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PHOTOELECTRICAL PROPERTIES OF SEMICONDUCTING AMORPHOUS Se-Te-Sb THIN FILMS

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The electrical properties of $Se_{70}Te_{30-x}Sb_x$ (x = 0, 2, 4, 6, 8) amorphous thin films prepared by thermal evaporation technique have been studied. The dark conductivity (σ_d), charge carrier concentration (n_σ) and photoconductivity (σ_{ph}) increases as the concentration of Sb additive increases upto x = 6 at. % in a-$Se_{70}Te_{30-x}Sb_x$ thin films. The activation energy (ΔE) and photosensitivity (σ_{ph}/σ_d) decreases sharply after Sb incorporation. As the Sb concentration is further increased (when x=8 at. %) a reverse in the trend has been observed for all these parameters. Intensity dependence of photoconductivity has also been studied at 303 K and follows a power law as $\sigma_{ph} \propto F^\gamma$, where γ lies between 0.5 and 1. The differential life time (τ_d) is determined from the decay of photocurrent with time. The differential life time increases as the Sb concentration increases upto x = 6 at. %. The results are explained on the basis of increase in the density of localized states present in the mobility gap and in terms of the electron affinity values of the various constituents of Se-Te-Sb thin films.

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1. Introduction

Chalcogenide glasses are a very important class of semiconductor materials because of their technological applications in xerography, switching and memory devices and theses glasses show a unique set of photo induced effects which makes them very interesting for optical fabrication and performance [1-2]. Besides, these glasses have attracted much attention for the development of active and passive infrared devices. These glasses are low-phonon energy materials and are generally transparent from the visible to infrared region. Chalcogenide glasses are normally p-type semiconductors owing to the fact that the number of electrons excited above the conduction band mobility edge is smaller than the number of holes excited below the valence band mobility edge [3-4]. These systems also contain positively and negatively charged defect states, known as valence alternation pairs (VAPs) [5-6]. The common feature of this class of glasses is the presence of localized states in the mobility gap due to the absence of long-range order as well as various inherent defects [7-8]. In pure state Se has several disadvantages because of its short life time and low sensitivity. To overcome these difficulties, certain additives are used, e.g. Te, Sb, In, Ge, etc and binary and ternary alloys are formed. Recently, it has been pointed out that Se-Te alloys have more advantages than a-Se from the technological point of view due to their greater hardness, higher crystallization temperature, higher photosensitivity and smaller ageing effects [9]. The electrical properties of amorphous Se-based chalcogenide glasses exhibit a large Fermi level shift and large photovoltaic effects.

These semiconductor chalcogenide glasses also exhibit many interesting properties, such as photodarkening, photodoping, photocrystallization and photoconductivity. The photoconductivity of these glasses is helpful in understanding the phenomenon of recombination kinetics, and the nature and distribution of localized states in the forbidden energy gap. In

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chalcogenide glasses, the localized states in the mobility gap are the D^+ and D^- states [10]. Chalcogenide glasses are sensitive to the absorption of electromagnetic radiation and show a variety of photo-induced effects as a result of illumination [11].

Transient photoconductivity measurements in chalcogenide glasses are important as the photocurrent rise and decay with time depends upon the presence of traps in the mobility gap of these materials. These traps originate from the defect states present in these materials. Therefore, such measurements made at different temperatures, intensities and illumination times give important information about the defect states [12].

In the present work, the photoconductive properties of thin films of the $Se_{70}Te_{30-x}Sb_x$ system have been studied in detail. Temperature-dependent dark conductivity, photoconductivity and intensity dependent steady-state photoconductivity have been measured for five samples with different compositions. The decay of photocurrent has also been measured at room temperature for all compositions.

2. Experimental procedure

Glassy alloys of $Se_{70}Te_{30-x}Sb_x$ (x = 0, 2, 4, 6, 8) were prepared by melt-quench technique. High purity 99.999% Bi, Sb and Te granules were weighted according to the formula of $Se_{70}Te_{30-x}Sb_x$ (x = 0, 2, 4, 6, 8). The powder mixture was loaded into quartz ampoule and sealed under vacuum at 10^{-4} Pa. The sealed quartz ampoule was loaded in a furnace and heated to 950°C at a rate of 3-4 ^{0}C/minute for 18 hours to ensure the composition homogeneity and quenched in liquid nitrogen. The ingots were crushed, separated, grounded and characterized. The glassy nature of alloys was checked by X-ray diffraction technique.

The thin films were synthesized by thermal evaporation technique under high vacuum conditions (~ 10^{-4} Pa) using a small piece of bulk alloy as a source material and glass as a substrate. For electrical measurements vacuum – evaporated indium electrodes were used. A coplanar structure (length ~ 1.8 cm and separation between electrodes ~ 0.7 mm) was used for present measurements.

A three terminal sample holder in which light could be shown through a transparent window has been used for the measurement of photoconductivity of thin films. A copper-constantan thermocouple has been inserted inside the sample holder and kept close to the sample to measure the correct temperature. A vacuum of the order of 10^{-4} to 10^{-5} Torr was achieved inside the sample holder using vacuum pump. The light source for these measurements was a 200 W tungsten lamp. Light intensity is measured by a digital Luxmeter (Testron, model TES-1332). The photocurrent (I_{ph}) is obtained after subtracting dark current (I_d) from the current measured in the presence of light. Before measurement, the films were first annealed below their glass transition temperature for two hours in a vacuum ~ 10^{-4} Torr for different samples and the dark conductivity, photoconductivity and transient photoconductivity measurements are carried out. The present measurements were made by applying only 10 V across the films using dc power supply (CROWN DC-regulated Power Supply 0-30V/2A) and the resulting current was measured with digital piccoammeter (Digital Piccoammeter DPM-111, Scientific equipment Roorkee).

3. Result and discussion

Fig. 1 shows the temperature dependence of dark conductivity (σ_d) for a $Se_{70}Te_{30-x}Sb_x$ (x = 0, 2, 4, 6 and 8) thin films. The $\ln\sigma_d$ verses 1000/T curves are straight lines in the investigated temperature range 253K to 343K. This indicates that the conduction in these glasses is through an activated process having single activation energy in the investigated temperature range. The σ_d can, therefore, be expressed by the usual relation

$$\sigma_d = \sigma_0 \exp(-\Delta E/k_B T) \qquad (1)$$

where σ_0 is the pre-exponential factor, ΔE is the activation energy for conduction and k_B is the Boltzmann constant. The values of σ_d at 303K and ΔE_d have been calculated from the curves plotted in Fig. 1. The value of σ_d increases from $5.38x10^{-8}$ $(\Omega\text{-cm})^{-1}$ to $1.13x10^{-5}$ $(\Omega\text{-cm})^{-1}$ as the Sb concentration increases from x = 0 to x = 6 followed by a decrease to $6.45x10^{-6}$ $(\Omega\text{-cm})^{-1}$ on increasing the Sb concentration to x = 8 at 303K. Correspondingly, the value of ΔE_d decreases from 0.48 eV to 0.38 eV when x increases from 0 to 6 and then ΔE increases to 0.4 eV as the Sb composition further increases.

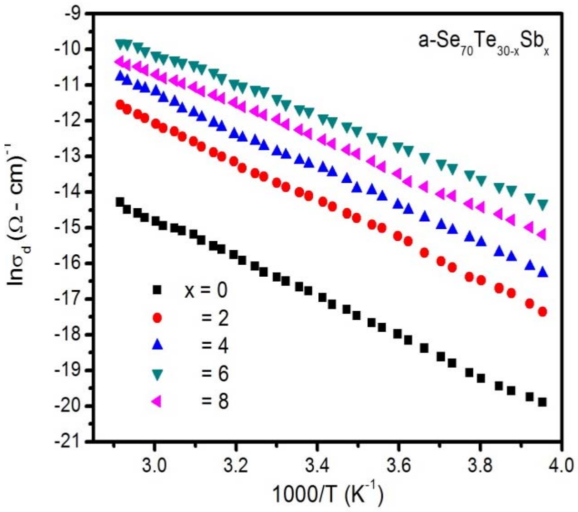

Fig. 1. Variation of σ_d with temperature for a-$Se_{70}Te_{30-x}Sb_x$ thin films.

Fig. 2 shows the temperature dependence of steady state photoconductivity (σ_{ph}) at a particular intensity (1043 lux) for all compositions. The value of σ_{ph} increases with temperature in the measured temperature range (253K to 343K). The activation energy of photoconduction is smaller than the dark conduction. The values of σ_{ph} have been calculated at 303 K and at intensity 1043 lux from the plots of Fig. 2 and given in Table 1. The values of σ_d and σ_{ph} follow the same pattern on Sb incorporation in the $Se_{70}Te_{30}$ as shown in Table 1.

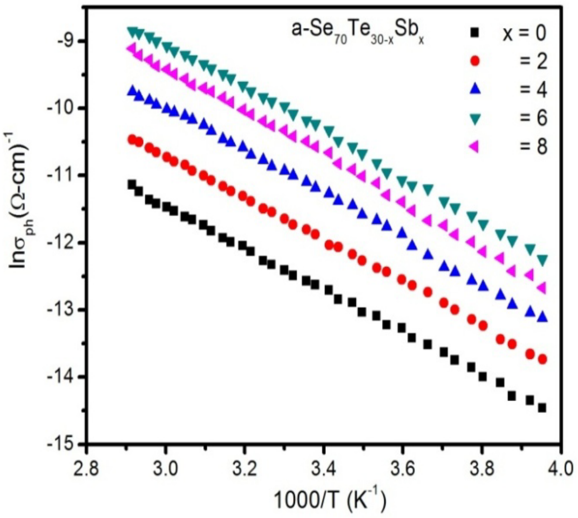

Fig. 2. Variation of σ_{ph} with temperature for a-$Se_{70}Te_{30-x}Sb_x$ thin films.

The charge carrier concentration (n_σ) for different samples can be calculated using the equation [13-14]

$$n_\sigma = 2(2\pi m k_B T/h^2)^{3/2}\exp(-\Delta E_d/k_B T) \qquad (2)$$

where 'm' is the mass of the charge carrier and 'k_B' is the Boltzmann constant. The calculated values of n_σ are given in the Table 1. It is evident from Table 1, that the values of n_σ increases with the increase of Sb concentration with a maximum at when x = 6 and then it again decreases on increase in the concentration of Sb additive to x = 8 at. %.

An important and useful parameter in the photoconductivity measurements is the photosensitivity (σ_{ph}/σ_d), which decides the use of that material in the photoconductive devices. From the measured values of σ_{ph} and σ_d, we have therefore calculated the σ_{ph}/σ_d for all the samples at a particular intensity (1043 Lux) and at temperature 303 K. The σ_{ph}/σ_d decreases quite appreciably after the incorporation of Sb additive and having a minimum at x = 6. As the concentration of Sb is further increased, the value of σ_{ph}/σ_d increases.

An increase in dark photoconductivity with a corresponding decrease in activation energy is generally found to be associated with the shift of Fermi level in impurity doped chalcogenide glasses [15]. On the other hand, an increase in dark conductivity after impurity doping has also been explained in terms of the increased hopping conduction in impurity induced states [16]. The dark activation energy (ΔE_d) alone does not provide any indication as to whether conduction takes place in extended states above the mobility edge or by hopping in the localized states. So, the increase in σ_d after Sb incorporation can be interpreted in terms of either of the two above mentioned processes. According to the second interpretation, the density of localized states should increase which should lower the photosensitivity at a particular temperature and intensity, but in the first interpretation, the density of states should not increase. Since the photosensitivity (σ_{ph}/σ_d) decreases sharply after the Sb incorporation indicating an increase in density of localized state, therefore, the first interpretation seems unlikely in the present case.

The photosensitivity (σ_{ph}/σ_d) depends on the lifetime of the excess charge carriers which in turn depends on the density of localized states in a particular material. The higher the density of states, the lower will be lifetime, as these defect states may act as recombination centers in presence of light. This is found to be due to the formation of intimate valence alternation pairs (IVAPs) under illumination. The defects are converted by bond switching reactions to random pairs of charged defects, known as light induce metastable defects (LIMDs) [17-19]. Such an increase in the density of defect states after incorporation of Sb additive may be understood in terms of the electron affinity of Sb [20]. When Te is added to Se, some of the Te atoms may not be incorporated in chains and act as ionized impurities (electron affinity of Te (1.97 eV) is lower than that of Se (2.02 eV)). The electron affinity of Sb (1.07 eV) is much lower than that of both Se and Te and addition of Sb will induce more and more positively charged localized states and hence defect states increases. So increase in defect state density after incorporating Sb additive in various concentrations to binary $Se_{70}Te_{30}$ alloy may be understood in terms of lower electron affinity of Sb as compared to Se and Te. When concentration of Sb is further increase, addition of Sb may satisfy the bonding states of Se-Te [21] and density of localized states decreases which leads to decrease in conductivity of $Se_{70}Te_{22}Sb_8$ as compared to $Se_{70}Te_{24}Sb_6$.

Table 1. Variation of electrical parameters at different Sb concentration in a- $Se_{70}Te_{30-x}Sb_x$ thin films

x	σ_d ($\Omega^{-1}cm^{-1}$)	σ_{ph} ($\Omega^{-1}cm^{-1}$)	ΔE_d (eV)	σ_{ph}/σ_d	n_σ(cm^{-3})	τ_d (sec)
0	$5.38x10^{-8}$	$5.65x10^{-6}$	0.48	105	$2.67x10^{11}$	19
2	$1.08x10^{-6}$	$8.76x10^{-6}$	0.44	8.11	$1.23x10^{12}$	42
4	$2.58x10^{-6}$	$1.79x10^{-5}$	0.41	6.94	$3.88x10^{12}$	57
6	$1.13x10^{-5}$	$4.65x10^{-5}$	0.38	4.12	$1.22x10^{13}$	98
8	$6.45x10^{-6}$	$3.25x10^{-5}$	0.40	5.04	$5.71x10^{12}$	85

Intensity dependence of photoconductivity has been studied at 303 K to investigate the nature of the recombination process in $Se_{70}Te_{30-x}Sb_x$ thin films. The plots of ln σ_{ph} and ln F are straight for all compositions as shown in Fig. 3, indicating that σ_{ph} follows a power law with F, i.e. $\sigma_{ph} \propto F^{\gamma}$, where γ is an exponent which characterizes the recombination mechanism. For $\gamma = 0.5$, recombination is bimolecular in nature, whereas for $\gamma = 1$, recombination is monomolecular. In our case, γ varies from 0.53 to 0.56 for all compositions, which is close to 0.5. This confirms the dominance of bimolecular recombination mechanism and which may be discussed on the basis of Street and Mott model [3]. These authors suggest that chalcogenide glasses contains higher number of frozen-in structural defects at chalcogen atom sites, leaving broken or dangling bonds on the neighboring atoms which could be the source of localized defect states. The dangling bond states are either unoccupied or occupied by pairs of electrons so that paired D^+ and D^- defects are formed, which have lower energy than the neutral singly occupied sites, according to the relation:

$$2D^0 = D^+ + D^-$$

The energy level of the neutral unpaired dangling bond D^0 lies intermediate between that of D^+ and D^-. The D^+ and D^- centres can act as discrete traps for electrons and holes generated by light excitation. This capture of photoexicted charge carriers leads to an excess concentration of D^0 centres. These trapped carriers can be released to the valance or conduction band enhancing the conductivity.

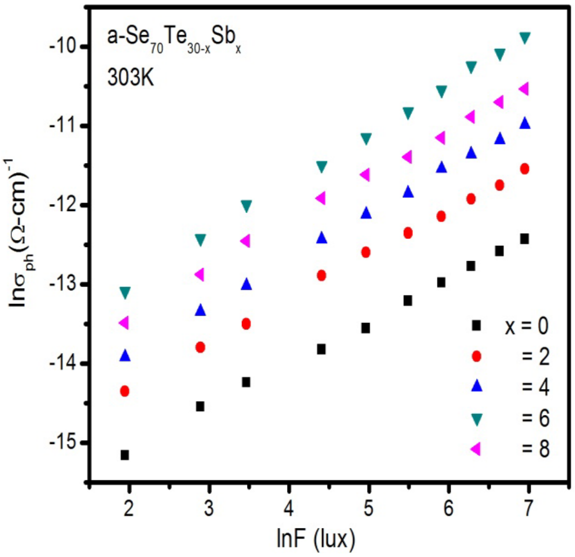

Fig. 3. Intensity dependence of photoconductivity for different a- $Se_{70}Te_{30-x}Sb_x$ glassy alloy thin films.

Transient photoconductivity measurements were conducted by exposing all samples to a light intensity of 1043 lux at 303 K and amorphous thin films of a-$Se_{70}Te_{30-x}Sb_x$ show slow decay of photocurrent (results not shown here). A persistent photocurrent (the asymptotic value of the current in the decay) is also measured for all samples. The persistent photocurrent was subtracted from the measured photocurrent and found that the decay of photocurrent is non exponential even after subtracting the persistent photocurrent. In discussing the non-exponential decay process we prefer to use the concept of differential lifetime as described by Fuhs and Meyer [22]. According to these researchers, the differential life time can be defined as follows:

$$\tau_d = -\left[\frac{1}{I_{ph}}\left[\frac{dI_{ph}}{dt}\right]\right]^{-1} \tag{3}$$

In the case of an exponential decay, the differential life time will be equal to the carrier lifetime. However, in the case of a non-exponential decay, τ_d will increase with time and only its value at t = 0 corresponds to the carrier lifetime. The values of τ_d are calculated at various times using slops of I_{ph} verses time curves. Fig. 4 shows a plot of the variation of τ_d with time at 303 K and 1043 lux intensity for x = 4 at. % sample. It is clear from the figure that τ_d increases with time. This confirms the non-exponential decay in the present case because for exponential decay τ_d should be constant with time. Other compositions also follow a similar behaviour in their variation of τ_d with time. To compare the value of τ_d for the different samples, at 303 K the value of τ_d at t = 50 s verses the Sb content is plotted in the insert of Fig. 4. The value of τ_d first increases as the concentration of Sb increases upto x = 6 at. % and then decreases from x = 6 at. % to x = 8 at. %.

The higher value of τ_d after the Sb incorporation, indicating a slower rate of decay of I_{ph} and hence an increased density of localized sates. One can therefore expect a higher density of localized states in the mobility gap of $Se_{70}Te_{30-x}Sb_x$.

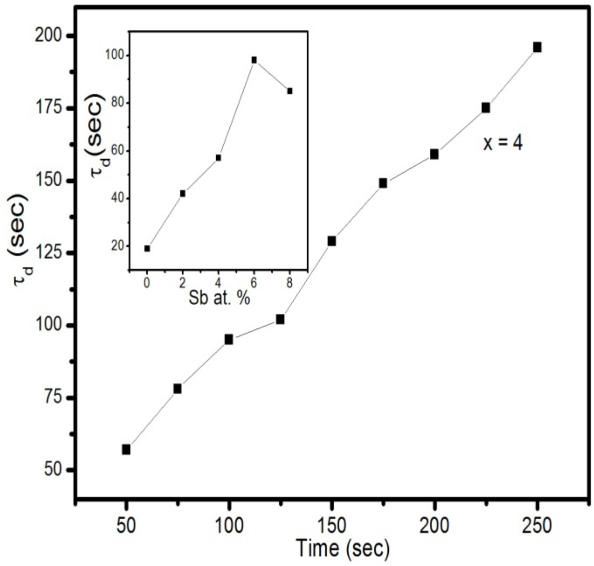

Fig. 4. Plot of τ_d verses time for $Se_{70}Te_{30-x}Sb_x$ thin films. Inset: Plot of τ_d verses Sb at. % for $Se_{70}Te_{30-x}Sb_x$ thin films.

4. Conclusion

The effect of Sb additive on the dark (σ_d) and photoconductivity (σ_{ph}) is studied in amorphous $Se_{70}Te_{30}$ binary alloy. The study of dark conductivity of $Se_{70}Te_{30-x}Sb_x$ thin films as a function of temperature (253-343 K) reveals that conduction is an activated process with single activation energy. The charge carrier concentration (n_σ) increases upto x = 6 at. % and these carriers act as localized states due to which dark conductivity (σ_d) and photoconductivity (σ_{ph}) increases after the addition of Sb. The increase in dark conductivity is also interpreted in terms of increased hopping conduction due to increase in the concentration of localized states. An increase in localized state density after incorporating Sb additive in various concentrations to binary $Se_{70}Te_{30}$ alloy may be understood in terms of lower electron affinity of Sb as compared to Se and Te. The photosensitivity (σ_{ph}/σ_d) decreases after the incorporation of Sb into the $Se_{70}Te_{30}$ system, due to increase in the number of localized states. Intensity dependence photoconductivity has also been studied showing the existence of bimolecular recombination in the thin films. The transient photoconductivity measurements follow the non-exponential decay (for all samples) as differential life time (τ_d) increases with time. The differential life time also increases with increase of Sb content upto x = 6 at. % indicating increase in density of localized states. When concentration of Sb is increased further a decrease in dark conductivity, photoconductivity, carrier concentration and an increase in dark activation energy, photosensitivity can be understood in term of structural changes because addition of Sb may satisfy the bonding states of Se-Te due to which density of localized states decreases.

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