TEMPERATURE AND INTENSITY DEPENDENCE OF PHOTOCONDUCTIVITY IN a – $Se_{70}Te_{26}Zn_4$: DETERMINATION OF DEFECT CENTRES

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Temperature and intensity dependence of photoconductivity is studied in vacuum evaporated amorphous thin films of $Se_{70}Te_{26}Zn_4$. Two temperature regions have been observed in temperature dependence of photoconductivity. In the first region, photoconductivity increases with increase in temperature while in second region, a decrease in the photoconductivity is observed with temperature. A maxima in photoconductivity is observed at a particular temperature. The activation energy obtained in these two regions are used to determine the location of prominent defect energy levels. The intensity dependence of photoconductivity measurements show that bimolecular recombination takes place in the intensity range used in the present study.

1. Introduction

Chalcogenide glassy semiconductors are some of widely used amorphous semiconductors for a variety of applications in optics, electronics, and optoelectronics such as ultra fast optical switches, waveguides, optical memories, gratings, optical sensors, holography, infrared lasers, ionic sensors etc. These glasses generally exhibits p type electrical conduction due to the pinning of Fermi level arising from the trapping of the charge carriers and localized gap states [1, 2]. In amorphous semiconductors the presence of localized defect states may act as traps for the charge carriers and hence affect many properties of materials presumably, the parameters of traps (their energy position, the character of energy distribution, trapping concentration and capture cross section of the traps) are substantially different in deferent materials and these parameters determine the specific feature of the kinetic process in each case.

Photoconductivity gives information about defect states as recombination centers. In chalcogenide glasses the Se centre are the defect with negative effective correlation energy (negative-U model [3]). These defects produce discrete energy levels in the gap of amorphous chalcogenide glasses [1]. Consequently, measurement of photoconductivity is a valuable technique to identify the position of these levels. The dependence of photocurrent on temperature and on intensity of illumination allows identification of the areas with monomolecular or bimolecular recombination. Behavior at high temperatures and at low light intensities where monomolecular recombination dominates, the photocurrent is positively activated with the reciprocal of temperature while at lower temperatures and at high intensities bimolecular recombination leads to a different and negative value of the activation energy. In terms of the activation energy in the two

regimes, the quantities of discrete trapping level in the gap can be specified [4, 5]. The two regimes have been observed on a large number of amorphous semiconductors [6, 10].

In the present work, steady state photoconductivity measurements have been investigated in amorphous thin films of $Se_{70}Te_{26}Zn_4$. The temperature dependence of dark and photoconductivity is studied at different light intensities and intensity dependence of photoconductivity is studied at different fixed temperatures.

2. Experimental

The glassy alloy of $Se_{70}Te_{26}Zn_4$ was prepared by quenching from the melt. Thin films were prepared by vacuum evaporation of the prepared glass at a base pressure of 10^{-5} Torr using a standard coating unit (IBP-TORR: EPR- 002), keeping the glass substrate at room temperature. Vacuum- evaporated indium electrodes were used for electrical contacts. The thickness of the films was about 500 nm. A coplanar structure (length ~ 1.3 cm and electrodes separation ~ 0.5 mm) was used for present measurements.

Steady - state photoconductivity measurements were performed by mounting the film in a specially designed sample holder in which light could be shown through a transparent window. A vacuum of about 10^{-2} Torr was maintained during these measurements. The temperature of these films was controlled by a heater mounted inside the sample holder and was measured using a copper - constantan thermocouple mounted very near to the films. The light source for these measurements was a 200W tungsten lamp, the intensity of which was measured by a lux meter (Testron, model LX-101). The photocurrent was measured by a digital electrometer (Keithley, model 614). Before measurement, the film were first annealed at their glass transition temperature (T_g ~ 350 K) for two hours in a vacuum ~ 10^{-3} Torr. Current voltage (I-V) characteristics were found to be linear and symmetric up to 30V. The present measurements were, however, made by applying only 10 V across the films.

3. Results

The temperature dependence of the dark current and the photocurrent (at the different intensities) were studied in a- $Se_{70}Te_{26}Zn_4$ thin films in the temperature range 302 K- 363 K. The results, at one particular intensity (1190 lux) are shown in Fig.1. The results at other intensities were also of the same nature. It is clear from Fig.1, that dark conductivity is thermally activated with Arrhenius behavior described by:

$$\sigma_d \ \alpha \ exp \ (-\Delta E_d \ / \ kT) \tag{1}$$

Where σ_d is the dark conductivity and ΔE_d is the activation energy for dc conduction.

In the photoconductivity curve, a maximum is clearly seen near a particular temperature ($T_m = 337$ K) at an intensity of 1190 lux. As is evident from Fig.1, the photoconductivity curve can be divided into two temperature regions according to the nature of its slope. Below T_m, ln σ_{ph} increases as T^{-1} and reaches a maximum value of σ_{ph} at $T = T_m$ and the activation energy of photoconduction is much smaller than the activation energy in the dark. $\sigma_{ph} > \sigma_d$ in this temperature range. The photoconductivity is negatively activated (activation energy ΔE_b) with the reciprocal of the temperature according to:

$$\sigma_{ph} \ \alpha \ exp \ (-\Delta E_b \ / \ kT) \tag{2}$$

Thereafter, above T_m, ln σ_{ph} decreases as T^{-1} and shows a positive value of activation energy ΔE_a as given below:

$$\sigma_{ph} \ \alpha \ exp \ (\Delta E_a \ / \ kT) \tag{3}$$
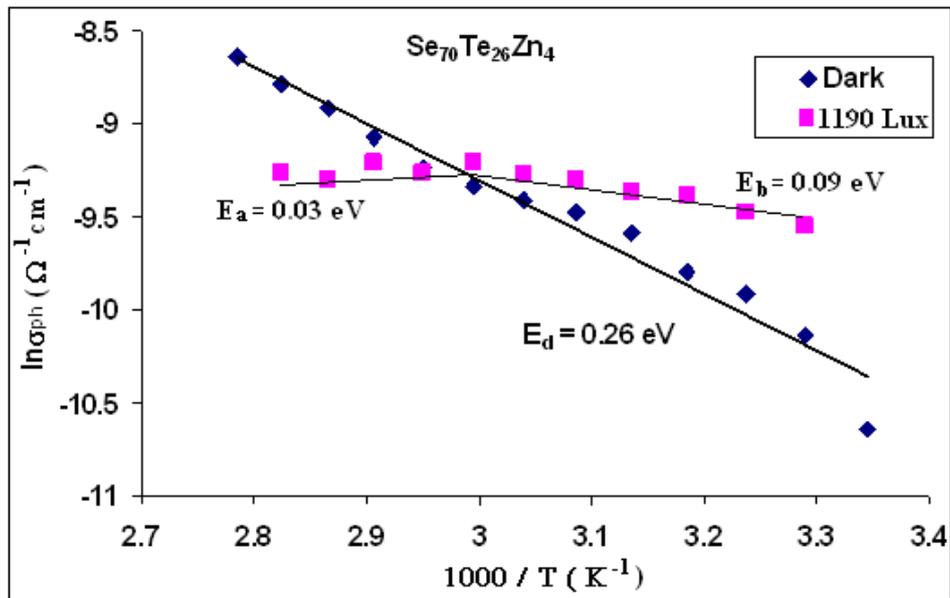
In this temperature range σ_{ph} is less than σ_d.

Fig. 1. Temperature dependence of steady–state photoconductivity in amorphous thin films of $Se_{70}Te_{26}Zn_4$ at a constant intensity 1190 lux.

The values of the activation energies, ΔE_d, ΔE_a and ΔE_b, calculated from the slopes of ln σ_{ph} vs. T^{-1} curves, are indicated in Fig. 1.

Steady state photoconductivity measurements as a function of light intensity were also performed on the a-$Se_{70}Te_{26}Zn_4$ thin films at room temperature (302 K) and at a temperature T (= 363 K). The results of these measurements are shown in Fig. 2. It is clear from this figure that, at both the temperatures, ln σ_{ph} vs. ln F curves are nearly straight lines which indicate that photoconductivity follows a power law with intensity ($\sigma_{ph} \propto F^{\gamma}$). The power γ has been calculated from the slopes of ln σ_{ph} vs. ln F curves. The value of γ are nearly to 0.5 in the temperature range (302 K to 363 K).

In case of a semiconductor with only one type of recombination centers, the excess electron density (Δn) can be related to the generation rate (g) as follows
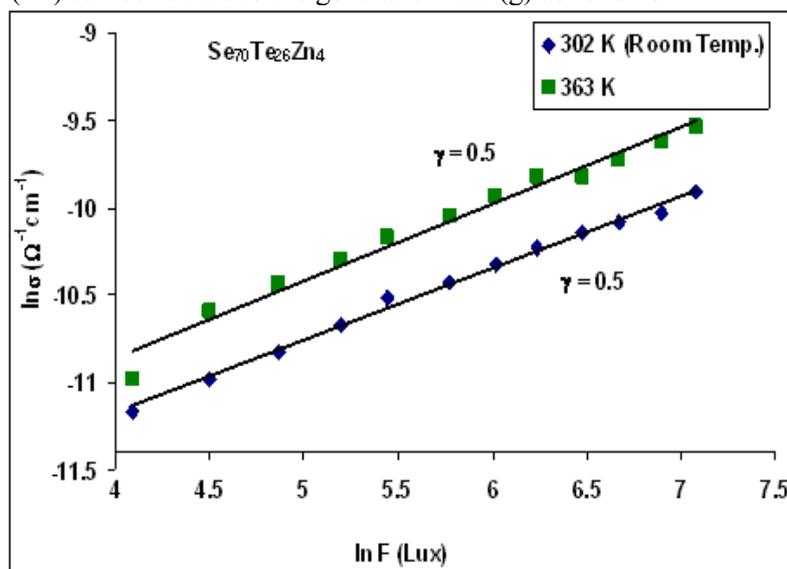

Fig. 2. Intensity dependence of photoconductivity at 302 K and 363 K.

$$g = C_n \, (\Delta n^2 + 2 \, n_0 \, \Delta n) \qquad (4)$$

Where C_n is the capture coefficient (the product of capture cross section and the thermal velocity of the carrier), n_0 is the density of thermal carriers. In the case of monomolecular recombination where $n_0 >> \Delta n$, equation (4) reduces to

$$\Delta n = g \, / \, 2C_n \, n_0 \qquad (5)$$

As the generation rate is proportional to the light intensity (F), the photoconductivity will vary linearly with light intensity in the above case. In case of bimolecular recombination where Δn >>

$$\Delta n = (g \, / \, C_n)^{1/2} \qquad (6)$$

Equation (5) shows that the photoconductivity will be proportional to square root of the light intensity in case of bimolecular recombination.

4. Discussion

As predicted by Simmons and Taylor [5], the photoconductivity σ_{ph} is a linear function of Intensity F (monomolecular recombination) up to the value of σ_m corresponding to T_m and in this range the photoconductivity decreases with increase in T. For $\sigma_{ph} > \sigma_m$, σ_{ph} increases as $F^{1/2}$ (bimolecular recombination), and in this range the photoconductivity increases with increasing T. The observed experimental findings in the present case show fair agreement with the model proposed by Simmons and Tayler [5].

The ESR experiments performed by Street and Biegelson [22] on glassy Se-Ge reveal the presence of two types of defects which have different densities and capture cross sections. One may be a dangling bond at a Se atom and other may be Se chain end that bond to another Se atom. Luminescence measurements [22] support this suggestion and show that the time constants of the two defect states are quite different. This implies that the two defect states, i.e., E_1 and E_2, are at two different positions in the mobility gap, separated by a large energy.

The models proposed by Simmons and Taylor [5] and Main and Owen [4] give information for the energy location of discrete sets of localized states between the band edges. With the help of experimental observations in term of the low – and high – temperature slopes, $\Delta E_a \sim 0.03$ eV and $\Delta E_b \sim 0.09$ eV, we can deduce the energy position for these two defect states in the mobility gap. We can not determine the value of ΔE_a precisely since only a limited number of data points are available in the higher temperature range. The activation energy calculated for the dark conductivity is $\Delta E_d = 0.26$ eV, which can be taken nearly half of the band gap of a $-Se_{70}Te_{26}Zn_4$ thin films. The position of the defects energy states E_1 and E_2 above the valance band edge can be written as

$$E_1 = \Delta E_d + \Delta E_a$$
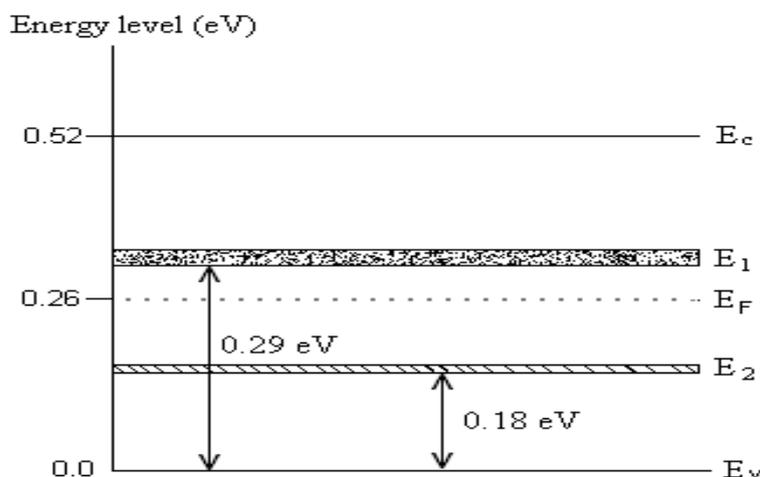and
$$E_2 = 2\Delta E_b$$

Fig. 3. Energy level diagram for defect states in the mobility gap of a-Se$_{70}$Te$_{26}$Zn$_4$ thin films

From this, the approximate location of the energy states E$_1$ and E$_2$ have been computed for a – Se$_{70}$ Te$_{26}$Zn$_4$ this films and are shown in Fig 3. It is clear from the figure that one state is below the Fermi level whereas another state is above it. It is known that in chalcogenide glasses the states in mobility gap may behaves as a D$^-$ and D$^+$ centres. These D$^+$ and D$^-$ centres capture electrons and holes via D$^+$ + e → D^0 and D$^-$ + h → D^0, creating neutral D^0 sites. These D^0 sites produce energy levels approximately midway between the band edges and the Fermi levels. The corresponding D^0 levels are at 0.18eV and ~ .29eV for a Se$_{70}$Te$_{26}$Zn$_4$. Some authors have also observed two defect states for the Se - Ge and Se – Ge - Cu system [10, 21].

Intensity dependence of photoconductivity has been studied in chalcogenide glasses by many workers [22, 27]. The value of γ is reported between 0.5 and 1.0 in various glassy systems. In the present case, γ is 0.5 in the temperature range 302 K to 363 K which indicates that bimolecular recombination is predominant in Se$_{70}$Te$_{26}$Zn$_4$.

5. Conclusion

The temperature dependence of the photoconductivity of amorphous Se$_{70}$Te$_{26}$Zn$_4$ thin films, has been measured at different intensities. Photoconductivity shows a maximum at a particular temperature for each intensity of measurements. From the intensity dependence of photoconductivity curve, it is clear that bimolecular recombination is predominant in this material. From the activation energies obtained for the two regions, prominent defect levels have been calculated in the present glass system whose positions comes out to be 0.18 eV and 0.29 eV from the valence band.

References

[1] R. A.Street, N.F.Mott, Phy.Rev. Lett.**35**,1293 (1975)
[2] A. I. Gubanov, Sov.Phy.Solid State **3**, 1964 (1962)
[3] P. W.Anderson, Phys. Rev. Lett. **34** 953 (1975).
[4] C.Main, A.E.,Owen, 1973 Electronic and Structural Properties of Amorphous
    Semiconductors editor Comber P G Le and Mort J (Academic Press- London).
[5] J. G. Simmons, G. W. Taylor J. Phys. C **7**, 3051 (1974)
[6] G. J. Adriaenssens Phil. Mag. B **62**, 79 (1990)
[7] T. C. Arnouldussen, C. A. Menezes, Y. Nakagawa, R. H. Bube Phys. Rev. B **9**, 3377 (1974).
[8] B. T. Kolomiets, V. M. Lyubin Phys. Stat. Solidi A **17**, 11 (1973)
[9] M. L. Benkhedir, M. S. Aida, N. Qamhieh, A. Stesmans, G. J. Adriaenssens, J. Optoelectron.

Adv. Mater. **7**, 329 (2005).

[10] N. Qamhieh, G. J. Adriaenssens, J. Non-Cryst.Solids **292**, 80 (2001).

[11] S.Kumar, R. Arora and A. Kumar, J. Electron. Mater.**22** 675(1993)

[12] A.Zolanvari, N. Goyal and S.K.

[13] A.Kumar, S. Goel and S.K.Tripathi, Phys.Rev. **B 38** 13432 (1988)

[14] A.Kumar, S.Goel and D.S.Mishra, Phys.Rev. **B35** 5635 (1987).

[15] K.M.Kandil, PhD thesis, ain Shams University, Egypt(1992)

[16] P.Boolchand, private communication.

[17] N. F. Mott and E. A.Davis, Electronic processes in Non-crystalline Materials (Clarendon Press, Oxford, 1979)

[18] J. M. Marshall, C. ain and E.E.Owen, J. Non-Cryst. Solids **8** 760 (1972)

[19] N. Kushwaha, V. S. Kushwaha, R. K. Shukla, et al., J. Non-Crystalline Solids **351** 3414 (2005)

[20] R.A.Street and D.K. Biegelson, J. Non-Crystalline Solids **32** ,339 (1979).

[21] A.Thakur, V.Sharma, G.S.Saini, et al., J. Phys. D **38**, 1959 (2005).

[22] N. Kushwaha, S.Singh, R. K.Shukla., A. Kumar, Journal of Alloys and Compounds 456 (2008) 46-50.

[23] R. K. Pal, A. Kumar, Journal of Ovanic Research **4**(5), 113 (2008).

[24] Sangeeta Singh, R. S. Sharma, R. K. Shukla and A.Kumar,Vacuum **1-9,** 72 (2004).

[25] S. Singh, R. K. Shukla, A. Kumar, Ind. J. Engg. And Matter. Sci. **12**, 461 (2005).

[26] R. S. Sharma, D. Kumar, A. Kumar, Turkish. J. Phys, **30**, 47 (2006)

[27] R. S. Sharma, R. K. Shukla, A. Kumar, J. Optoelectronics and Advanced Materials, **9**, 3700 (2007).