Study of defect state chemistry of chalcogens elements (Se/Te) in binary $Se_{100-x}Te_x$ glassy system using low-temperature d.c. conductivity measurements

SHOBHIT SARASWAT[a], V. K. TOMAR[a], N. CHANDEL[b], N. MEHTA[c]

[a]Department of Electronics and Communications, Institute of Engineering and Technology, GLA University, Mathura, India
[b]Department of Physics, Sunbeam College for Women, Varanasi-221005, India
[c]Department of Physics, Institute of Science, Banaras Hindu University, Varanasi-221005, India

The density of defect states (DDS) has always been a subject of curiosity in electronic materials as the knowledge of this parameter is a key parameter for determining the applications of these materials. Chalcogenide glasses are well known as electronic materials because of their excellent electrical properties (e.g., resistive switching, thermally activated a.c. and d.c. conduction, dielectric relaxation, etc). In the present paper, the d.c. conductivity has been measured for chalcogens elements Se and Te based binary glasses in the low-temperature region to apply the Mott's theory of electronic conduction. The conduction mechanism in this region follows the Mott's temperature dependence. The further investigations provide the estimation of the density of defect states (DDS) in $Se_{100-x}Te_x$ alloys. The value of DDS is decreased with the increase in Te concentration. We have observed a correlation between the DDS and the electronegativity of the chalcogens elements Se and Te. The compositional dependence of the hopping parameters indicates that the condition becomes easier for the variable range hoping with the rise in the Te concentration.

1. Introduction

The Group 16 elements are frequently named as chalcogens ('ore builders'). From the geographical point of view, they are known as chalcophiles which are the soft elements (keeping in mind the terminology of the hard/soft acids and bases concept). In the geographical sense, chalcophiles preferably form minerals with sulfur (S), selenium (Se), and tellurium (Te). However, oxygen (O) tends to bind preferably to lithophiles, which are hard elements such as the alkali metals, early transition metals, and silicon. The special position of oxygen amongst the chalcogen elements is its association with its very high electronegativity, which in turn correlates with its high ionization energy and the small atomic radius; which makes it difficult for oxygen to act as a central atom in electron-rich multicentre bonds. The nature of the charged defect states is a subject of great interest in physics, chemistry, electronics and, materials science [1-5]. The density of defect states is found to be important in determining the role of various multifunctional materials (e.g., perovskites, ceramics, and glasses) for the applications in a specific direction.

The nature of the gap states, which have been pinning the Fermi level near the gap center has very different characteristics in the two major classes of amorphous semiconductors: (i) the tetrahedrally coordinated materials such as Si and Ge (ii) the chalcogenide glasses. In reality, the tetrahedrally amorphous semiconductors contain a large number of voids and vacancies and hence produce many dangling bonds which yield electronic states near the gap center [6-9]. The density of defect states (DDS) is a key parameter in amorphous semiconductors for determining the semiconducting properties i.e. electrical, optical, thermal properties. The defect population is often the limiting factor in determining the electronic performance of an amorphous semiconductor. To measure DDS in amorphous semiconductors, different methods have been mentioned in literature with their advantages and limitations [10-14].

Defects play an important role in the case of semiconductors as their electronic properties are particularly sensitive to the presence of defects and some of these properties are sometimes a direct consequence of this presence. The vast utilization of semiconductors in modern electronics demands an extensive study on the nature of defects present in these semiconducting materials. Amorphous materials are prepared by the rapid cooling of the melt or condensing vapors on a cold substrate. Due to rapid cooling, many kinds of defects are produced in amorphous materials. The defect density is therefore in general higher in amorphous materials as compared to crystalline materials. Due to the high density of localized defects, not all amorphous materials can be used for making solid-state devices. Several materials can, therefore, be investigated with an emphasis on reducing the density of defect states (DDS). Thus, the determination of DDS in the non-crystalline solids like amorphous

semiconductors and glasses is an on-going research activity [15-18]. In the present work, we have determined the DDS in glassy alloys of $Se_{100-x}Te_x$ system by using low temperature d.c. conductivity measurements.

2. Synthesis technique

To acquire the glassy alloys of $Se_{100-x}Te_x$ system, Se and Te elements of very high purity were purchased (Sigma Aldrich USA). The desired compositions of powdered samples were weighed in the quartz tubes of identical geometry. Each ampoule was sealed under a sufficiently high vacuum (~ 10^{-6} Torr) by using a vacuum sealing unit (Hindhivac, Model: VS65D). The heating and the rocking of the sealed tubes were done in an electronic furnace. The rocking of ampoules was done to make sure of the homogeneity of the samples. The rapidly quenching of molten samples was done in chilled water to obtain the samples in a glassy form.

3. Experimental

For measurements of conductivity, all the glassy alloys were ground to a very fine powder and pellets (diameter ~ 10 mm and thickness ~ 1 mm) were obtained by compressing the powder in a die at a load of 5 Tons. The pellets were coated with indium film to ensure good electrical contact between the sample and the electrodes. For the conductivity measurements, the pallets were mounted in a specially designed sample holder between the steel electrodes in a vacuum ~10^{-3} Torr. A liquid nitrogen trap attached to the lower part of the sample holder was used for lowering the temperature. The sample holder has two parts. The upper part consists of two electrodes and an evacuation port. The samples were mounted between the jaws of two electrodes having a spring arrangement. At the end of two electrodes, two UHF connectors were used for the electrical connections of the sample. A calibrated copper-constantan thermocouple was mounted very near to the sample to measure the temperature of the sample. An O-ring was provided between the two parts of the sample holder for proper evacuations inside the chamber. A liquid nitrogen trap is attached around the wall of the lower part of the sample holder for cooling the samples up to the low-temperature regime during d.c. conductivity measurements.

4. Results and discussion

The glassy nature of the quenched samples was confirmed by the XRD technique using Cu target and K_α radiation ($\lambda = 1.5405$ Å). The respective values of applied voltage and current in the X-ray tube were 30 kV and 20 mA. Fig. 1(a) shows the XRD pattern of $Se_{80}Te_{20}$ alloy. The nonexistence of any sharp peaks ensures the glassy character of the present sample. For further structural

characterization of as-prepared samples, we used a transmission electron microscopy (TEM) [Model: FEI-Technai 20 G^2] and a high-resolution scanning electron microscope (SEM) [Model: JEOL-840A, made in Japan].
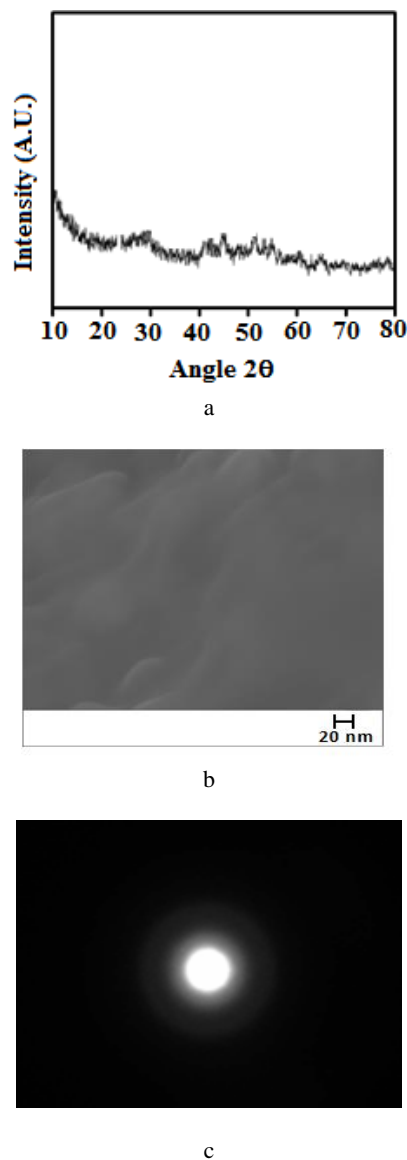

a

b

c

Fig. 1. (a) XRD pattern, (b) SEM image and (c) the electron diffraction pattern of glassy $Se_{80}Te_{20}$ alloy

Fig. 1(b) exemplifies the SEM image of $Se_{80}Te_{20}$ alloy. This image clearly shows a dark and smooth region only is observed for the present sample. This is again a signature of the glassy character of as-prepared samples. Similar results were obtained for the other two alloys. Fig. 1(c) shows the electron diffraction pattern of the as-prepared sample of $Se_{80}Te_{20}$ alloy. From this figure, it is clear that the electron diffraction pattern exhibits a diffuse ring. This diffused ring also confirms the amorphous character $Se_{80}Te_{20}$ alloy.

Se$_{90}$Te$_{10}$
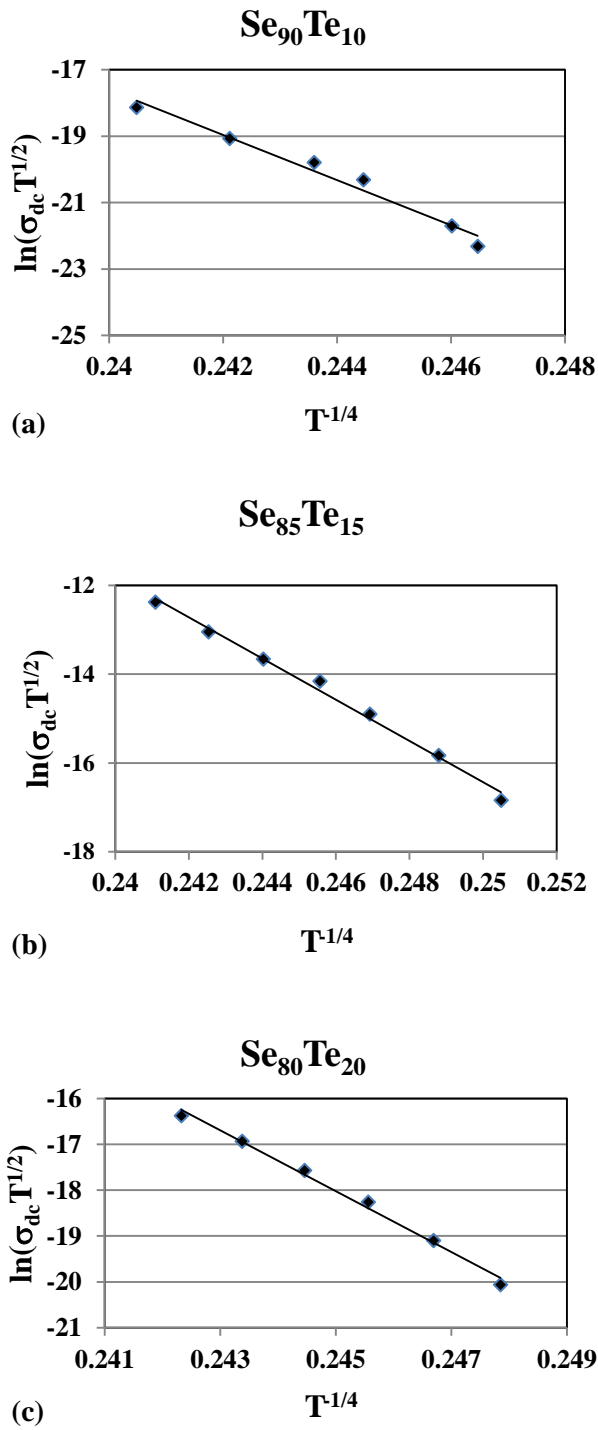

(a)

Se$_{85}$Te$_{15}$

(b)

Se$_{80}$Te$_{20}$

(c)

Fig. 2. Plots of ln ($\sigma_{dc}T^{1/2}$) vs $T^{-1/4}$ for glassy Se$_{100-x}$Te$_x$ alloys

Plots of ln ($\sigma_{dc}T^{1/2}$) against $T^{-1/4}$ are shown in Fig. 2. From this figure, it is clear that in the low-temperature range (206-311 K), the temperature dependence of show linear relation between ln ($\sigma_{dc}T^{1/2}$) against $T^{-1/4}$. This implies that conduction occurs via variable range hopping of the charge carriers in the localized states near the Fermi level and is characterized by Mott's variable range hopping relation [19]:

$$\sigma_{dc} = \left(\frac{\sigma'_0}{T^{1/2}}\right) exp\left[-\left(\frac{T_0}{T}\right)^{1/4}\right] \qquad (1)$$

Here:

$$\sigma'_0 = 3e^2\upsilon\left[\frac{N(E_F)}{8\pi\alpha K_B T}\right]^{1/2} \qquad (2)$$

and

$$T_0 = \frac{\lambda\alpha^3}{K_B N(E_F)} \qquad (3)$$

Here $N(E_F)$ is the density of localized states at the Fermi level, α^{-1} is the degree of localization, T_0 is the degree of disorder, λ is a dimensionless quantity (≈ 18), K_B is Boltzmann constant, e is electronic charge and υ is typical phonon frequency approximately 10^{13} Hz.

Solving Equations (2) and (3), we obtain:

$$\alpha = 22.52\sigma'_0 T_0^{1/2} \qquad (4)$$

and

$$N(E_F) = 2.12 \times 10^9 (\sigma'_0)^3 T_0^{1/2} \qquad (5)$$

The average hopping distance R and hopping energy W are given by:

$$R = \left[\frac{9}{8\pi\alpha K_B T N(E_F)}\right]^{1/4} \qquad (6)$$

$$W = \frac{3}{4\pi R^3 N(E_F)} \qquad (7)$$

Various Mott parameters T_0, α'_0, α, $N(E_F)$, R, and W have been calculated from Eqs. (1) to (7) and are listed in Table 1.

Table 1. Mott's parameters for present samples of Se$_{100-x}$Te$_x$ system

Mott's Parameters	Sample		
	Se$_{90}$Te$_{10}$	Se$_{85}$Te$_{15}$	Se$_{80}$Te$_{20}$
T_0 (K)	2.1×10^{11}	4.6×10^{10}	1.8×10^6
α (cm)$^{-1}$	1.5×10^9	4.8×10^8	4.3×10^6
$N(E_F)$ (eV^{-1}cm^{-3})	3.1×10^{21}	4.5×10^{20}	8.5×10^{18}
R (cm)	4.1×10^{-8}	8.8×10^{-8}	7.8×10^{-7}
W (meV)	1114.1	760.2	59.7
αR	62.7	42.8	3.4

Similar results have been observed by other research groups in diversified glassy systems [20, 21]. Mott and Davis suggested [19] that when the conduction is governed by the variable range hopping then the respective values of W and αR should be larger than $K_B T$ and unity. Table 1 manifests that $W > K_B T$ and $\alpha R > 1$. Thus, our present results

confirm the applicability of Mott's theory (i.e., the condition for which the dominant conduction mechanism is variable range hopping). Further, it is also clear from this table that the density of localized states changes, i.e., the reduction in the localized defects occurs when we replace Se atoms by Te atoms in the glassy network of binary Se-Te system.

In the last seven decades, an extensive investigation of the structure and properties of amorphous selenium (a-Se) has been done [22, 23]. Extensively, it was assumed that the structural elements long selenium chain (Se_n) and the selenium 8-ring (Se_8) are mixed together as the constituents of the amorphous phase. The idea of this model was put forward with the information that the crystalline phase of selenium consists of α-monoclinic Se (α-Se) phase and trigonal Se (γ-Se) phase. The Se_8 rings and the Se_n chains are the building block in the former and the later phases respectively. It is therefore plausible that we can think about a structure for the amorphous phase which is made of a mixture of ring and chain members. Various research groups have studied the structure of amorphous Se (a–Se) [24-27] and the consequence of alloying Te into glassy Se [28-31]. The outcome of their research work demonstrates the presence of the dangling bonds in the widespread polymeric chains of Se in the form of the localized defect states. Thus, the reduction in the number of such localized defects is possible due to the cross-linking of Te with breaking end of chains after the incorporation of Te in glassy Se. Consequently, the DDS is decreased with the increase in the Te content in binary Se–Te system. This explanation is a qualitative basis but we may explain the present observation (i.e., the decrease in DDS after the incorporation of Te as a foreign element) quantitatively in terms of the average electronegativities of the present glassy alloys. Defect states in glassy materials are found to be correlated with the electronegativities [ξ_{Se} = 2.55 and ξ_{Te} = 2.1] of the composing atoms [32-38].
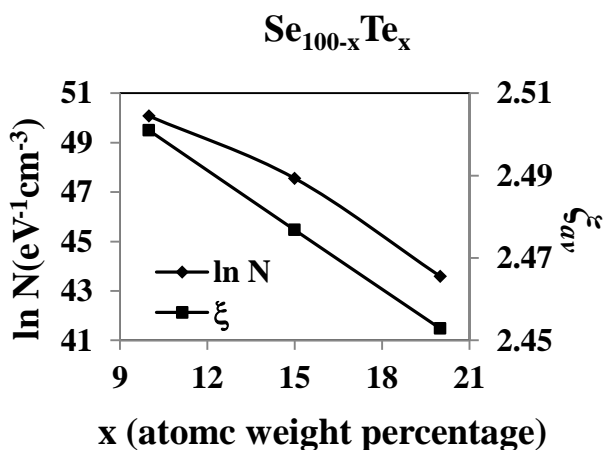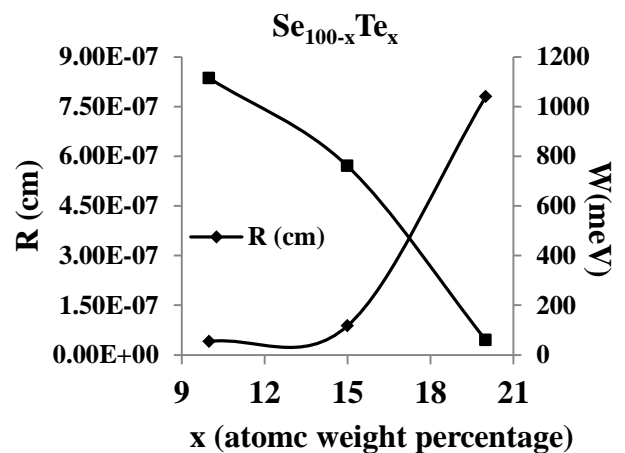

Fig. 4. Composition dependence of Mott parameters W and R for glassy $Se_{100-x}Te_x$ alloys

Thus, one would expect that the probability of defect formation is connected with the average electronegativity (ξ_{av}) of the glasses [11]. The plots of DDS and ξ_{av} against the composition of Te are shown in Fig. 3, which indicates that the values of DDS are decreased with a decrease in the average electronegativity.

Further, the plots of average hopping distance R and hopping energy W against the composition of Te are shown in Fig. 4.

These plots show that there is only a slight increment in average hopping distance with the increase in the Te concentration while the hopping energy W is decreased appreciably. Thus, the addition of Te provides more favorable conditions for the hopping conduction mechanism. Such studies directly related to the determination of DDS in Se rich chalcogenide glasses are necessary to check their candidature for different optoelectronic applications like non-volatile phase-change RAM [39, 40].

5. Conclusions

The d.c. conductivity σ_{dc} of Se-Te glasses has been measured in the low-temperature region. The detailed temperature dependence of d.c. conductivity confirms that σ_{dc} follows Mott's $T^{1/4}$ law. The further analysis of the results concludes that the conduction is due to variable range hopping in the present binary glasses. The reduction in the DDS is found to be correlated with the electronegativity of the chalcogens elements Se and Te. The condition becomes more and more favorable for the variable range hoping with the increase in the Te concentration as indicated by the values of hopping parameters (R and W).

Fig. 3. Composition dependence of DDS and ξ_{av} for glassy $Se_{100-x}Te_x$ alloys

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*Corresponding author: dr_neeraj_mehta@yahoo.co.in