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TEMPERATURE AND COMPOSITION DEPENDENCE OF PHOTOCONDUCTIVITY IN AMORPHOUS $Se_{80-x}Te_{20}Cd_x$ THIN FILMS*

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The present paper reports the composition dependence of steady state and transient photoconductivity measurements in vacuum evaporated thin films of amorphous $Se_{80-x}Te_{20}Cd_x$ (x =0, 5, 10 and 15) at different temperatures and intensities. Temperature dependence of conductivity in dark as well as in presence of light shows that conduction is through a thermally activated process in both the cases. The activation energy is found to decrease with the increase in light intensity. This indicates the shift of Fermi level with intensity. The Photosensitivity (σ_{ph}/σ_d) decreases with the increase of Cd concentration. This is explained in terms of the increase in the density of defect states with the increase of Cd in a-$Se_{80-x}Te_{20}Cd_x$ glassy system. It has been observed that the rise of the photocurrent shows an anomalous behavior in case of $Se_{80}Te_{20}$ binary glassy alloy only which could not be observed in any ternary compositions. Transient photoconductivity measurements at different temperatures indicate that the decay of photoconductivity is quite slow which is found to be non-exponential in the present case indicating the presence of continuous distribution of defect states in the aforesaid glassy alloys.

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1. Introduction

Amorphous semiconductors, in particular Se-Te alloys have gained much importance among chalcogenide glasses because of their higher photosensitivity, greater hardness, higher crystallization temperature and smaller aging effects as compared to pure Se glass. Because of these advantages, these alloys are now days preferred in xerography [1]. The semi-conducting compounds belonging to the cadmium chalcogenide family such as $CdSe_xTe_{1-x}$ can be advantageously used for various technical applications in particular for the conversion in photovoltaic or photo-electrochemical devices. This material with its near-ideal band gap and a high optical absorbance is a promising material for low-cost terrestrial applications [2-5]. Attempts have been made to produce stable glasses which have good photosensitive properties and can be doped n or p type. The effect of incorporation of third element in binary chalcogenide glassy alloys has always been an interesting problem in getting relatively stable glassy alloys as well as to change the conduction from p to n as most of these glasses show p type conduction only. In Ge-Se and Se-In systems, some metallic additives have been found [6-11] to change conduction from p type to n type and hence these binary systems are of great importance.

Though the electrical and optical properties of these glasses have been studied by various workers the photo-conducting properties of these glasses have not been studied in detail. Since the photoconductivity kinetics of amorphous semiconductors are to a great extent determined by the process of trapping of non-equilibrium charge carriers on localized centers of various depths, such studies are important to understand the energy distribution of the traps. From application point of view also photoconductive properties are important.

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The present paper reports the steady state photoconductivity measurements in amorphous thin films of $Se_{80-x}Te_{20}Cd_x$ (x =0, 5, 10 and 15) prepared by vacuum evaporation technique. Temperature dependence of steady state photoconductivity is studied at different light intensities. Intensity dependence of photoconductivity is studied at different fixed temperatures. Composition dependence of various photoconductive parameters is also discussed. 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

Glassy alloys of $Se_{80-x}Te_{20}Cd_x$ (x =0, 5, 10 and 15) are prepared by quenching technique. High purity (99.999 %) materials are weighed according to their atomic percentages and are sealed in quartz ampoules (length ~ 5 cm and internal dia ~ 8 mm) with a vacuum ~ 10^{-5} Torr. The ampoules containing the constituent materials are heated to 1000°C and held at that temperature for 10 - 12 hours. The temperature of the furnace is raised slowly at a rate of 3 - 4 °C/min. During heating, all the ampoules are constantly rocked, by rotating a ceramic rod to which the ampoules are tucked away in the furnace. This is done to obtain homogenous glassy alloys.

After rocking for about 10 hours, the obtained melts are cooled rapidly by removing the ampoules from the furnace and dropping to ice-cooled water. The quenched samples of $Se_{80-x}Te_{20}Cd_x$ are taken out by breaking the quartz ampoules. The amorphous nature of samples was confirmed by the absence of any sharp peak in the X-ray diffraction pattern. Compositional analysis was performed using electron probe micro- analysis (EPMA) technique.

Thin films of these glasses are prepared by vacuum evaporation technique keeping glass substrates at room temperature. Vacuum evaporated indium electrodes at bottom are used for the electrical contact. The thickness of the films is ~ 500 nm. The co-planar structure (length ~ 1.4 cm and electrode separation ~ 0.5 mm) are used for the present measurements. A vacuum ~ 10^{-2} Torr is maintained in the entire temperature range (300K to 340K).

Before measuring the d. c. conductivity, the films are first annealed at 340K for one hour in a vacuum ~ 10^{-2} Torr. I-V characteristics are found to be linear and symmetric up to 100 V. The present measurements are, however, made by applying a voltage of 10 V across the films so that the resulting current comes in the measuring range of the instrument. The resulting current is measured by a digital electrometer (Keithley 6517 A). The heating rate is kept quite small (0.5 K/min) for these measurements so that the films could follow the temperature change with time properly.

The dark and photo-conductivity of the amorphous films were studied by mounting them in a specially designed metallic sample holder in which illumination could be achieved through a transparent window. The light source used for these measurements was a 200 W tungsten lamp. Light intensity was measured by a digital lux meter(Testron, model LX-101). The photocurrent (I_{ph}) was obtained after subtracting the dark current (I_d) from the current measured in the presence of light.

3. Results and discussion

3.1 Temperature and composition dependence of dark conductivity:

Fig. 1 shows the temperature dependence of dark conductivity (σ_d) for pure and Cd-doped $Se_{80}Te_{20}$ binary alloys. It is clear from this figure that ln σ_d vs 1000/T curves are straight lines, indicating that the conduction in these glasses is through an activated process having a single activation energy in the temperature range 300K to 340K. The d. c. conductivity (σ_d) can, therefore, be expressed by the usual relationship

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

Where ΔE is called the activation energy for d. c. conduction, σ_0 is called the pre-exponential factor and k is Boltzmann's constant.

The values of ΔE were calculated for various samples using the slopes of the curves of Fig. 1. These values are listed in Table 1. The values of σ_d at room temperature (300 K) are also given in Table 1. Figs. 2-3 plot the values of σ_{dc} (at 300 K) and ΔE as a function of the Cd concentration. It is clear from these figures that σ_{dc} increases and ΔE decreases with increasing Cd concentration.

Table -1: Electrical Parameters in a- $Se_{80-x}Te_{20}Cd_x$ Thin Films

Glassy Alloys	σ_d (Ω^{-1} cm^{-1})	ΔE (eV)	σ_{ph} (Ω^{-1} cm^{-1})	σ_{ph} / σ_d
$Se_{80}Te_{20}$	2.50 X 10^{-9}	0.44	1.19 X 10^{-7}	47.7
$Se_{75}Te_{20}Cd_5$	2.58 X 10^{-8}	0.43	2.08 X 10^{-7}	6.3
$Se_{70}Te_{20}Cd_{10}$	1.04 X 10^{-6}	0.42	2.46 X 10^{-6}	2.4
$Se_{65}Te_{20}Cd_{15}$	7.50 X 10^{-6}	0.40	1.70 X 10^{-5}	2.3

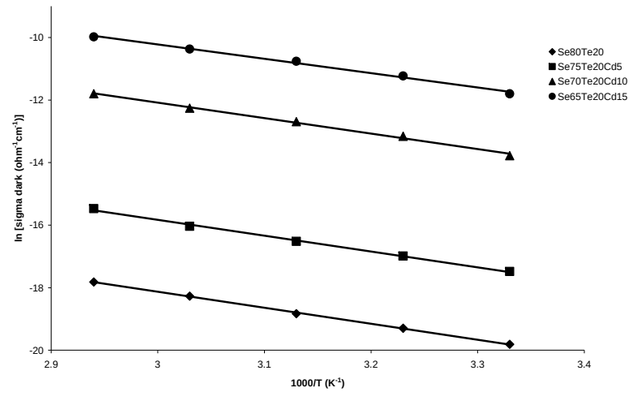

Fig.1 Temperature dependence of dark photoconductivity in $Se_{80-x}Te_{20}Cd_x$ thin films.

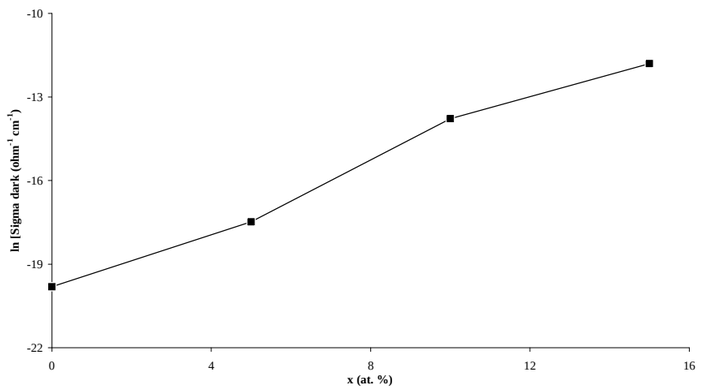

Fig.2 Composition dependence of dark conductivity at 300 K in $Se_{80-x}Te_{20}Cd_x$ thin films.

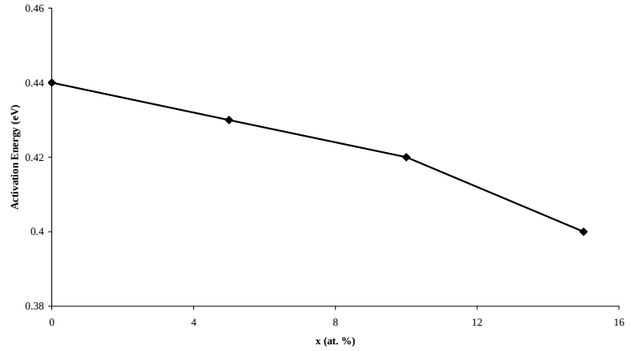

Fig.3 Composition dependence of Activation Energy in $Se_{80-x}Te_{20}Cd_x$ thin films.

An increase in σ_{dc} with a decrease in ΔE may be associated with the decrease of the mobility gap upon increasing Cd concentration in the $Se_{80-x}Te_{20}Cd_x$ glassy system. The value of σ_0 also decreases as the Cd concentration increases, which indicates that the density of localized states (DOS) may be affected by Cd incorporation.

3.2 Temperature and composition dependence of steady state photoconductivity:

The thermally activated dc conduction is a common feature of chalcogenide glasses due to their semi-conducting nature. In presence of light, Fermi level splits into quasi Fermi levels and move towards valence band for holes and towards conduction band for electrons. The position of these quasi Fermi levels depends on light intensity [12]. The activation energy therefore becomes smaller in presence of light as compared to in dark.

Fig. 4 shows the temperature dependence of photoconductivity (σ_{ph}) at a particular intensity (13000 lux). It is clear from this figure that σ_{ph} increases with increasing temperature in the temperature range of the present measurements. At a particular temperature σ_{ph} increases as the Cd concentration increases. This is shown in Fig.5. A similar variation was also observed in the dark conductivity (see Fig. 2.).

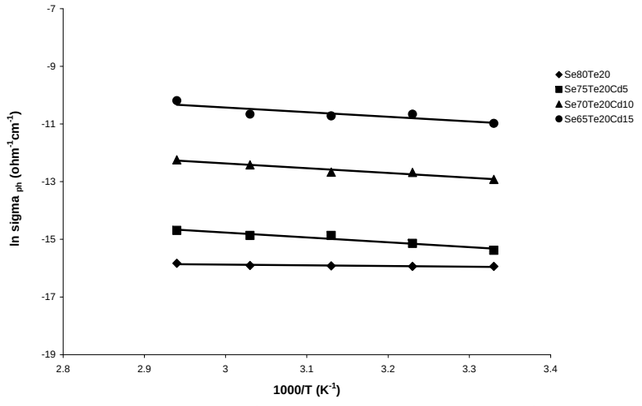

Fig.4 Temperature dependence of the photoconductivity in $Se_{80-x}Te_{20}Cd_x$ thin films.

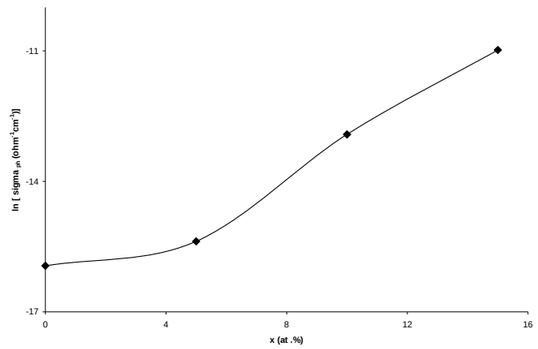

Fig.5 Composition dependence of photoconductivity at 300 K in $Se_{80-x}Te_{20}Cd_x$ thin films.

The important parameter in photoconductivity measurements is the photosensitivity (σ_{ph} / σ_d) at a particular temperature and intensity. The value of σ_{ph} / σ_d for a particular material determines the use of that material in photoconductive devices. We have therefore calculated σ_{ph} / σ_d at various temperatures for all of the samples at a particular intensity (13000 lux). The values of σ_{ph} / σ_d at room temperature are given in Table 1 and plotted in Fig. 6 as a function of x in $Se_{80-x}Te_{20}Cd_x$ glassy system. It is clear from this figure that an appreciable reduction in σ_{ph} / σ_d is observed at room temperature. Similar results were also obtained at other temperatures.

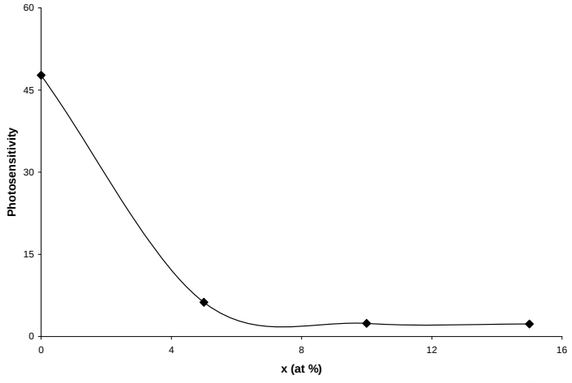

Fig.6 Composition dependence of photosensitivity at 300K in$Se_{80-x}Te_{20}Cd_x$ thin films.

3.3 Temperature and composition dependence of transient photoconductivity:

To measure the rise and decay of photoconductivity with time, thin film samples were mounted in the same metallic sample holder and light of desired wavelength was shown through a transparent window. After a certain time of exposure, the light was turned off and the decay of current was measured as a function of time. The initial dark value of current was subtracted to obtain photoconductivity during decay.

Figs. 7-10 show the results of the transient photoconductivity measurements in all the samples. It is clear from fig.7 that the rise of the photocurrent shows an anomalous behavior in case of $Se_{80}Te_{20}$ binary glassy alloy. The photocurrent passes through a maximum before attaining the steady state. The same kind of the results has also been reported previously by some other groups [13-14]. The results indicate that the anomalous behavior increases as the steady state

photocurrent increases at higher intensities or higher temperatures. This anomalous behavior could be understood in terms of non-equilibrium recombination as suggested by them. Our results are also in agreement with their results. However, the aforesaid behavior could not be observed by us in any Cd doped composition chosen in the present study. This could be due to enhance in the density of defect states with Cd concentration.

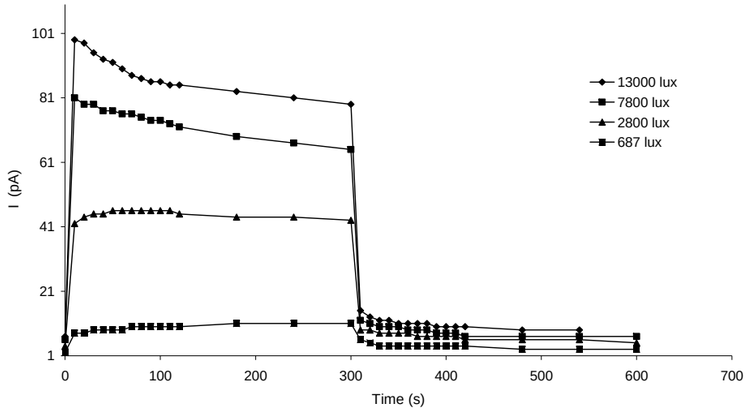

Fig.7 Time dependence of photocurrent at different intensities during rise and decay at 300 K in $Se_{80}Te_{20}$ thin film.

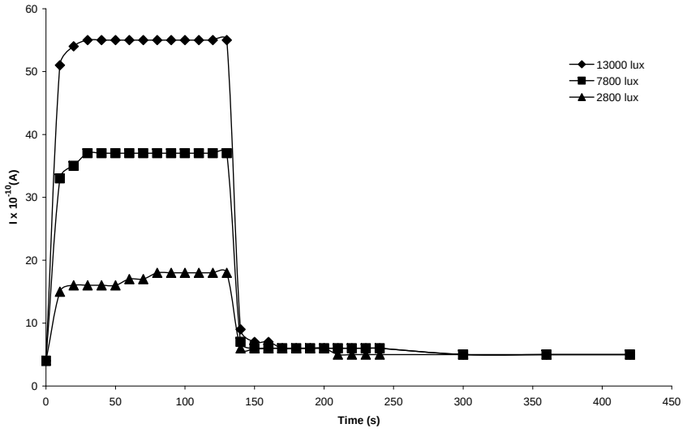

Fig.8 Time dependence of photocurrent at different intensities during rise and decay at 300K in $Se_{75}Te_{20}Cd_5$ thin film.

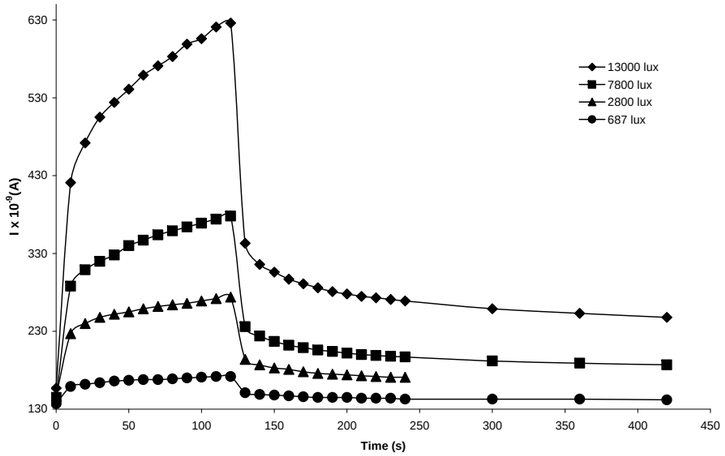

Fig.9 Time dependence of photocurrent at different intensities during rise and decay at 300K in $Se_{70}Te_{20}Cd_{10}$ thin film.

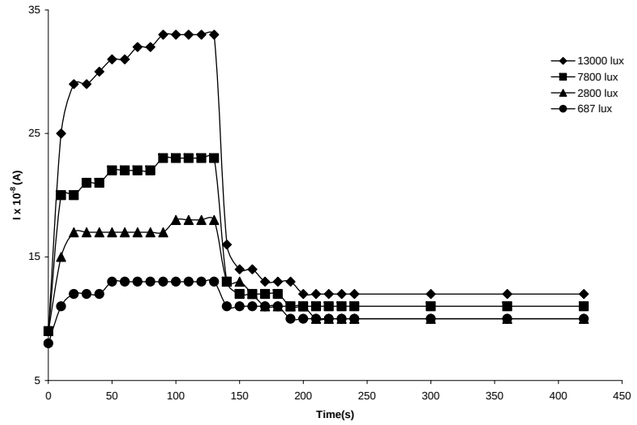

Fig.10 Time dependence of photocurrent at different intensities during rise and decay at 300K in $Se_{65}Te_{20}Cd_{15}$ thin film.

Figs. 8-10 show the results of the transient photoconductivity measurements in Cd doped samples. It is clear from these figures that the rise and decay of photocurrent is quite slow in all the samples. A persistent photocurrent (the asymptotic value of the current in the decay curve) was also observed in all the samples. This type of decay of photocurrent was observed [15-16] in various kinds of chalcogenide glasses. To simplify the analysis, we have subtracted the persistent photocurrent from the measured photocurrent and found that the decay of photocurrent is non-exponential even after subtracting the persistent photocurrent. The slower decay after incorporation of Cd in binary $Se_{80}Te_{20}$ glassy alloy shows that the density of defect states increases with increase in percentage of Cd in the present glassy system.

4. Conclusions

Temperature and composition dependence of conductivity is studied in dark and in presence of light in amorphous thin films of $Se_{80-x}Te_{20}Cd_x$ (x =0, 5, 10 and 15), prepared by

vacuum evaporation technique. The temperature range of measurement was 300 K to 340K. These measurements at different intensities indicate that photoconductivity is also thermally activated in the above temperature range in all the samples studied as in case of dark conductivity. The activation energy of photoconduction is found to decrease with the increase in the intensity which indicates the shift of the Fermi level on light shining due to splitting of Fermi level into quasi Fermi levels.

The present measurements also indicate that the photosensitivity (σ_{ph} / σ_d) decreases on increase in Cd concentration in this glassy system. This indicates that the density of defect states must be larger for samples containing higher and higher concentration of Cd.

Transient photoconductivity measurements have been also studied in all the glassy samples. It has been observed that the rise of the photocurrent shows an anomalous behavior in case of $Se_{80}Te_{20}$ binary glassy alloy only which could not be observed in any ternary compositions. This anomalous behavior could be understood in terms of non-equilibrium recombination Non-exponential decay with quite slow decay rate has been observed, in the other samples which indicates the increase of density of defect states with increasing content of Cd in the present glassy system.

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