Composition Dependence of Photoconductivity in Amorphous Thin Films of $Se_{.80-x}Te_{.20}Ge_x$

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Abstract

The present paper reports the dependence on composition of photoconductivity in vacuum evaporated thin films of amorphous $\operatorname{Se}_{.80-x}\operatorname{Te}_{.20}\operatorname{Ge}_x$ (x = .05, .10, .15 and .20). Temperature dependence of conductivity in dark as well as in presence of light show that conduction is through a thermally activated process in both cases. The activation energy is found to decrease with increase in light intensity, indicating shift of the Fermi level with intensity. A correlation between activation energy and the pre-exponential factor is observed in all the compositions, which could be fitted to the Meyer-Neldel rule.

Measurements on the dependence of photoconductivity on intensity show that photoconductivity increases with intensity as a power law, where the power is found to be between 0.5 and 1.0. The photosensitivity σ_{ph}/σ_d increases with Ge concentration. This is explained in terms of the decrease in the density of defect states with increase of Ge content in a-Se_{.80-x} Te_{.20}Ge_x. This is consistent with the conclusions reported in the literature by dielectric loss measurements.

Key Words: Chalcogenide Glasses, Photoconductivity, Amorphous Thin films

1. Introduction

For many years, it was believed that the physical properties of chalcogenide glasses can not be modified by foreign atoms. Doping could not be achieved with conventional impurities. Recently however, p to n transitions has been reported [1–6] in binary Ge–Se and In-Se chalcogenide alloys, when a third element is introduced in these glasses. Though the electrical and optical properties of these glasses have been studied by various workers [1–12], the photoconducting 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, investigations into their characterization and mechanism are important to understand the energy distribution of the traps.

In a study of dielectric relaxation in a-Se_{.80-x}Te_{.20}Ge_x [13] it is concluded that the density of defect states decreases on addition of Ge to the binary Se_{.80}Te_{.20} alloy. Since the photoconductivity depends on the density and the energy distribution of defect states, it is interesting to see the effect of adding Ge to the Se-Te system.

The present paper reports the steady state photoconductivity measurements in amorphous thin films of $\text{Se}_{.80-x}\text{Te}_{.20}\text{Ge}_x(x = .05, .10, .15 \text{ and } .20)$ prepared by vacuum evaporation technique. Temperature

dependence of steady state photoconductivity is studied at different light intensities. Photoconductivity as a function of intensity 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 $Se_{.80-x}Te_{.20}Ge_x$ are prepared by quenching technique. Component materials of high purity (99.999%) are weighed according to their atomic percentages and are sealed in quartz ampoules (of length ~5 cm and internal diameter ~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. To obtain homogenous glassy alloys, all the ampoules are constantly rocked during heating by rotating a ceramic rod to which the ampoules are connected in the furnace.

After rocking for about 10 hours, the ampoules are removed from the furnace and are cooled rapidly in ice-cooled water. The quenched samples of $\text{Se}_{.80-x}\text{Te}_{.20}\text{Ge}_x$ are removed by breaking the quartz ampoules.

Thin films of these glasses were prepared by vacuum evaporation technique, keeping glass substrates at room temperature. Vacuum evaporated indium electrodes below the deposited films are used for the electrical contact. The thickness of the films is ~ 500 nm. The co-planar structure (of length ~ 1.4 cm and electrode separation ~ 0.5 mm) is used for the present measurements. A vacuum of $\sim 10^{-2}$ Torr is maintained throughout the entire temperature range (305 K to 335 K).

Before measuring the dc conductivity, the films are first annealed at 340 K for one hour in a vacuum at $\sim 10^{-2}$ 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 50 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 picoammeter (Model DPM-111, Scientific Equipment Co., India). 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.

3. Results and Discussions

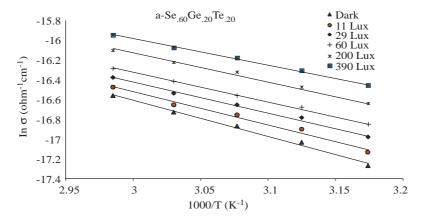
3.1. Temperature dependence of conductivity in dark and in the presence of light

The temperature dependence of the conductivity is studied in dark and in the presence of light at different intensities. For these measurements, thin film samples were mounted in a specially designed sample holder, which has a transparent window through which a sample can be illuminated. A vacuum of $\sim 10^{-2}$ Torr is maintained throughout the measurements. The temperature of the films is controlled by mounting a heater inside the sample holder, and measured by a calibrated copper-constant thermocouple mounted very near the films.

The source of light is a 200 W tungsten lamp. Interference filters are used to get the desired wavelength of 620 nm. The intensity of light is varied by changing the voltage across the lamp and measured by a luxmeter.

Figure 1 shows the temperature dependence of conductivity for amorphous thin films of a-Se_{.60}Te_{.20}Ge_{.20} between 305 K and 335 K. The conductivity σ in dark as well as in the presence of light varies exponentially with temperature, with the relationship ln σ vs. 1000/T appearing as straight lines (see Figure 1). Similar results were also obtained in the case of other glass compositions. From the present results it is evident that the conductivity, in the present glassy system, is thermally activated in dark as well in the presence of light following the well known relation in case of semiconductors:

$$\sigma = \sigma_{\circ} \exp[-\Delta E/kT],\tag{1}$$



where ΔE is called the activation energy and σ_{\circ} is called the pre-exponential factor.

Figure 1. Conductivity as a function of reciprocal temperature at different light intensities in a-Se_80-x Te₂₀Ge_x.

From the slope and the intercepts of Figure 1, the values of ΔE and σ_{\circ} have been calculated at different intensities and the values are listed in Table 1 for the case of Se_{.60}Te_{.20}Ge_{.20} amorphous thin films. Similar results were also obtained in other glassy compositions used in the present study. The thermally activated dc conduction is a common feature of chalcogenide glasses due to their semiconducting nature. In presence of light, the Fermi level splits into quasi Fermi levels and move towards the valence band for holes and towards the conduction band for electrons. The position of these quasi Fermi levels depends on light intensity [14]. The activation energy therefore becomes smaller in the presence of light as compared to in dark. Similar type of behavior has also been reported by Singh et al. [15] in the case of amorphous Se-Ge-In thin films.

Intensity (Lux)	$\Delta E \; (eV)$	$\sigma_{\circ} (\Omega^{-1} \mathrm{cm}^{-1})$
0	0.305	3.71×10^{-3}
11	0.280	1.64×10^{-3}
29	0.261	9.23×10^{-4}
60	0.250	6.76×10^{-4}
200	0.246	7.09×10^{-4}
390	0.226	3.92×10^{-4}

Table 1. Semiconduction parameters for a-Se_{.60}Te_{.20}Ge_{.20}.

Table 2. Electrical parameters in a-Se_{.80-x} Te_{.20}Ge_x thin films.

Glassy Alloy	$\sigma_d \; (\Omega^{-1} \; \mathrm{cm}^{-1})$	$\sigma_{ph} \; (\Omega^{-1} \; \mathrm{cm}^{-1})$	$\sigma_{ph} \ / \ \sigma_d$
$\mathrm{Se}_{.75}\mathrm{Te}_{.20}\mathrm{Ge}_{.05}$	2.46×10^{-6}	3.57×10^{-7}	0.14
$\mathrm{Se}_{.70}\mathrm{Te}_{.20}\mathrm{Ge}_{.10}$	1.43×10^{-6}	3.57×10^{-7}	0.25
$\mathrm{Se}_{.55}\mathrm{Te}_{.20}\mathrm{Ge}_{.15}$	2.86×10^{-8}	2.86×10^{-8}	1.00
$\mathrm{Se}_{.60}\mathrm{Te}_{.20}\mathrm{Ge}_{.20}$	4.29×10^{-9}	4.57×10^{-8}	10.67

It is interesting to note that the values of σ_{\circ} are not constant at different intensities in a particular glassy alloy. The values of σ_{\circ} decreases with increasing intensity similar to decrease in ΔE . This indicates that there is a correlation between σ_{\circ} and ΔE . Such a correlation is shown in Figure 2, where $\ln \sigma_{\circ}$ vs. ΔE is found to be a straight line, indicating that σ_{\circ} varies exponentially with ΔE the relation

$$\sigma_{\circ} = \sigma_{\circ\circ} \exp[\Delta E/kT_{\circ}]. \tag{2}$$

Slope of the ln σ_{∞} (ΔE) curve yields the values of $(kT_{\circ})^{-1} \sim 28 \text{ eV}^{-1}$ and $\sigma_{\circ} \sim 6.51 \times 10^{-7} \text{ ohm}^{-1} \cdot \text{cm}^{-1}$ for a-Se_{.60}Te_{.20}Ge_{.20} thin films. Similar results were found in other compositions also. It may be mentioned here that such type of correlation has been observed in many amorphous materials and is known as the Meyer-Neldel Rule [16–20].

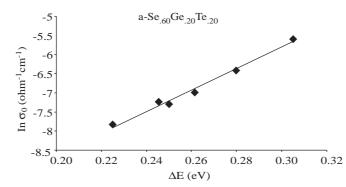


Figure 2. Plot of pre-exponential factor σ_{\circ} vs. activation energy ΔE in a-Se_{.60}Te_{.20}Ge_{.20}.

Photoconductivity σ_{ph} as a function of intensity F has been studied at different temperatures. The results for a-Se_{.60}Te_{.20}Ge_{.20} films are shown in Figure 3. Similar results were found in case of other glass compositions also [21–22]. It is clear from Figure 3 that, at all temperatures, curves of $\ln \sigma_{ph}$ vs. $\ln F$ are nearly straight lines, indicating that photoconductivity follows a power law with intensity ($\sigma_{ph} \propto F^{\gamma}$). The exponent γ is found to vary between 0.5 and 1.0 for all the glassy alloys studied here. Rose [14] has pointed out that the γ between 0.5 and 1.0 can not be understood by assuming a set of discrete trap levels, but demands the existence of continuous distribution of traps. In the present case also, γ is between 0.5 and 1.0 which indicates that a continuous distribution of localized states exists in the mobility gap of the present glassy system.

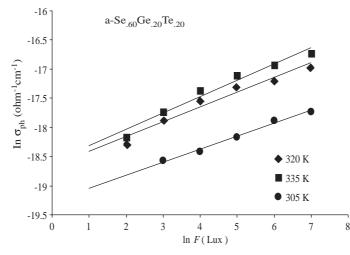


Figure 3. Photoconductivity as a function of intensity at different temperatures in $a-Se_{.60-x}Te_{.20}Ge_{.20}$.

3.2. Composition dependence of photoconductivity

Table 2 shows the compositional dependence of the dark conductivity σ_d , photoconductivity σ_{ph} , and photosensitivity σ_{ph}/σ_d at room temperature. It is clear from this table that σ_d and σ_{ph} both decrease with

the increasing Ge concentration in a-Se_{.80-x}Te_{.20}Ge_x. Since the decrease in $\sigma_d(x)$ is greater than the decrease in $\sigma_{ph}(x)$, the photosensitivity σ_{ph} / σ_d increases with Ge concentration in this glassy system (see Figure 4). This indicates that the excess carriers experience longer lifetime in samples with higher Ge concentration. Longer lifetime further indicates lower recombination rate for the excess carriers, which is expected when the density of the defect states is lesser in composition for x=.20 as compared to other compositions. Goel et al. [13] have measured dielectric constant as a function of Ge concentration in a-Se_{.80-x}Te_{.20}Ge_x, where they have also concluded that the density of defect states decreases in samples containing higher concentration of Ge. The conclusions from the present measurements are therefore consistent with the conclusions drawn by Geol et al. [13] in the same glassy system.

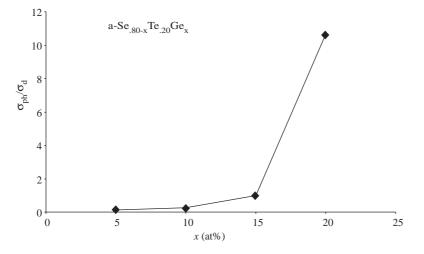


Figure 4. Photosensitivity as a function of concentration in $a-Se_{.80-x}Te_{.20}Ge_x$.

Binary Se-Te system contains Se-Te chains and mixed Se-Te ring structure. When Ge is added to such a binary system it induces the formation of Ge-Se tetrahedral units in addition to chain structures [23]. Since the tetrahedral structure is more rigid, structural flexibility decreases, reducing the density of defect states in the Se-Te-Ge ternary glass system below what would be found in the binary Se-Te system.

4. Conclusion

Temperature dependence of conductivity is studied in dark and in presence of light in amorphous thin films of a-Se_{.80-x}Te_{.20}Ge_x (x = .05, .10, .15 and .20), prepared by vacuum evaporation technique. The films were characterized over the temperature range 305 K to 335 K. These measurements at different intensities indicate that photoconductivity is also thermally activated in the above temperature range in all the samples studied. The activation energy of photoconduction is found to decrease with increasing light intensity, which indicates illumination causes a shift in the Fermi level due to splitting of the Fermi level into quasi Fermi levels. A correlation between the activation energy and the pre-exponential factor is observed in all the compositions following the Meyer-Neldel rule.

The present measurements also indicate that the photosensitivity σ_{ph} / σ_d increases with increasing Ge concentration in this glassy system. This indicates that the density of defect states must be lower for samples containing increasing concentrations of Ge. The conclusions from the present measurements are consistent with the conclusions drawn by Geol et al. [13] in the same glassy system.

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