSe compound revealed that it is attractive for heterojunction device applications [2] and photovoltaic devices in the visible range [3]. It has been used as device like radiation detector that operates at room temperature [4].

Fundamentally, for amorphous materials the temperature dependence of conductivity is determined by three mechanisms [5], extended state conductivity, conduction in band tail and conduction in localized sites. In first case of an extended state conductivity, it is assumed that beyond mobility edge the mean free path for conduction is short and nearly equal to the average separation between atoms. The conduction in this case is an activated process and the conductivity is given as

$$\sigma_d = \sigma_{\text{min}} \exp \left[ \frac{-(E_C - E_F)}{kT} \right]$$

(1)
In the second mechanism, i.e., conduction in the band tails, the conduction occurs due to the tunneling of the carriers to the unoccupied nearest neighbour. Since the tunneling process involves the emission or absorption of phonons, it requires a tunneling energy $\Delta W_1$. The conductivity due to this mechanism can be written as

$$\sigma_d = \sigma_1 \exp \left[ -\frac{E_1}{kT} \right]$$

(2)

Where the activation energy ($E_1$):

$$E_1=\frac{\Delta W_1}{k} + E_f \pm \frac{D}{k}$$

The third conduction in localized states at Fermi-energy is proportional to $T^{-3/4}$. At low temperature, the activation energy of the conductivity decreases gradually with decreasing temperature, the conduction may be mainly due to hopping. Below about 220 K, $\sigma_d$ varies exponentially with $T^{-1/4}$, indicating that charge transport is due to variable range hopping in states close to the Fermi level $E_f$. Following the model proposed by Mott [6], the conductivity is given by

$$\sigma_d = \sigma_2 \exp \left[ -\left( \frac{\Delta W_1}{kT} \right) \right]$$

(3)

Here $\sigma_1$ is less than $\sigma_2$. As the temperature reached lower, the number and the energy of phonons decreases, hence the hopping between the nearest neighbours will become less mobility and instead the carriers will hop to larger distances i.e. to the sites within the range $kT$. For such conduction, Mott [5] proposed the Variable Range Hopping (VRH) in which the conductivity is proportional to $T^{-3/4}$. At low temperature, the activation energy of the conductivity decreases gradually with decreasing temperature, the conduction may be mainly due to hopping. Below about 220 K, $\sigma_d$ varies exponentially with $T^{-1/4}$, indicating that charge transport is due to variable range hopping in states close to the Fermi level $E_f$. Following the model proposed by Mott [6], the conductivity is given by

$$\sigma_d = \sigma_2 \exp \left[ -\left( \frac{\Delta W_1}{kT} \right) \right]$$

(4)

The pre-exponential $\sigma_2$ depends mainly on frequencies, while $T_d$ has been shown to be approximately

$$T_d = C_0 \alpha^2 / kN (E_f)$$

(5)

Where $N (E_f)$ is the density of hopping sites at the Fermi level, and $C_0$ is numerical constant which depends on the detailed assumptions.

2. Experimental

Glassy alloys material of $\text{Sb}_x\text{Se}_{1-x}$ ($x=40, 50, 60$) were prepared by a melt-quenching technique. Materials of 99.99% purity were sealed in quartz glass ampoules (length ~ 16 cm, internal diameter ~1.2 cm) with a vacuum of about $2 \times 10^{-5}$ Torr. The sealed ampoules were kept inside a furnace where the temperature degree was raised slowly up to 1100°C. The ampoules were stayed in tilt position 30 degree for 12 h at the maximum temperature to make the material melt homogeneous. Quenching state was done in ice water 4°C. Thin films of glassy alloys were prepared by vacuum evaporation technique using a standard coating unit (national made), well degassed corning glass plates, having pre-deposited Aluminium electrodes, were used as a substrate for depositing amorphous films in the planer geometry (length ~ 2 cm) and electrode gap (~1mm).

These thin films were deposited at room temperature and at a base pressure of about $2 \times 10^{-2}$ Torr using molybdenum boat. The thickness of these films was ~ 400 nm. The films were kept in deposition chamber. This done to allow sufficient annealing at RT so that a meta-stable thermodynamic equilibrium may be attained in the samples of chalcogenide glasses as suggested by Abkowitz [7]. The amorphous nature of the resulting glassy alloys was verified by X-ray diffraction.

For DC conductivity measurements, the samples were mounted in a specially designed metallic sample holder. a vacuum of about $2 \times 10^{-2}$ Torr could be maintained throughout the measurements. A DC voltage was applied across the sample and the resulting current was measured by a digital electrometer (Keithley, model 6517B). The temperature was measured by mounting a calibrated Pt 100 sensor near the sample with digital readout.

3. Results and Discussion

Fig. 1. shows the X-ray diffraction pattern of $\text{Sb}_x\text{Se}_{1-x}$ thin films deposited at room temperature in the glass slides. It is clear from the figure that there is no prominent peaks which verify the amorphous nature of those thin films. The similar curves have been obtained for other samples (i.e. $x=50, 60$) also.

The Temperature dependence of the DC conductivity ($\sigma$) of amorphous $\text{Sb}_x\text{Se}_{1-x}$ ($x=40, 50, 60$) thin films, prepared by thermal evaporation technique, have been studied and plotted in figures 2-4. In all samples, the ln $\sigma \propto 1000/T$ the curves found to be straight lines indicating a thermally activated process for DC conduction in these samples.

![SbSe thin film](Image)

**Fig. 1.** X-ray diffractogram of a-SbSe thin films deposited at room temperature.

The Temperature dependence of the DC conductivity ($\sigma$) of amorphous $\text{Sb}_x\text{Se}_{1-x}$ ($x=40, 50, 60$) thin films, prepared by thermal evaporation technique, have been studied and plotted in figures 2-4. In all samples, the ln $\sigma \propto 1000/T$ the curves found to be straight lines indicating a thermally activated process for DC conduction in these samples.
The incorporation of Sb atoms in Se matrix leads to an increase in the electrical conductivity with increase in Sb content and decrease in the thermal activation energy. In the temperature range (150-400 K), we found two temperature regions (two different activation energies) divided at approximately high ranges and low ranges temperatures in all samples.

In Figs. 2 & 3 the thermal activation energy of conduction of a-Sb$_2$Se$_3$ and a-SbSe thin films are 0.64eV and 0.67eV which lies in the temperature range 250-400 K, where the conduction mechanism is due to excitation of the holes to the extended valence band with an activation energy. The conductivity in this region is associated with the transport of carriers through the extended states of the relative transport band of Eq. 1. The second region of thermal activation energy of conduction are 0.075eV and 0.076eV in the temperature range 150-250 K which is due to hopping conduction near the Fermi level $E_F$ that obeys for low activation energy, and $\sigma_d$ varies exponentially with $T^{-1/4}$ following the model proposed by Mott [6]. In Eq 4, the phonons do not have enough energy for transferring to a nearest neighbour atom and the charge carrier hops from a neutral atom to another neutral atom situated at the same energy level, which can be many interatomic distance away [8-12].

Figure 4 shows that have one activation energy for a-Sb$_3$Se$_2$. The activation energy (0.33eV) lie in the range(150-400 K). The $\sigma$ at high temperature obeys the law: $\ln \sigma \propto 1/T$ and in the low temperature range obeys the law $\ln \sigma \propto T^{-1/4}$, indicating variable range hopping in localized states near the Fermi level in the later case[13-17]. All data listed in table 1.

### Table 1. Results of activation Energy gap.

<table>
<thead>
<tr>
<th>Thin films Materials</th>
<th>Activation energy at High temperature $E_a_1$ (eV)</th>
<th>Activation energy at Low temperature $E_a_2$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-Sb$_2$Se$_3$</td>
<td>0.64 (250-400 K)</td>
<td>0.075 (150-250 K)</td>
</tr>
<tr>
<td>a-SbSe</td>
<td>0.67 (250-400 K)</td>
<td>0.076 (150-250 K)</td>
</tr>
<tr>
<td>a-Sb$_3$Se$_2$</td>
<td>0.33 (150-400 K)</td>
<td></td>
</tr>
</tbody>
</table>

Results shows the plot the DC electrical conductivity of SbSe thin films, in the temperature range 150-400K, increases with increase in concentration of Sb metal. The electrical conductivity for a-Sb$_2$Se$_3$ is $1\times10^8$ $(\Omega\cdot cm)^{-1}$ increases to $9.2\times10^4(\Omega\cdot cm)^{-1}$ for thin film a-Sb$_3$Se$_2$ at 300K. Whereas the thermal activation energy decreases from 0.64eV to 0.67 eV for conduction in extended state and from 0.074eV to 0.076eV for conduction in localized sites for a-SbSe and a-Sb$_3$Se$_2$thin films respectively. All these values are listed in table 2.

We have calculated carrier concentration and the nature of the charge carriers at room temperature (300K), by Hall measurements from the slope of current vs. Hall voltage by using the relation $p = (I/V)B/qt$, where B is magnetic filed in (tesla), q electronic charge (coul) and t is the thickness of thin film (~0.400nm), we have found that the incorporation of Sb atoms in Se matrix leads to an increase in carrier
concentration. Its value for a-Sb$_2$Se$_3$ is $1.3 \times 10^{10}$ cm$^{-3}$ and increases to $3.7 \times 10^{14}$ cm$^{-3}$ for thin film of a-Sb$_3$Se$_2$ thin film. On the other hand, we have found the nature of the charge carriers change from p-type to n-type for a-Sb$_x$Se$_{1-x}$ at $x=0.6$. We have calculated carrier mobility for all SbSe thin films by using the relationship $\sigma = pq\mu$.

The experimental data of the conductivity for different compositions of SbSe thin films in the region below 250 K. In accordance with relation that obeys the $T^{-1/4}$ law. We have evaluated the constant $T_o$ from the slope of the $\ln (\sigma T^{1/2})$ vs. $T^{-1/4}$ and then we have calculated the density of states $N(E_F)$ at the Fermi level by using the relation, where: $T_o = 18.1/(\alpha^3 a k N(E_F))$

Table 2. Results of Carrier concentration, Conductivity and Hall mobility for SbSe thin films.

<table>
<thead>
<tr>
<th>Thin films Materials</th>
<th>Carrier concentration type (cm$^{-3}$) at 300K</th>
<th>Conductivity (Ohm.cm)$^{-1}$ At 300K</th>
<th>Mobility (cm/ V. sec) At 300K</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-Sb$_2$Se$_3$</td>
<td>$p=1.3E+10$</td>
<td>1.0E-8</td>
<td>5</td>
</tr>
<tr>
<td>a-SbSe</td>
<td>$p=5.3E+10$</td>
<td>2.4E-7</td>
<td>28</td>
</tr>
<tr>
<td>a-Sb$_3$Se$_2$</td>
<td>$n=3.7E+14$</td>
<td>9.2E-4</td>
<td>16</td>
</tr>
</tbody>
</table>

4. Conclusions

The DC conductivity measurements were made on the deposited of SbSe thin films in the room temperature. The conduction in the low temperature range (< 250 K) exhibits relatively less thermal activation and was found to be due to variable range hopping, while in the high temperature range (250-400 K), the conductivity increases with increasing temperature according to the semiconductor behavior.

References