

Photoconductivity and high-field effects in amorphous $\text{Se}_{83}\text{Te}_{15}\text{Zn}_2$ thin film

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Abstract. The glassy alloy of $\text{Se}_{83}\text{Te}_{15}\text{Zn}_2$ has been prepared by conventional rapid melt-quenching technique. The glassy nature of the prepared alloy is confirmed through X-ray diffraction (XRD) technique. A thin film of the aforesaid material was prepared by thermal evaporation technique. Coplanar indium electrode was used. Current–voltage (I – V) characteristics and photoconductivity measurements were obtained. At low electric field, ohmic, and at high electric fields ($E \sim 10^4$ V/cm), non-ohmic behaviour was observed. An analysis of the experimental data confirms the presence of space charge limited conduction (SCLC) in the glassy material studied in the present case. From the fitting of the data to the theory of SCLC, the density of defect states (DOS) near the Fermi level was calculated. Temperature dependence of conductivity in dark as well as in the presence of light shows that conduction is through a thermally activated process in both the cases. The activation energy is found to decrease with the increase in light intensity. This indicates the shift of the Fermi level with intensity. Transient photoconductivity measurements at different temperatures indicate that the decay of photoconductivity is quite slow, which is found to be non-exponential in the present case, indicating the presence of a continuous distribution of defect states in the aforesaid glassy alloy.

Keywords. Thin film; chalcogenide glasses; SCLC; photoconductivity; defect states.

1. Introduction

The phenomenon related to electronic conduction in amorphous chalcogenide semiconductors has attracted a great deal of scientific attention since the discovery of electrical switching in chalcogenide glasses in 1968 (Ovshinsky 1968). The study of doped amorphous semiconductors is becoming of great interest to scientists. It was believed earlier (Mott 1967) that impurities have little effect on the properties of amorphous semiconductors as each impurity atom can satisfy its valence requirements by adjusting its nearest-neighbour environment. However, several reports indicate that drastic changes in the conductivity and activation energy can be achieved by suitable preparation techniques (Ovshinsky 1977; Fritzsche *et al* 1978; Kastner 1978).

The electrical properties of amorphous Se-based chalcogenide glasses exhibit a large Fermi level shift and large photovoltaic effects (Watanabe and Yamamoto 1985; Watanabe and Sekiya 1987). I – V characteristics and the consequent field effect study of several chalcogenide glasses have been reported by different investigators (El-Kady 1999). In pure state this Se has several disadvantages because of its short life time and low sensitivity. To overcome these difficulties, certain additives

are used, e.g. Te, Sb, In, Ge, etc and binary and ternary alloys are formed (Moharram *et al* 2002). Recently, it has been pointed out that Se-Te alloys have more advantages than a-Se from the technological point of view due to their greater hardness, higher crystallization temperature, higher photosensitivity and smaller ageing effects. Therefore, glassy Se–Te alloys are used to extend the utility of a-Se (Shimakawa 1985; Saitar *et al* 1998).

Since network connectivity, rigidity and nature of bonding play important roles in electronic conduction process (Ovshinsky and Sapru 1977), and hence in order to understand the conduction phenomena, a great deal of experimental data is required. Many workers have carried out investigations of the electrical and optical properties of binary and ternary chalcogenide glasses (Saraswat *et al* 2006; Soltan 2005). The photoconductivity kinetics of amorphous semiconductors are to a great extent determined by the process of trapping of non-equilibrium charge carriers on localized centres of various depths – such studies are important to understand the energy distribution of the traps. From the application point of view also photoconductive properties are important.

The effect of incorporation of a third element in binary chalcogenide glassy alloys has always been an interesting problem in getting relatively stable glassy alloys as well as to change the conduction type from p to n as most of these glasses show p -type conduction only. In the present study we measured the electrical properties of chalco-

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genide $\text{Se}_{83}\text{Te}_{15}\text{Zn}_2$ glassy alloy. The selection of Zn as a chemical modifier in Se–Te system is based on its attractive and important applications in chalcogenide glasses. Like Ag, Zn can also be used for photo-doping in chalcogenide glasses (KoloBov *et al* 1985; Kolobov and Bedelbaeva 1991; Faschinger *et al* 1994). There are successful reports of doping of Zn–Se–Te in the literature that are suitable for the development of light-emitting diodes and lasers.

As high-field effects are most readily observed in these materials because of their low conductivity (Joule heating is negligibly small at moderate temperatures) and have been studied by various groups working in this field (Kumar *et al* 1993; Nikam and Aher 1996; Abou El-Hassan 2001). The results of these workers have been interpreted in terms of heating effect, space charge limited conduction (SCLC) and high field conduction due to the Poole–Frenkel effect. This indicates that the interpretation of the high field data is highly intriguing in these materials and much has to be done in this field.

Keeping this fact in mind, we report in this paper the high-field conduction and photoconductivity measurements in glassy $\text{Se}_{83}\text{Te}_{15}\text{Zn}_2$ thin film. The experimental data fits well with the theory of space charge limited conduction (SCLC) in the high-electric-field region. From the fitting of the data, the density of defect states (DOS) near the Fermi level is calculated.

Temperature dependence of steady state photoconductivity was also studied at different light intensities. Intensity dependence of photoconductivity is studied at different fixed temperatures. Transient photoconductivity measurements at different temperatures have also been obtained. Section 2 describes the experimental details. The results have been presented and discussed in §3. The conclusions have been presented in the last section.

2. Experimental

2.1 Sample preparation

A glassy alloy of $\text{Se}_{83}\text{Te}_{15}\text{Zn}_2$ system was prepared by melt-quenched technique. High-purity elements (99.999% pure), selenium, tellurium and zinc, were weighed by electronic balance (Shimadzu, AUX 220) according to their atomic percentages, with a least count of 10^{-4} g. The properly weighed materials were put into clean quartz ampoule (length ~ 5 cm and internal diameter ~ 8 mm) and then sealed under vacuum of 1.3×10^{-3} Pa. This sealed ampoule was heated in electric furnace up to 1000°C and kept at that temperature for ~ 10 h. The temperature of the furnace was raised slowly at a rate of $3\text{--}4^\circ\text{C}/\text{min}$. During the heating process, the ampoule was constantly rocked, by rotating a ceramic rod to which the ampoule was attached in the furnace. This was done to obtain homogenous glassy alloy.

After rocking for ~ 10 h, the obtained molten material ampoule was rapidly quenched by removing the ampoule from the furnace and dropping it into ice-cooled water. The quenched sample of the glassy alloy was taken out by breaking the quartz ampoule. The amorphous nature of the sample was confirmed by the absence of any sharp peak in the X-ray diffraction pattern, as shown in figure 1. Compositional analysis was performed using electron probe micro-analysis (EPMA) technique.

2.2 Preparation of thin films

Thin films of the glassy alloy of $\text{Se}_{83}\text{Te}_{15}\text{Zn}_2$ were prepared by vacuum evaporation technique; keeping the glass substrate at room temperature. Vacuum-evaporated indium electrodes at the bottom were used for the electrical contact. The thickness of the film was ~ 500 nm. The co-planar structure (length ~ 1.2 cm and electrode separation ~ 0.12 mm for high-field measurements and 0.5 mm for photoconductivity measurements) was used for the present measurements. A vacuum ~ 1.3 Pa was maintained in the entire temperature range ($300\text{--}340$ K).

2.3 Procedure of measurements

The thin film was kept in the deposition chamber in the dark for 24 h before it was mounted 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 sample as suggested by Abkowitz (1984). Before measuring the d.c. conductivity, the film was first annealed at 340 K (below their glass transition temperature, T_g) for 1 h in a vacuum ~ 1.3 Pa.

As co-planar structure of the film was used for the present measurements, a d.c. voltage was applied across the

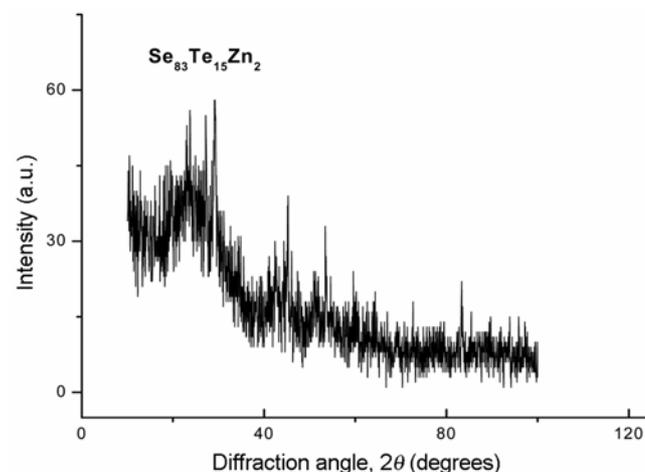


Figure 1. XRD pattern of $\text{Se}_{83}\text{Te}_{15}\text{Zn}_2$ glassy alloy.

electrodes to measure I - V characteristics and found to be linear and symmetric up to 10 V. The present measurements were, however, made by applying a voltage up to 300 V across the films. The resulting current was measured by a digital Pico-Ammeter. The heating rate was kept quite small (0.5 K/min) for these measurements. The thin film sample was mounted in a specially designed sample holder. A vacuum ~ 1.3 Pa was maintained throughout the measurements. The temperature of the film was controlled by mounting a heater inside the sample holder, and measured by a calibrated copper-constantan thermocouple mounted very near to the film.

The dark and photoconductivity of the amorphous film was studied by mounting it in a specially designed metallic sample holder in which illumination could be achieved through a transparent window. The light source used for these measurements was a 200 W tungsten lamp. Light intensity was measured by a digital lux meter (Testron, model LX-101). The photocurrent (I_{ph}) was obtained after subtracting the dark current (I_d) from the current measured in the presence of light.

3. Results and discussion

3.1 High-field conduction measurements

Results of I - V characteristics at different temperature shows that in the glassy sample studied here, ohmic behaviour is observed at low voltages, i.e. up to 10 V. However, at higher voltages ($E \sim 10^4$ V/cm), a super-ohmic behaviour is observed in the sample. Here, $\ln I/V$ vs V curves are found to be straight lines. Figure 2 shows such curves in the case of the $Se_{83}Te_{15}Zn_2$ glassy alloy. According to the theory of SCLC, in the case of a uniform distribution of localized states having density g_0 , the current (I) at a particular voltage (V) is given by (Lampert and Mark 1970):

$$I = (2eA\mu n_0 V/d)[\exp(SV)]. \quad (1)$$

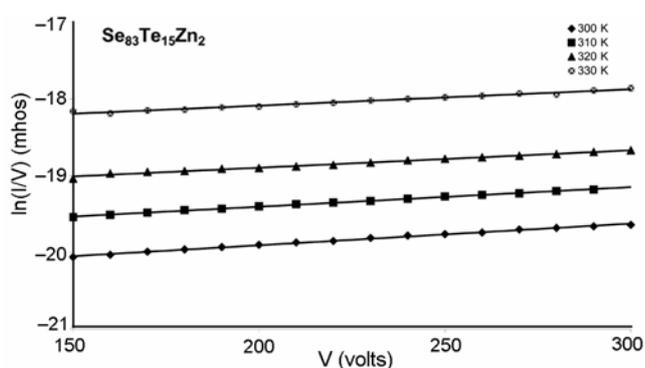


Figure 2. Plots of $\ln(I/V)$ vs V curves for $Se_{83}Te_{15}Zn_2$ film at different temperatures.

Here, e is the electronic charge, A the cross-sectional area of the film, n_0 the density of free charge carriers, d the electrode spacing and S is given by

$$S = 2\varepsilon_r\varepsilon_0/eg_0kTd^2, \quad (2)$$

where ε_r is the static value of the dielectric constant, ε_0 the permittivity of free space, g_0 the density of traps near the Fermi level and k the Boltzmann's constant.

It should be noted that (1) is not an exact solution of SCLC equation, but is a very good approximation of the one carrier SCLC under the condition of a uniform distribution of traps. In the present case, the one carrier assumption is justified as these glasses are known to behave as p -type materials. As present measurements scan a very limited range of energy near the Fermi level, the assumption of uniform distribution of traps is also not unjustified.

According to (1), $\ln I/V$ vs V curves should be straight lines whose slope should decrease with increase in temperature as evident from (2). It is clear from figure 2 that the slope (S) of $\ln I/V$ 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 figure 3 for the glassy system used in the present study. It is clear from this figure that the slope decreases linearly with the increase in temperature. These results indicate the presence of SCLC in the present samples.

Using (2), we have calculated the density of localized states from the slope of figure 3. The value of the relative dielectric constant ε_r is measured by using capacitance measuring assembly model 'Hioki 3532-50 LCR Hi TESTER', employing the four terminal techniques. The results of these calculations are given in table 1.

3.2 Temperature and intensity dependence of dark and photoconductivity

Figure 4 shows the temperature dependence of dark conductivity and steady state photoconductivity at different

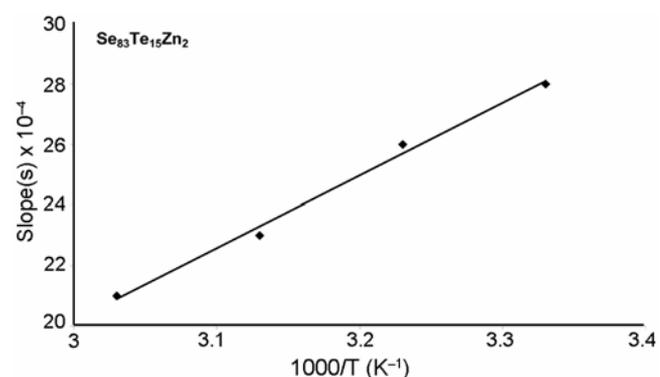


Figure 3. Plot of S vs $1000/T$ curve for $Se_{83}Te_{15}Zn_2$ glassy system.

intensities (F). It is clear from figure 4 that $\ln \sigma$ vs $1000/T$ curves are straight lines having the same slope, indicating that the dark conductivity as well as photoconductivity is due to an activated process having single activation energy in the present range of temperature. The conductivity can, therefore, be written as

$$\sigma = \sigma_0 \exp(-\Delta E/kT), \tag{3}$$

where ΔE is the activation energy for conduction and k the Boltzmann's constant.

The values of ΔE are calculated using the slope of figure 4 and (3). The results of these calculations are given in table 2.

It is clear from this table that the activation energy decreases at different intensities of light and is much smaller than the activation energy in dark. Hence, the activation energy in this case depends on the light intensity, which clearly indicates the shift of the Fermi level with intensity.

Table 1. Density of localized states (g_0) in $\text{Se}_{83}\text{Te}_{15}\text{Zn}_2$ glassy system.

Glassy alloy	Slope of S vs $1000/T$ curves	ϵ_r (at 120 Hz, 305 K)	$eV^{-1}g_0$ ($\text{eV}^{-1}\text{cm}^{-3}$)
$\text{Se}_{83}\text{Te}_{15}\text{Zn}_2$	2.4×10^{-3}	26	9.64×10^{14}

Table 2. Dark and photoconductivity along with activation energy at various intensities in $\text{Se}_{83}\text{Te}_{15}\text{Zn}_2$ glassy system.

Intensities (Lux)	σ ($\Omega^{-1}\text{cm}^{-1}$) at 300 K	ΔE (eV)
Dark	2.92×10^{-6}	0.39
2800	8.75×10^{-6}	0.16
7800	2.00×10^{-5}	0.15
13,000	3.21×10^{-5}	0.14

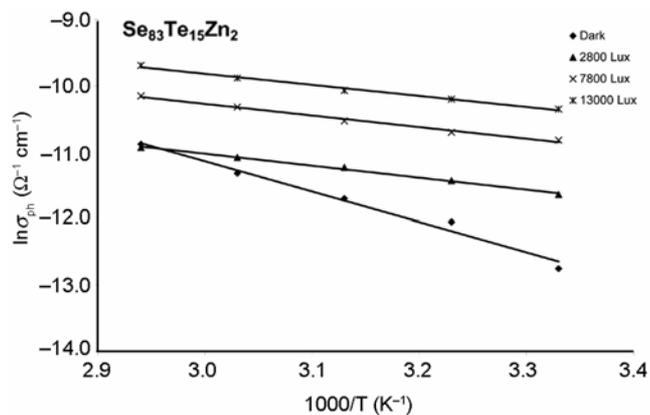


Figure 4. Temperature dependence of dark and photoconductivity at different intensities in $\text{Se}_{83}\text{Te}_{15}\text{Zn}_2$ thin film.

Intensity (F) dependence of photoconductivity (σ_{ph}) is studied at different temperatures. The results for $\text{Se}_{83}\text{Te}_{15}\text{Zn}_2$ glassy alloy are shown in figure 5. It is clear from figure 5 that, at all temperatures, $\ln \sigma_{ph}$ vs $\ln F$ curves are nearly straight lines, which indicates that photoconductivity follows a power law with intensity ($\sigma_{ph} \propto F^\gamma$).

3.3 Transient photoconductivity measurements

To measure the rise and decay of photoconductivity with time, the thin film sample was mounted in the same metallic sample holder and light of desired wavelength was shown through a transparent window. After a certain time of exposure, the light was turned off and the decay of current was measured as a function of time. The initial dark value of current was subtracted to obtain photoconductivity during decay.

Figures 6–7 show the results of the transient photoconductivity measurements at different intensities and temperatures in the sample studied at present. It is clear from these figures that the rise and decay of photocurrent is quite slow. Photoconductivity rises monotonically with time and saturates after a long time (a few minutes).

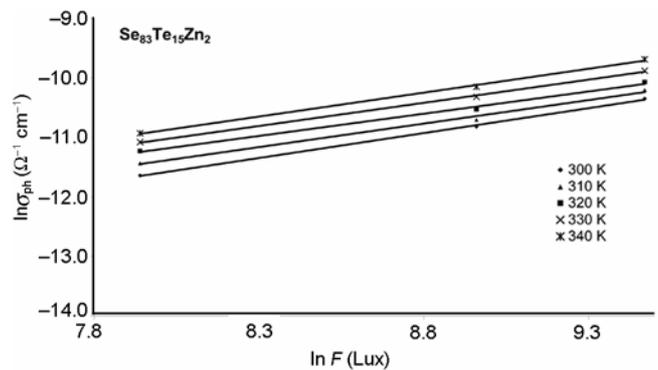


Figure 5. Intensity dependence of photoconductivity at different temperatures in $\text{Se}_{83}\text{Te}_{15}\text{Zn}_2$ thin film.

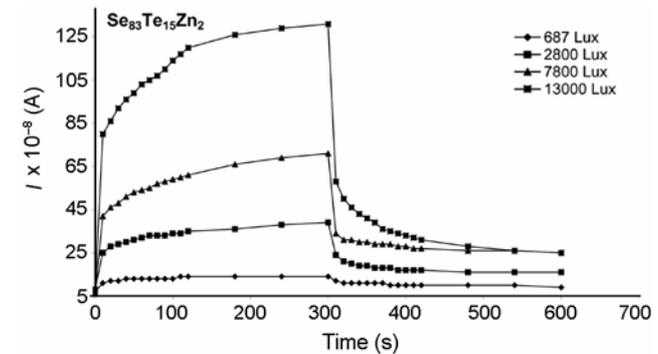


Figure 6. Time dependence of photocurrent at different intensities during rise and decay at 300 K in $\text{Se}_{83}\text{Te}_{15}\text{Zn}_2$ thin film.

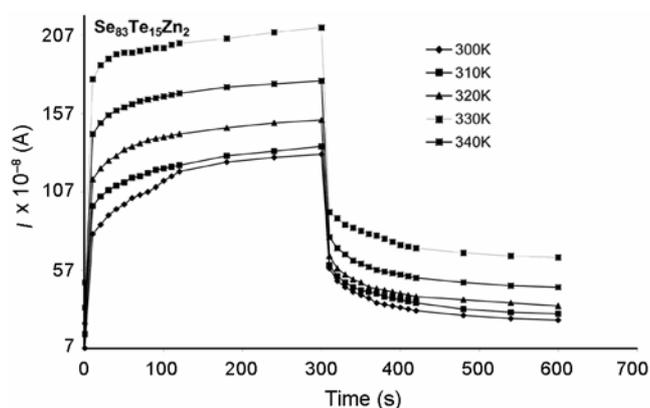


Figure 7. Time dependence of photocurrent at different temperatures during rise and decay in $\text{Se}_{83}\text{Te}_{15}\text{Zn}_2$ thin film at a light intensity of 13000 Lux.

Initially, it increases rapidly and then become slower before reaching to steady state value. After attaining the steady state, light was turned off and the decay of photoconductivity was measured as the function of time. Initially, the photoconductivity decay is quite fast and then becomes slow as time lapses. Figure 6 shows the results of these measurements at different intensities. It is clear from this figure that the behaviour of the decay curves is of the same nature at different intensities.

Another measurement was made at different temperatures keeping the intensity of light constant. The rise and decay of photoconductivity in such a case is shown in figure 7. The behaviour of rise and decay curves is found to be similar as above.

4. Conclusions

High-field conduction and photoconductivity measurements in glassy $\text{Se}_{83}\text{Te}_{15}\text{Zn}_2$ thin films have been obtained. The experimental data, fits well with the theory of space charge limited conduction (SCLC) in the high-electric-field region. From the fitting data, the density of defect states (DOS) near the Fermi level was calculated.

Temperature dependence of steady state photoconductivity is also studied at different light intensities. Intensity dependence of photoconductivity was studied at different fixed temperatures. Temperature dependence of photoconductivity at different light intensities is found to be through a thermally activated process. It is also found that the activation energy decreases at different intensities of light and is much smaller than the activation energy in dark. Hence, the activation energy in this case

depends on the light intensity, which clearly indicates the shift of the Fermi level with intensity.

Transient photoconductivity measurements at different temperatures and intensities indicate that the decay of photoconductivity has two components: initially, it is little faster and then become quite slow. This component is found to be non-exponential in the present case, indicating the presence of a continuous distribution of defect states.

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References

- Abkowitz M 1984 *Polymer Eng. Sci.* **24** 1149
- Abou El-Hassan S 2001 *Physica* **B307** 86
- El-Kady Y L A 1999 *Phys. Stat. Solidi (a)* **175** 577
- Faschinger W, Ferreira S and Sitter H 1994 *Appl. Phys. Lett.* **64** 2682
- Fritzsche H, Gaszi P J and Kastner M 1978 *Philos. Mag.* **B37** 593
- Kastner M 1978 *Philos. Mag.* **B37** 127
- Kolobov A V and Bedelbaeva G E 1991 *Philos. Mag.* **B64** 21
- Kolobov A V, Kolomiets B T, Lyubin V M and Tagirdzhanov M A 1985 *Solid State Commun.* **54** 379
- Kumar S, Arora R and Kumar A 1993 *Physica* **B183** 172
- Lampert M A and Mark P 1970 *Current injection in solids* (New York: Academic Press)
- Moharram A H, Abu-Sehly A A, Abu-El-Oyoun M and Soltan A S 2002 *Physica* **B324** 344
- Mott N F 1967 *Adv. Phys.* **16** 49
- Mott N F 1976 *Philos. Mag.* **34** 1101
- Nikam P S and Aher H S 1996 *Ind. J. Pure Appl. Phys.* **34** 393
- Ovshinsky S R 1968 *Phys. Rev. Lett.* **21** 1450
- Ovshinsky S R 1977 *Proceedings of the international conference on amorphous liquid semiconductors* (ed.) W E Spear (Edinburgh: CICL) p. 519
- Ovshinsky S R and Sapru K 1977 *Proc. 7th int. conf. amorphous liquid semiconductors* (ed.) W E Spear (Bristol: Institute of Physics Publishing) **Vol. 447**, 65
- Saitar J M, Ledru J, Hamou A and Saffarini G 1998 *Physica* **B245** 256
- Saraswat V K, Kishore V, Saxena N S and Sharma T P 2006 *Ind. J. Pure Appl. Phys.* **44** 196
- Shimakawa K 1985 *J. Non-Cryst. Solids* **77-78** 1253
- Soltan A S 2005 *Appl. Phys.* **A80** 117
- Watanabe I and Sekiya T 1987 *Jpn. J. Appl. Phys.* **26** 663
- Watanabe I and Yamamoto T 1985 *Jpn. J. Appl. Phys.* **24** 1282