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Electrical transport in thin films of glassy $\text{Ge}_{40}\text{Te}_{60-x}\text{Sb}_x$ alloys*

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Abstract. Glassy alloys of $\text{Ge}_{40}\text{Te}_{60-x}\text{Sb}_x$ (where $x = 2, 4, 6$ and 10) were prepared by conventional rapid melt-quenching technique. The nature of the alloys was ascertained through X-ray diffraction pattern of the samples. Thin films of the aforesaid materials could be prepared over the glass substrate by thermal evaporation technique. Vacuum evaporated indium electrodes were used here to perform electrical measurements. Coplanar structure of thin films was used in this case. The dc electrical conductivity measurements have been carried out. The dark conductivity, pre-exponential factor and activation energy have been calculated for various compositions. It has been found that the dark conductivity and pre-exponential factor increase, while the activation energy decreases with Sb concentration in $\text{Ge}_{40}\text{Te}_{60-x}\text{Sb}_x$ system. The results can be reserved as an evidence for the chalcogenide nature defects in the above material.

Keywords: chalcogenide glass, thin films, conductivity.

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1. Introduction

Present-day computers and numerous multimedia applications require faster and denser memories [1]. Phase-change materials based on chalcogenide alloys are found to be suitable for optical and electrical memories due to its fast crystallization. The operation principle of these devices is based on the ability of the active materials to reversibly transform between amorphous and crystalline phases. Chalcogenide materials, especially those containing Ge and Te, are of importance in modern technology due to the following reasons: (1) large change in optical constants between crystalline and amorphous state and (2) rapid phase transition between amorphous and crystalline (two stable states) states [2]. This indicates that it can be used as an optical recording material (in optical memory devices such as CD or DVD). Also, this material has high piezoelectricity, which makes it applicable in many other applications.

The most commonly used phase-change materials are Ge-Sb-Te ternary alloys which show pronounced differences in electrical conductivity and optical reflectivity between the amorphous and crystalline states [3, 4]. Moreover, the speed of the phase transformation is very fast within the nanosecond time scale, indicating that it is potentially applicable for use in memory devices, that is, phase change random access memory

(PC-RAM) using Ge-Sb-Te alloy is considered to be essentially close to practical use [5-7]. Research on these alloys is already in progress. Some measurements related to structural studies [8-15], crystallization kinetics [16-21] and others [22, 23] have been reported by various groups working in this field. Despite this, nobody can claim to have these glasses well understood and well characterized. Problems yet to be solved are the basic parameters affecting the electrical and optical transport related to the structure of these glasses. The rapid and reversible amorphous-to-crystalline phase transformation is accompanied by increase in the optical reflectivity and the electrical conductivity. However, uncertainties about the optical band gap and electrical properties of this material have persisted.

The common feature of these glasses is the presence of localized states in the mobility gap. This is due to the absence of long-range order as well as various intrinsic defects. In chalcogenide glasses, it is assumed that the localized states in the mobility gap are the charged defects D^+ and D^- with a negative effective correlation energy. This type of defects usually pins the Fermi energy level in the middle of the forbidden energy gap and result in the absence of electron spin resonance signal [24, 25]. The investigation of electrical conductivity in chalcogenide glasses is a valuable tool for determining the position of the Fermi energy level in the energy gap of semiconductor materials.

Keeping these facts in mind, we report in this paper the results of dc conductivity measurements for $\text{Ge}_{40}\text{Te}_{60-x}\text{Sb}_x$ (where $x = 2, 4, 6$ and 10) ternary chalcogenide glassy system. Section 2 describes the experimental details. The results have been presented and discussed in section 3. The conclusions have been presented in the last section.

2. Experimental details

2.1. Sample preparation

Glassy alloys of $\text{Ge}_{40}\text{Te}_{60-x}\text{Sb}_x$ (where $x = 2, 4, 6$ and 10) systems were prepared by melt quenched technique. High purity (99.999 %) elements, germanium, antimony and tellurium, were weighed using electronic balance according to their atomic percentages. The properly weighed materials were put into clean silica ampoule (length ~ 5 cm and internal diameter ~ 8 mm) and then sealed under vacuum of 1.3×10^{-3} Pa. These sealed ampoules were heated in electric furnace up to 1000°C and kept at that temperature for 10-12 hours. The temperature of the furnace was raised slowly at the rate $3\text{-}4^\circ\text{C}/\text{min}$. During the heating process, ampoules were constantly rocked by rotating a ceramic rod to which the ampoules were tucked away in the furnace. This was done to obtain homogenous glassy alloy.

After rocking for about 10 hours, the obtained molten material in ampoules was rapidly quenched by removing the ampoules from the furnace and dropping into ice-cooled water. The quenched samples of the glassy alloys were taken out by breaking the ampoules. Compositional analysis was performed using the electron probe microanalysis (EPMA) technique.

The amorphous to crystalline nature of samples was ascertained by X-ray diffraction pattern as given in Fig. 1. According to this figure, it is clear that the only sample containing $x = 2$ is amorphous, and in all other samples the structure goes on converting amorphous to polycrystalline as we increase the content of Sb in the $\text{Ge}_{40}\text{Te}_{60-x}\text{Sb}_x$ system.

2.2. Preparation of thin films

Thin films of glassy alloys of $\text{Ge}_{40}\text{Te}_{60-x}\text{Sb}_x$ were prepared using the vacuum evaporation technique by keeping the glass substrate at room temperature. Vacuum evaporated indium electrodes at bottom were used for the electrical contact. The thickness of the film was close to 500 nm. The co-planar structure (length ~ 1.2 cm and electrode separation ~ 0.12 mm and 0.5 mm) was used for these measurements. The pressure close to 1.3 Pa was maintained in the entire temperature range (300 up to 340 K). The thin films were kept in the deposition chamber in the dark for 24 hours before mounting that in the sample holder. This was done to allow sufficient annealing at room temperature, so that metastable thermodynamic equilibrium may be attained in the sample as suggested by Abkowitz [26].

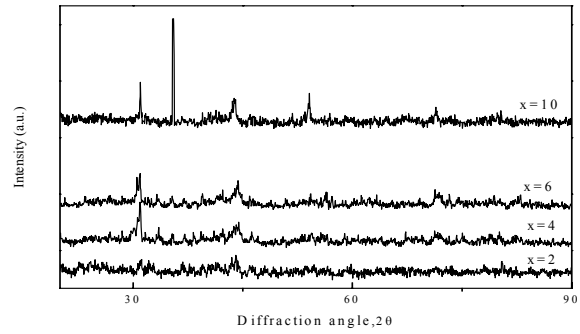


Fig. 1. XRD patterns of $\text{Ge}_{40}\text{Te}_{60-x}\text{Sb}_x$ for $x = 2, 4, 6$ and 10 .

2.3. Measurement procedure

Before measuring the dc conductivity, the film was first annealed at 340 K (below its glass transition temperature, T_g) for one hour in vacuum ~ 1.3 Pa. Thin-film sample was mounted into a specially designed sample holder. The pressure ~ 1.3 Pa was maintained throughout the measurements. The temperature of the film was controlled by mounting a heater inside the sample holder, and measured by a calibrated copper-constantan thermocouple mounted very near to the film.

3. Results and discussion

Fig. 2 shows the temperature dependence of the dark conductivity. It is clear from this figure that $\ln \sigma_{dc}$ vs $1000/T$ curves are straight lines having the single slope indicating that the dark conductivity is due to an activated process having the single activation energy in the used measuring range of temperatures. The dc conductivity can, therefore, be expressed by the usual conductivity relation

$$\sigma_{dc} = \sigma_0 \exp(-\Delta E/kT), \quad (1)$$

where σ_0 is the pre-exponential factor, ΔE is the activation energy for dark conductivity, and k is the Boltzmann constant.

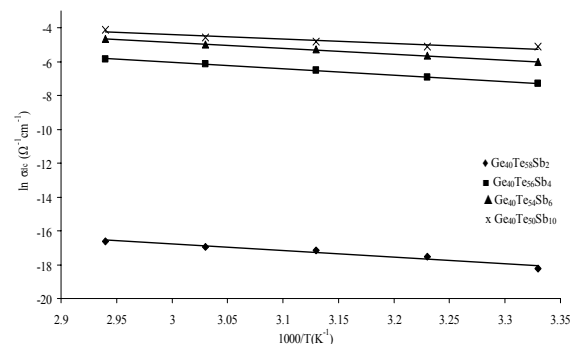


Fig. 2. Plots of $\ln \sigma_{dc}$ vs $1000/T$ curves for $\text{Ge}_{40}\text{Te}_{60-x}\text{Sb}_x$ thin films.

Table. Electrical parameters of the $\text{Ge}_{40}\text{Te}_{60-x}\text{Sb}_x$ (where $x = 2, 4, 6$ and 10) glassy system.

Number	Samples	ΔE (eV)	σ_{dc} ($\Omega^{-1}\text{cm}^{-1}$) at 300 K	σ_0 ($\Omega^{-1}\text{cm}^{-1}$) at 300 K
1.	$\text{Ge}_{40}\text{Te}_{58}\text{Sb}_2$	0.34	1.20×10^{-8}	6.32×10^{-3}
2.	$\text{Ge}_{40}\text{Te}_{56}\text{Sb}_4$	0.33	6.69×10^{-4}	1.97×10^2
3.	$\text{Ge}_{40}\text{Te}_{54}\text{Sb}_6$	0.30	2.43×10^{-3}	2.59×10^2
4.	$\text{Ge}_{40}\text{Te}_{50}\text{Sb}_8$	0.22	5.96×10^{-3}	2.89×10^1

The values of σ_0 and ΔE were calculated using the slopes of curves in Fig. 2 and Eq.(1). The results of these calculations are given in Table that also contains the values of σ_{dc} at room temperature (300 K). Figs 3 to 4 plot the values of σ_{dc} (at 300 K) and ΔE as a function of the Sb concentration. It is clear from these figures that σ_{dc} increases by several orders of magnitude, and ΔE decreases with increasing the Sb concentration. The sharp increase in conductivity and decrease in ΔE in the case of annealed samples with $x \geq 4$ obviously indicates their partial crystallization.

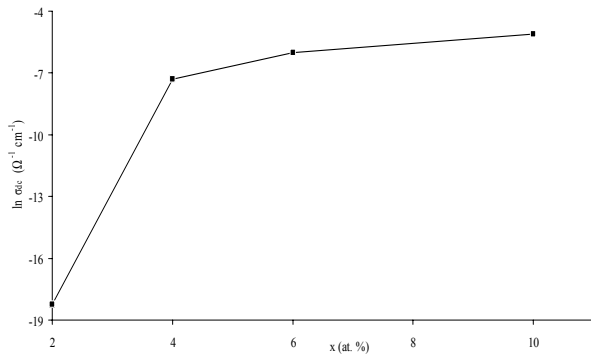


Fig. 3. Composition dependence of dark conductivity at 300 K in $\text{Ge}_{40}\text{Te}_{60-x}\text{Sb}_x$ thin films.

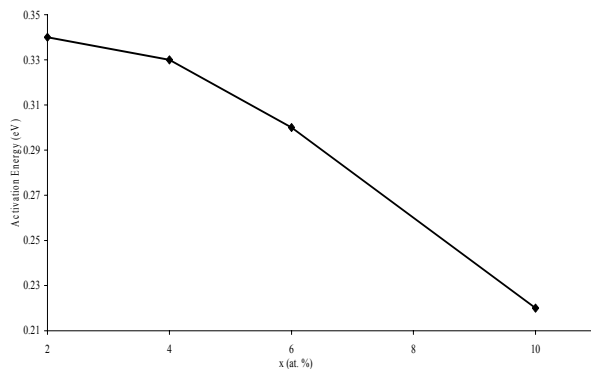


Fig. 4. Composition dependence of activation energy at 300 K in $\text{Ge}_{40}\text{Te}_{60-x}\text{Sb}_x$ thin films.

An increase in σ_{dc} with a decrease in ΔE may be associated with the decrease of the mobility gap with increasing the Sb concentration in the $\text{Ge}_{40}\text{Te}_{60-x}\text{Sb}_x$ glassy system. It may be assumed that the decrease in activation energy due to the addition of Sb may modify the energy band diagram of Ge-Te by creating new charged centers in the mobility gap. It may result in unpinning the Fermi energy level that in the undoped chalcogenides is located midway between the deep line levels of the charged centers.

When Sb is added to the Ge-Te system, it induces structural changes in the host network Ge-Te, which leads to a readjustment in the local environment. This might disturb the balance of characteristic charged defects in a chalcogenide semiconductor, which can change the electronic conduction. In such a situation, distribution and the density of localized states are modified, and even some new trap states can appear in the gap of semiconductor. So, we assume that the Fermi energy level is shifted after addition of Sb owing to changes in the energy spectrum of states in the mobility gap. The value of σ_0 also increases with the Sb concentration, which indicates that the density of localized states may be affected by Sb incorporation.

However, with this mechanism of structural transformations that result in creation of new charged centers in the mobility gap, the changes in conductivity parameters are, as a rule, not so essential.

4. Conclusions

Temperature dependence of dc conductivity has been measured in vacuum-evaporated thin films of $\text{Ge}_{40}\text{Te}_{60-x}\text{Sb}_x$ (where $x = 2, 4, 6$ and 10). It has been found that the dark conductivity is due to an activated process having the single activation energy in the used measuring range of temperatures. The values of ΔE , σ_{dc} and σ_0 have been calculated. The results of these calculation show that σ_{dc} and σ_0 increase while ΔE decreases with increasing the concentration of Sb in $\text{Ge}_{40}\text{Te}_{60-x}\text{Sb}_x$ amorphous and crystallized films. The high values of σ_{dc} in the samples with $x \geq 4$ are caused by structural transformations and by creation of crystalline inclusions in amorphous matrix when the samples are annealed.

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