Persistent photoconductivity in a-Se$_{90}$Ge$_{10-x}$In$_x$ thin films

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Transient photoconductivity has been studied in amorphous Se$_{90}$Ge$_{10-x}$In$_x$ thin films prepared by vacuum evaporation. It is observed that the decay of photoconductivity is quite slow in these samples. A persistent photoconductivity, with an extremely slow decay rate is also observed during decay process. The magnitude of persistent photoconductivity increases with increase in illumination time, intensity of light and temperature of the films. The results indicate that some kind of photo induced structural changes occur in these samples, which are of reversible nature and have time constants of a few hours. Studies made on various compositions under identical conditions show that the persistent photoconductivity is minimum at 4 at. % of Indium. This discontinuity at an average coordination number $<Z> = 2.2$ is closer to the value suggested by topological models based on constraints theory.

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The common feature of chalcogenide glasses is the presence of localized states in the mobility gap due to the absence of long-range order as well as various inherent structural defects. These glasses when exposed to light having photon energy comparable to the band gap, exhibit a number of interesting changes$^{1,4}$. On the basis of mode of induction, photo induced phenomenon in chalcogenide glasses can be grouped into three categories: the photon mode in which the photo electronic excitation directly induces atomic structural changes. An example is the photo darkening changes$^{5,7}$ in which light illumination induces a red shift in the optical absorption edge, so that the sample becomes darker, while the red shift can be reversed with annealing of the glasses. Sample volume, elastic and chemical properties also change with illumination. The photo thermal mode, in which photo electronic excitation induces changes with the aid of the thermal activation. The illumination with linearly polarized light can add some anisotropy$^{2,3}$ such as dichroism, birefringence and axial strains. Even unpolarised light can induce anisotropy if light irradiates a side surface of a sample. The third mode, i.e., heat mode, in which the temperature rise induced by optical absorption is essential, may be the optical phase change or so called optical Ovonic effect$^{2,8}$.

Transient photoconductivity measurements act as a tool to understand the recombination kinetics, which, in turn, give information about the localized states in the mobility gap of amorphous semiconductors. Not only from theoretical point of view but also from application point of view these measurements are very important.

In general, in chalcogenide glassy semiconductors, the decay in the photoconductivity is found to have two components, a fast decay in the beginning and a slow decay later. In some of the cases, the later component of residual photoconductivity is found to have extremely slow rate of decay, which leads to the long tail in the decay curves$^9$. The light induced conductivity, which persists for a long time after the removal of the illumination, is often referred to as ‘persistent photoconductivity’. This type of persistent photoconductivity has been observed by many researchers in the case of amorphous semiconductors$^{9-23}$ as well as in the case of many other materials$^{24-28}$.

The present paper reports a detailed study of persistent photoconductivity in vacuum evaporated thin films of a-Se$_{90}$Ge$_{10-x}$In$_x$ for $x = 2, 4, 6$ and $10$. The effect of increase in illumination time, intensity of light, temperature of the films and concentration of In in a-Se$_{90}$Ge$_{10-x}$In$_x$ on the persistent photoconductivity is studied in detail.

**Experimental Procedure**

Glassy alloys of Se$_{90}$Ge$_{10-x}$In$_x$ with $x = 2, 4, 6$ and $10$ were prepared by quenching technique$^{12}$. Thin films of these glasses were prepared by vacuum evaporation technique at a base pressure of $10^{-5}$ Torr using a standard coating unit (IBP-TORR, TYPE: H01L27/00).
After a certain time of exposure, the light was turned off and the decay in conductivity was measured as a function of time. The initial value of dark conductivity was subtracted from the measured conductivity after turning off the illumination. The subtraction of these two values gives the value of photoconductivity.

Studies made on Se-Ge-In glassy system show that the system exhibits a large photo response upon illumination with white light of different illumination intensities. Fig. 1 shows the decay of photoconductivity at room temperature at 10750 Lux for different exposure times (5 and 30 min). The decay in the photoconductivity is found to have two components, a fast decay in the beginning and a slow decay later. In the present case the latter component of residual photoconductivity is found to have extremely slow rate of decay, which leads to the long tail in the decay curves. A long tail in the decay curves, i.e., persistent photoconductivity is observed at all the illumination time.

It is observed that the persistent photocurrent is enhanced with increasing illumination time for all the
studied samples. This suggests that the residual photoconductivity is produced due to some kind of defects, which is accumulated during illumination.

Fig. 2 shows the dependence of persistent photoconductivity at different illumination intensities (6400, 8600 and 10750 Lux) keeping the temperature of the films at room temperature. In all these cases, samples were exposed to white light for 5 min. A long tail in the decay curves, i.e., persistent photoconductivity is also observed at all the intensities. The results are plotted only up to 10 min. However, the photocurrent persists for a few hours. The magnitude of persistent photoconductivity increases with increase in illumination intensities.

![Graphs showing the dependence of persistent photoconductivity on different illumination intensities.](image1)

![Graphs showing the dependence of persistent photoconductivity on different temperatures.](image2)
This may be due to increase in photo-induced structural changes at higher and higher intensity.

In order to obtain further information about the persistent photoconductivity we tried to perform a similar experiment at different fixed values of temperatures (306 K, 341 K and 374 K) of the films. Fig. 3 shows the plot of these measurements at 10750 Lux, keeping the illumination time constant (30 min). A persistent photoconductivity is observed which takes a few hours to decay. The results are plotted only up to 30 minutes in Fig. 3. The persistent photoconductivity is found to be more when the samples are exposed to higher temperatures. This may be due to increase in photo-induced structural changes at higher temperatures.

Dependence of residual photoconductivity on compositions has also been studied. Fig.4 shows \( \ln \sigma_{ph} \) versus time curves for different compositions at 306 K at 10750 Lux. It is clear from this figure that the magnitude of persistent photoconductivity decreases up to \( x = 4 \) at.% of In. After that, it increases with increasing concentration of In. Similar nature has been observed at other temperatures and intensities also (results not shown here).

Persistent photoconductivity in the decay curve of photoconductivity has already been reported by various researchers\(^9\)\(^-\)\(^{23}\). Fuhs and Meyer\(^14\) tried to explain the slow decay in a-\( \text{As}_2\text{Se}_3 \) by assuming localized electron and hole trap levels in the gap, in which recombination occurs directly between the two localized levels. The recombination rate depends on the spatial distance of the level, and increases during the decay with time. Chamberlain \textit{et al.}\(^{16}\) explained the slow decay in a-\( \text{Ge-Se} \) by applying the Street-Mott model\(^{29}\). Kumeda \textit{et al.}\(^{17}\) observed that the slow decay of the photoconductivity in a-\( \text{Ge}_{4x}\text{S}_{8x} \) film occurs with an accompanying decrease in the photoinduced ESR signal. The decrease in the ESR signal provides evidence that the metastable defect \( D^0 \) acts the limiting process of the photoconductivity. Shimakawa \textit{et al.}\(^{15}\) explained the slow decay in a-\( \text{As}_2\text{Se}_3 \) film by the dispersive diffusion-controlled monomolecular recombination of excess neutral defects \( D^0 \) through the reaction \( 2D^0 \rightarrow D^+D^- \). Watanabe and Sekiya\(^*\) explained extremely long lived residual photocurrent in a-\( \text{In}_2\text{Se}_3 \) films by reporting that neutral defects are created by the illumination through any structural change, and thus produced localized levels in the gap. The photocurrent is derived from the variable range hopping conduction at the quasi-Fermi levels. Persistent photoconductivity effect arising from deep defect states were observed by Harea \textit{et al.}\(^{13}\) in a-\( \text{As}_2\text{Se}_3 \) films with Sn impurity. The origin of persistent photoconductivity in hydrogenated a-\( \text{Si:H} \) has been explained by Lee \textit{et al.}\(^{23}\) by concluding that hole induced dopant conversion and following dangling bond formation processes are responsible for persistent photoconductivity in both doping-modulated super lattices and compensated films.

From the above discussion it is clear that though persistent photoconductivity has been observed by many researchers, and various models have been proposed to explain this, but exact mechanism of persistent photoconductivity is still unclear. In the present case, the persistent photoconductivity has a very large time constant involved which can not be understood by simply considering the charge carriers trapped in defect states which act as traps. Moreover, the persistent photoconductivity strongly depends on illumination time, intensity of light and temperature of the film, we expect that reversible light induced structural changes are possible in the present case. Such type of structural changes\(^1\)^4 may have large time constants, some times a few hours as observed in the present samples.

In the present case, it is also observed that the persistent photoconductivity is highly composition dependent in the present glassy system. It shows a minimum at 4 at. % of In which can be understood as follows:

Many approaches have been proposed to explain the compositional dependence of various physical properties of chalcogenide glasses\(^30\)^\(^-\)\(^{38}\). One of these approaches is the so-called chemically ordered network model (CONM)\(^30\)^\(^-\)\(^{33}\) in which the formation of hetropolar bonds is favored over the formation of
homopolar bonds. In this model, the glass structure is assumed to be composed of cross-linked structural units of the stable chemical compounds (hetropolar bonds) of the system and excess, if any, of the elements (homopolar bonds). Due to chemical ordering, features (such as extremum, a change in slope or kink) occur for the various properties at the so-called the tie line or stoichiometric compositions at which the glass structure is made up of cross-linked structural units consisting of hetropolar bonds only. The tie line compositions, where the features seen have chemical origin, are also referred as the chemical threshold of the system$^{39,40}$.

Other approaches are the so-called topological models, which are based on the constraint theory$^{34-38}$ and on the structural dimensionality considerations$^{38}$. In these models, the properties can be discussed in terms of the average coordination number ($Z$), which is indiscriminate of the species or valence bond. In the constraints model$^{34-37}$, by equating the number of operating constraints to the number of degrees of freedom, $Z$ of the most stable glass is shown to be $\sim 2.4$. At this value of $Z$, the glass network has a mechanical threshold or critical composition, at which the network changes from an elastically floppy (polymeric glass) type to a rigid (amorphous solid) type.

By extension of the topological model to the medium-range structures, other features at $Z > 2.67$ have also been observed$^{38}$. However, the features observed at $Z > 2.67$ were attributed to a change from two-dimensional layered structure to a three-dimensional network arrangement due to cross-link.

In the present case the magnitude of persistent photoconductivity is found to be minimum at 4 at. % of In showing a discontinuity at an average coordination number $< Z > = 2.2$, which is closer to the topological models based on constraints theory described above.

**Conclusions**

Persistent photoconductivity has been observed in a-Se$_{90}$Ge$_{10-x}$In$_x$ thin films for different exposure times, different illumination intensities, different temperatures of the film and different compositions. These measurements indicate that persistent photoconductivity has very large time constant and strongly depends on the above parameters. The results indicate that some kind of reversible light induced structural changes occur in the present samples which may have time constants of a few hours.

**References**