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Electrical conduction and photoconduction in $Se_{80-x}Te_{20}Bi_x$ thin films

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Abstract

The dark conductivity and photoconductivity of $Se_{80-x}Te_{20}Bi_x$ ($0 \leqslant x \leqslant 1$) thin films have been studied. The values of dc activation energy, optical band gap and photoconduction activation energy are found to decrease with the addition of bismuth content. The optical energy gap has been found to be approximately equal to twice the dark thermal activation energy in all the compositions studied. The variation of photocurrent with illumination intensity indicates that the recombination mechanism is bimolecular.

1. Introduction

The chalcogenide materials are one of the most widely known families of amorphous semiconductors; they find vast applications in optical fibres, memory devices, reversible phase change optical recording, etc [1], and the study of these materials is becoming a great field of interest. These materials generally show p-type conduction, as evidenced by thermoelectric power measurements [2]. In chalcogenide materials the Fermi level is pinned near the middle of the gap due to the presence of large number of defect states ($\approx 10^{26}$ m^{-3}). The position of the Fermi level is insensitive to doping, as explained by Mott [3, 4]. The modification of the density of states by the presence of electrically active impurities is too small to shift the Fermi level, except perhaps at such high concentrations that the material is outside the glass-forming region. Selenium is selected because of its wide commercial applications. Its device applications like switching, memory, and xerography have made it attractive [5–8]. It also exhibits an interesting property of reversible phase transformation. This property makes it very useful in optical memory devices. But in the pure state it has disadvantages because of its short lifetime and low sensitivity. This problem can be overcome by alloying Se with some impurity atoms (Bi, Te, Ge, Ga, Sb, As, etc), which gives higher sensitivity, higher crystallization temperature and smaller ageing effects. Several workers have studied the effect of bismuth on the optical and electrical properties of chalcogenide materials [9–11]. However, not much work has been reported on the effect of bismuth on the photoconductivity of the

Se–Te matrix. In the present work, the effect of Bi addition on the dark and light conductivity in $Se_{80-x}Te_{20}Bi_x$ ($x = 0, 0.2, 0.5, 1.0$) is reported.

2. Experimental details

Glassy alloys of a-$Se_{80-x}Te_{20}Bi_x$ ($0 \leqslant x \leqslant 1$) were prepared by a conventional melt quenching technique. High-purity specimens (99.999% pure) were used for preparing the amorphous materials. The ampoule was kept inside the furnace and the temperature was raised up to 1123 K slowly (3–4 K min^{-1}). The ampoule was inverted at regular intervals of time to ensure homogeneous mixing of the constituents. The ampoule was then quenched in ice-cold water. The material was separated from the quartz ampoule by dissolving it in $HF + H_2O_2$ solution for approximately 48 h. The bulk alloy obtained was used to prepare thin films on well-cleaned Corning glass substrates by a thermal evaporation technique in a vacuum better than 10^{-5} mbar using a Hind high vacuum coating unit (model 12A4D). Talysurf (Taylor Hobson: model 2015) was used to measure thickness of the films. The thickness was found to be ~2300 Å for all samples. The amorphous nature was confirmed by the absence of peaks in the x-ray diffractograms of both the bulk and thin films. The optical transmission spectrum was recorded at room temperature using a UV–visible spectrophotometer (Shimadzu, Japan) in the wavelength interval of 300–1100 nm. The absorption coefficient, α, was calculated using the relation

$$\alpha = (1/t)^* \ln(100/T')$$

where t is the thickness of the films and T' is the percentage transmission. The optical band gap (E_g^{opt}) was obtained by taking the intercept on the energy axis in the $(\alpha h\nu)^{1/2}$ versus $(h\nu)$ plot. The conductivity of all the samples was measured in a vacuum of 10^{-5} mbar. Electrical contacts were made on the thin films using silver paint electrodes in a coplanar geometry (length 0.9 cm and gap between electrodes 0.3 cm) for all the samples. During photoconductivity studies the electrodes were well covered using aluminium foil, so that photo-diffusion did not take place. The sample was mounted inside a metallic cryostat with a transparent window. For photoconductivity measurements, the samples were illuminated using a tungsten halogen lamp (Halonix, India) of 500 W. Infrared filters were used to avoid the heating of the samples. The intensity of light was measured with a digital lux meter (LX-101, Taiwan). The photocurrent was measured using a digital picoammeter (DPM-111 Scientific Equipments, Roorkee).

3. Results and discussions

3.1. Temperature-dependent dark conductivity and optical band gap studies

The dark conductivity of the $Se_{80-x}Te_{20}Bi_x$ ($0 \leqslant x \leqslant 1$) samples, measured as a function of temperature, is shown in figure 1. The conductivity of the samples increases with increase in temperature, as observed from the figure. The dc conductivity can be expressed by the relation

$$\sigma = \sigma_0 \exp[\Delta E_d/kT]$$

where σ_0 is the pre-exponential factor, ΔE_d is the dc activation energy and is calculated from the slope of σ and $1000/T$ plots, k is the Boltzmann constant and T is the absolute temperature. Table 1 shows the variation of ΔE_d with bismuth concentration. It is seen from the table that the activation energy decreases with increase in bismuth content. Increase in dark conductivity and decrease in activation energy as seen from the figure 1 and table 1 respectively are found to be associated with the shift in Fermi level in impurity-doped chalcogenide glasses [9, 12–15]. Figure 2 shows a plot of $(\alpha h\nu)^{1/2}$ versus $(h\nu)$ for different bismuth concentrations. The

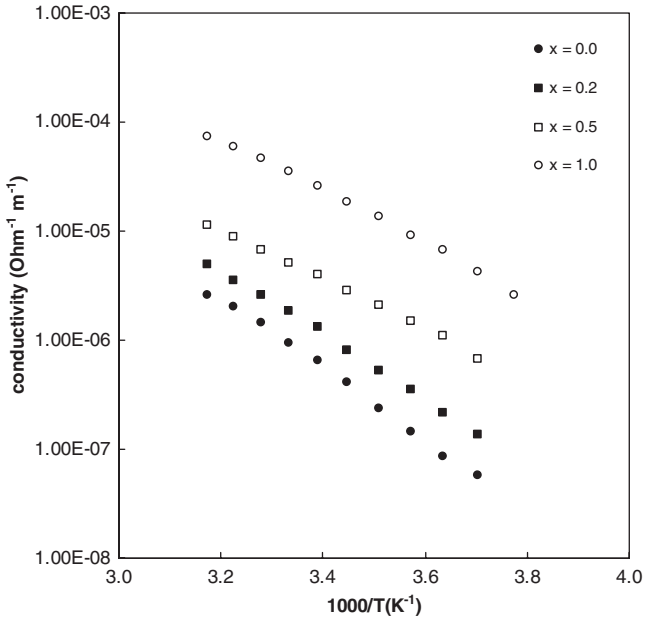

Figure 1. Variation of dark conductivity with temperature in $Se_{80-x}Te_{20}Bi_x$ ($x = 0, 0.2, 0.5, 1.0$) thin films.

Table 1. The variation of optical bandgap (E_g^{opt}) and conductivity activation energy in the dark (ΔE_d) and in the light (ΔE_{ph}) on bismuth content (x) in $Se_{80-x}Te_{20}Bi_x$ ($x = 0, 0.2, 0.5, 1.0$) thin films.

		Conductivity activation energy	
Composition x	Optical bandgap, E_g^{opt} (eV)	In the dark, ΔE_d (eV)	In the light, ΔE_{ph} (eV)
0.0	1.46	0.73	0.20
0.2	1.41	0.60	0.17
0.5	1.38	0.56	0.16
1.0	1.32	0.50	0.14

values of bandgap calculated from the above plot for different bismuth concentrations are given in table 1. From this table it can be seen that the optical bandgap decreases with bismuth concentration. Optical absorption depends upon both the short-range order in the amorphous state and the defects associated with it. A decrease in optical bandgap in our system may be due to the reduction in the amount of disorder in the system and an increase in the density of defect states [9]. It may be noted from the results that the band gap is approximately twice that of the dc activation energy. The variation of both ΔE_d and E_g^{opt} follows the same trend as that reported for antimony addition to the Se–Te system [16, 17].

3.2. Temperature- and intensity-dependent photoconductivity

The temperature dependence of steady state photoconductivity has been studied in the a-$Se_{80-x}Te_{20}Bi_x$ system in the temperature range 253–333 K. The temperature dependence of photoconductivity at 800 lx for different samples ($x = 0.0, 0.2, 0.5, 1.0$) is shown in figure 3.

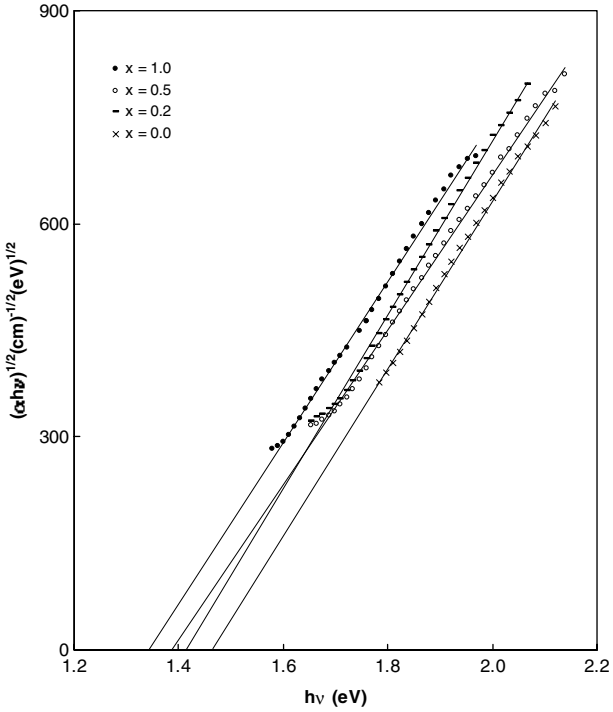

Figure 2. Plot showing the variation of $(\alpha h\nu)^{1/2}$ with $(h\nu)$ for $Se_{80-x}Te_{20}Bi_x$ $(x = 0, 0.2, 0.5, 1.0)$ thin films.

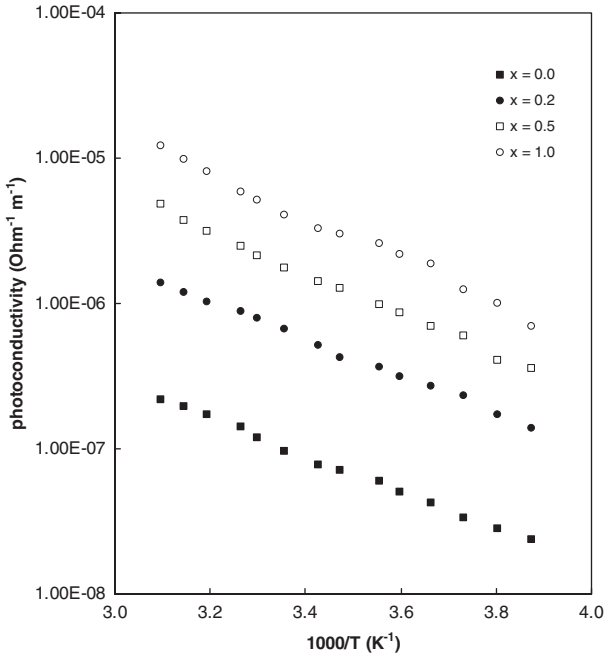

Figure 3. Variation of photoconductivity with temperature in $Se_{80-x}Te_{20}Bi_x$ $(x = 0, 0.2, 0.5, 1.0)$ thin films.

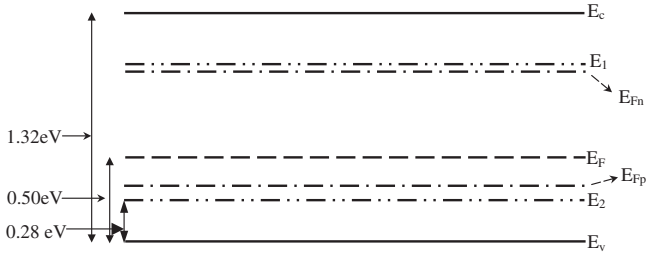

Figure 4. Energy level diagram for $Se_{80-x}Te_{20}Bi_x$ ($x = 1.0$) during illumination.

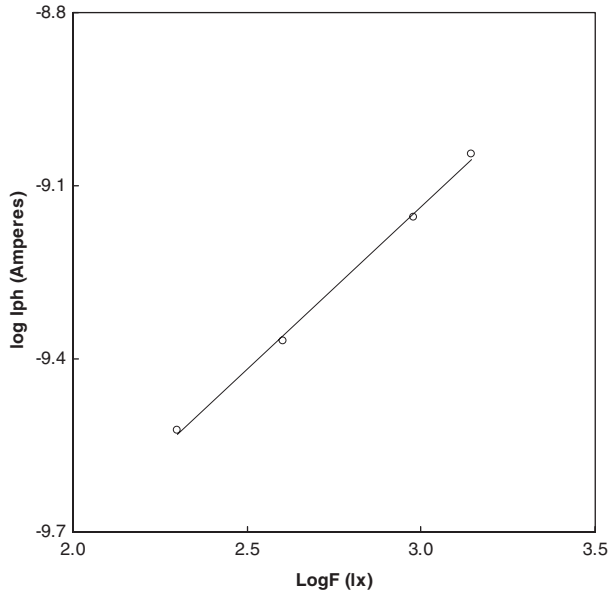

Figure 5. Variation of photocurrent with light intensity in $Se_{80-x}Te_{20}Bi_x$ ($x = 1.0$) thin films.

The variation of photoconductivity with temperature is similar to the variation of the dark conductivity. The values of the activation energy in the light (ΔE_{ph}) have been calculated from the slopes of photoconductivity and $1000/T$ plots and are given in table 1. It is clear from the above table that the activation energy in the light is less than the activation energy in the dark. The lower activation energy under illumination can be explained by assuming the presence of electron and hole traps in the bandgap. In the presence of light, the Fermi level splits into electron and hole quasi-Fermi levels and move towards the conduction band for electrons (E_{Fn}) and towards the valence band for holes (E_{Fp}). The position of the quasi-Fermi level depends on the light intensity [18, 19]. Simmons and Taylor [20] have shown in their theoretical model for photoconductivity that for moderate and intermediate level illumination, the photoconduction is mainly due to holes, and the hole concentration in the light, p, is proportional to $\exp[-(E_2 - E_v)/2kT]$, where E_2 is the energy level of the hole traps near the valence band. They also assumed electron traps at E_1 below the conduction band such that $(E_c - E_1) > (E_2 - E_v)$. A model constructed on similar lines for the present $Se_{79}Te_{20}Bi_1$ system is shown in figure 4. The photocurrent dependence on temperature is the same as that

of the hole concentration dependence on temperature. It can be seen from the above relation that the photocurrent will be activated with activation energy equal to $(E_2 - E_v)/2$.

The variation of photocurrent with light intensity for samples with $x = 1.0$ is shown in figure 5. This variation of photocurrent with light intensity obeys the power law

$$I_{ph} = F^{\gamma}$$

where I_{ph} is the photocurrent (total current minus dark current), F is the intensity of light and γ is the exponent that characterizes the recombination mechanism. In the present case the value of γ calculated from the slope of figure 5 is 0.5, which shows that the bimolecular recombination process is the dominant mechanism [18, 21] that controls the photoconductivity in $Se_{80-x}Te_{20}Bi_x$. In these materials the recombination is between an electron trapped at D^+ and a hole at D^-, which is nothing but the exchange of an electron between two D^0 centres. A value of $\gamma = 0.5$ has been predicted by Simmons and Taylor [20] for amorphous semiconductors for moderate light intensities. This value is observed for all the samples.

4. Conclusion

Thin films of $Se_{80-x}Te_{20}Bi_x$ were grown by a thermal evaporation process. The activation energy and optical energy gap decrease with addition of bismuth. The photocurrent is found to be square root dependent on the illumination, which indicates bimolecular recombination.

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