Transient Photoconductivity in Amorphous Se-Ge-Ag System

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Abstract

Transient Photoconductivity measurements have been made in vacuum evaporated thin films of $Se_{0.80-x}Ge_{0.20}Ag_x$ at different intensities, temperatures and illumination times. The films exhibit long-lived residual photoconductivity, called persistent photoconductivity, with an extremely slow decay rate. The persistent photoconductivity (PPC) increases with an increase in intensity and illumination time. However, this quantity decreases with increase in temperature. These results indicate that the decay of photoconductivity is not only governed by the carrier trapped in the intrinsic defects but also gets affected by the light induced defect creation through structural changes The persistent photoconductivity effect is found to be suppressed on increase of Ag concentration in a- $Se_{0.80-x}Ge_{0.20}Ag_x$, which may be understood in terms of smaller effect of light induced defects due to higher concentration of inherent structural defects in dark at higher concentration of Ag.

Key Words: Persistent photoconductivity, Chalcogenide Glasses, Photoconductivity.

1. Introduction

The difference between crystalline and disordered semiconductors is mainly the presence of localized states. The presence of monoenergetic localized centers is the most characteristic feature of crystalline semiconductors, while in disordered materials and, primarily in amorphous and glassy semiconductors, the individual groups of localized centers are energetically spread, following from theoretical studies. 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.

Ge-Se glassy system is an interesting system as it is a combination of two different kinds of amorphous semiconductors: a-Ge, which contains unpaired electrons; and a-Se, where defects are charged and unpaired electrons are not present, as evident from electron spin resonance and magnetic susceptibility measurements. This difference arises from the dissimilarity in the short-range structures of these two systems. a-Ge has tetrahedral structure which is more rigid than the flexible structure of a-Se, which has chain structure in two fold co-ordination.

The addition of another element in binary systems has been quite useful in improving some of the properties of glassy semiconductors. Though the addition of the third element stabilizes the structure,

which makes the ternary system more stable thermally, the density of defect states is increased, which affects the photoconductive properties [1–3].

Ag-containing chalcogenide glasses have attracted widespread interest for applications in optical recording and as solid electrolytes. The importance of this combination was first established when the effect of silver photo-diffusion in chalcogenide glasses was discovered [4]. In the following years, great contributions have been made to the field [5, 6] and the photo-diffusion effect has been applied in the fabrication of optical elements using relief images [7], in micro-photo-lithographic systems [8, 9] and in direct imaging by photo-induced silver surface deposition [10, 11]. The low free energy of crystallization of Ag (48 kcal/mol.) was a further reason to consider the introduction of Ag in chalcogenide glasses used for phase change optical recording [12, 13]. This enabled one for the attainment of the main requirements for good optical recording-high phase transformation rate. For this reason, the crystallization kinetics of Ag-containing chalcogenide glasses have been studied by various workers [14–16] for the development of new and better phase change recording materials.

Another aspect of interest regarding silver's influence in Ag-containing chalcogenide glasses, is that the electrical conductivity of the glasses changes by several orders of magnitudes when Ag is introduced. Therefore, investigations into the influence of Ag on the electrical properties of chalcogenide glasses are relevant both from the points of view of basic science and application.

Transient photoconductivity measurements in chalcogenide glasses are important as the photocurrent rise and decay with time depends upon the presence of traps in the mobility gap of these materials. These traps originate from the defect states present in these materials. Therefore, such measurements made at different temperatures, intensities and illumination times give important information about the defect states.

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 cases, 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 [17].

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 [17–32] as well as in the case of many other materials [33–37].

The present paper reports the transient photoconductivity measurements in amorphous films of $Se_{0.80-x}$ $Ge_{0.20}Ag_x$ ($x = 0.0$, 0.05 and 0.10) deposited by vacuum evaporation technique. Persistent photocurrent is observed in all the glasses used in the present study. Effect of Ag addition on PPC is discussed in terms of the light induced structural defects in these materials.

2. Experimental

Glassy alloys of $Se_{0.80-x}Ge_{0.20}Ag_x$ ($x = 0.0$, 0.05 and 0.10) were prepared from the melt by quenching technique. The exact proportions of high purity (99.999%) elements, in accordance with their atomic percentages, were weighed using an electronic balance to an accuracy of 10^{-4} g. The materials were then sealed in evacuated ($\sim 10^{-5}$ Torr) quartz ampoules of about 8 mm diameter. The ampoules containing the materials were heated to 1000 °C and were held at that temperature for 12 hours. The temperature of the furnace was raised slowly at a rate of 3–4 °C/min.

During heating, all the ampoules were constantly rocked, by rotating a ceramic rod to which the ampoules were tucked away in the furnace. This was done to obtain homogenous glassy alloys. The melts were cooled rapidly by removing the ampoules from the furnace and dropping them to ice-cooled water. The quenched samples were then taken out 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 at bottom were used for the electrical contact.

The thickness of the films was $\sim$500 nm. The co-planar structure (length $\sim$1.2 cm and electrode separation $\sim$0.5 mm) was used for the present measurements.

For the measurement of photoconductivity, thin film samples were mounted in a specially designed sample holder which has a transparent window to shine light for these measurements in a vacuum $\sim$10^{-2} Torr. The temperature of the films was controlled by mounting a heater inside the sample holder and measured by a calibrated copper-constantan thermocouple mounted very near to the films.

The source of light was a 200 W tungsten lamp. The intensity of light was varied, by changing the voltage across the lamp. The intensity was measured by a lux meter. A dc voltage of 10 V is applied across the film and the resulting current is measured by a digital Electrometer (Keithley, model 614). The heating rate is kept quite small (0.5 K/min) for these measurements.

The photoconductivity is calculated by measuring the increase in current upon illumination. For this purpose, the current was measured in presence of light as well as in dark. The subtraction of these two values gave the value of photocurrent.

Before measuring the dark and photoconductivity, the films were first annealed at 370 K for one hour in a vacuum $\sim$10^{-2} Torr. I-V characteristics were found to be linear and symmetric up to 30 V in all the glasses studied. The present measurements are, however, made by applying only 10 V across the films.

3. Results

To measure the rise and decay of photoconductivity with time, thin film samples were mounted in a metallic sample holder and light 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 photocurrent during decay.

To study the persistent photoconductivity behaviour in the present glassy system, we performed three sets of measurements for the rise and decay of photoconductivity, as described below.

The first set of measurements was taken at room temperature by varying the light intensity, keeping the illumination time constant (45 min, in the present case). A vacuum of $\sim$10^{-2}Torr was maintained during the measurements. The experimental data for the rise and decay at different intensities for the case of $Se_{0.75}Ge_{0.20}Ag_{0.05}$ in white light is plotted as a function of time in Figures 1 and 2, respectively. The results for other glasses were also of the same nature.
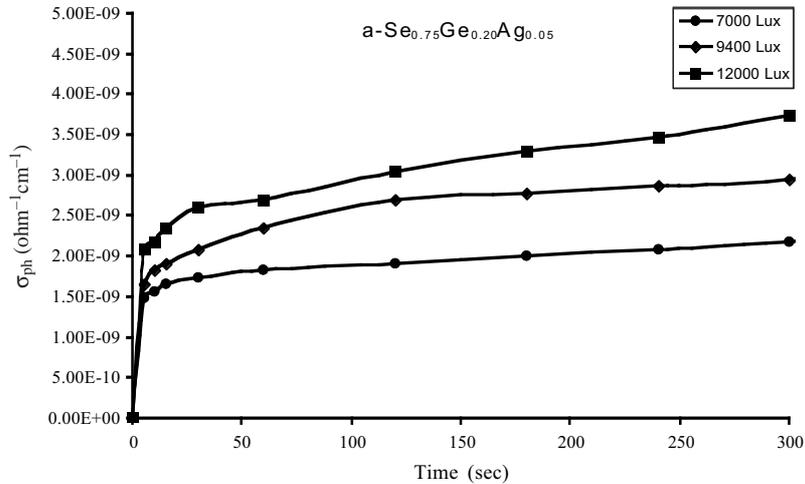
Figure 1. Rise of photoconductivity with time in a-$Se_{0.75}Ge_{0.20}Ag_{0.05}$ at different intensities at 297 K.
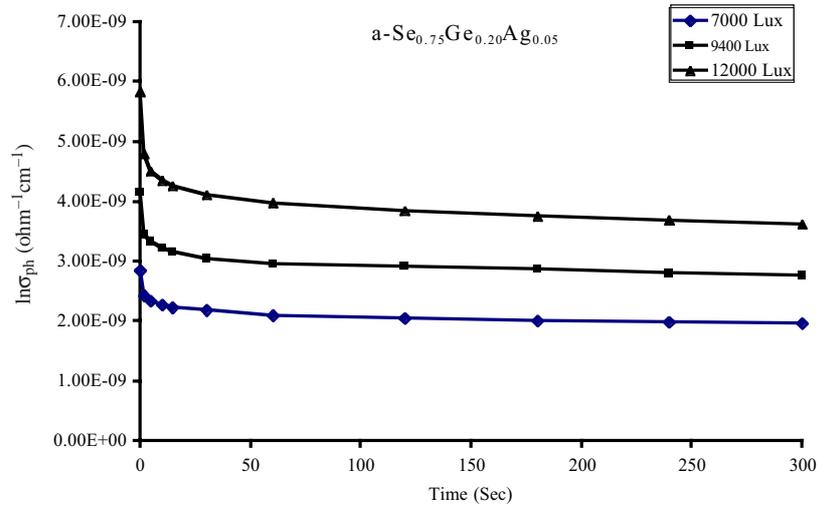
Figure 2. Decay of photoconductivity with time in a-$Se_{0.75}Ge_{0.20}Ag_{0.05}$ at different intensities at 297 K.

It is clear from Figure 1 that the photocurrent initially rises fast then slows, saturating after much time. The nature of the curves is similar at different intensities. The behaviour of the decay curves (shown in Figure 2) is also of the same nature at different intensities. Initially, the photocurrent decays fast and then becomes slow as time elapses. A persistent photocurrent is also observed which takes many hours to decay.

Another set of measurements was made at different temperatures keeping the intensity of light constant at 12000 Lux. The illumination time for the present measurements was 45 minutes. The rise and decay of photocurrent in case of a-$Se_{0.75}Ge_{0.20}Ag_{0.05}$ is shown in Figures 3 and 4, respectively. In this case also, the behaviour of the rise and decay curves is similar at different temperatures. The rise as well as decay both are initially fast, then becomes slow as time elapses. A persistent photocurrent is observed in this case also, which takes many hours to decay. The results for other glasses were also of the same nature.
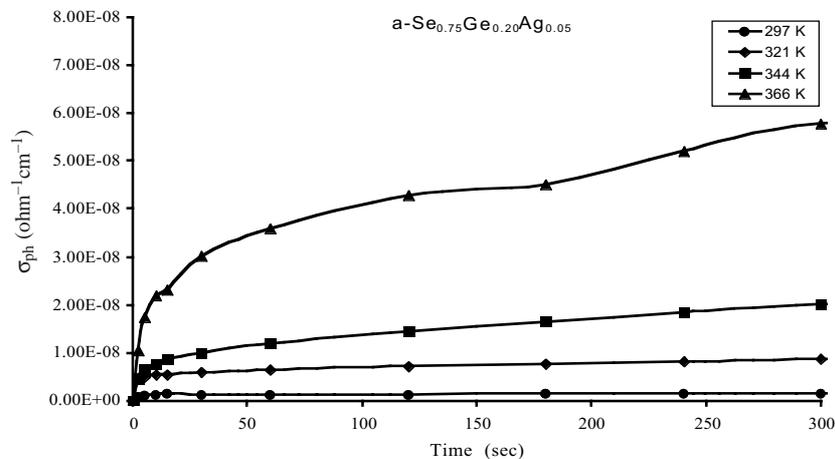
Figure 3. Rise of photoconductivity with time in a-$Se_{0.75}Ge_{0.20}Ag_{0.05}$ at different temperatures at 12000 Lux.
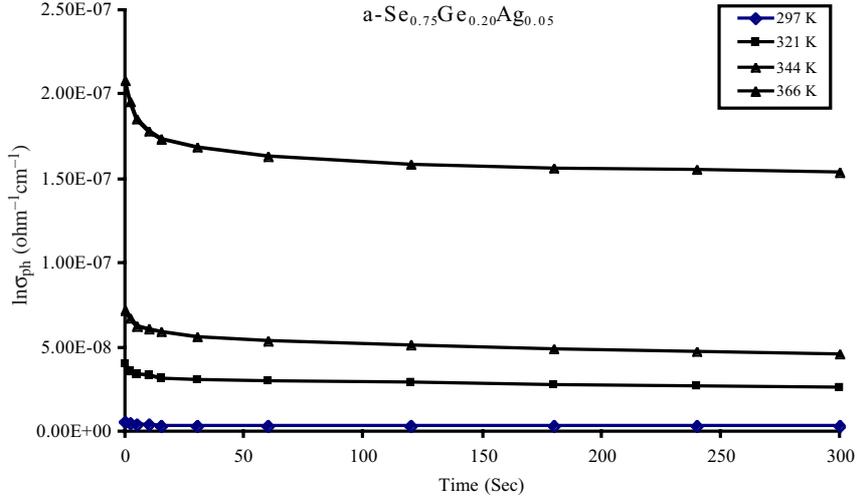
Figure 4. Decay of photoconductivity with time in a-$Se_{0.75}Ge_{0.20}Ag_{0.05}$ at different temperatures at 12000 Lux.

The third set of measurements has been taken at different illumination times. Figure 5 shows the results of decay of photoconductivity measurements in case of a-$Se_{0.75}Ge_{0.20}Ag_{0.05}$. In this case also, persistent photoconductivity is observed even at the lower illumination time of 5 minutes. The results for other glasses were also of the same nature.
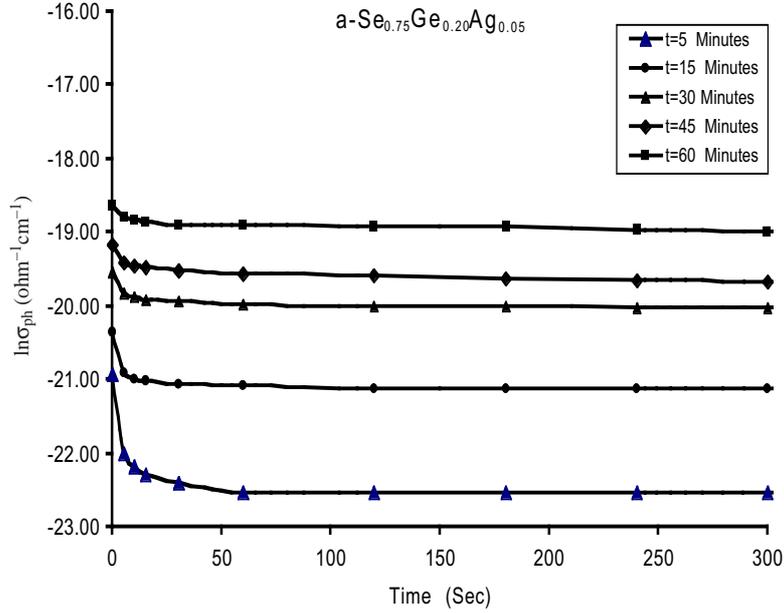
Figure 5. Decay of photoconductivity with time in a-$Se_{0.75}Ge_{0.20}Ag_{0.05}$ at different illumination times at 297 K and 12000 Lux.

To compare the persistent photocurrent effect as a function of intensity, temperature and illumination time, we define the quantity Persistent Photoconductivity (PPC) as

$$PPC = (\sigma_l - \sigma_d)/\sigma_d, \tag{1}$$

where σ_l is the total conductivity of the light induced state, i.e. the total conductivity after the decay of 300 sec, and σ_d is the dark conductivity of the amorphous state. $(\sigma_l - \sigma_d)$ will therefore represent the remaining photoconductivity σ_{ph} in the decay curves of Figures 2, 4 and 5.

PPC is calculated for the decay curves and these values are plotted as a function of intensity, temperature and illumination time in Figures 6, 7 and 8, respectively. It is clear from these figures that PPC increases with illumination intensity and illumination time at particular temperature of measurement (297 K, in the present case). However, PPC is found to decrease on increase in temperature at a particular illumination intensity and illumination time. Similar results were also obtained in other glasses. To see the effect of Ag addition on the PPC in binary Se-Ge alloy, the intensity dependence of PPC is plotted for different samples in Figure 9. It is clear from this figure that PPC decreases on addition of Ag in $Se_{0.80-x}Ge_{0.20}Ag_x$ at all intensities.
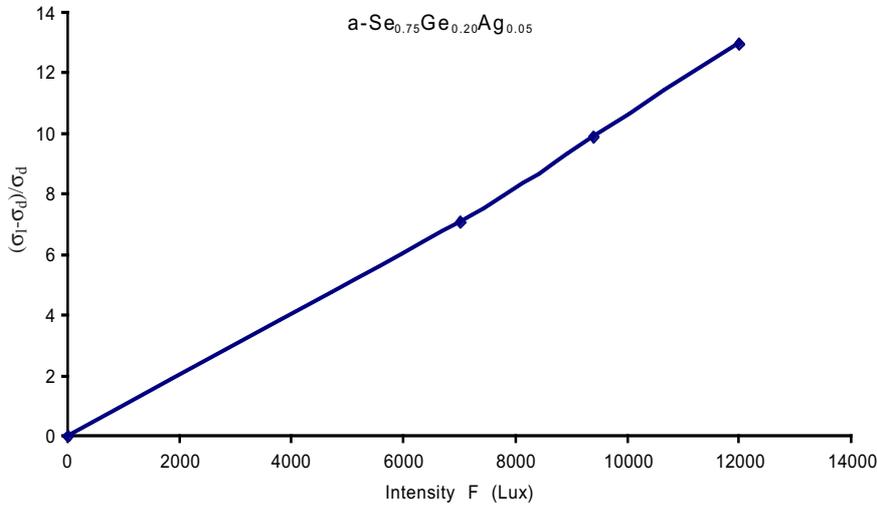
Figure 6. PPC at different intensities in a-$Se_{0.75}Ge_{0.20}Ag_{0.05}$.
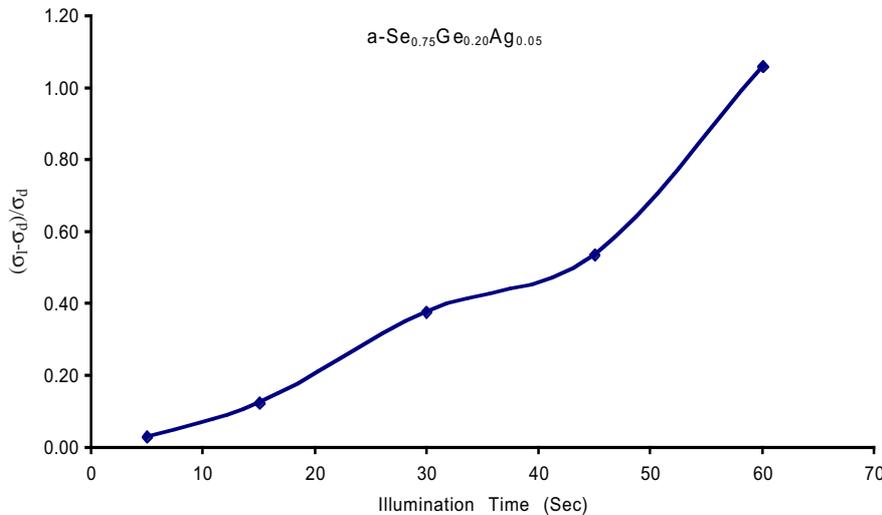
Figure 7. PPC at different illumination times in a-$Se_{0.75}Ge_{0.20}Ag_{0.05}$.
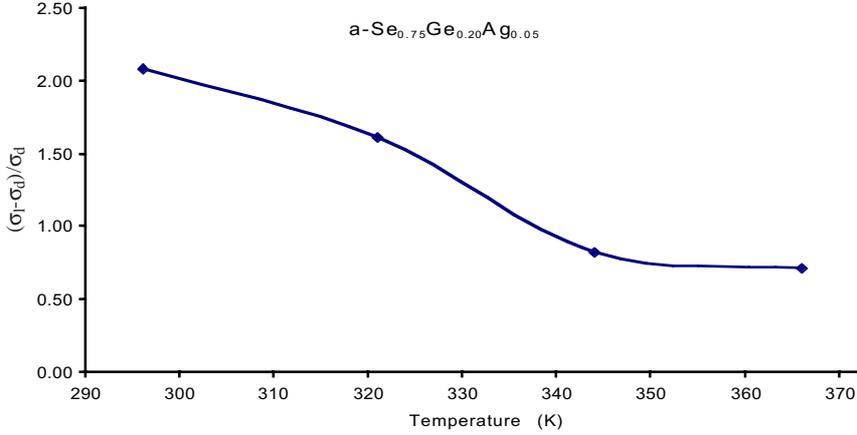
Figure 8. PPC at different temperatures in a-$Se_{0.75}Ge_{0.20}Ag_{0.05}$.
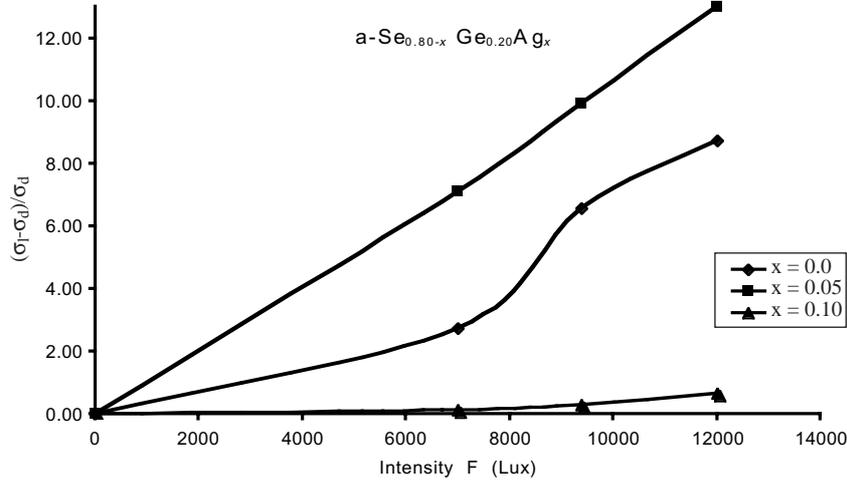
Figure 9. Comparison of PPC for various samples at different intensities in a-$Se_{0.80-x}Ge_{0.20}Ag_x$.

Since the persistent photocurrent increases with light intensity as well as illumination time, it is expected that the persistent photocurrent may be due to light-induced structural defects, which are accumulated during the illumination through structural changes. The decrease in PPC at higher temperatures is consistent with this concept as light induced effects are expected to be removed more quickly at higher temperatures.

Such long-lived photocurrent has also been observed in other chalcogenide glasses [17–33]. It is believed that such a large decay constant can not be due to carriers trapped in the intrinsic defects. It may be due to light-induced defects through structural changes on light shining which are of reversible kind, i.e., they are removed on annealing at room temperature for longer times.

4. Discussion

Persistent photoconductivity in the decay curves of photoconductivity has already been reported by various researchers [18–37]. Fuhs and Meyer [22] tried to explain the slow decay in a-As_2Se_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 et al. [24] explained the slow decay in a-Ge-Se by applying the Street-Mott model [38]. Kumeda et al. [25] observed that the slow decay of the photoconductivity in a-$Ge_{0.42}S_{0.58}$ film occurs with an accompanying decrease in the photo-induced ESR signal. Decrease in the

ESR signal provides evidence that the metastable D^0 defect acts to limit the photoconductivity. Shimakawa et al. [23] explained the slow decay in a-As$_2$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 [17] explained extremely long-lived residual photocurrent in a-In$_2$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 et al. [21] in a-As$_2$Se$_3$ films with Sn impurity. The origin of persistent photoconductivity in hydrogenated a-Si:H has been explained by Lee et al. [31] 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 which can not be understood by simply considering the charge carriers trapped in defect states. Moreover, as the persistent photoconductivity strongly depends on illumination time, intensity of light, we expect that reversible light-induced structural changes are possible. Such type of structural changes may have large time constants, some times as high as a few days, as observed in the present samples.

The smaller PPC at higher concentration of Ag may be understood in terms of lesser effect of light induced defects in Ag rich samples in Se-Ge-Ag system, as the inherent structural defects states may be higher in ternary Se-Ge-Ag system [1–3] compared to binary Se-Ge system.

5. Conclusion

Transient photoconductivity measurements at different temperatures, intensities and illumination times indicate that decay of photoconductivity has two components. Initially it is very fast and then become quite slow. A persistent photocurrent is observed in all the cases. PPC increases at higher intensities and for longer illumination times. However it decreases with increase in temperature. This effect is attributed to light induced effects in these materials. These effects are reversible as the persistent photocurrent vanishes on annealing at room temperature for longer times. The decrease in PPC at higher temperatures is consistent with this concept as light induced defects are expected to be removed faster at higher temperatures. The persistent photoconductive effect is found to be suppressed on increase of Ag concentration in a- Se$_{0.80-x}$Ge$_{0.20}$Ag$_x$, which may be understood in terms of smaller effect of light induced defects due to higher concentration of inherent structural defects in dark at higher concentration of Ag.

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