Physical properties of amorphous Se$_{0.75}$Ge$_{0.25-y}$Sb$_y$ semiconductors

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Effect of the addition of varying amounts of antimony in concentrations from 0.01 to 0.20 at % on dc conductivity of Se:Ge glass is analysed. The electrical conductivity of amorphous Se$_{0.75}$Ge$_{0.25-y}$Sb$_y$ films have been determined during and after light exposure and at different temperatures. The time dependence of the electrical conductivity measured in darkness or when exposed to light has been studied for films of different compositions and different thicknesses. The conduction activation energy $\Delta E$ and the pre-exponential factors $\sigma_0(0,T)$ are found to decrease with increasing Sb content. The mean value of the threshold voltage, $V_{th}$, was measured in darkness and after exposure of light for different compositions and temperatures. The pronounced glass-forming tendencies of alloys of Se and Ge with Sb were discussed in terms of the chemical bonds expected to be present in these materials. These chemical bonds have been used to estimate the cohesive energies (CE) of these glasses.

1 Introduction

Chalcogenide glasses have been recognized as promising materials for infrared optical element, infrared optical fibres, Xerography, switching and memory devices, photolithographic process, and in the fabrication of inexpensive solar cells, and more recently for reversible phase change optical records. The addition of an impurity has a pronounced effect on the conduction mechanism and the structure of the amorphous glass and this effect can be widely different for different impurities.

In our earlier communication, preliminary results on the electrical properties of antimony-doped Se$_{0.75}$Ge$_{0.25-y}$Sb$_y$ glassy alloy with Sb concentration from 0.01 at % were explained on the basis of Sb acting as a Ge-chain terminator causing decreased disorder.

Much effort has been devoted towards the preparation and properties of chalcogenide glasses of Se-Ge-Sb system. Also, the effect of illumination on the distribution of mobile charge carriers in a semiconductor is a topic of interest in several branches of optoelectronics.

The aims of the present work for the system Se$_{0.75}$Ge$_{0.25-y}$Sb$_y$ ($y = 0.01, 0.05, 0.10, 0.15, 0.18$ and $0.20$) were: (i) to obtain the density by Archimedes method, (ii) to study the effect of illumination on the electrical properties as a function of time, temperature and film thickness, (iii) to obtain the conduction activation energy, the pre-exponential factor, for dark $E_a$, $\sigma_0$, and the mean value of threshold voltage for switching $V_{th}$, for illuminated conductivity $E_{il}$, $\sigma_{il}$, $V_{th,il}$ and for photoconductivity behaviour $\Delta E_{il}$ and $\Delta \sigma_{il}$. (iv) to investigate the effect of light on switching phenomenon, and (v) to correlate the experimental data with the chemical bond expected to be present.

2 Experimental Technique

Six compositions of the system Se$_{0.75}$Ge$_{0.25-y}$Sb$_y$ ($y = 0.01, 0.05, 0.10, 0.15, 0.18$ and $0.20$) were prepared by the conventional melt quenching technique. Commercial grade elements from Balzers Company (99.999% pure) are sealed in evacuated (to about 10$^{-5}$ torr) fixed silica ampoule and placed in a special rotary furnace held at a temperature at 1000°C for 15 h, followed by quenching in water.

Density measurements for bulk samples of the system Se$_x$Ge$_{0.75-y}$Sb$_y$ ($x = 0.75$ and $y = 0.01, 0.05, 0.10, 0.15, 0.18$ and $0.20$) were made by the Archimedes method using the hydrostatic weighing in toluene. A single crystal of germanium was used as a reference material for characterizing the toluene. Five separate determinations were made on each sample and the average of these was corrected for the buoyancy of air. The precision of measurement was ± 0.05.

Thin films of the six compositions were prepared by the thermal evaporation technique using high vacuum plant (Edward 306A) on cleaned glass and pyrographite substrates. Film thickness was measured during deposition using an hf crystal monitor (Edward...
FTMS). The amorphicity of the samples was confirmed by the absence of any sharp peak in the X-ray diffraction pattern.

For electrical measurements, the film resistance was measured with a digital electrometer (Keithly type E616A) in a coplanar configuration with Al electrodes evaporated into a glass substrate at an interval of width 1-2 mm and length 3 mm, before evaporation of the samples under investigation.

The conductivity-time dependence measurements, were measured at room temperature, directly after film preparation either in darkness (curve a) or during exposure to a tungsten lamp (curve b). The 60 W lamp was 10 cm away from the sample, and produced a luminous intensity of 56 candela, at the surface of the sample.

The effect of illumination on the variation of $\rho_{0}$ with temperature was also investigated. Firstly, at room temperature (~ 25°C), the author exposed the film sample to tungsten lamp for about 12s. During the exposure, the threshold $\rho_{0,11}$ was recorded; thereafter, the illumination was stopped and the temperature increased to 50°C and $\rho_{0,11}$ recorded by exposing the sample kept at different temperatures, to light.

3 Results and Discussion

3.1 Density measurements

Density of the as-prepared glasses were measured to determine whether density measurement could be used as a quality control technique for bulk synthesized material, and are listed in Table 1. The density increases with increasing Sb content.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Thickness, nm</th>
<th>Density, g/cm³</th>
<th>$\Delta E_{1} = \Delta E_{2}$, eV</th>
<th>$\sigma_{01} = \sigma_{04}$ (Ωcm)$^{-1}$</th>
<th>$E_{11}$, eV</th>
<th>$\sigma_{011}$, (Ωcm)$^{-1}$</th>
<th>$\Delta E_{11}$, eV</th>
<th>$\Delta \sigma_{11}$ theoretical (Ωcm)$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SeO.75 GeO.25 Sb0.01</td>
<td>77.60</td>
<td>4.49</td>
<td>0.842</td>
<td>3.85 x 10$^6$</td>
<td>0.79</td>
<td>2.02 x 10$^5$</td>
<td>0.719</td>
<td>3.65 x 10$^6$</td>
</tr>
<tr>
<td>SeO.75 GeO.20 Sb0.05</td>
<td>32.49</td>
<td>4.50</td>
<td>0.821</td>
<td>3.16 x 10$^6$</td>
<td>0.730</td>
<td>3.09 x 10$^6$</td>
<td>0.70</td>
<td>7 x 10$^5$</td>
</tr>
<tr>
<td>SeO.75 GeO.15 Sb0.10</td>
<td>1073.0</td>
<td>4.62</td>
<td>0.803</td>
<td>3.25 x 10$^6$</td>
<td>0.713</td>
<td>2.37 x 10$^6$</td>
<td>0.69</td>
<td>8.8 x 10$^5$</td>
</tr>
<tr>
<td>SeO.75 GeO.10 Sb0.15</td>
<td>982.2</td>
<td>4.65</td>
<td>0.780</td>
<td>2.85 x 10$^6$</td>
<td>0.690</td>
<td>1.74 x 10$^5$</td>
<td>0.639</td>
<td>2.68 x 10$^6$</td>
</tr>
<tr>
<td>SeO.75 GeO.07 Sb0.18</td>
<td>1004.5</td>
<td>4.66</td>
<td>0.730</td>
<td>1.22 x 10$^6$</td>
<td>0.677</td>
<td>1.37 x 10$^5$</td>
<td>0.628</td>
<td>1.08 x 10$^6$</td>
</tr>
<tr>
<td>SeO.75 GeO.05 Sb0.20</td>
<td>250.0</td>
<td>4.68</td>
<td>0.628</td>
<td>3.66 x 10$^5$</td>
<td>0.639</td>
<td>9.99 x 10$^3$</td>
<td>0.595</td>
<td>3.56 x 10$^5$</td>
</tr>
</tbody>
</table>
Fig. 1 — The time dependence of electrical conductivity for Se$_{0.75}$ Ge$_{0.25-y}$ Sb$_{y}$ (0.01 $\leq y \leq 0.20$) thin films (a) without illumination, and (b) illuminated samples

(b) Temperature dependence

Fig. 2 depicts the variation of dc dark conductivity $\sigma_d$ with inverse temperature (in the range 293-455 K) for thin films of Se$_{0.75}$ Ge$_{0.25-y}$ Sb$_{y}$. It is observed that $\sigma$-$T$ data cannot be approximated by single activation energy over the entire temperature range. The plot shows that there are two types of conduction processes. The linearity of $\sigma$-$T$ data in the high temperature region indicates that the conductivity in this region exhibits activated behaviour in accordance with the relation

$$\sigma_d(0,T) = \sigma_{01} \exp \left( \frac{-\Delta E_1}{kT} \right)$$

where the symbols have their usual meaning. Supposing $\Delta E_1 = E_d$ and $\sigma_{01} = \sigma_{0d}$, where $E_d$ can be calculated from the slopes of the straight lines of Fig. 2. Table 1 lists the electrical conductivity parameters of these films.

Fig. 3 depicts the temperature dependence of the dark electrical conductivity for Se$_{0.75}$ Ge$_{0.05}$ Sb$_{0.20}$ thin films of different thicknesses (30, 100, 150 and 250 nm), in the temperature range 294-417 K. The obtained relations of $\sigma = F(1/T)$, are parallel straight lines, indicating that
Fig. 2 — The dependence of dark electrical conductivity, $\sigma_d$, of the system $\text{Se}_{0.75}\text{Ge}_{0.25}\text{Sb}_y$ films on temperature and after exposure of the samples to white light for a certain duration.

Fig. 3 — $\sigma_d$ as a function of $1000/T$ for $\text{Se}_{0.75}\text{Ge}_{0.05}\text{Sb}_{0.20}$ films.
Fig. 4 — Temperature dependence of electrical conductivity in dark, $\sigma_d$, and in illumination $\sigma_0$ for the Se-Ge-Sb glasses.
the dark activation energy $E_d$ ($E_d = 0.63$ eV) is independent of the film thickness.

(c) Illumination dependence

Fig. 4 (a and b) depicts the temperature dependence of dark electrical conductivity $\sigma_d$ (curve a), under illumination with white light $\sigma_{il}$ (curve b) as a function of 1000/T. Photoconductivity $\Delta \sigma_d$ was calculated by subtracting $\sigma_{il}$ from $\sigma_d$ and is represented in Fig.5 for the various compositions. It is clear from this figure that this dependence is linear in the high temperature range, which indicates that the photoconductivity is an activated process in this region.

The conduction activation energy values for photoconductivity $\Delta E_d$ which were calculated from the slopes of the data of Fig.5 are listed in Table 1. It is obvious that $\Delta E_d$ is less than $E_d$ and $E_{th}$, which may be explained by the presence of charge carrier trapping level in the pseudogap of the studied glass.

(d) Effect of light on switching phenomenon

Both dynamic and static characteristic curves were obtained on a pyrographite substrate for thin film samples. The dynamic curve was displayed on the screen of a cathode ray oscilloscope, using an ac source, and the static curves were used on the dc source. Both dynamic and static characteristic curves are typical for a memory switch.

Room temperature static current-voltage curves for amorphous Se$_{0.75}$ Ge$_{0.25}$ Sb$_y$ films of thickness $\pm 450$ nm are given in Fig.6. The curves have three states, off-state with high resistance, negative resistance state beyond the threshold voltage and the on-state with low resistance. These facts indicate that the system is characterized by negative resistance and memory phenomena.

Fig.7 depicts the effect of illumination on the variation of $V_{th}$ with temperature. It is observed from Fig.7(a,b) and Table 2 that $V_{th,il}$ are less than $V_{th}$ especially at room temperature, where $V_{th,il}$ decreases rapidly at first, this is attributed to the effect of illumination. This behaviour is similar to that observed in experimental results of Fig.1.

From figures and tables, it is obvious that the photoconductivity values of pre-exponential factor $\sigma_{0il}$, activation energy $\Delta E_d$ and threshold voltage $V_{th,il}$ are less than the dark conductivity $\sigma_d$ (from Fig.2), $E_d$ and $E_{th}$ (from Fig.4) and $V_{th}$ (from Fig.7) decreases with increasing Sb content. The decrease of $\sigma_{0il}(0,T)$, with the addition of Sb, in the present work indicated that the conduction in the linear part is in confirmation with the thermally assisted tunnelling of charge carriers in the extended states present in the energy band, where $\sigma_{0il}(0,T) > 10^6$ (Ref.18). But around room temperature (see Figs 2 and 4), the conduction occurs via variable-range hopping of the charge carriers in the localized state near the Fermi level.

To discuss the mechanism of the change in conduction type, information as to the glass structure is very important. The structure of these glasses is predominantly made up of structural units (S.U.) tetrahedal GeSe$_2$, trigonal Sb$_2$Se$_3$ and some connecting Se$_x$ chain. Only Ge-Se, Sb-Se and Se-Se bonds exist in this system.

The stoichiometric glasses Se$_{0.75}$ Ge$_{0.25}$ Sb$_y$ exhibit a decrease of Tg and Sb is increased. As Sb is progressively increased, more and more Sb-Se S.U. with weaker Sb-Se bonds replace Ge Se$_2$ S.U. with stronger
Fig. 5 — Temperature dependence of $\Delta\sigma_a = \sigma_a$ for the Se$_{0.75}$Ge$_{0.25-y}$Sb$_y$ (0.01 $\leq y \leq 0.20$) amorphous thin films.

Fig. 6 — Room temperature state $I-V$ curves for Se$_{0.75}$Ge$_{0.25-y}$Sb$_y$ (0.01 $\leq y \leq 0.20$) thin film of thickness $\approx 450$ nm.
Fig. 7 — Static I-V characteristic curve for Se-Ge-Sb films of thickness 450 nm at different elevated temperature (298 - 423 K)
The resulting weakening of the lattice structure accounts for the observed decrease of \( T_g \). As a mixed network derives its \( T_g \) from its weakest bonds\(^{21}\), the addition of a small concentration of relatively weaker Sb-Se bond to a network of Ge-Sb bonds has a large effect in initially reducing the \( T_g \) of GeSe\(_2\) glass.

The chemical bond approach has been used successfully by Pauling\(^ {22}\) to explain the electrical behaviour of amorphous systems. Such an approach explains the behaviour in terms of cohesive energy (CE), which reflects the average bond strength at a given composition.

Therefore, one can estimate the bond energies \( E_{A,B} \) for heteronuclear bonds by using the relation
\[
E_{A,B} = [E_{A,A} - E_{B,B}]^{1/2} + 30 (X_A - X_B)^2
\]
where \( E_{A,A} \) and \( E_{B,B} \) are the energies of the homonuclear bonds, and \( X_A \) and \( X_B \) are the electronegativity of the atoms. The values of \( X_A \) are 2.6 for Se, 1.8 for Ge and 1.9 for Sb. The types of bonds expected to occur in the investigated system are listed in Table 2. After all these bonds are formed, there are still unsatisfied Se valences "Excess Bonds" which must be satisfied by the formation of Se-Se bond. The number of excess bonds also are given in Table 2. Knowing the bond energies, one can estimate the cohesive energy (CE), i.e. the stabilization energy of an infinitely large cluster of the material per atom, by summing the bond energies over all the bonds expected in the system under test. The results of CE are listed in Table 2.

The chemical bond approach can also help us to understand why Sb which is present in such small amount \((0.12 \leq \text{Sb} \leq 0.26)\) plays a crucial role in the memory glasses, by enhancing the reversibility of these films in memory process\(^ {23}\).

References