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Dependence of activation energy and pre-exponential factor on electric field in amorphous thin films of $Se_{70}Te_{30-x}Zn_x$

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ABSTRACT

The present paper reports the effect of electric field on the electrical parameters (activation energy and pre-exponential factor) in amorphous thin films of $Se_{70}Te_{30-x}Zn_x$ ($x = 0, 6, 8$). It is observed that, in a particular composition, at low electric field up to 10^3 V/cm neither activation energy nor pre-exponential factor depend on electric field as expected in case of ohmic region. However, at higher electric fields where non ohmic region is observed, activation energy and pre-exponential factor both vary with electric field. Similar behavior is observed in all the compositions used in this study. A correlation between activation energy and pre-exponential factor is also observed in these alloys, which is known as Meyer–Neldel rule (MN rule). Further MN rule is also observed in the present case which is explained by the model suggested by Yelon and Movaghar responsible for MN rule in chalcogenide glasses.

1. Introduction

Chalcogenide glasses are an important class of glassy materials as they behave as semiconductor and hence can be used for semi-conducting devices similar to crystalline ones. However, it is found experimentally that it is difficult to have efficient doping (*n* type or *p* type) in these materials due to large density of defect states in the band gap. Though, all chalcogenide glasses could not be doped, the properties of chalcogenide glassy semiconductors are usually affected by the addition of impurities when third element is added to the binary alloys. Experimental results reported by various researchers have shown that the addition of impurity atoms in binary Se–Ge and Se–In systems does change the electrical properties of chalcogenide glasses significantly [1–3]. It has also been found that the effect of impurities depends strongly on the composition of the glass, the chemical nature of the impurity and the method of doping. Several physical properties are found to be improved by the addition of certain impurities.

Se–Te alloys are thought to be promising media which can be used for phase change between an amorphous and crystalline state. These alloys are found to have some significant problems when used as a recording layer material in optical phase change technique (PC) [4,5]. It is also reported [6,7] that chalcogenide glasses are also promising materials for application of electrical phase change in the non-volatile memories.

The two serious problems are the limited reversibility [8], low glass transition and crystallization temperature. These problems can be removed by adding third element as a chemical modifier in Se–Te binary alloys. A lot of work has been done on ternary chalcogenide glasses having different compositions like Se–Te–Sb, Se–Te–Ge, Se–Te–In [9,10]. In the present work, Zn has been added as a third element in binary Se–Te alloys to study the electrical parameter.

The reason for the selection of Zn as a chemical modifier in Se–Te system is based on it's attractive and important applications in chalcogenide glasses. Like Ag, Zn can also be used for photo-doping in chalcogenide glasses [11–16]. There are successful reports of doping of $ZnSe_xTe_{1-x}$ in the literature that are suitable for the development of light emitting diodes and lasers.

The present paper reports the measurements of d.c. conductivity as a function of temperature at low and high electric fields. The results are found to be dependent on electric field in high field region ($\sim 10^4$ V/cm). Section 2 describes the experimental details. The results have been presented and discussed in Section 3. Last section deals with the conclusions of the present work.

2. Experimental

Glassy alloys of $Se_{70}Te_{30-x}Zn_x$ ($x = 0, 6, 8$) were prepared by quenching technique. High purity (99.999%) materials were weighed according to their atomic percentages and were sealed in quartz ampoules (length ~5 cm and internal diameter ~8 mm) with a vacuum $\sim 10^{-5}$ Torr. The ampoules containing the materials were heated to 900 °C and held at that temperature for 10–12 h. The temperature of the furnace was raised slowly at a rate ~3–4 °C/min. During heating, all the ampoules were constantly rocked, by rotating a ceramic rod to which the ampoules are tucked away in the furnace. This was done to obtain homogenous glassy alloys.

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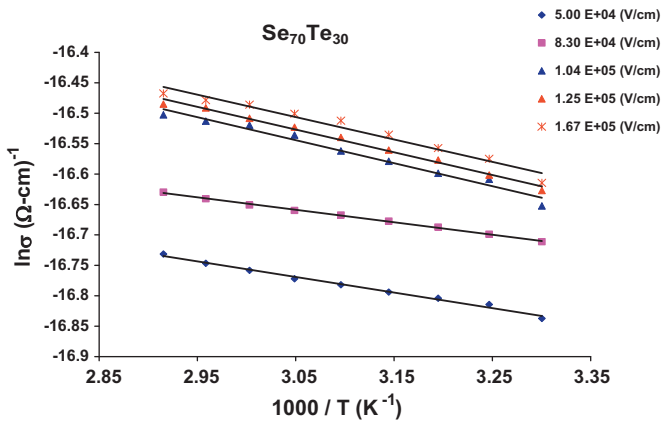

Fig. 1. Plot of $\ln\sigma$ versus 1000/T at different electric fields for $Se_{70}Te_{30}$ thin film.

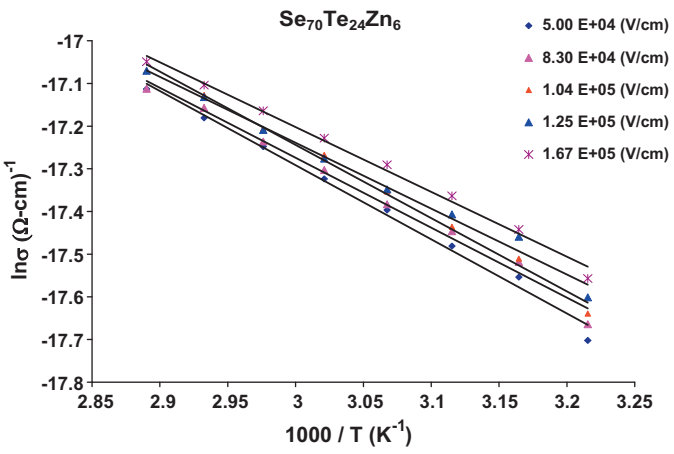

Fig. 2. Plot of $\ln\sigma$ versus 1000/T at different electric fields for $Se_{70}Te_{24}Zn_6$ thin film.

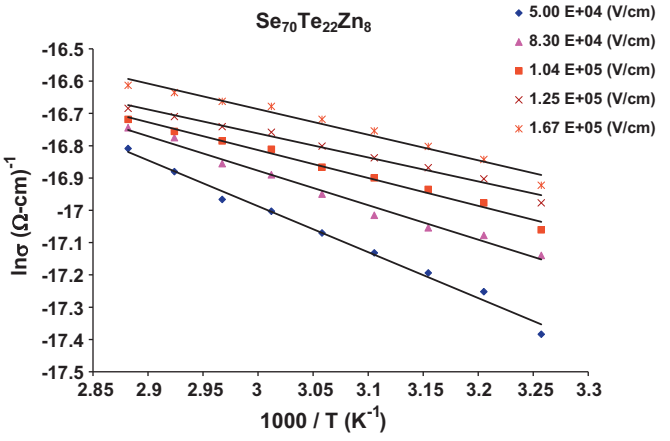

Fig. 3. Plot of $\ln\sigma$ versus 1000/T at different electric fields for $Se_{70}Te_{22}Zn_8$ thin film.

After rocking for about 10 h, the obtained melts were cooled rapidly by removing the ampoules from the furnace and dropping to ice-cooled water. The quenched samples were taken out by breaking the quartz ampoules. The glassy nature of the materials was checked by XRD technique.

Thin films of these glasses 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 co-planar structure (length ~1.2 cm and electrode separation ~0.12 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. The deposition parameters were kept almost the same for all samples so that a comparison of results could be made for the various glassy samples. The amorphous nature of the thin films was ascertained by X-ray diffraction.

For the measurements of high field conduction, thin film samples were mounted in a specially designed sample holder in a vacuum $\sim10^{-3}$ Torr. Thin films were mounted above the copper substrate holder with the help of two phosphor bronze clips. These clips are fixed by two Teflon screws to the substrate holder. The electrical connections are taken through a Teflon insulated BNC connector. A heating element is wounded around a copper rod to heat the thin film. A calibrated copper-constantan thermocouple was mounted very near to the sample to measure the temperature of thin film. An O-ring was provided between the upper and lower parts of the sample holder for proper evacuations inside the chamber.

A vacuum $\sim10^{-3}$ Torr was maintained throughout the measurements. A d.c voltage (0–300 V) was supplied across the sample and the resultant current was measured by digital Pico-ammeter. *I–V* characteristics were measured at various fixed temperatures (285–328 K) in these films. The temperature of the films was controlled by mounting a heater inside the sample holder and measured by a calibrated copper-constantan thermocouple mounted very near the films. Before measuring *I–V* characteristics, thin films were annealed in a vacuum $\sim10^{-3}$ Torr near glass transition temperature for 2 h in the same sample holder that was used for the above measurements.

3. Results and discussion

The temperature dependence of conductivity 'σ' at different electric fields is studied in thin films of glassy $Se_{70}Te_{30-x}Zn_x$ ($x = 0$, 6, 8) alloys. $\ln\sigma$ vs. $1000/T$ are found to be straight lines in all the samples in the temperature ranges 300–350 K at all the electric fields. At low electric fields upto 10^3 V/cm such curves are found to be independent of electric field applied. However, at higher fields $\sim10^4$ V/cm or more, the slopes of such curves are found to be dependent on electric field. Figs. 1–3 show such plots at different electric fields for thin films of glassy $Se_{70}Te_{30-x}Zn_x$ alloys ($x = 0$, 6, 8).

These figures indicate that the thermally activated conduction occurs at high field also consistent with Arrhenius equation:

$$\sigma = \sigma_0 \exp\left(\frac{-\Delta E}{kT}\right) \quad (1)$$

Here ΔE is the activation energy of electrical conduction and σ_0 is called the pre-exponential factor.

From the slopes and the intercepts of these curves the value of ΔE and σ_0 are calculated at different electric fields for each glassy alloy. The values of these parameters are given in Table 1.

In semiconductors conductivity increases exponentially with temperature and the activation energy should not depend on electric field applied as long as ohmic behavior is observed in the measuring range of temperature and electric field. However, when electric field applied is much higher, current density may not be proportional to field due to increase in charge carriers at higher fields. The current density becomes super-ohmic at these fields and hence the activation energy may also depend on applied field. Such type of behavior is possible due to charge injection from the electrodes at the higher field which is known as space charge limited conduction.

In the present case, ΔE is different for different fields in high field region which may be understood in terms of shift of Fermi level in presence of high fields due to injection of charge carriers from the electrodes [17–20] or due to Poole–Frenkel conduction [21–23] at high fields.

Table 1
Semi-conducting parameters ΔE (in eV) and $\ln\sigma_0$ ($\Omega^{-1}\,cm^{-1}$) for glassy $Se_{70}Te_{30-x}Zn_x$ alloys.

Electric Field (V/cm)	$Se_{70}Te_{30}$		$Se_{70}Te_{24}Zn_6$		$Se_{70}Te_{22}Zn_8$	
	ΔE	$\ln\sigma_0$	ΔE	$\ln\sigma_0$	ΔE	$\ln\sigma_0$
5.00E+04	0.032	−15.39	0.149	−12.07	0.122	−12.72
8.30E+04	0.031	−15.40	0.147	−12.09	0.134	−12.32
1.04E+05	0.029	−15.51	0.141	−12.35	0.068	−14.31
1.25E+05	0.022	−15.90	0.133	−12.60	0.064	−14.53
1.67E+05	0.017	−16.03	0.130	−12.64	0.070	−14.22

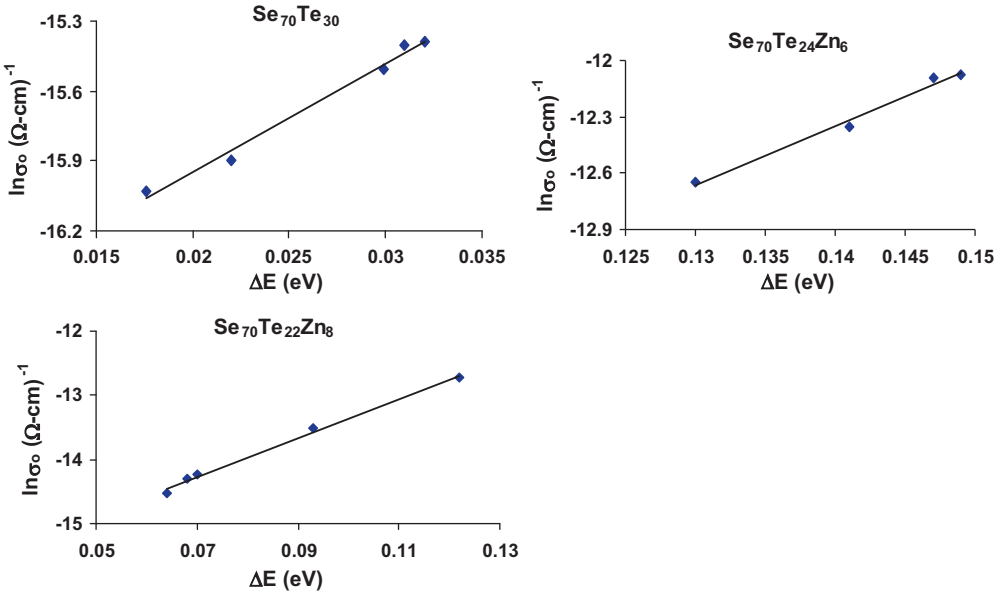

Fig. 4. Plots of $\ln \sigma_0$ vs. ΔE for thin films of glassy $Se_{70}Te_{30-x}Zn_x$ ($x = 0, 6, 8$) alloys at each value of x.

In addition to the variation of ΔE with field, we have observed that pre-exponential factor σ_0 is not same at all electric fields in a particular glass composition (see Table 1).

Fig. 4 represents the plots of $\ln \sigma_0$ vs. ΔE for thin films of glassy $Se_{70}Te_{30-x}Zn_x$ ($x = 0, 6, 8$) at each value of x. These plots indicate that σ_0 varies exponentially with activation energy ΔE according to a following relation:

$$\sigma_0 = \sigma_{00} \exp\left(\frac{\Delta E}{E_{MN}}\right) \tag{2}$$

Here σ_{00} is a constant and E_{MN} is frequently called as the Meyer–Neldel characteristic energy. Above equation is also called MN rule.

From the slopes and intercepts of the lines of $\ln \sigma_0$ vs. ΔE curves, we have calculated the values of E_{MN} and σ_{00}. These values are given in Table 2. It is clear from this table that the characteristic energy (E_{MN}) is different at different electric field and there exists a strong correlation between the MN conductivity pre-factor and characteristic energy as shown in Fig. 5. This figure indicates that σ_{00} varies exponentially with E_{MN}, which can be expressed as:

$$\ln \sigma_{00} = \alpha + \beta E_{MN} \tag{3}$$

where α and β are constants.

The above relation between σ_{00} and E_{MN} given by Eq. (3) is called "Further MNR in σ_{00} and E_{MN}" [24,25].

To explain the puzzles associated with MN rule, Yelon and Movaghar has proposed a model, called YM model [26,27]. According to this model, the MN rule may be understood as arising naturally when the activation energy for a process is significantly larger than the typical excitations available and kT both. Yelon et al. suggest that the optical phonons are the source of the excitation energy in such process. It is assumed that many phonons involve in trapping and de-trapping of electrons, either by cascade or by multi-phonon process. They have explained MNR with entropy term, which may vary the pre-factor by many orders of magnitude. It applies equally well to crystalline or amorphous materials.

In this model, Emin has calculated the hopping rates due to multi-phonon effects, using small polaron theory and the Kubo–Greewood formula. The result is

$$R(\Delta E) \propto \exp\left[\left(\frac{\Delta E}{h\upsilon_0}\right) \ln S\right] \exp\left(\frac{-\Delta E}{kT}\right) \tag{4}$$

where $h\upsilon_0$ is the optical phonon energy. That is,

$$E_{MN} = \frac{h\upsilon_0}{\ln S} \tag{5}$$

where

$$S = \frac{2E_b}{h\upsilon_0} \tag{6}$$

In Eq. (6), E_b is the small polaron binding energy, so that S represents a normalized coupling strength.

In order to understand the variation of E_{MN} with $\ln \sigma_{00}$ observed by Shimakawa and Abdel-Wahab, we start by assuming that electron hopping induced by optical phonons and the associated variation in σ_{00}, must be due to variation in $\ln S$. Actually, Emin's model predicts that the hopping rate, and as a result, the conductivity, will be extremely sensitive to variation in $\ln S$. The most complete expression for the hopping rate at low temperatures is presented by Emin [28]. If we limit our consideration to hops

Table 2
The values of $\ln \sigma_{00}$ and MN Energy (E_{MN}) for glassy $Se_{70}Te_{30-x}Zn_x$ alloys.

Composition	E_{MN} (meV)	$\ln \sigma_{00}$ (Ω^{-1} cm^{-1})
$Se_{70}Te_{30}$	21.3	16.88
$Se_{70}Te_{24}Zn_6$	31.1	16.70
$Se_{70}Te_{22}Zn_8$	32.9	16.64

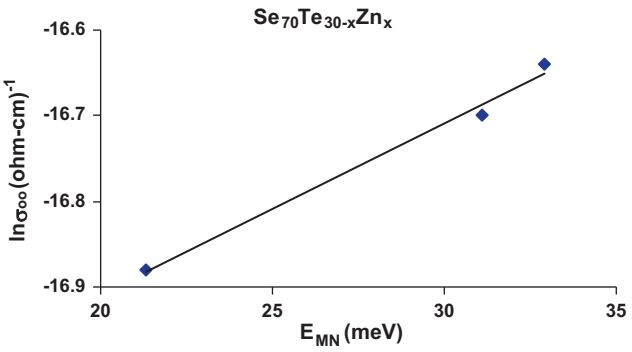

Fig. 5. plots of $\ln \sigma_{00}$ vs. E_{MN} showing strong co-relation (i.e., further relation) between σ_{00} and E_{MN}.

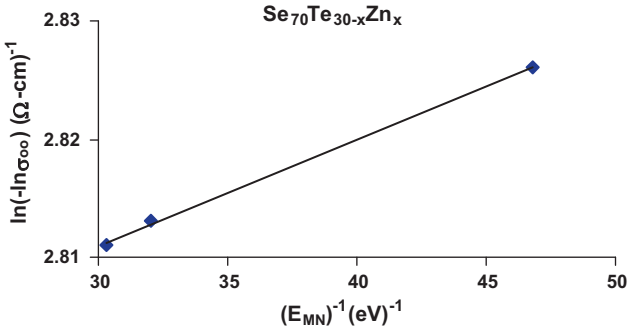

Fig. 6. A plots of $\ln(-\sigma_{00})$ vs. $(E_{MN})^{-1}$.

upward in energy, and use the present notation, this may be written as

$$R(\Delta E) = \frac{2\pi}{\omega_0}\left(\frac{J}{h}\right)^2 e^{-s}\frac{\exp(-\Delta E/E_{MN})\quad \exp(-\Delta E/kT)}{(-\Delta E/h\upsilon_0)!} \times \left[\sum_{\pi-\infty}^{\infty}(A_n)^{(-\Delta E/h\upsilon_0)} \times \cos\left(\frac{\Delta E\phi_n}{h\upsilon_0}\right)\right] \quad (7)$$

where J is the electron transfer integral connecting the initial and final sites, A_n is a lattice-relaxation amplitude function and ϕ_n is the lattice-relaxation phase shift. As it can be easily seen the MN energy depends upon $\ln S$, whereas the hopping rate depends upon the $\exp(-S)$. Combining Eqs. (5) and (7) leads the prediction that

$$\ln\sigma_{00} = r - \exp\left(\frac{h\upsilon_0}{E_{MN}}\right) \quad (8)$$

Here it has been assumed that 'r' is a constant. Using the data of σ_{00} and E_{MN}, curves are plotted between σ_{00} and E_{MN}, (see Fig. 6). The value of $h\upsilon_0$ for the above cases is 9.0 meV. The lower values of $h\upsilon_0$ may be due to high field electric conduction in the present case, whereas Yelon et al. developed above theory without using high electric field. The present results, therefore supports the model given by Yelon and Movaghar to explain the observation of MN rule between σ_{00} and EMN for high field conduction.

4. Conclusions

Temperature dependence of conductivity is measured in presence of high field in thin films of glassy $Se_{70}Te_{30-x}Zn_x$ alloys. Conductivity is found to be thermally activated at all the values of electric field. The values of ΔE and σ_0 are calculated at various electric fields for each composition. σ_0 and ΔE follow MN rule for all the glasses studied here. The value of σ_{00} and E_{MN}, obtained for each glassy alloy, is found to have a further correlation, which is explained by the model suggested by Yelon and Movaghar responsible for MN rule in chalcogenide glasses.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jallcom.2010.08.141.

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