

OBSERVATION OF MEYER-NELDEL N RULE IN AMORPHOUS Se_{100-x}Te_x THIN FILMS

N. Kushwaha, N. Mehta, R. K. Shukla, D. Kumar^a, A. Kumar^{*}

Department of Physics, Harcourt Butler Technological Institute, Kanpur-208 002, India

^aDepartment of Physics, Pranveer Singh Institute of Technology, Kanpur, India

In the present paper, we report the thermally activated conductivity in thin films of Se_{100-x}Te_x in three different states (amorphous state, partially crystalline state and crystalline state) obtained by exposure of light in thin films for different exposure times. We have observed Meyer-Neldel rule (MN rule) between pre-exponential factor and activation energy in the first case when Se_{100-x}Te_x thin films are in amorphous state. However, in the second phase, it has been found that the plot of $\ln \sigma_0$ vs ΔE deviates from MN rule. This deviation increases further in crystalline phase. This indicates that MN rule is associated with the disorder of some form in the chalcogenide glasses due to their short-range order structure.

(Received July 4, 2005; accepted September 22, 2005)

Keywords: Chalcogenide glasses, Meyer-Neldel rule, Pre-exponential factor

1. Introduction

Substitutional doping is a defining property of semiconductors. The resulting changes in the magnitude and type of conductivity permits use in a wide range of devices. Amorphous semiconductors mostly belong to two broad classes, one of which contains the hydrogenated group IV materials. The other group comprises the glasses, of which the chalcogenides are best known. Selenium and tellurium belong into the VI b group elements have gained much importance among chalcogenide glasses and are proved to be an efficient material for thin films circuits [1], fabrication of semiconductor devices, xerography, transistors, detectors [2,3]. A great number of studies have been undertaken to understand the characteristics of electronic, thermal, optical and structural properties of Se-Te based chalcogenide glasses due to their potential importance in scientific area and in applications [4-11].

It is known that free holes dominate the electronic transport at relatively high temperature in chalcogenide glasses. It is then expected that the electric conductivity be expressed by standard band-transport model. Mathematically it can be expressed as

$$\sigma = \sigma_0 \exp (-\Delta E / kT) \quad (1)$$

where ΔE is called the activation energy and σ_0 is called the pre-exponential factor. Note that σ_0 should be taken a constant value in the standard transport model. However, as described below, the conductivity is found to obey the Meyer-Neldel Rule (MNR) [12], and the pre-exponential factor correlates with the activation energy ΔE as

$$\sigma_0 = \sigma_{00} \exp (\Delta E / E_{MN}) \quad (2)$$

where σ_{00} and E_{MN} is often called as the Meyer-Neldel characteristic energy [13].

^{*}Corresponding author: dr_ashok_kumar@yahoo.com

This phenomenon (also known as the Compensation Effect) can occur in any situation, which involves an activated process and is generally observed in disordered materials. In the class of amorphous semiconductors, the MN rule has been reported in a-Si:H films in which ΔE is varied by doping, by surface absorption, light soaking or by preparing films under different conditions [14-16]. This rule has been observed in liquid semiconductors and fullerenes [13,17] also.

The validity of MN rule has been reported in the case of chalcogenide glasses also. In case of glassy semiconductors, MN rule is observed by the variation of ΔE on changing the composition of the glassy alloys in a specific glassy system [18-21] or by the variation of intensity of light [22,23]. Arora et al. [24] have observed MN rule in $\text{Se}_{100-x}\text{Te}_x$ alloys in the bulk form by the variation of ΔE on changing the composition.

In the present study, we have tried to fit MN rule in the glassy samples in different phases, i.e., amorphous, partially crystalline and crystalline state obtained by exposing the light for different exposure times. We have investigated the $\text{Se}_{100-x}\text{Te}_x$ thin films for this purpose. Our results show that observation of the MN rule in chalcogenide glasses is probably due to some fundamental characteristics arising due to their short-range order structure.

2. Material preparation

Glassy alloys of $\text{Se}_{100-x}\text{Te}_x$ ($x = 5, 10, 15$ & 25) were prepared by quenching technique. The exact proportions of high purity (99.999%) Se and Te elements, in accordance with their atomic percentages, were weighed using an electronic balance (LIBROR, AEG-120) with the least count of 10^{-4} gm. The material was then sealed in evacuated ($\sim 10^{-5}$ Torr) quartz ampoules (length ~ 5 cm and internal diameter ~ 8 mm). The ampoules containing material were heated to 800°C and were held at that temperature for 12 hours. The temperature of the furnace was raised slowly at a rate of $3-4^\circ\text{C} / \text{minute}$. During heating, the ampoules were constantly rocked, by rotating a ceramic rod to which the ampoules were tucked away in the furnace. This was done to obtain homogeneous glassy alloys.

After rocking for about 12 hours, the obtained melts were cooled rapidly by removing the ampoules from the furnace and dropping to ice-cooled water rapidly. The quenched samples were then taken out by breaking the quartz ampoules. The glassy nature of the alloys was ascertained by X-ray diffraction.

Thin films of $\text{Se}_{100-x}\text{Te}_x$ were prepared by vacuum evaporation technique keeping glass substrates at room temperature. Vacuum evaporated indium electrodes at bottom were used for the electrical contact. The thickness of the films was ~ 500 nm. The coplanar structure (length ~ 1.2 cm and electrode separation ~ 0.5 mm) was used for present measurements. The amorphous nature of the films was verified by X-ray diffraction and the composition was checked by Electron Probe Micro Analyzer (EPMA).

3. Experimental

The electrical conductivities of $\text{Se}_{100-x}\text{Te}_x$ thin films in dark were studied by mounting them in a specially designed sample holder. A vacuum of about 10^{-3} Torr was maintained throughout these measurements. The temperature of the films was controlled by mounting the heater inside the sample holder and measured by a calibrated copper constantan thermocouple.

The photo crystallization was achieved by shining white light at room temperature for different exposure times. The temperature of the thin films was not allowed to increase to more than glass transition temperature to avoid thermally induced crystallization.

It has already been reported by us that photo -crystallization occurs in $\text{Se}_{100-x}\text{Te}_x$ amorphous films [25]. The conductivity as well as the activation energy changes on increasing exposure time. However, after a certain exposure time, no further change is observed in these parameters. The initial state is amorphous state and the final state may be called fully crystalline state and the intermediate state is called partially crystalline state. It is also reported [25] that X-ray diffraction experiment confirms that initially films are in amorphous state and crystallization peaks occurs in

light exposed samples. In the present study, we have done similar experiments on four glassy alloys of Se-Te system and found that 1020 min exposure saturates the crystallization process. We have chosen state A as amorphous state, state B as partially crystalline state (exposure time 540 min) and state C as fully crystalline state (exposure time 1020 min).

4. Results

The electrical conductivity measurements have been made as a function of temperature on various thin films of $\text{Se}_{100-x}\text{Te}_x$ (5, 10, 15 & 25). To observe the effect in different states (states A, states B and states C), three sets of measurements have been undertaken.

First set comprises the temperature dependence of conductivity in unexposed thin films of $\text{Se}_{100-x}\text{Te}_x$ (5, 10, 15 & 25) say amorphous phase (State A). The conductivity (σ) varies exponentially with the temperature as $\ln \sigma$ vs $1000/T$ curves are straight lines for all compositions shown in Fig. 1. Such behaviour is consistent with the equation-1. From the slope and intercept, the activation energy ΔE and σ_0 have been computed and the values are inserted in Table 1. It is clear from this table that, at all the temperatures of measurements, the values of ΔE in $\text{Se}_{100-x}\text{Te}_x$ alloy, increases with the addition of Te. The second set of ΔE and σ_0 for various composition of $\text{Se}_{100-x}\text{Te}_x$ thin films exposed to light for 540 min, say partially crystalline phase ((State B). The results in this state are also given in the same table. In the similar way, the ΔE and σ_0 calculated for exposure time 1020 min (State C) is also given in same table. It is clear from this table that the activation energy decreases with increasing exposure time in the same composition. The increase in conductivity (σ) with exposure time can be attributed to the increase in the mobility of the carriers in the localized states. Further, this table shows that ΔE and σ_0 both are composition dependent and σ_0 is not a constant but depends on ΔE .

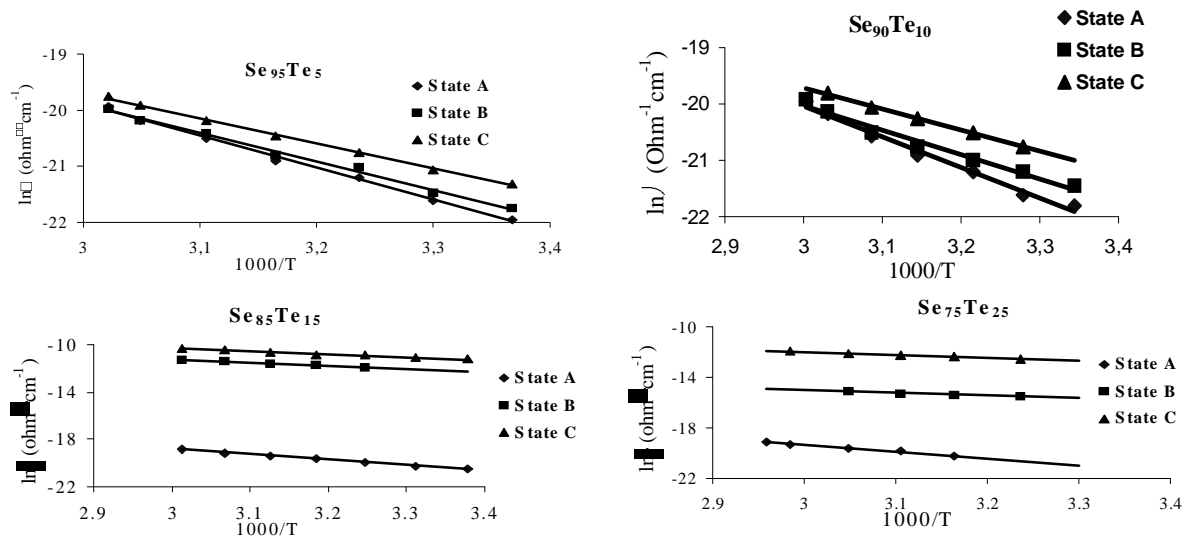


Fig. 1. $\ln \sigma$ versus $1000/T$ plots for $\text{Se}_{100-x}\text{Te}_x$ thin films in three states.

Table 1. Semi-conduction Parameters for $\text{Se}_{100-x}\text{Te}_x$ thin films in states A, B and C.

Composition	State A		State B		State C	
	ΔE (eV)	$\ln \sigma_0$ ($\text{Ohm cm})^{-1}$	ΔE (eV)	$\ln \sigma_0$ ($\text{Ohm cm})^{-1}$	ΔE (eV)	$\ln \sigma_0$ ($\text{Ohm cm})^{-1}$
$\text{Se}_{95}\text{Te}_5$	0.49	-2.70	0.42	-5.33	0.39	-6.25
$\text{Se}_{90}\text{Te}_{10}$	0.46	-3.73	0.37	-7.09	0.32	-8.55
$\text{Se}_{85}\text{Te}_{15}$	0.39	-5.17	0.21	-3.20	0.21	-2.89
$\text{Se}_{75}\text{Te}_{25}$	0.32	-7.80	0.21	-4.71	0.19	-8.64

To observe the MN rule in three phases, $\ln \sigma_0$ vs ΔE curve is plotted in Figs. 2,3 & 4, respectively. Curve fitting is done by least square method and the correlation coefficients (R^2) of the lines are indicated in these figures.

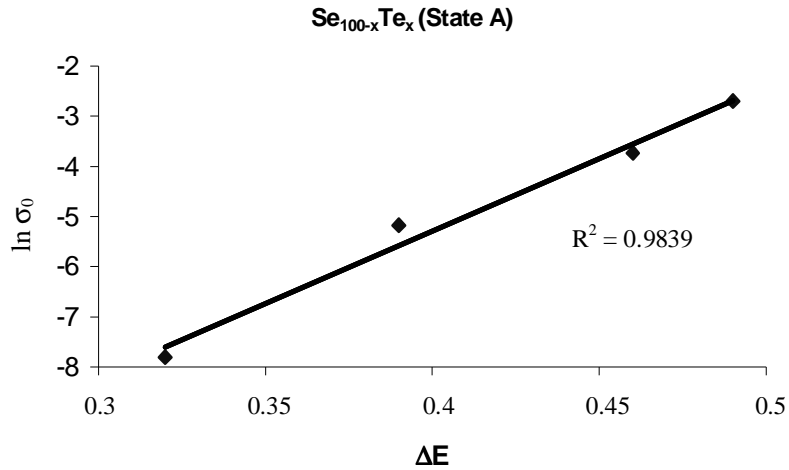


Fig. 2. $\ln \sigma_0$ versus ΔE plots for Se_{100-x}Te_x thin films in state A.

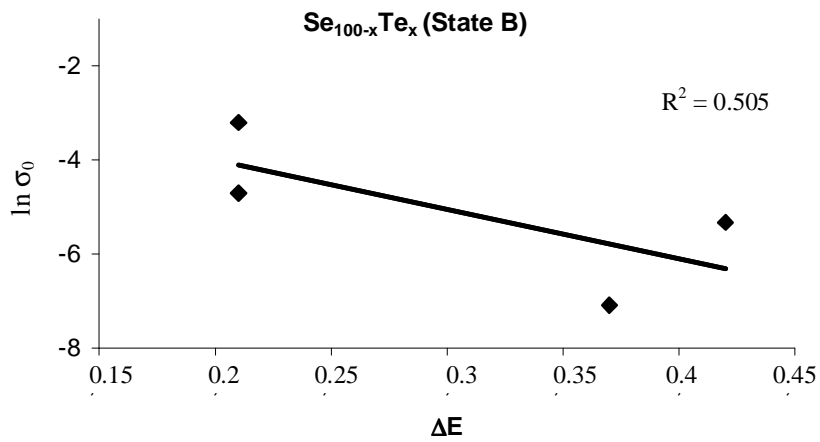


Fig. 3. $\ln \sigma_0$ versus ΔE plots for Se_{100-x}Te_x thin films in state B.

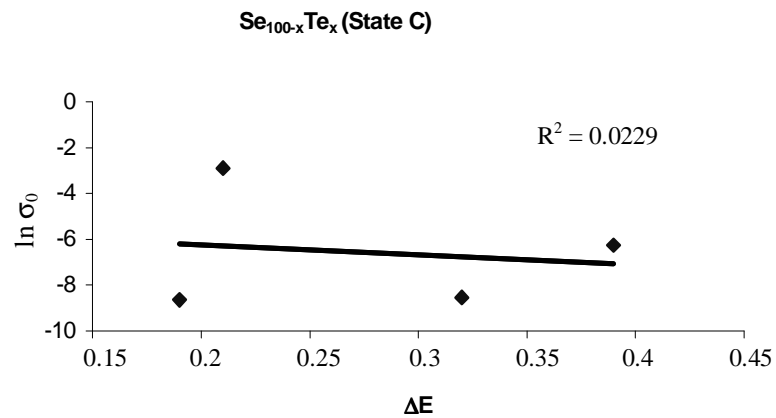


Fig. 4. $\ln \sigma_0$ versus ΔE plots for Se_{100-x}Te_x thin films in state C.

It is clear from this figure that $\ln \sigma_0$ vs ΔE plot is a straight line of good correlation coefficient for only state A indicating that σ_0 varies exponentially with ΔE satisfying the relation (2).

From the slope and intercept of the line, we have calculated the values of $E_{MN} = 28.9$ eV and $\sigma_{00} = 4.87 \times 10^{-8} (\Omega\text{-cm})^{-1}$ for state A. Using these values, the expected σ_0 values have been calculated for state A and compared with the reported values (see Table 2). An overall good agreement between these two values confirms the validity of MN rule in amorphous $\text{Se}_{100-x}\text{Te}_x$ thin films in state A.

Table 2. Semi-conduction Parameters for amorphous $\text{Se}_{100-x}\text{Te}_x$ thin films.

Composition	ΔE (eV)	$\ln \sigma_0 (\text{ohm cm})^{-1}$	$\ln \sigma_0 = \ln \sigma_{00} + [\Delta E/kT_0]$
$\text{Se}_{95}\text{Te}_5$	0.49	-2.70	-2.68
$\text{Se}_{90}\text{Te}_{10}$	0.46	-3.73	-3.55
$\text{Se}_{85}\text{Te}_{15}$	0.39	-5.17	-5.57
$\text{Se}_{75}\text{Te}_{25}$	0.32	-7.80	-7.60

For states B and C, i.e., partially crystalline and crystalline phase, the slope of $\ln \sigma_0$ vs ΔE is negative which shows the MN Rule is not followed in these states. A negative slope is observed by various workers [26-28] which is known as Anti MN Rule. The poor correlation coefficients in the present case, however, indicate that even the anti MN Rule is not completely applicable in the present case in these states. It is interesting to note that the correlation coefficient becomes poorer in crystalline state (state C) as compare to partially crystallize state (state B).

This shows that MN rule is followed in chalcogenide glasses if they remain in amorphous phase and when the structure of the alloy transforms from short-range order to long-range order structure, the deviation from MN rule is observed.

5. Discussion

The discussion of whether there is one universal explanation for the MNR in different systems is not yet settled. Various plausible models have been proposed. One common interpretation is based on an exponential density of states distribution that induces a shift in the Fermi level. In this model [29] it is assumed that there is exponential tailing of localized states with energy and distance near valence and conduction bands, which is, in general, accepted in case of glassy semiconductors. The increase of the dc conductivity with temperature is believed to be due to an increase in the free carrier concentration (holes) due to the statistical shift of the Fermi level (E_f).

In case of semiconductors, the Fermi level (E_f) is temperature dependent and the position of E_f is determined by the charge neutrality. Normally, only states within a couple of kT above E_f have any significant occupancy and control the temperature dependence of E_f . If the ratio of conduction band tail states to the midgap density of states is large, then states $\gg kT$ from E_f have significant occupancy and can influence the motion of E_f and in turn gives rise to the MNR. This happens because the density of localized states increases at least as fast as the Fermi function falls off the energy due to exponential distribution of density of states with energy. The view that the position of the Fermi level is controlled by the midgap localized states has been supported by a.c. conductivity measurements in chalcogenide glasses [30, 31].

The present results in state A are consistent with the above model as MN rule is obeyed in this case. The absence of MNR in states B and C may be due to the different distribution of defect states in these states.

6. Conclusions

The temperature dependence of conductivity measurements has been performed in $\text{Se}_{100-x}\text{Te}_x$ thin films. The electrical conductivity is found to be thermally activated in all the three states.

We have shown that, in amorphous state, the MN rule is observed in thin films of $\text{Se}_{100-x}\text{Te}_x$ alloys by the variation of ΔE on changing the composition. The explanation is based on the exponential distribution of density of states with energy. However, in partially crystalline and crystalline states, the MN rule is not respected showing that the defect states energy distribution may be different in these states. This indicates that MN rule is associated with the disorder of some form in the chalcogenide glasses due to their short-range order structure.

References

- [1] P. K. Weimer, H. Borken, G. Sadasiva, L. Merry-Horvath & F. V. Shallcross, Proc. IEEE 52 (1967).
- [2] L. Cheung, GMT Foley, P. Fournia, BE. Springett, *photogr. Sci. Eng. (USA)* **26**, 245 (1982).
- [3] H. L. Wilson & W. A. Gutierrez, *proc. IEEE (USA)* **52**, 417 (1967).
- [4] A. El-Korashy, H. El-Zahed, H. A. Zayed, M. A. Kenwy *Sol. Stat. commun.* **95**, 335 (1995).
- [5] S. P. Singh, S. Kumar, A. Kumar *Vacuum* **75**, 313 (2004).
- [6] R. Misra, S. K. Tripathi, A. K Agnihotri, A. Kumar, *Sol. Stat. Commun.* **77**, 797 (1991).
- [7] N. Tomozeiu, I. Munteanu, *FIZIKA A* **5**, 127 (1996).
- [8] N. Mehta, M. Zulfequar, A. Kumar, *J. Optoelectron. Adv. Mater.* **6**(2), 441 (2004).
- [9] V. S. Kushwaha, A. Kumar, *J. Optoelectron. Adv. Mater.* **6**(4), 1159 (2004).
- [10] N. Mehta, R. K. Shukla, A. Kumar, *J. Optoelectron. Adv. Mater.* **6**(4), 1185 (2004).
- [11] V. S. Kushwaha, N. Mehta, N. Kushwaha, A. Kumar, *J. Optoelectron. Adv. Mater.* **7**(4), 2035 (2005).
- [12] W. Meyer, H. Neldel *Z. Tech. Phys.* **18**, 588 (1937).
- [13] K. Simkawa, F. Abdel-Wahab, *Appl. Phys. Lett.* **70**, 652 (1997).
- [14] W. E. Spear, D. Allan, P. Lecomber, A. Gaith *Phil. Mag. B* **41**, 419 (1980).
- [15] M. Tanielian *Phil. Mag. B* **45**, 435 (1982).
- [16] R. S. Crandall *Phys. Rev. B* **43**, 4057 (1991).
- [17] A. Abd-El Mongy, *Egypt. J. Sol.* **24**, 1 (2001).
- [18] S. K. Dwivedi, M. Dixit, A. Kumar *J. Mater. Sci. Lett.* **17**, 233 (1998).
- [19] Sangeeta Singh, R. K. Shukla, A. Kumar *J. Non-Cryst. Solids* **351**, 1577 (2005).
- [20] Y. L. A. Ei-Kady *Physica B* **305**, 259 (2001).
- [21] V. S. Kushwaha, N. Mehta, N. Kushwaha, A. Kumar, *J. Optoelectron. Adv. Mater.* (Accepted).
- [22] D. Kumar, S. Kumar *Vacuum* **74**, 113 (2004).
- [23] D. Kumar, S. Kumar *J. Optoelectron. Adv. Mater.* **6**, 777 (2004).
- [24] A. Arora, A. Kumar *Phys. Stat. Sol. A* **1125**, 273 (1991).
- [25] R. Misra, Ph. D. Thesis Kanpur University, India 1991.
- [26] R. Flückiger, J. Meier, M. Goetz, A. Shah, *J. Appl. Phys.* **77**, 712 (1995).
- [27] H. Meiling, R. E. I. Schropp, *Appl. Phys. Lett.* **74**, 1012 (1999).
- [28] J. H. Schon, Ch. Kloc, B. Batlogg, *Phys. Status Solidi B* **121**, R4 (2000).
- [29] G. G. Roberts, *J. Phys. C* **4**, 3167 (1971).
- [30] R. Arora, A. Kamar *Rev. Phys. Appl.* **25**, 169 (1989).
- [31] R. Arora, S. K. Tripathi, A. Kamar *J. Mater. Sci. Lett.* **9**, 348 (1990).