Anomalous decay of photocurrent in amorphous thin films of $Ge_{22}Se_{78}$

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The transient photocurrent has been studied in vacuum-evaporated thin films of amorphous $Ge_{22}Se_{78}$. It has been observed that, under certain experimental conditions, the decay of the photocurrent shows anomalous behavior. Instead of decaying monotonically to zero, the photocurrent becomes negative very fast and then returns to zero slowly. The negative value of the photocurrent is found to be greater at higher temperatures and intensities, lower wavelengths, and longer illumination times. A model has also been proposed to explain these results.

I. INTRODUCTION

Recently, chalcogenide glasses have attracted a great deal of attention from scientists and engineers because of their potential use in various solid-state devices. A common feature of these materials is the presence of localized states in the mobility gap due to inherent defects and the absence of long-range order. As the photocurrent behavior is controlled by carrier localization and delocalization processes, transient photoconductivity measurements are expected to give information about the localized states in these materials.

Transient photoconductivity measurements have been carried out by various workers[1-7] in different kinds of chalcogenide glasses. In general, the decay of the photocurrent is found to have two components: a fast one in the beginning and a slow one later. In some cases,[1,2,7] the decay of the photocurrent can be fitted by taking a sum of exponential decay curves and, in few other cases,[3,4] the decay can be fitted to a power law. However, in all the cases, the decay is found to be monotonic and devoid of any structure.

The present paper, for the first time, reports a photocurrent decay which, under certain experimental conditions, is quite different than the normal behavior observed so far in chalcogenide glasses. The measurements of photoconductive decay have been made in amorphous thin films of $Ge_{22}Se_{78}$ prepared by vacuum evaporation. The anomalous behavior of the photoconductive decay has been studied at different temperatures, intensities, wavelengths, and illumination times. On the basis of recent findings[8] regarding the nature of defect states in Ge_xSe_{1-x} alloys, a model has been proposed to explain this anomalous behavior.

Section II describes the experimental details and the characteristics of the sample. The results of the transient photocurrent measurements are presented in Sec. III and discussed in Sec. IV. Section V deals with the conclusion of the present work.

II. EXPERIMENT

A glassy alloy of $Ge_{22}Se_{78}$ is prepared by the quenching technique. The materials (99.999% pure) are weighed according to their atomic percentages and sealed in a quartz ampoule (length ~ 5 cm and internal diameter ~ 8 mm) with a vacuum $\sim 10^{-5}$ Torr. The sealed ampoule is kept inside a furnace where the temperature is raised to 950 °C at a rate of 3—4 °C/min. The ampoule is frequently rocked for 10 h at the maximum temperature to make the melt homogeneous. Quenching is done in air.

Thin films of the glassy alloy are prepared at room temperature by vacuum evaporation at a base pressure $\sim 10^{-5}$ Torr on well-degassed glass substrates which had predeposited Nichrome electrodes. The coplanar structures (length ~ 1.2 cm and electrode gap ~ 0.5 mm) are used for the photoconductivity measurements.

For the measurement of photoconductivity, the sample is mounted inside a metallic cryostat with a transparent window which allowed light to shine on the sample. A vacuum of $\sim 10^{-3}$ Torr is maintained throughout the measurements. The temperature of the sample is controlled by a heater mounted inside the cryostat and measured by a calibrated copper-Constantan thermocouple.

The source of the light is a 200-W tungsten lamp. Interference filters are used to obtain light of the desired wavelength. The intensity of the light is varied by changing the voltage across the lamp. The relative intensity is measured by measuring the short-circuit current in a photocell.

To measure the decay of the photocurrent, light is shone on the sample until the steady state is reached (90 sec in the present case). The light is then turned off and the current is measured with time by a $3\frac{1}{2}$-digit digital picoammeter (Achme, model SD-100). All the measurements are done after annealing the sample, in a vacuum $\sim 10^{-3}$ Torr, at 150 °C for 2 h inside the same cryostat.

The dark conductivity (σ_d) is measured as a function of temperature (302 to 450 K). The value of σ_d at 302 K is

$5\times10^{-9}\ \Omega^{-1}\,\mathrm{cm}^{-1}$ and the conductivity is thermally activated with a single activation energy (0.9 eV) as also reported elsewhere.[9] The sample is found to be highly photoconducting in the steady state. At room temperature, the photosensitivity (I_{ph}/I_d), at the highest intensity used, is ~ 100 in white light. The stability of the same to light exposure is also studied. No permanent change in the dark conductivity, activation energy for dc conduction, and photosensitivity is observed after exposing the sample to white light (200 W tungsten lamp) for 8 h in a vacuum of $\sim 10^{-3}$ Torr.

The sample is found to be ohmic up to 30 V in the dark as well as in the presence of light. The present measurements are, however, made at very low voltage (1.5 V) which is applied by a dry cell.

III. RESULTS

Figures 1 and 2 show the decay of the photocurrent with time at different temperatures for red (660 nm) and violet (420 nm) light, respectively. These measurements have been taken after illuminating the sample for 90 sec at the maximum light intensity (210 arbitrary units). It is clear from Fig. 1 that, in red light, the photocurrent decays monotonically to zero at all temperatures. The decay is found to be nonexponential and can be fitted by taking a sum of various exponential decay curves (results not shown here). Such type of decay of photocurrent is common in chalcogenide glasses[1,2,7] and we, therefore, call it normal behavior. In the case of violet light (see Fig. 2), the decay of the photocurrent is similar to that in red light at 302 and 322 K. However, at higher temperatures (≥ 344 K) the decay is found to be quite different. In this case, the photocurrent becomes negative very fast (less than 30 sec) and then grows slowly and reaches zero in a very long time (more than 4 min). We call this behavior anomalous as such type of decay has not so far been observed in chalcogenide glasses. It is clear from Fig. 2 that the anomalous effect increases at higher temperatures.

To study the effect of wavelength on the anomalous behavior, we have studied the decay of photocurrent at

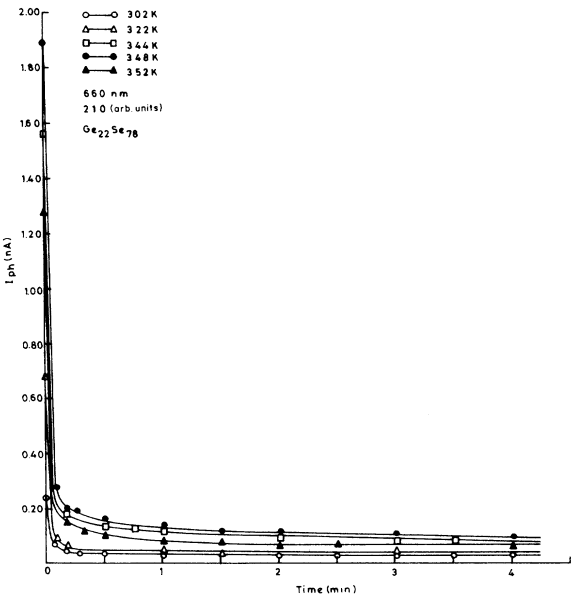

FIG. 1. Decay of photocurrent with time at different temperatures after illuminating the sample for 90 sec in red light (660 nm).

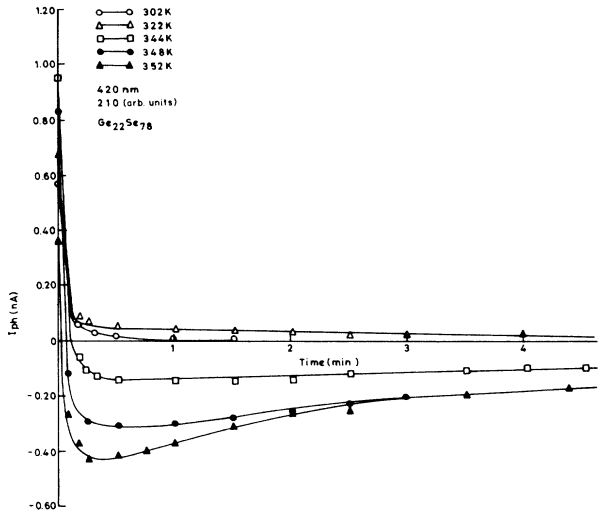

FIG. 2. Decay of photocurrent with time at different temperatures after illuminating the sample for 90 sec in violet light (420 nm).

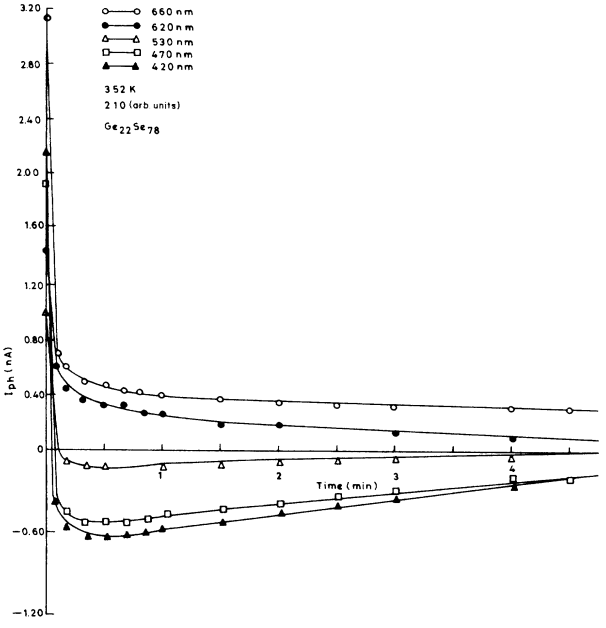

FIG. 3. Decay of photocurrent with time at 352 K after illuminating the sample for 90 sec in the light of different wavelengths.

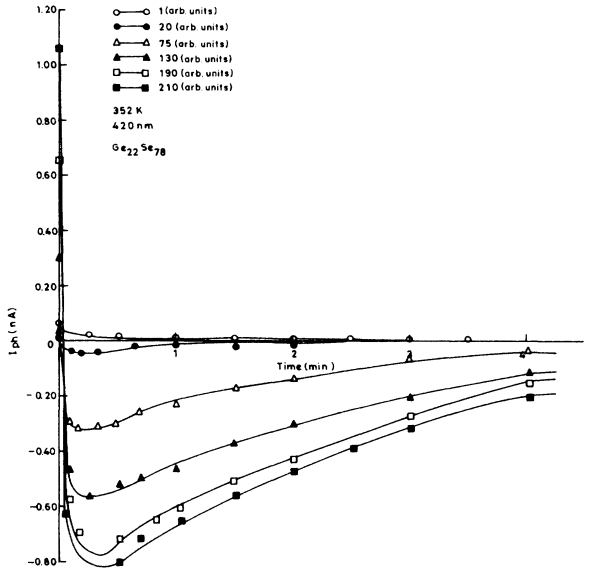

FIG. 4. Decay of photocurrent with time at 352 K after illuminating the sample for 90 sec in violet light (420 nm) of different intensities.

various wavelengths (420, 470, 530, 620, and 660 nm). These measurements are done at 352 K and at the highest intensity (210 arb. units). The results of these measurements are shown in Fig. 3. It shows that the decay of photocurrent starts showing anomalous behavior at about 530 nm and the effect increases as the wavelength of light further decreases.

To study the effect of intensity on the anomalous behavior, we have measured the decay of photocurrent at 352 K for different intensities. Violet light (420 nm) is used for these measurements as the effect is maximum for this wavelength. The illumination time is kept the same (90 sec) for all intensities. The results of these measurements are shown in Fig. 4. It is evident from this figure that the anomalous effect decreases as the intensity of light is decreased. At the lowest intensity (1 arbitrary unit) used, the anomalous effect is not seen at all.

We have also studied the anomalous behavior after illuminating the sample for different time periods ($t=10$, 15, and 30 sec). These measurements are also taken in violet light (420 nm) at 352 K and for highest intensity (210 arb. units). The results of these measurements are shown in Fig. 5. It is clear from this figure that the anomalous effect increases as the illumination time increases.

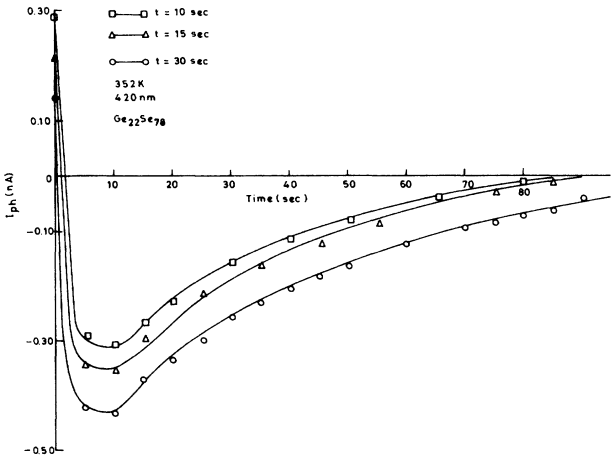

FIG. 5. Decay of photocurrent with time at 352 K after illuminating the sample in violet light (420 nm) for different time period.

IV. DISCUSSION

Figures 2–5 show that the decay of photocurrent becomes anomalous under certain experimental conditions. As this kind of decay of photocurrent has not been reported so far in any chalcogenide glass system, we expect that the special kinds of defects in this particular glass system may be responsible for this anomalous behavior.

The nature of defect states in Ge_xSe_{1-x} alloys has been studied in detail by Street and Biegelsen[8] by ESR and photoluminescence experiments. According to them, two types of defects are anticipated in these alloys. One may be a Ge dangling bond which bonds to a Se atom (I) and other may be a Se chain end which bonds (in its positive state) to a neighboring Se atom (II). They also emphasized that the density of the second kind of defect (II) should be large in Se-rich alloys (as in the present case) as compared to that of the first (I) kind. From ESR measurements, Street and Biegelsen[8] could resolve these two kinds of defects clearly. This is confirmed by their photoluminescence measurements also. Furthermore, it is also found in their luminescence measurements that the time constants of the two defect states are quite different: One kind of defect has a small time constant and other kind a larger time constant. This implies that the two defect states are at two different positions, in the mobility gap, separated by large energy.

Based on the above discussion, the following model can be formulated which may explain the anomalous decay of photocurrent observed in the present material. The majority charge carriers, in this material, are considered to be holes as the thermoelectric power measurements[10] show that p-type conduction takes place in Ge-Se alloys.

Figure 6 shows a model to explain the anomalous decay of photocurrent in $Ge_{22}Se_{78}$. Two major defect levels are shown, separated by a large energy. As discussed earlier, the density of the type-I defect is assumed to be smaller than the that of the type-II. We further assume that the capture cross section for the electrons and holes is also much smaller for type-I defects as compared to the type-II. It is also assumed that the rate of thermal exchange between type-I defect states and the valence band is negligibly small.

In presence of light, the quasi-Fermi levels (E_{Fn} and E_{Fp}) for electrons and holes move towards the conduction and valence bands, respectively. The I and II types of de-

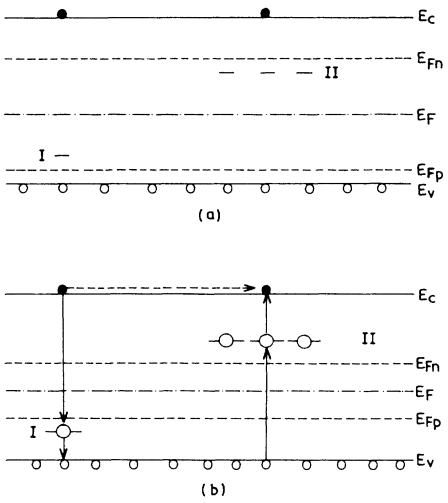

FIG. 6. A model to explain the anomalous decay of photocurrent (a) in presence of light (b) after putting the light off (but not in steady state).

fects, therefore, become recombination centers [see Fig. 6(a)] and the steady-state condition is reached. When light is turned off, the two quasi-Fermi levels move away from the valence and conduction bands towards the dark Fermi level (E_F); the defect states (I and II) now start behaving as traps when the quasi-Fermi levels fall in between these two defect states [see Fig. 6(b)]. As assumed earlier, the rate of thermal exchange between states I and the valence band is small, the excess holes (which were generated by light) will remain trapped resulting in a negligible change in the density of thermally generated holes. In the mean time, the excess electrons are captured by states II. As the capture cross section for electrons and holes is assumed to be higher for the II states, these states become the sink for the thermally generated holes resulting in a negative value of photocurrent while decaying. As there is no continuous generation of excess electrons (the light is put off), this process will not continue and an equilibrium will not be obtained. With the density of excess electrons approaching zero, the holes, which were going to states II, will now start contributing to the current which will make the transient photocurrent to go to zero value.

The model discussed above is similar to the model described by Stöckmann[11] to explain the negative photoconductivity in germanium. The assumptions made may appear to be unlikely but not impossible as pointed out by Rose.[12]

In the above analysis, we have assumed only two special kinds of defects states. However, the possibility of other types of defect states cannot be ruled out as the chalcogenide glasses are known to have a continuous distribution of localized states. The decay of photocurrent will, therefore, be a sum of decay curves arising due to each type of defect states. The anomalous behavior described above may, therefore, be dominated over the normal behavior (shown in Fig. 1) only in certain experimental conditions (high temperatures, high intensities, and low wavelengths). In the absence of the knowledge of the exact distribution and the nature of all kinds of defect states, it is difficult to point out the reasons for not observing this kind of anomalous behavior under other experimental conditions.

V. CONCLUSIONS

The decay of photocurrent has been studied in vacuum-evaporated thin films of $Ge_{22}Se_{78}$ at various temperatures, intensities, wavelengths, and illumination times (shorter than the rise time). It has been observed that, under certain experimental conditions, the decay of the photocurrent shows anomalous behavior. Instead of decay to zero monotonically, the photocurrent becomes negative very fast and then grows slowly and then reaches zero in a very long time.

The anomalous effect is found to be greater at higher temperatures, higher intensities, shorter wavelengths, and longer illumination times. The results are explained on the basis of a model which is based on the two different kinds of major defect states in the present material. These two different kinds of defect states have been observed experimentally in ESR and photoluminescence measurements by Street and Biegelsen.[8]

The model, though qualitative in nature, could successfully explain the anomalous behavior of photoconductive decay which is observed by us for the first time in chalcogenide glasses.

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