SPACE CHARGE LIMITED CONDUCTION IN Ge,Se_{100-x}

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The present paper reports the measurements on space charge limited conduction in vacuum evaporated thin films of Ge,Se_{100-x}, where 5 ≤ x ≤ 40. Current, at high fields (10^4 V cm^{-1}), could be fitted to the theory of space charge limited conduction in case of an uniform distribution of localized states in the mobility gap of these materials. The results indicate that a minimum density of localized states occurs at x = 22 which is in agreement with the other experiments reported in the literature.

1. INTRODUCTION

AMORPHOUS semiconductors have drawn great attention from scientists because of their potential use in various solid state devices. The major drawback of amorphous semiconductors over its crystalline counterpart is the presence of inherent defect states in the mobility gap of these materials. The density of such localized states g(E) in the mobility gap controls many physical properties of amorphous semiconductors. The determination of g(E) has, therefore, been an important issue in these materials. One of the most direct methods for the determination of g(E) involves the measurements of space charge limited current (SCLC) which can easily be observed in low conductivity amorphous materials. Such a technique has already been applied [1-8] to hydrogenated amorphous silicon (a-Si:H) and it is observed that g(E) obtained by this method is lower by a factor of 3-5 as compared to field effect technique as SCLC technique is not influenced by surface states unlike field effect experiment where surface states may come into picture [1].

In the present paper we report SCLC measurements in an important glassy system Ge,Se_{100-x}, where properties have been found to be highly composition dependent. The measurements of SCLC have been made on amorphous thin films of Ge,Se_{100-x} prepared by vacuum evaporation technique. Using the theory of SCLC for the case of an uniform distribution of localized states, g(E) = \kappa_0, the density of localized states is calculated and found to be minimum at x = 22 in Ge,Se_{100-x} glassy system which is explained in terms of the structure of this glassy system.

2. EXPERIMENTAL

Glassy alloys of Ge,Se_{100-x}, (x = 5, 10, 15, 22, 30 and 40) were prepared by a melt quenching technique. 5N pure materials were sealed in quartz ampoules (length ~ 5cm, internal diameter ~8 mm) with a vacuum ~ 10^{-5} Torr. The sealed ampoules were kept inside a furnace where the temperature was raised slowly (3-4°C min^{-1}) to 950°C. The ampoules were rocked frequently for 10 h at the maximum temperature to make the melt homogeneous. Quenching was done in air by an air blower. The glassy nature of the alloys was ascertained by the X-ray diffraction technique.

Thin films of the glassy alloys were prepared by vacuum evaporation technique using a standard coating unit (IBP Torr model EPR 002). Well degassed corning glass plates, having predeposited indium electrodes, were used as a substrate for depositing amorphous films in the planar geometry (length ~ 1.2 cm and electrode gap ~ 0.12 mm). These films were prepared at a base pressure 10^{-5} Torr by keeping substrates at room temperature. The thickness of the amorphous films was ~ 5000 Å. The deposition parameters were kept almost the same for all the samples so that a comparison of results could be made for various glassy samples.

For the measurements of SCLC, the samples were mounted in a specially designed metallic sample holder where a vacuum ~ 10^{-3} Torr could be maintained throughout the measurements. A d.c. voltage (0-300 V) was applied across the sample and the resulting current was measured by a digital electrometer (Keithley, model 614). Current-voltage (I-V) characteristics were made at various fixed tem-
peratures (299 to 365 K) for all the glassy alloys studied. The temperature was measured by mounting a copper-constantan thermocouple near to the sample. Before measuring $I-V$ characteristics, thin film samples were annealed in a vacuum $\sim 10^{-3}$ Torr near glass transition temperature of each alloy for 2 h in the sample holder which was used for the above measurements.

3. RESULTS

$I-V$ characteristics were studied at various temperatures (299 to 365 K) in amorphous thin films of Ge$_x$Se$_{1-x}$, where $x = 5, 10, 15, 22, 30$ and 40. Planar geometry of the films was used for these measurements. At low fields ($< 10^3$ V cm$^{-1}$) an ohmic behaviour was observed at various temperatures in all the glassy samples used in the present study. However, at higher fields ($> 10^3$ V cm$^{-1}$), a non-ohmic behaviour was observed where $\ln I/V$ vs $V$ curves were found to be straight lines at all the measuring temperatures (299 to 365 K). The results of one particular glassy alloy, Ge$_x$Se$_{1-x}$, are plotted in Fig. 1. Similar results were obtained in other glassy alloys (results not shown here). It is clear from Fig. 1 that the slope ($S$) of $\ln I/V$ vs $V$ curves is not same at all the measuring temperatures. The values of these slopes is plotted as a function of temperature in Fig. 2 for various glassy alloys used in the present study. It is clear from this figure that the slope decreases linearly with the increase of temperature.

According to the theory of Space Charge Limited Conduction (SCLC) in case of an uniform distribution of localized states, $g(E) = g_s$, current ($I$) at a particular voltage ($V$) is given by

$$I = KV \exp (SV),$$

(1)

where $K$ is a constant and $S$ is given by

$$S = \frac{2e_i\varepsilon_0}{q\varepsilon_0 kTd^2}$$

(2)

Here $\varepsilon_i$ is the relative dielectric constant, $d$ is the electrode gap, $\varepsilon_0$ is the permittivity of the free space and $k$ is the Boltzmann’s constant.

It may be mentioned that equation (1) is not an exact solution of the SCLC equations, but it is a very good approximation for high-injection currents.

As evident from equation (1), in case of SCLC, $\ln I/V$ vs $V$ curve, at a particular temperature, should be a straight line as found in the present samples (see Fig. 1). The slope ($S$) of these curve should decrease linearly
with temperature [equation (2)] as also found in the present samples (see Fig. 2). These results indicate the presence of SCLC in the present samples.

It is clear from equation (2) that $g_0$ can be obtained from the slope of $S$ vs $1/T$ curves (Fig. 2) if the value of $\varepsilon_1$ is known. Using the measured values of relative dielectric constant in Ge$_x$Se$_{100-x}$, glassy system [10], the values of $g_0$ are calculated from the slopes of $S$ vs $1/T$ curves shown in Fig. 2. In Ge$_x$Se$_{100-x}$, $\varepsilon_1$ is found [10] to be independent of frequency (100 Hz to 10 kHz) and temperature (305 to 365 K). Hence the value of $\varepsilon_1$ at 305 K and 1 kHz is used for the present calculations. Such values are given in Table 1 which also consists the values of slopes of $S$ vs 1000/T curves.

The values of $g_0$ are given in Table 1 for various glassy alloys and plotted as a function of $x$ in Fig. 3. Though there are small variations at all compositions but they are not very significant except at $x = 22$ where a drastic decrease is observed. The value of $g_0$ at $x = 22$ is minimum in Ge$_x$Se$_{100-x}$ glassy system (see Fig. 3). The reason for such a minimum is given in the following section.

4. DISCUSSIONS

Phillips [11] proposed that the molecular structure of melt-quenched Ge$_x$Se$_{100-x}$ is much more ordered than would be expected from a continuous random network model. According to him, Ge$_x$Se$_{100-x}$ alloys may be described by chemically ordered clusters embedded in a continuous network. Some of these clusters are (Se)$_4$ chains, Ge$_2$(Se)$_6$ corner-sharing tetrahedra and Ge$_2$(Se)$_2$ ethane-like structural units. The first two types dominate for $x \leq 33$ and the third type is expected to occur at higher concentration of Ge ($x > 33$).

An analysis of Raman spectra for Ge$_x$Se$_{100-x}$ glasses showed [12] that (GeSe$_{12}$)$_4$ units are randomly distributed within the glass structure. Based on this argument, Feltz et al. [13] proposed that, at a composition GeSe$_x$ ($x = 20$), the (GeSe$_{12}$)$_4$ groups should be predominantly linked by Se-Se bridges. The number of Se-Se bridges may be reduced by the introduction of longer chains when $x < 20$.

From the above discussion it is clear that some sort of chemical ordering takes place near $x = 20$. At low concentration of Ge, longer Se-Se chains predominate. As the concentration of Ge increases, (GeSe$_{12}$)$_4$ units are linked by Se-Se bridges. At high concentration of Ge ($20 < x < 33$) this effect decreases owing to the presence of single-bridging Se atom.

The above mentioned non-crystalline compound (GeSe$_x$) formation was first observed by Feltz et al. [13] in their dielectric measurements in Ge$_x$Se$_{100-x}$ glassy system. This was further supported by X-ray spectroscopic measurements of Agnihotri et al. [14] where they could observe a discontinuity in the K-absorption edge of Ge and Se at $x = 22$ in

![Fig. 3. Density of states vs x curve in Ge$_x$Se$_{100-x}$ glassy system.](image-url)
Ge, Se	extsubscript{100}, glassy system. Similar discontinuity was also observed by Kumar et al. [15] in their photo-conductivity measurements where they found a maximum in photo-sensitivity at \( x = 22 \) in Ge, Se	extsubscript{100}, glassy system.

Our SCLC measurements also indicate a minimum density of states for \( x = 22 \) in Ge, Se	extsubscript{100}, glassy system (see Fig. 3) which is in agreement with the maximum photo-sensitivity at this composition [15].

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Chalcogenide glasses have recently attracted great attention from solid-state physicists due to their application in various solid-state devices. The effect of impurities on the transport and structural properties has been an important issue since the discovery of these glasses. Among these glasses impurity effects in the Ge–Se system have drawn more attention as some metallic impurities have been found [1–3] to change the conduction type from p to n in these glasses. Since the density of localized states in the mobility gap controls many physical properties of amorphous semiconductors, the determination of the density of such states becomes an important issue in these materials.

One of the most direct methods for the determination of \( g(E) \) involves the measurements of space-charge-limited current (SCLC) which can easily be observed at high fields in amorphous materials because of their low conductivity. Such a technique has already been applied [4–11] to hydrogenated amorphous silicon and it is generally observed that \( g(E) \) obtained by this method is lower by a factor of 3–5 than by other techniques as surface states do not come into the picture in this experiment.

This letter reports the measurements of SCLC in an a-Ge\(_{20}\)Se\(_{80–x}\)In\(_x\) system with the specific aim of seeing the effect of a third element on \( g(E) \) in binary Ge–Se alloys. Crystallization kinetics and X-ray spectroscopic studies of the Ge\(_{20}\)Se\(_{80–x}\)In\(_x\) glassy system have already been reported [12, 13]. The results indicated that the physical properties are highly composition-dependent in this system.

Glasses of Ge\(_{20}\)Se\(_{80–x}\)In\(_x\) (0 ≤ x ≤ 20) were prepared by a melt-quenching technique. Materials of 99.999% purity were sealed in quartz ampoules (length about 5 cm, internal diameter about 8 mm) in a vacuum of about 1.3 mPa. The sealed ampoules were kept inside a furnace where the temperature was raised slowly (3–4 °C min\(^{-1}\)) to 950 °C. The ampoules were rocked frequently for 10 h at the maximum temperature to make the melt homogeneous. Quenching was done in air by an air blower. The glassy nature of the alloys was ascertained by the X-ray diffraction technique.

Thin films of the glassy alloys were prepared by a vacuum evaporation technique using a standard coating unit (IBP Torr model EPR 002). Well-doped Corning glass plates, having pre-deposited indium electrodes, were used as the substrate for depositing amorphous films in the planar geometry (length about 1.2 cm and electrode gap about 0.12 mm). These films were prepared at a base pressure of about \( 10^{−4} \) torr by keeping the substrates at room temperature. The thickness of the amorphous films was about 500 nm. The deposition parameters were kept almost the same for all of the samples, so a comparison of results could be made for various glassy samples.

For the measurements of SCLC, the samples were mounted in a specially designed metallic sample holder where a vacuum of about 0.13 Pa could be maintained throughout the measurements. A d.c. voltage (0–300 V) was applied across the sample and the resultant current was measured by a digital electrometer (Keithley model 614) Current–voltage (I–V) characteristics were measured at various fixed temperatures (291–362 K) for all glassy alloys studied, the temperature was measured by mounting a copper–constantan thermocouple near to the sample. Before measuring the I–V characteristics, thin film samples were annealed in a vacuum of about 0.13 Pa near the glass transition temperature of each alloy for 2 h in the same sample holder that was used for the above measurements.

The I–V characteristics were studied at various temperatures (291–362 K) in amorphous thin films of Ge\(_{20}\)Se\(_{80–x}\)In\(_x\) (0 ≤ x ≤ 20). The planar geometry of the films was used for these measurements. At low fields (< \( 10^3 \) V cm\(^{-1}\)) an ohmic behaviour was observed at various temperatures in all of the glassy samples used in the present study. However, at higher fields (about \( 10^3 \) V cm\(^{-1}\)), a non-ohmic behaviour was observed where \( \ln(I/V) \) versus \( V \) curves were found to be straight lines at all measuring temperatures (291–362 K). The results for Ge\(_{20}\)Se\(_{80}\) and Ge\(_{20}\)Se\(_{80}\)In\(_{20}\) glassy alloys are plotted in Figs 1 and 2, respectively. Similar results were obtained in other glassy alloys (results not shown here).

It is clear from Figs 1 and 2 that the slope (S) of the \( \ln(I/V) \) versus \( V \) curves is not the same at all measuring temperatures; the values of these slopes is plotted as a function of temperature in Fig. 3 for various glassy alloys used in the present study. It is clear from this figure that the slope decreases linearly with increasing temperature.

According to the theory of space-charge-limited conduction, in the case of a uniform distribution of localized states, \( g(E) = g_o \), current \( (I) \) at a particular voltage \( (V) \) is given by [14]

\[
I = KV \exp(SV)
\]

(1)

where \( K \) is a constant and \( S \) is given by

\[
S = 2e_A \epsilon \frac{1}{|q|g_o kT d^2}
\]

(2)

Here \( \epsilon \) is the relative dielectric constant, \( d \) is the
Figure 1. In(I/V) versus V curves at different temperatures for a-Ge_{x}Se_{1-x}: (O) 303, (●) 314, (□) 324, (■) 348 and (▲) 362 K.

It may be mentioned that Equation 1 is not an exact solution of the SCLC equations, but it is a very good approximation for high injected currents. According to Equation 1, in the case of SCLC, the In(I/V) versus V curve, at a particular temperature, should be a straight line as found in the present samples (see Figs 1 and 2). The slope (S) of these curves should decrease linearly with temperature (Equation 2) as also found in the present samples (see Fig. 3). These results indicate the presence of SCLC in the present samples.

Figure 2. In(I/V) versus V curves at different temperatures for a-Ge_{x}Se_{1-x}: (O) 291, (●) 306, (▲) 321, (▲) 335 and (□) 349 K.

Figure 3. S versus 10^3/T curves for a-Ge_{x}Se_{1-x}: x = (O) 0, (●) 5, (△) 10, (▲) 15 and (□) 20.
It is clear from Equation 2 that $g_0$ can be obtained from the slope of $S$ versus $1/T$ curves (Fig. 3) if the value of $\varepsilon_r$ is known. Using the measured value of relative dielectric constant at room temperature and at frequency $1 \text{ kHz}$, the values of $g_0$ were calculated for the present samples. The results of these calculations are given in Table 1 and plotted in Fig. 4. It is clear from this figure that $g_0$ increases monotonically with increasing In concentration in a-Ge$_{20}$Se$_{80}$,In$_x$.

When the third element (In in the present case) is added to the Ge-Se system, the atoms of the third element induce structural changes in the host network Ge-Se. This leads to readjustments in the local environment, which disturbs the balance of characteristic charged defect states which may result in the shift of the Fermi level as observed by Kosek et al. [15] in the Ge-Se-In system. In addition to the above readjustments, some new trap states can also appear in the mobility gap of the host material on addition of the third element, as evident from the present measurements.

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**References**


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SPACE CHARGE LIMITED CONDUCTION IN a-Se_{1-x}Te_x

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The present paper reports the measurements on space charge limited conduction in vacuum evaporated amorphous thin films of Se_{100-x}Te_x, where 0 \leq x \leq 25. Current, at high fields (\sim 10^4 \text{V cm}^{-1}), could be fitted to the theory of space charge limited conduction (SCLC) in case of a uniform distribution of localized states in the mobility gap of these materials. The results indicate that the density of localized states increases with the concentration of Te in a-Se-Te.

1. INTRODUCTION

DUE TO THEIR wide range of applications in various solid state devices, e.g. switching and memory, image converters and optical mass memories etc., chalcogenide glasses have recently received a lot of attention from scientists and engineers. The common feature of these glasses is the presence of localized states in the mobility gap due to the absence of long range order as well as various inherent defects.

Se–Te alloys have created extreme interest due to their greater hardness, higher photosensitivity, higher crystallization temperature and smaller ageing effects as compared to pure amorphous Se. Se–Te alloys have therefore certain advantages over amorphous Se as far as their use in xerographic photoreceptors is concerned [1]. This laboratory has been engaged these days in studying the transport and structural properties of various Se–Te amorphous alloys. The photoconductivity [2–4], dielectric behaviour [5], crystallization kinetics [6–9], X-ray spectroscopic measurements [10] of such alloys have recently been reported by us. Since the density of localized states (DOS) in the mobility gap controls many physical properties of amorphous semiconductors, an independent measurement of these states is required for a better understanding of these materials and possible improvement thereof.

One of the most direct methods for the determination of density of localized states (g(E)) involves the measurements of space charge limited conduction (SCLC) which can easily be observed at high fields in disordered materials because of their low conductivity. Such a technique has already been applied to hydrogenated amorphous silicon [11–18] and it is generally observed that g(E) obtained by this method is lower by a factor of 3–5 as compared to other techniques as surface states do not come into the picture in this experiment. Recently, we have applied [19, 20] the same method in some germanium based glassy alloys and obtained composition dependence of the localized states near Fermi level.

The aim of the present paper is to report similar measurements in amorphous Se_{100-x}Te_x (0 \leq x \leq 25) with a specific aim to see the effect of Te incorporation on the density of defect states in amorphous Se. The results indicate that the DOS increases with Te concentration.

Section 2 describes the experimental details of sample preparation and SCLC measurements. The results are presented and discussed in Sections 3 and 4 respectively. The last section deals with the conclusions drawn from the present work.

2. EXPERIMENTAL DETAILS

2.1. Sample preparation

Glassy alloys of Se_{100-x}Te_x, where 0 \leq x \leq 25, were prepared by a quenching technique. Materials (99.999% pure) were weighed according to their atomic percentages and were sealed in quartz ampoules (length ~ 5 cm, internal diameter ~ 8 mm) in a vacuum ~ 10^{-5} \text{Torr}. The sealed ampoules were kept inside a furnace where the temperature was raised to maximum temperature 600°C at a rate of 3–4°C min^{-1}. The ampoules were rocked frequently for a period of 10 h at the maximum temperature to make the melt homogeneous. The quenching was done in ice water.

Thin films of the glassy alloys were prepared by a vacuum evaporation technique keeping the substrates at room temperature at a base pressure ~ 10^{-5} \text{Torr}, using molybdenum boats. Predeposited thick indium electrodes on well degassed glass substrates were used for the electrical contact. The thickness of the films was ~ 5000 Å.
The planar geometry of the amorphous films (width ~ 1.7 cm and electrode gap ~ 0.12 mm) was used for the SCLC measurements. The films were kept in the deposition chamber in the dark for 24 h before mounting them in the sample holder. This was done to allow sufficient annealing at room temperature so that the metastable thermodynamic equilibrium may be attained in the samples as stressed by Abkowitz [21] in chalcogenide glasses.

2.2. SCLC measurements

For the measurements of SCLC, the samples were mounted in a specially designed metallic sample holder where a vacuum ~ 10^{-3} Torr could be maintained throughout the measurements. A d.c. voltage (0-300 V) was applied across the sample and the resulting current was measured by a digital electrometer (Keithley, model 614). Current voltage (I-V) characteristics were made at various fixed temperatures (285 to 336 K) for all the glassy alloys studied. The temperature was measured by mounting a copper constantan thermocouple very near to the sample. Before measuring I-V characteristics, thin film samples were annealed in a vacuum ~ 10^{-3} Torr near glass transition temperature of each sample for two hours in the same sample holder which was used for the above measurements.

3. RESULTS

I-V characteristics were studied at various temperatures (285 to 336 K) in amorphous thin films of Se_{100-x}Te_{x}, where 0 ≤ x ≤ 25. At low fields (< 10^4 V cm^{-1}), an ohmic behaviour was observed at various temperatures in all the glassy samples used in the present study. However, at higher fields (~ 10^4 V cm^{-1}), a non-ohmic behaviour was observed where ln J/V vs V curves, where J is current density, were found to be straight lines at all the measuring temperatures (285 to 336 K). The results of a-Se and a-Se_{80}Te_{20} are plotted in Figs. 1 and 2 respectively. Similar results were obtained in other glassy systems also (results not shown here). It is clear from Figs. 1 and 2 that the slope (S) of ln J/V vs V curves is not the same at all the measuring temperatures. The value of these slopes is plotted as a function of temperature in Fig. 3 for various glassy systems used in the present study. It is clear from this figure that the slope decreases linearly with the increase in temperature.

According to the theory of SCLC, in case of a uniform distribution of localized states, \( g(E) = g_0 \) current density \( J \) at a particular voltage \( V \) is given by the following equation [22].

\[
J = e\mu_0 \frac{V}{d} \exp (SV),
\]
where \( d \) is the electrode spacing, \( \rho_0 \) is the density of the thermally generated carriers, \( \mu \) is the mobility, \( e \) is the electronic charge and \( S \) is given by

\[
S = \frac{2e\rho_0}{\varepsilon_0\kappa Td^2}.
\]

It may be mentioned that equation (1) is not an exact solution of SCLC equations, but it is a very good approximation for one carrier space charge limited currents under the condition of uniform distribution of traps.

In the present case, one carrier assumption is justified as these glasses are known to behave p-type. As the present measurements scan a very limited energy range near Fermi level, the assumption of uniform distribution is also not unjustified.

As evident from equation (1), in case of SCLC, \( \ln J/V \) vs \( V \) curve, at a particular temperature, should be a straight line as found in the present samples (see Figs. 1 and 2). The slope (\( S \)) of these curves should decrease linearly with temperature equation (2) as also found in the present samples (see Fig. 3). These results indicate the presence of SCLC in the present samples.

It is clear from equation (2) that \( g_0 \) can be obtained from the slope of \( S \) vs \( 1/T \) curves (Fig. 3) if the value of \( \varepsilon \) is known. The static value of the relative dielectric constant is, however, not reported for these glasses. Hence the measured values [5] of \( \varepsilon \) at lower frequency (120 Hz) and at room temperature is used for the calculation of \( g_0 \) in the present samples. The results of these calculations are given in Table 1, and plotted in Fig. 4 as a function of Te concentration. It is clear that \( g_0 \) increases monotonically with the increase of Te concentration in \( a-\text{Se}-\text{Te} \) system.

Touraine et al. [23] have also measured high field conductivity in amorphous Se films and have demonstrated that the results can be interpreted in terms of space charge limited conduction in case of a uniform distribution of traps in the mobility gap of this material. Using these measurements, they obtained a trap density \( \sim 5 \times 10^{14} \text{cm}^{-3}\text{eV}^{-1} \). In the present case, the density of traps comes out to be \( \sim 1.33 \times 10^{14} \text{cm}^{-3}\text{eV}^{-1} \) which is quite close to the value obtained by the above workers. A small difference in the trap density may be associated with the different conditions of preparation of films in the two cases.

### Table 1. Density of localized states in various glassy alloys

<table>
<thead>
<tr>
<th>Glassy alloy</th>
<th>Slope of $S$ vs $1000/T$ curve</th>
<th>( \varepsilon ) (120 Hz, 303 K) [5]</th>
<th>( g_0 ) (density of localized states) in eV$^{-1}$ cm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se</td>
<td>$3.47 \times 10^{-3}$</td>
<td>5.17</td>
<td>$1.33 \times 10^{14}$</td>
</tr>
<tr>
<td>Se$<em>{90}$Te$</em>{10}$</td>
<td>$2.07 \times 10^{-3}$</td>
<td>5.75</td>
<td>$2.48 \times 10^{14}$</td>
</tr>
<tr>
<td>Se$<em>{80}$Te$</em>{20}$</td>
<td>$2.52 \times 10^{-3}$</td>
<td>10.16</td>
<td>$3.59 \times 10^{14}$</td>
</tr>
<tr>
<td>Se$<em>{75}$Te$</em>{25}$</td>
<td>$9.50 \times 10^{-4}$</td>
<td>18.38</td>
<td>$1.73 \times 10^{15}$</td>
</tr>
</tbody>
</table>

Fig. 4 as a function of Te concentration curve in \( a-\text{Se}_{100-x}\text{Te}_x \).
effect of Te alloying on the electronic gap of amorphous Se by a combination of drift mobility and xerographic measurements. The measurements indicated that the addition of Te to Se progressively decreases both electron and hole drift mobility and increases the integrated number of deep traps and broadens the distribution of both deep and shallow electronic gap states. Hjartarson and Kao [25] made photo-response measurements in the same system and concluded that the density of defects increases on addition of Te in a-Se. In our earlier measurements [5] we found that the density of Te concentration in dielectric loss increases on increasing Te concentration in glassy a-Se. In the present measurements also we found that the density of defect states increases with the increase of Te concentration in a-Se, Te, system which is in agreement with the above measurements. This increase in the density of defects may be understood as follows:

Selenium glass is considered to be a continuous random network consisting of chains and a few rings of atoms with two fold co-ordination. The introduction of Te decreases the number of Se rings and increases the number of long Se–Te polymeric chains and Se–Te mixed rings making the system more rigid and hence improving the properties of a-Se as mentioned earlier in this paper. However, since the electron affinity of tellurium is lower than selenium, not all Te atoms are mixed in selenium atom chains and would act as ionized impurities as suggested by Onozuka et al. [26]. This is probably the reason why the density of defect states increases on Te incorporation in a-Se as observed in the present case.

CONCLUSIONS

Space charge limited conduction studies are made in vacuum evaporated amorphous thin films of a-Se, Te, where 0 ≤ x ≤ 25. The density of localized states in the mid gap is calculated by fitting the data to the theory of SCLC in case of a uniform distribution of localized states (g0). It is observed that g0 increases as concentration of Te increases in a-Se–Te system. These results are in agreement with the other experiments in the same glassy system.

REFERENCES

High-field conduction in $a\text{-Se}_{80}\text{Te}_{20}$ and $a\text{-Se}_{80}\text{Te}_{10}\text{M}_{10}$

($\text{M} = \text{Ag, Cd or Sb}$)

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The present paper reports the measurement of DC conductivities at high fields in various binary and ternary glassy semiconducting alloys. The analysis of the data shows the existence of space charge limited conduction in $a\text{-Se}_{80}\text{Te}_{20}$ and $a\text{-Se}_{80}\text{Te}_{10}\text{M}_{10}$ ($\text{M} = \text{Ag, Cd or Sb}$). Using these measurements, the density of localized states near the Fermi level is also calculated for these alloys.

Due to their low conductivity, amorphous semiconductors are most suitable for high-field conduction studies as the joule heating is negligibly small in these materials at moderate temperatures. Some such studies have been reported [1–11] in chalcogenide glassy semiconductors and the results have been interpreted in terms of the space-charge limited currents [2–8] or in terms of high field conduction due to the Poole–Frenkel effect of screened charged intrinsic defects and field induced lowering of energy barriers for the charge carrier hopping within localized states at the band edges [1, 9, 10, 11]. It is interesting to note that space-charge limited currents for a uniform distribution of traps as well as the high-field conduction theories mentioned above lead to a similar kind of field dependence of the conductivity at different temperatures. To distinguish between these two processes, the measurements on samples having different electrode gaps are therefore necessary.

In view of the above the field dependence of the conductivity is measured at different temperatures on vacuum-evaporated thin films of Se$_{80}$Te$_{20}$ and Se$_{80}$Te$_{10}$M$_{10}$ having different electrode separation. The dependence of DC conductivity on the electrode separation confirms the presence of space-charge limited conduction (SCLC) in the present samples. Using the theory of SCLC for the case of a uniform distribution of traps, the density of localized states near the Fermi level is calculated for various samples used in the present study.

Chalcogenide glasses were prepared by a quenching technique. Materials (99.999% pure) were weighed according to their atomic percentages and were sealed in quartz ampoules (length ~5 cm, internal diameter ~8 mm) in a vacuum of ~$10^{-4}$ Torr. The sealed ampoules were kept inside a furnace where the temperature was raised to a maximum temperature of 600°C at a rate of 3–4°C mm. The ampoules were rocked frequently for a period of 10 h at the maximum temperature to make the melt homogeneous. The quenching was done in ice water.

Thin films of the above glasses were prepared by a vacuum evaporation technique keeping the substrates at room temperature at a base pressure of ~$10^{-6}$ Torr, using molybdenum boats. Predeposited thick indium electrodes on well degassed glass substrates were used for the electrical contact. The thickness of the films was ~5000 Å.

The planar geometry of the amorphous films
(width ~1.2 cm and electrode gap ~0.12–0.37 mm) was used for the present measurements. The films were kept in the deposition chamber in the dark for 24 h before mounting them in the sample holder. This was done to allow sufficient annealing at room temperature so that a metastable thermodynamic equilibrium may be attained in the samples as suggested by Abkowitz [12] for chalcogenide glasses.

For the measurements of SCLC, the samples

![Graph](https://via.placeholder.com/150)

**Fig. 1.** $\ln I / V$ vs. $V$ curves at different temperatures for a Se$_{1-x}$Te$_x$.
were mounted in a specially designed metallic sample holder where a vacuum of \( \sim 10^{-3} \) Torr could be maintained throughout the measurements. A DC voltage (0–300 V) was applied across the sample and the resulting current was measured by a digital electrometer (Keithley, model 614) and current voltage \((I-V)\) characteristics were measured at various fixed temperatures (296 K to 337 K) for all the chalcogenide glasses studied. The temperature was measured by mounting a copper–constantan thermocouple very near the sample. Before measuring the \( I-V \) characteristics, thin film samples were annealed in a vacuum of \( \sim 10^{-3} \) Torr near the glass transition temperature \( (T_g) \) for two hours in the same sample holder as used for the above measurements.

At low fields (\(< 10^3 \) V/cm), an ohmic behaviour was observed at various temperatures in all the glassy samples used in the present study. However, at higher fields (\( \sim 10^4 \) V/cm), a non-ohmic behaviour was observed where \( \ln I/V \) vs.

**Fig. 2.** Temperature dependence of the slope of \( \ln I/V \) vs. \( V \) curves.
$V$ curves were found to be straight lines at all the measuring temperatures (296 K to 337 K). The results for a-Sc$_{80}$Fe$_{20}$ are plotted in fig. 1. Similar results were obtained in other glassy systems also (results not shown here). It is clear from this figure that the slope ($S$) of In $I/V$ vs. $V$ curves is not the same at all the measuring temperatures. The value of these slopes is plotted as a function of temperature in fig. 2 for various glassy systems used in the present study. It is clear from this figure that the slope decreases linearly with the increase in temperature.

According to the theory of SCIC, in the case of a uniform distribution of localized states, $g(l)$ = $g_0$, the current ($I$) at a particular voltage ($V$) is given [13] by the following equation:

$$I = cA \mu n_a \frac{d}{d} \exp(MV)$$

where $d$ is the electrode spacing, $n_a$ is the density
of the thermally generated charge carriers, $\mu$ is the mobility, $A$ is the area of cross section of thin films, $e$ is the electronic charge and $S$ is given by

$$S = \frac{2r_1 e A}{e \varepsilon_0 k T d^2}$$

(2)

where $r_1$ is the static value of the relative dielectric constant, $\varepsilon_0$ is the permittivity of free space and $K$ is Boltzmann's constant.

It may be mentioned that eq. (1) is not an exact solution of the SCLC equations, but it is a very good approximation for one carrier of

![Graph](image)

Fig. 4. $S$ vs. $1/d^2$ curve for different electrode gaps.
space-charge limited currents under the condition of uniform distribution of traps.

In the present case, the one-carrier assumption is justified as these glasses are known to behave as p-type material. As the present measurements scan a very limited range of energy near the Fermi level, the assumption of uniform distribution is also not unjustified.

As evident from eq. (1), in the case of SCLC, the \( \ln I/V \) vs. \( V \) curve should be a straight line for each temperature of measurement as found in the present samples (see fig. 1). The slope \( S \) of these curves should decrease linearly with temperature (see eq. (2)) as also found in the present samples (see fig. 2). These results indicate the presence of SCLC in the present samples.

It may be mentioned here that nearly linear plots of \( \ln I/V \) vs. \( V \) as well as a linear decrease of \( S \) with temperature can also be explained in terms of high field conduction due to the Poole-Frenkel effect of screened charged intrinsic defects and field induced lowering of energy barriers for the charge-carrier hopping within localized states at the band edges. However, in the case of field dependent conductivity, the plot of \( \ln I/V \) vs. \( V \) must be independent of the electrode spacing \( 'd' \). On the other hand, for any SCLC mechanism, the same plot gives different curves for different values of \( d \). We have therefore measured \( I-V \) characteristics at room temperature for various samples having different electrode spacing. The results for one particular sample \( \text{Se}_{95}\text{Te}_{5} \) are plotted in fig. 3. It is clear from this figure that different slopes are obtained at different electrode spacings. The values of these slopes are given in table 1 and plotted against \( 1/ d \) in fig. 4. This confirms the validity of eq. (2) in the present case and excludes the possibility of high field conduction processes mentioned above. Hence the present measurements confirm the presence of SCLC in the present samples.

It is clear from eq. (2) that \( g \) can be obtained from the slope of \( S \) vs. \( 1/I \) curves (fig. 2) if the value of \( r \) is known. The static value of the relative dielectric constant is, however, not reported for these glasses. Hence the measured values \([13]\) of \( r \) at lower frequency \((120\text{Hz})\) and at room temperature \((303\text{K})\) is used for the calculation of \( g \) in the present samples. The results of these calculations are given in table 2.

It is clear from this table that the density of localized states near the Fermi level is not significantly changed on addition of a third element to binary chalcogenide \( \text{Se}_{x}\text{Te}_{1-x} \).

Acknowledgements

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References


Table 1

<table>
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<tr>
<th>Electrode gap ((d)) in mm</th>
<th>(1/d) ((\text{in mm}^{-1}))</th>
<th>Slop of (I/V) of (\ln I/V) vs. (V) at (1_{\text{G}})</th>
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<tr>
<td>0.12</td>
<td>69.44</td>
<td>5.10 \times 10^3</td>
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<td>0.19</td>
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<td>0.30</td>
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<td>9.40 \times 10^3</td>
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<tr>
<td>0.37</td>
<td>7.31</td>
<td>5.45 \times 10^3</td>
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Table 2

<table>
<thead>
<tr>
<th>Glassy alloy</th>
<th>Slope of (\ln I/V) curve at (1_{\text{G}}) (\text{K}^{-1})</th>
<th>(g), density of localized states (\text{meV}^{-1}\text{cm}^{3})</th>
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</thead>
<tbody>
<tr>
<td>Se_{95}Te_{5}</td>
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