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DEFECT ENERGY LEVELS IN a- $Se_{80}Te_{20}$ AND a- $Se_{80}Te_{10}Cd_{10}$ CHALCOGENIDE THIN FILMS

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Temperature dependence of photoconductivity at different intensities of light, is studied in vacuum evaporated amorphous thin films of $Se_{80}Te_{20}$ and $Se_{80}Te_{10}Cd_{10}$. Two temperature regions have been observed in temperature dependence of photoconductivity in case of these films. In the first region, photoconductivity increases with increase in temperature while in second region, a decrease in the photoconductivity in these samples is observed with temperature. A maxima in photoconductivity is observed at a particular temperature. The activation energy obtained in these two region is used to determine the location of prominent defect energy levels in present glassy alloys. The intensity dependence of photoconductivity measurements show that bimolecular recombination takes place in the intensity range used in the present study.

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1. Introduction

Chalcogenide glasses have many current and potential applications in optics, optoelectronics, chemistry and biology such as optical elements, gratings, photo-doping, optical memories, micro lenses, waveguides, holography, bio- and chemical- sensors, solid electrolytes, batteries etc. [1-10]. 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 [11, 12], In amorphous semiconductors, the presence of localized defect states may act as traps for the charge carriers and hence affect many properties of materials. 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.

Measurement of photoconductivity is a valuable technique to identify the position of discrete energy levels. Temperature and intensity dependence photoconductivity allows identification of the areas with monomolecular or bimolecular recombination. Behavior at high temperatures and at low light intensities where monomolecular recombination dominates, the photoconductivity 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 [14, 15]. The two regimes have been observed on a large number of amorphous semiconductors [16, 20].

In the present work, steady state photoconductivity measurements have been made in amorphous thin films of $Se_{80}Te_{20}$ and $Se_{80}Te_{10}Cd_{10}$. The temperature dependence of dark and

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photoconductivity is studied at different light intensities and intensity dependence of photoconductivity is studied at different fixed temperatures.

2. Material preparation

Glassy chalcogenide material of $Se_{80}Te_{20}$ and $Se_{80}Te_{10}Cd_{10}$ was prepared by quenching technique. High purity materials (5N pure) were weighed according to their atomic percentages and were sealed in a quartz ampoule under the vacuum of 10^{-5} Torr. Ampoule was kept inside the furnace at an appropriate temperature (where the temperature was raised at a rate of 3-4 ^{o}C /min.). The ampoule was rocked frequently for 10 hrs at the maximum temperature (800 ^{o}C) to make the melt homogeneous. Quenching was done in liquid nitrogen and the glassy nature of alloy was checked by x-ray diffraction technique. Absence of any sharp peaks in XRD pattern confirms the glassy nature of $Se_{80}Te_{20}$ and $Se_{80}Te_{10}Cd_{10}$ alloys.

3. Experimental

Thin films of glassy alloys $Se_{80}Te_{20}$ and $Se_{80}Te_{10}Cd_{10}$ 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 ~ 1.7 cm and electrodes separation ~ 0.2 mm) was used for present measurements.

Steady - state photoconductivity measurements were performed by mounting the films 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 ~ 353 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 1.5 V across the films in case of a- $Se_{80}Te_{20}$ thin film and applying only 20 V across thin film in case of a- $Se_{20}Te_{10}Cd_{10}$ thin film.

4. Results

The temperature dependence of the dark conductivity and the photoconductivity (at the different intensities) were studied in a- $Se_{80}Te_{20}$ and $Se_{20}Te_{10}Cd_{10}$ thin films in the temperature range 301 K- 370 K and 298 K to 355 K respectively. The results in case of amorphous thin film of $Se_{80}Te_{20}$, at intensities of 559 lux and 904 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:

$$\sigma_d \alpha \exp(-\Delta E_d / kT) \quad (1)$$

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 = 356 K) at an intensity of 559 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:

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

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

$$\sigma_{ph} \alpha \exp(\Delta E_a / kT) \quad (3)$$

In this temperature range σ_{ph} is less than σ_d.

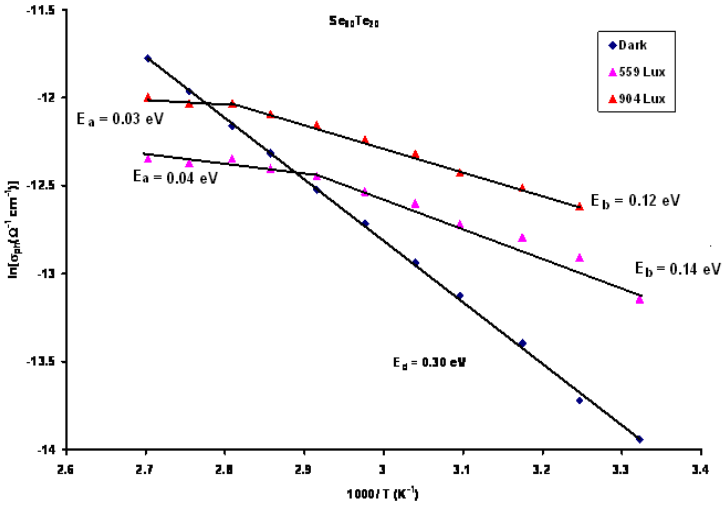

Fig. 1. Temperature dependence of photoconductivity in amorphous thin films of $Se_{80}Te_{20}$ at intensities of 559 lux and 904 lux.

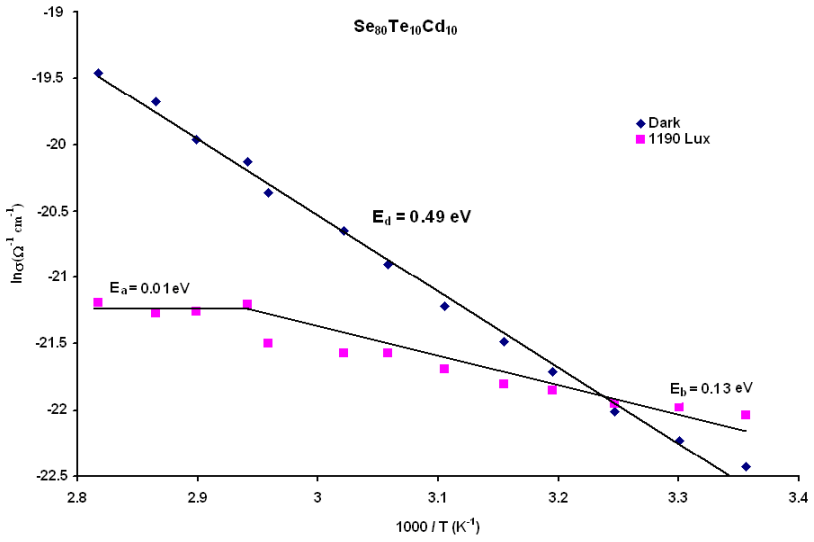

Fig. 2. Temperature dependence of photoconductivity in amorphous thin films of a-$Se_{80}Te_{10}Cd_{10}$ at a intensity of 1190 Lux.

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.

In the case of amorphous thin films of $Se_{80}Te_{10}Cd_{10}$, a maximum is clearly seen in the photoconductivity curve near a particular temperature (T_m = 340 K) at an intensity of 1190 lux as shown in Fig. 2. In this case also the photoconductivity curve can be divided into two temperature regions according to the nature of its slope as describe above.

Steady state photoconductivity measurements as a function of light intensity (F) were also performed on the a-$Se_{80}Te_{20}$ thin films at temperatures from 305 K to 330 K. The results of these measurements are shown in Fig. 3. It is clear from this figure that, at all temperatures, ln σ_{ph} vs. ln F curves are nearly straight lines which indicate that photoconductivity follows a power law with intensity ($\sigma_{ph} \alpha F^{\gamma}$). 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 (305 K to 330 K).

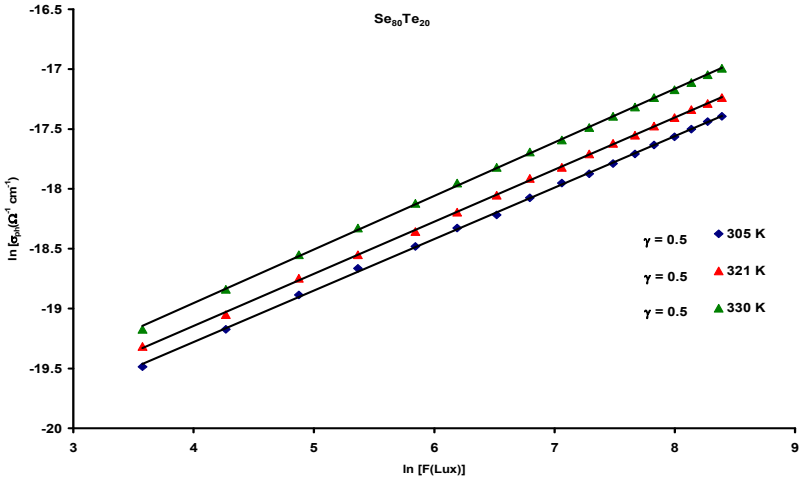

Fig. 3. Intensity dependence of photoconductivity at various temperatures in a- $Se_{80}Te_{20}$.

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

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

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

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

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 $\Delta n > > n_0$, equation (4) reduces to

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

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

Intensity dependence of photoconductivity has been studied in chalcogenide glasses by many workers [32, 37]. 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 305 K to 330 K which indicates that bimolecular recombination is predominant in $Se_{80}Te_{20}$. Similar results are found in amorphous thin film of $Se_{80}Te_{10}Cd_{10}$.

5. Discussion

As predicted by Simmons and Taylor [15], 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 [15].

The models proposed by Simmons and Taylor [15] and Main and Owen [14] 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, $\Delta E_a \sim 0.04$ eV and $\Delta E_b \sim 0.14$ eV, we can deduce the energy position for these two defect states in the mobility gap in case of a- $Se_{80}Te_{20}$ at an intensity 559 lux. 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 $\Delta E_d = 0.30$ eV, which can be taken nearly half of the band gap of a –Se_{80} Te_{20} thin films. Similar calculation has been done for the sample of thin film of a-$Se_{80}Te_{10}Cd_{10}$ is shown in Fig.5. 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

$$E_2 = 2\Delta E_b$$

From this, the approximate location of the energy states E_1 and E_2 have been computed for a – Se_{80} Te_{20} thin 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 $D^+ + e \rightarrow D^0$ and $D^- + h \rightarrow D^0$, 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 0.28eV and ~ .34eV for a- $Se_{80}Te_{20}$.Similarly the position of defect centers have been calculated in case of amorphous $Se_{80}Te_{10}Cd_{10}$ and the results are shown in Fig.5. Some other authors have also observed two defect centres for the Se - Ge and Se – Ge - Cu system [20, 31].

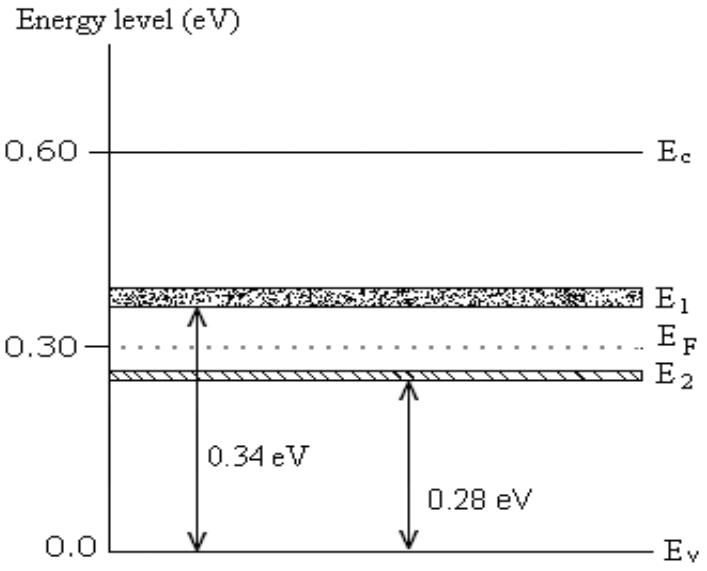

Fig. 4. Energy level diagram for defect states in the mobility gap of a-$Se_{80}Te_{20}$ thin films at intensity of light 559 Lux.

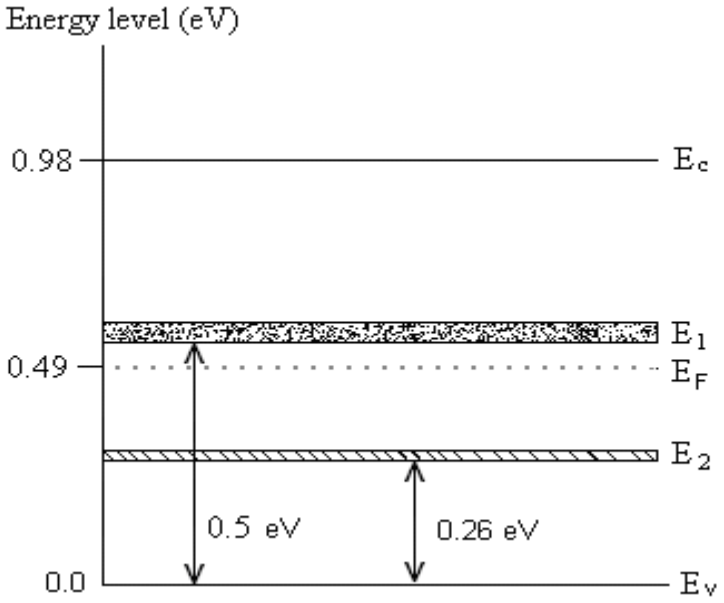

Fig. 5. Energy level diagram for defect states in the mobility gap of a-$Se_{80}Te_{10}Cd_{10}$ thin films at a particular intensity of light 1190 Lux.

6. Conclusion

The temperature dependence of the photoconductivity of a- $Se_{80}Te_{20}$ and a- $Se_{80}Te_{10}Cd_{10}$ thin films has been measured at different intensities. Photoconductivity shows a maximum at a particular temperature for both the cases. From the activation energies obtained for the two regions, prominent defect levels have been calculated in the present glass systems whose positions comes out to be 0.28 eV and 0.34 eV from the valence band in case of a- $Se_{80}Te_{20}$. However, in case of a- $Se_{80}Te_{10}Cd_{10}$ thin films, the positions of defect levels comes out to be 0.26 eV and 0.50 eV from the valence band.

References

[1] A. B Seddon, J Non-Cryst Sol, **184**, 44 (1995)
[2] L. Men, F. Jiang & F. Gan, Mater Sci Eng *B*, **47**, 18 (1997).
[3] D. Lezel, J Optoelectron, Adv Mater, **5**, 23 (2003).
[4] Guo-Fu. Zhou, Mater Sci Enginn *A*, **304**, 73 (2001).
[5] A. M. Andriesh, M. S. Iovu & S. D. Shutov, J. Optoelectron. Adv. Mater. **4**, 631 (2002).
[6] T. Ohta, J. Optoelectron. Adv Mater, **3**, 609 (2001).
[7] Tz. Babeva, D. Dimitrov, S. Kitova & I. Konstantinov, Vacuum, **58**, 496 (2000).
[8] V. I. Mikla, I. P. Mikhalko & V. V. Mikla, Mater Sci Eng B, **83**, 74 (2001).
[9] A. K. Kolobov & J. Tominaga, J Optoelectron Adv Mater, **4**, 679 (2002).
[10] A. Zakery & S. R. Elliott, J Non-Cryst Sol, **330**, 1 (2003).
[11] R. A.Street, N. F. Mott, Phy.Rev. Lett.**35**, 1293 (1975)
[12] A. I. Gubanov, Sov.Phy.Solid State **3**, 1964 (1962)
[13] P. W. Anderson, Phys. Rev. Lett. **34**, 953 (1975).
[14] C. Main, A. E. Owen, 1973 Electronic and Structural Properties of Amorphous Semiconductors editor Comber P G Le and Mort J (Academic Press- London).
[15] J. G. Simmons, G. W. Taylor J. Phys. C **7**, 3051 (1974).
[16] G. J. Adriaenssens Phil. Mag. B **62**, 79 (1990).
[17] T. C. Arnouldussen, C. A. Menezes, Y. Nakagawa, R. H. Bube Phys. Rev. B **9**, 3377 (1974).

[18] B. T. Kolomiets, V. M. Lyubin Phys. Stat. Solidi A **17**, 11 (1973)
[19] M. L. Benkhedir, M. S. Aida, N. Qamhieh, A. Stesmans, G. J. Adriaenssens, J. Optoelectron. Adv. Mater. **7**, 329 (2005).
[20] N. Qamhieh, G. J. Adriaenssens, J. Non-Cryst.Solids **292**, 80 (2001).
[21] S.Kumar, R. Arora and A. Kumar, J. Electron. Mater.**22** 675(1993)
[22] A.Zolanvari, N. Goyal and S.K.
[23] A.Kumar, S. Goel and S.K.Tripathi, Phys.Rev. **B 38** 13432 (1988)
[24] A.Kumar, S.Goel and D.S.Mishra, Phys.Rev. **B35** 5635 (1987).
[25] K.M.Kandil, PhD thesis, ain Shams University, Egypt(1992)
[26] P.Boolchand, private communication.
[27] N. F. Mott and E. A.Davis, Electronic processes in Non-crystalline Materials (Clarendon Press, Oxford, 1979)
[28] J. M. Marshall, C. ain and E.E.Owen, J. Non-Cryst. Solids **8** 760 (1972)
[29] N. Kushwaha, V. S. Kushwaha, R. K. Shukla, et al., J. Non-Crystalline Solids **351** 3414 (2005).
[30] R.A.Street and D.K. Biegelson, J. Non-Crystalline Solids **32**, 339 (1979).
[31] A.Thakur, V.Sharma, G.S.Saini, et al., J. Phys. D **38** ,1959 (2005).
[32] N. Kushwaha, S.Singh, R. K.Shukla., A. Kumar, Journal of Alloys and Compounds **456**, 46-50 (2008).
[33] R. K. Pal, A. Kumar, Journal of Ovanic Research **4**(5), 113-121 (2008)
[34] Sangeeta Singh, R. S. Sharma, R. K. Shukla and A.Kumar,Vacuum **1-9,** 72 (2004).
[35] S. Singh, R. K. Shukla, A. Kumar, Ind. J. Engg. And Matter. Sci. **12**, 461 (2005).
[36] R. S. Sharma, D. Kumar, A. Kumar, Turkish. J. Phys, **30**, 47 (2006).
[37] R. S. Sharma, R. K. Shukla, A. Kumar, J. Optoelectronics and Advanced Materials **9**, 3700 (2007).