Steady-state and transient photoconductivity in amorphous thin films of $Ge_x Se_{100-x}$

A. Kumar, S. Goel, and S. K. Tripathi

Department of Physics, Harcourt Butler Technological Institute, Kanpur 208 002, Uttar Pradesh, India

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The present paper reports the steady-state and transient photoconductivity (σ_{ph}) in amorphous thin films of $Ge_x Se_{100-x}$. It is observed that the photosensitivity (σ_{ph}/σ_d) shows a maxima at $x = 22$. A study of the decay of photocurrent with time shows that the decay is fastest at the same composition. The results indicate that the defect states are minimum for $x = 22$, which is explained in terms of chemical ordering because of noncrystalline compound $(GeSe_4)$ formation as suggested by Feltz et al. [J. Non-Cryst. Solids **55**, 179 (1983)].

I. INTRODUCTION

A sharp transition in the physical properties of a glassy $Ge_x Se_{100-x}$ system is reported at a particular value of $x = 33$ by various workers,[1-5] indicating a change in the bonding arrangements at higher concentration of Ge in the $Ge_x Se_{100-x}$ system. However, recently, Feltz et al.[6] have reported that dielectric parameters show some discontinuity at $x = 20$ where some other physical properties are not much affected. From their studies, they concluded that at $x = 20$, a new noncrystalline compound $GeSe_4$ exists in the $Ge_x Se_{100-x}$ system. Our recent measurements[7] of x-ray K absorption edge also supported the above argument, as a discontinuity in the shift of the K absorption edge versus x curve was observed at $x = 22$. The present paper reports the steady-state and transient photoconductivity measurements on amorphous thin films of $Ge_x Se_{100-x}$ where $5 \leq x \leq 40$. dc conductivity is also measured on the same samples.

Thin films of glassy $Ge_x Se_{100-x}$ alloys are prepared by the vacuum evaporation technique. The details of the sample preparation and the techniques of photoconductivity measurements are the same as reported earlier.[8] The present measurements are made at 20 V. The light source is a 200-W tungsten lamp.

II. RESULTS

Figure 1 shows the temperature dependence of dark current (I_d) for amorphous thin films of $Ge_x Se_{100-x}$. It is clear from this figure that, in all the samples, the plots of $\ln I_d$ versus $1000/T$ are straight lines, indicating that the conduction in these glasses is through an activated process having a single activation energy in the temperature range 300–375 K. The dc conductivity (σ_{dc}) can therefore be expressed by the usual relation:

$$\sigma_{dc} = \sigma_0 \exp\left[-\frac{\Delta E}{kT}\right], \tag{1}$$

where ΔE is the activation energy for dc conduction and k is Boltzmann's constant.

The values of ΔE and σ_0 are calculated using the slopes of the curves of Fig. 1 and Eq. (1). The results of these calculations are given in Table I. It is clear from this table that ΔE and σ_0 are highly composition dependent in the $Ge_x Se_{100-x}$ system.

Figure 2 shows the temperature dependence of photocurrent at a particular intensity (3000 lux) for amorphous thin films of $Ge_x Se_{100-x}$ where $5 \leq x \leq 40$. A maximum in photoconductivity is observed in $Ge_{22}Se_{78}$. However, this maximum is not seen in other samples. Below the maximum, $\ln I_{ph}$ versus $1000/T$ curves are straight lines for all the samples (see Fig. 2). This shows that the photoconductivity is an activated process. The activation energy for photoconduction (ΔE_{ph}) is calculated from the slopes of $\ln I_{ph}$ versus $1000/T$ curves and the values are inserted in Table I. A maximum in photoconductivity is a common feature of chalcogenide glasses. However, in some cases[9] this maximum is not seen at all.
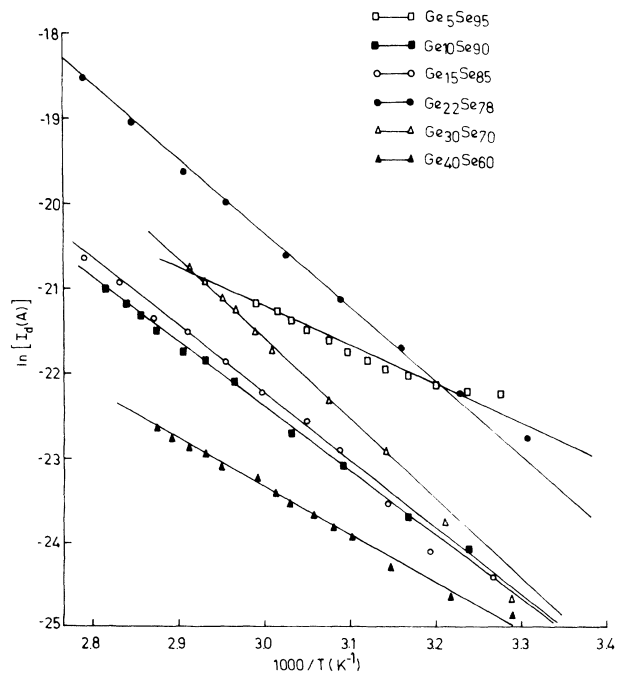

FIG. 1. Temperature dependence of dark current for amorphous thin films of $Ge_x Se_{100-x}$.

TABLE I. Electrical parameters in amorphous thin films of Ge_xSe_{100-x} at 300 K.

Composition x	σ_d ($\Omega^{-1}cm^{-1}$)	ΔE (eV)	σ_0 ($\Omega^{-1}cm^{-1}$)	σ_{ph} ($\Omega^{-1}cm^{-1}$)	I_{ph}/I_d	ΔE_{ph} (eV)	τ_d (sec)
5	1.2×10^{-7}	0.43	2.8	3.8×10^{-8}	0.4	0.41	107
10	5.0×10^{-10}	0.67	6.9×10^{1}	1.5×10^{-9}	3.0	0.63	77
15	9.2×10^{-10}	0.71	5.6×10^{2}	4.4×10^{-9}	5.0	0.59	65
22	1.4×10^{-8}	0.90	1.3×10^{7}	2.7×10^{-7}	19.7	0.32	54
30	7.5×10^{-10}	0.75	2.2×10^{3}	3.4×10^{-9}	4.0	0.59	79
40	6.6×10^{-10}	0.50	2.1×10^{-1}	1.0×10^{-9}	1.5	0.47	95

Intensity (F) dependence of photoconductivity (σ_{ph}) has also been studied (results not shown here) at room temperature, 300 K, in the intensity range 30–3000 lux. For all the samples, σ_{ph} increases with the increase of intensity following a power law $\sigma_{ph} \propto F^\gamma$, where the value of γ is found to be between 0.5 and 1.0 for various samples. This indicates a distribution of localized states in the mobility gap of these materials as pointed out by Rose.[10]

The important parameter in photoconductivity measurements is 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 I_{ph}/I_d at various temperatures for all the samples at a particular intensity (3000 lux) using the results shown in Figs. 1 and 2. The values of I_{ph}/I_d at room temperature are given in Table I and plotted in Fig. 3 as a function of

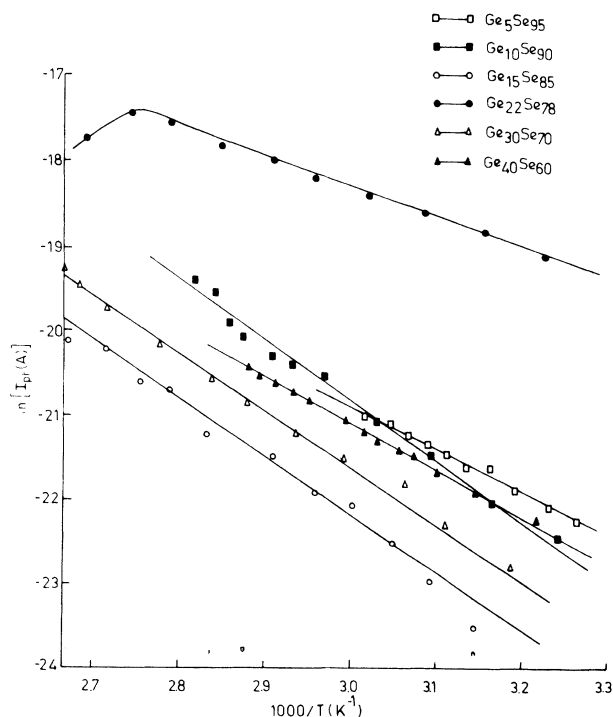x in the Ge_xSe_{100-x} system. It is clear from this figure that I_{ph}/I_d is maximum at $x=22$. Similar results are also obtained at other temperatures.

Figure 4 shows the decay of photocurrent with time at room temperature for various samples of Ge_xSe_{100-x} where $5 \leq x \leq 40$. It is clear from this figure that the decay of photocurrent is quite slow in amorphous thin films of Ge_xSe_{100-x}. A persistent photocurrent (the asymptotic value of the current in the decay curve) is also observed in all the samples. This type of decay of photocurrent is observed[11–13] 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 nonexponential even after subtracting the persistent photocurrent.

In discussing the nonexponential decay process we prefer to use the concept of differential lifetime as described by Fuhs and Meyer.[13] According to these workers, the differential lifetime can be defined as

$$\tau_d = -\left[\frac{1}{I_{ph}}\frac{dI_{ph}}{dt}\right]^{-1}. \tag{2}$$

The values of τ_d are calculated at various times using the slopes of I_{ph} versus t curves. The corrected value of I_{ph} is used for these calculations.

FIG. 2. Temperature dependence of steady-state photocurrent at a particular intensity for amorphous thin films of Ge_xSe_{100-x}.
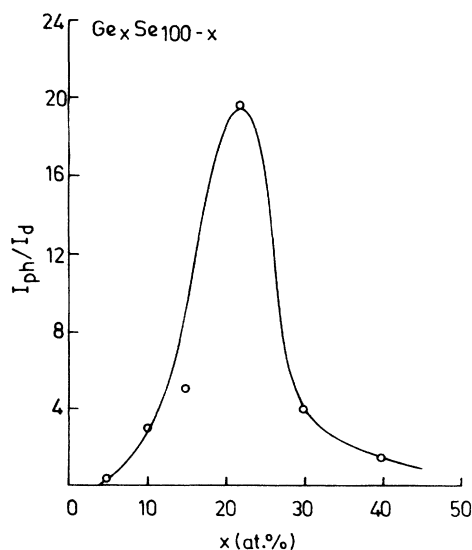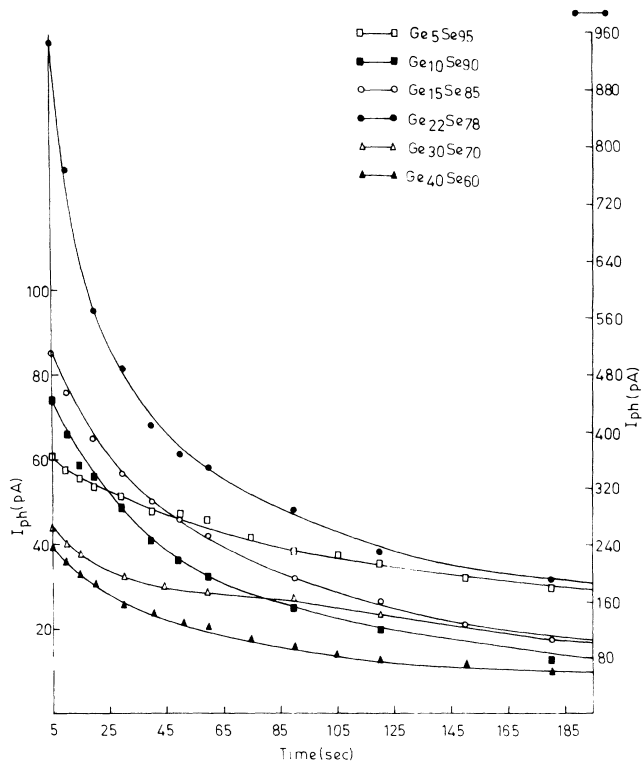

FIG. 3. Composition dependence of I_{ph}/I_d at room temperature.

FIG. 4. The decay of photocurrent with time at room temperature for amorphous thin films of $Ge_x Se_{100-x}$.

FIG. 5. Composition dependence of τ_d ($t = 30$ sec) at room temperature.

To compare the rate of decay for various samples, we have chosen the value of τ_d at $t = 30$ sec and we expect that, at this time, the slow decay will be predominant in all the samples studied. The values of τ_d ($t = 30$ sec) are given in Table I and plotted as a function of x in Fig. 5. It is clear from this figure that τ_d is highly composition dependent and is minimum for $x = 22$. The smaller value of τ_d in the case of $Ge_{22}Se_{78}$ indicates the faster decay in this material. One can therefore expect a lower density of localized states in the mobility gap of this sample ($x = 22$) as compared to other samples. Similar conclusions are also drawn from steady-state photoconductivity measurements.

III. DISCUSSIONS

Phillips[14] has proposed that the molecular structure of melt-quenched $Ge_x Se_{100-x}$ is much more ordered than would be expected from a continuous random network model. According to him, $Ge_x Se_{100-x}$ alloys may be described by chemically ordered clusters embedded in a continuous network. Some of these clusters are $(Se)_n$ chains, $Ge(Se_{1/2})_4$ corner-sharing tetrahedra, and $Ge_2(Se_{1/2})_6$ ethanelike structural units. The first two types dominate for $x \leq 33$ and the third type is expected to occur at a higher concentration of Ge ($x > 33$). Street and Biegelsen[1] have explained their photoluminescence and optical-gap measurements assuming the introduction of Ge—Ge bonds at a higher concentration of Ge ($x > 33$). It is interesting to note that such a b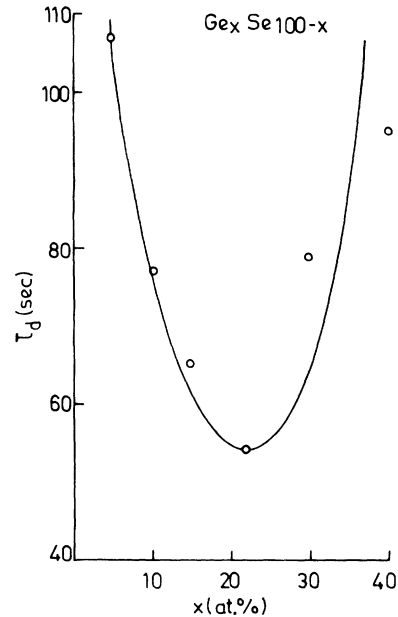onding change does not produce drastic changes in the photo-conductive properties, as in the present case no discontinuity in I_{ph}/I_d or the τ_d versus x curve is observed at $30 \leq x \leq 40$. Kim et al.[15] have studied the photoconductivity in $Ge_x Se_{100-x}$ glasses for $x = 33$ and 40 and found the photoconductive behavior similar in two samples.

We have observed a drastic difference in the various electrical parameters for $x = 22$ which indicates some kind of structural changes at this composition. Tronc et al.[16] have deduced from the analysis of Raman spectra for $Ge_x Se_{100-x}$ glasses that $(GeSe_{1/2})_4$ units are randomly distributed within the glass structure, i.e., without cluster formation. Based on this argument, Feltz et al.[6] have proposed that at a composition $GeSe_4$ ($x = 20$) the $(GeSe_{1/2})_4$ groups should be predominantly linked by Se—Se bridges. The results of the radial-distribution function also support[17] the above argument. Feltz et al.[6] have also proposed that the content of Se—Se bridges is reduced by the introduction of longer chains when $x < 20$.

From the above discussion, it is clear that some sort of chemical ordering takes place near $x = 20$. At low concentration of Ge, longer Se—Se chains predominate. As the concentration of Ge increases, $(GeSe_{1/2})_4$ units are linked with Se—Se bridges. However, at higher concentration of Ge ($x > 20$) this effect decreases due to the single-bridging Se atom.

A chemical ordering because of noncrystalline compound $(GeSe_4)$ formation as suggested by Feltz et al.[6] may be responsible for the lower density of defect states at $x = 22$ in the present case. Due to lower density of defect states, photosensitivity becomes quite large for $Ge_{22}Se_{78}$ as compared to other alloys. A smaller density of defect states makes the decay of photocurrent faster as observed in the present case for $x = 22$.

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