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Effect of Ag impurity on photoconductive properties of selenium-tellurium glasses

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The paper reports the effect of silver impurity on photoconductive properties of selenium-tellurium glassy system. Steady state and transient photoconductivity is reported in Se-Te glassy alloy with and without silver impurity. The dark conductivity of $Se_{70}Te_{30}$ increase, while activation energy is found to decrease with silver concentration. Photosensitivity also decreases with silver impurity. It has been observed that under certain experimental conditions, the transient measurement shows anomalous behaviour (i.e. peak in photoconductivity and negative photoconductivity in rise) in samples having Ag impurity. The recovery process of transient photoconductivity also takes a long time in Ag contained samples. This anomalous behaviour of photoconductivity has been studied at various temperatures and various illumination times. The results have been explained on the basis of the interaction of Ag^+ ions and photo-excited holes.

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Keywords: Chalcogenide glasses**,** Transient photoconductivity, Amorphous thin films

1. Introduction

Chalcogenide glasses are promising materials because of their potential application in various solid-state devices and in optical applications [1-3]. Selenium exhibits the unique property of reversible phase transformation [4]. Its various device applications like rectifiers, photocells, xerography, switching and memory, etc. have made it attractive, but pure selenium has disadvantages like short lifetime and low photo-sensitivity. This problem can be overcome by alloying Se with Te, which gives higher photo-sensitivity, higher crystallization temperature and smaller aging effects [5–7]. Several researchers [8–15] have reported the impurity effects in various chalcogenide glasses. The electrical properties of chalcogenide glasses are not, in general, affected appreciably by the incorporation of impurity because the random network of atoms can accommodate an impurity without creating an extra electron - hole pair. This concept is based on the fact that an impurity atom can satisfy its valance requirements by adjusting its nearest neighbour environment, thus causing negligible effect on electrical properties [16]. However, experimental results reported by various workers have shown that there are a few cases in which the addition of impurity atom does change the electrical properties significantly [17-21]. It has been observed that (by alloying Ag with As_2S_3) the conductivity of As_2S_3 increases [21-23] and the large increase in the conductivity has been explained on the basis of the increase in the number of charged dangling bonds. The photo - dissolution of Ag into chalcogenide glasses is a promising phenomenon for ultrahigh resolution photolithographic process and for fabrication of optical components [24-26]. The investigations have shown the possibility to use Ag photo doped chalcogenide glasses (Ge-Te, As-Ge- Te) for temperature and voltage sensors [27-28]. The results of the measurements indicate that the conductivity of chalcogenide glasses increases with photo/thermal dissolution of Ag into these glasses. The conductivity of glasses for given voltage/temperature increases tremendously after dissolution of Ag. Structural studies using Raman spectra have indicated that the silver photo-doped films of $As_{30}S_{70}$ are homogeneous and have a structure similar to that of bulk glass $Ag_{30}As_{22}S_{48}$ [29-30]. As ionic in nature, Ag doped chalcogenide glasses exhibit interesting electrical and optical properties, characteristic of ionic conductors and semiconductors. That is, the electrical conductivity is governed by Ag^+ ionic conduction since the hole conductivity is substantially smaller and electron conductivity is not detected [31-33].

The present paper reports the measurements of electrical and photoconductive properties of $Se_{70}Te_{30}$ before and after Ag incorporation into it and show how the electrical properties and photoconductive behaviour of $Se_{70}Te_{30}$ changes after the silver addition. The interesting results of a peak in transient measurements and the negative photoconductivity, in silver doped samples, is presented here and explained on the basis of the interaction of Ag^+ ions and photo-excited holes.

2. Experimental

Glassy alloys of Se_{70} $Te_{30-x}Ag_x$ (x = 0, 2, 4, 6, 8) have been prepared from the melt by quenching technique. The exact proportion of the high purity (5N) elements, in accordance with their atomic percentage, are weighed using an electronic balance (LIBROR, AEG-120) with a least count of 10^{-4} gm. The material are then sealed in evacuated (~ 10^{-5} Torr) quartz ampoules of 8 mm internal diameter and 5 cm length. The ampoules containing the materials are heated to 1000 ^oC and held at that temperature for 10–12 hours. The temperature of the furnace is raised slowly at a rate of 3-4 ^oC /min. During heating all the ampoules are constantly rocked, by rotating

ceramic rod to which ampoules were tucked away in the furnace. This was done to obtain homogeneous glassy alloys. Thereafter, the obtained melt is cooled rapidly by removing the ampoules from the furnace and dropping them to ice cooled water. The quenched samples are taken out by breaking the ampoules.

Amorphous materials are often defined by their diffraction patterns, which consist of few broad halos rather than sharp Bragg's reflections. Keeping this in view, the glassy nature of the alloy was ascertained by X-ray diffraction pattern. Glass transition temperature (T_g) was obtained from Differential Scanning Calorimetry measurements.

Thin films of the glassy alloys are prepared by vacuum evaporation technique using a standard coating unit (IBP Torr, EPR 002). The micro slides of size 2.5 cm length, 1.0 cm width and 2.0 mm thick were used as substrate. Vacuum evaporated indium electrodes at bottom are used for electrical contacts. The thickness of film is ~ 500 nm. The co-planar structure (length ~ 1.2 cm and electrode separation ~ 05 mm) is used for these measurements.

The electrical conductivities in dark as well as in presence of light are studied by mounting them in a specially designed sample holder, in which the illumination could be achieved through a transparent window in a vacuum of 10^{-2} Torr. The source of light is a 200 Watt tungsten lamp. The intensity of light is varied by changing the voltage across the lamp. The intensity is measured by a lux meter (Testron model LX – 101). A dc voltage of 10 volt is applied across the film and the resulting current is measured by a digital electrometer (Keithley, model 614). I-V characteristics are found to be linear and symmetric upto 30 volts in all the glasses studied. The heating rate is kept quite small (0.5 K/min) for these measurements.

3. Results

3.1 Temperature dependence of dark conductivity

The dark conductivity is measured as a function of temperature (306 K – 327 K) in thin films of $Se_{70}Te_{30}$ with and without silver impurity. The results of these measurements are plotted in Fig. 1. It is clear from this figure that ln σ_d vs 1000/T curves are straight lines for all the samples indicating that the conduction in these glasses is through an activated process having a single activation energy in the above temperature range. The dark conductivity can, therefore, be written as

$$\sigma_d = \sigma_o \exp(-\Delta E/kT) \quad (1)$$

where ΔE is the activation energy for dark conduction and k is the Boltzmann's constant.It is clear from the Table 1 that σ_d increases and ΔE decreases as silver concentration is increased in $Se_{70}Te_{30}$. These results are plotted in Fig. 2.

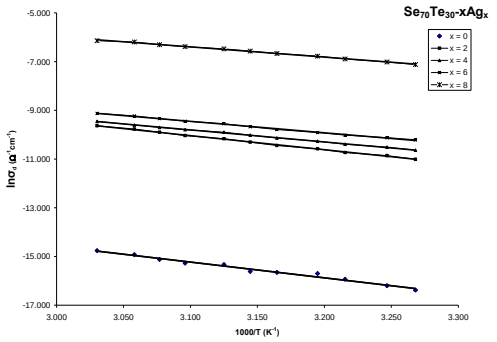

Fig. 1. Temperature dependence of dark conductivity for various samples in amorphous $Se_{70}Te_{30-x}Ag_x$ thin films.

Table 1. Electrical parameters in amorphous $Se_{70}Te_{30-x}Ag_x$ thin films.

	σ_d ($\Omega^{-1}cm^{-1}$) at 306 K	ΔE (eV)	σ_o ($\Omega^{-1}cm^{-1}$) at 306 K	σ_{ph}/σ_d at 306 K, 7700 lux
$Se_{70}Te_{30}$	7.69×10^{-8}	0.56	1.24×10^{2}	8.1
$Se_{70}Te_{28}Ag_2$	1.65×10^{-5}	0.50	2.89×10^{3}	3.3
$Se_{70}Te_{26}Ag_4$	2.40×10^{-5}	0.43	2.42×10^{2}	3.0
$Se_{70}Te_{24}Ag_6$	3.68×10^{-5}	0.40	1.60×10^{2}	1.4
$Se_{70}Te_{22}Ag_8$	8.08×10^{-4}	0.36	7.47×10^{2}	0.7

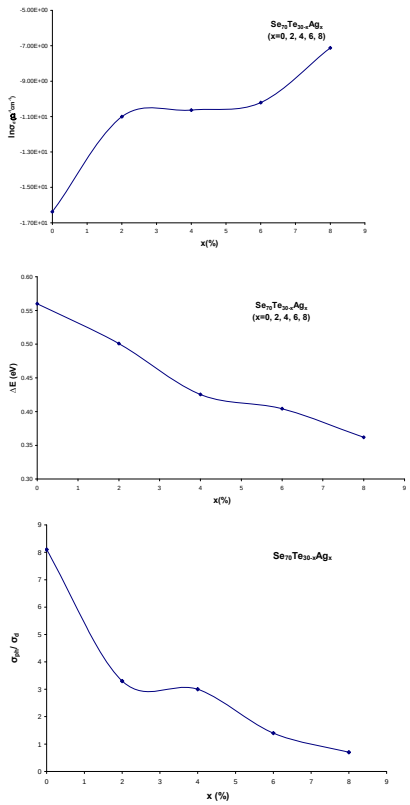

Fig. 2. Composition dependence of dark conductivity (σ_d), activation energy (ΔE) and photosensitivity (σ_{ph}/σ_d) in amorphous $Se_{70}Te_{30-x}Ag_x$ thin films.

3.2 Transient photoconductivity

Transient photoconductivity measurements have been made in amorphous thin films of $Se_{70}Te_{30-x}Ag_x$ for x = 0, 2, 4, 6, 8. However, the results of samples having x = 0 and 2 are being reported here as for other samples (x = 4, 6, 8), the photoconductivity behaviour is found to be similar as in case of x = 2.

Fig. 3 shows the rise of photoconductivity with time, at different intensities (2900-7700 lux) at 306 K in amorphous $Se_{70}Te_{30}$ and $Se_{70}Te_{28}Ag_2$. For these measurements, light was shone on the sample for 120 sec. Fig. 4 shows the subsequent decay of photoconductivity with time. The decay was recorded for 300 sec. From Fig. 3, it is clear that photoconductivity rises monotonically to the steady state value in pure as well as in the presence of Ag at 306 K. The photoconductivity takes about 120sec to reach the steady state value in the present case. Such a rise of photoconductivity is common in chalcogenide glasses [37, 38, 39, 40, 41and 42], and we, therefore, call it a normal behaviour.

It is clear from Fig. 4 that the photoconductivity decays monotonically to zero value in the above case. The decay is found to be non-exponential, and can be fitted by taking the sum of various exponential decay curves (results not shown here). Such type of decay of photoconductivity is also common in chalcogenide glasses, and we, therefore, call it normal behaviour.

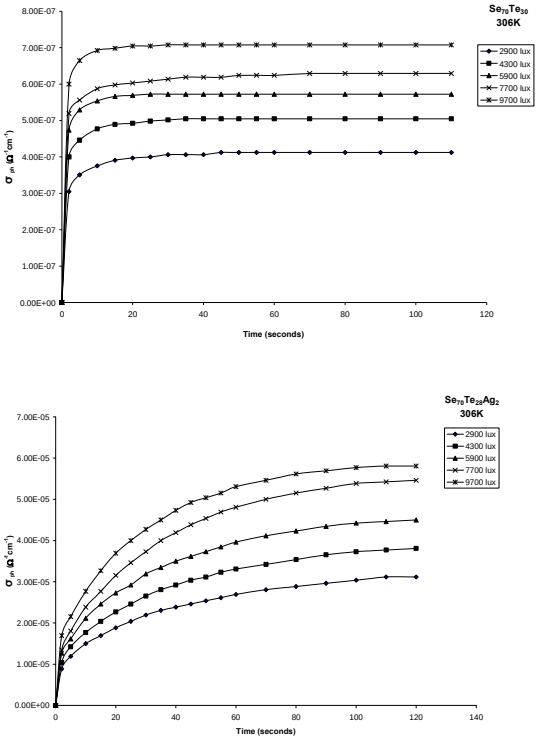

Fig. 3. Rise of photoconductivity at different intensities in amorphous $Se_{70}Te_{30}$ and $Se_{70}Te_{28}Ag_2$ thin films.

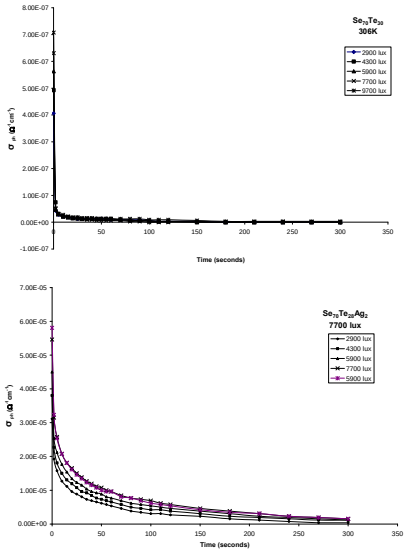

Fig. 4. Decayof photoconductivity at different intensities in amorphous $Se_{70}Te_{30}$ and $Se_{70}Te_{28}Ag_2$ thin films.

Figs. 5 and 6 show the rise and decay of photoconductivity with time at different temperatures (306, 313, 320 and 327 K) at the highest intensity (7700 lux) of light. It is clear from these figures that, at higher temperatures, rise and decay show normal behaviour in pure sample of $Se_{70}Te_{30.}$ However, with Ag impurity the photoconductivity becomes negative during illumination, and that the subsequent photoconductivity decay starts from a negative value and becomes more negative before reaching to zero value. The rise is found to be quite different. In the rise curve, the photoconductivity also becomes maximum at a particular time. We call this behaviour anomalous, as this type of behaviour is not common in chalcogenide glasses. Only in a few more glass systems (As_2Se_3, $Ge_{22}Se_{78}$, AgAs(Ge)S), this type of anomalous behaviour in the rise of photocurrent has been reported [43, 44, 45].

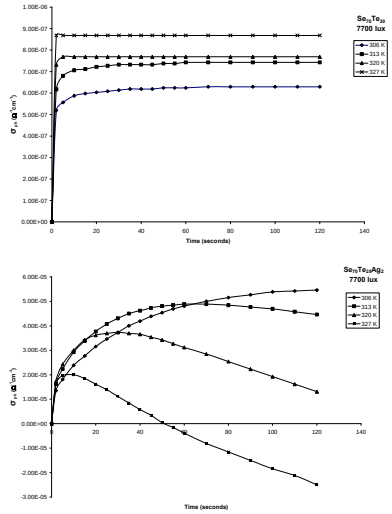

Fig. 5. Rise of photoconductivity at different temperatures in amorphous $Se_{70}Te_{30}$ and $Se_{70}Te_{28}Ag_2$ thin films.

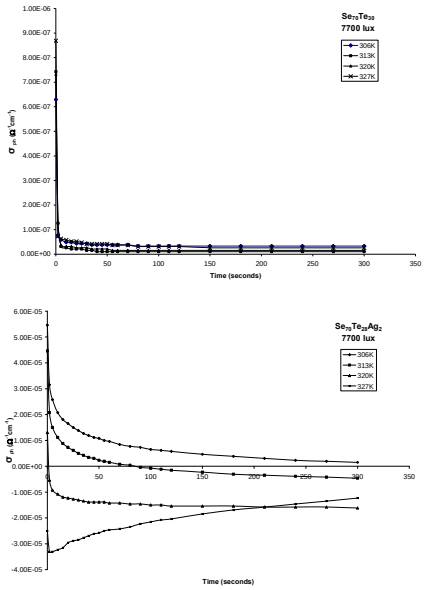

Fig. 6. Decay of photoconductivity at different temperatures in amorphous $Se_{70}Te_{30}$ and $Se_{70}Te_{28}Ag_2$ thin films.

Figs. 7 and 8 show the rise and decay of photoconductivity at different illumination times (60, 120, 300, 600 and 1800 sec) at room temperature (306 K) at the highest intensity (7700 lux) of light. It is clear from these figures that, for lower illumination times (<120 sec), the anomalous behaviour of photo-conductivity in rise and decay is not seen, even at the highest intensity of light (7700 lux). As illumination time increases, the anomalous behaviour of photoconductivity in rise and decay is observed. No anomalous behaviour is, however, observed in case of $Se_{70}Te_{30}$ thin films even at higher illumination times. The above results indicate that the anomalous behaviour is due to Ag impurity in $Se_{70}Te_{30}$ system.

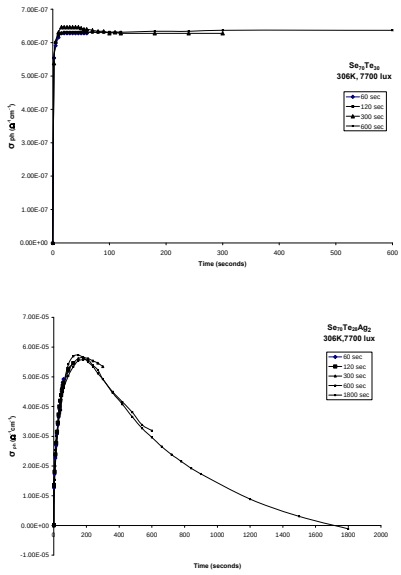

Fig. 7. Rise of photoconductivity at different temperatures in amorphous $Se_{70}Te_{30}$ and $Se_{70}Te_{28}Ag_2$ thin films.

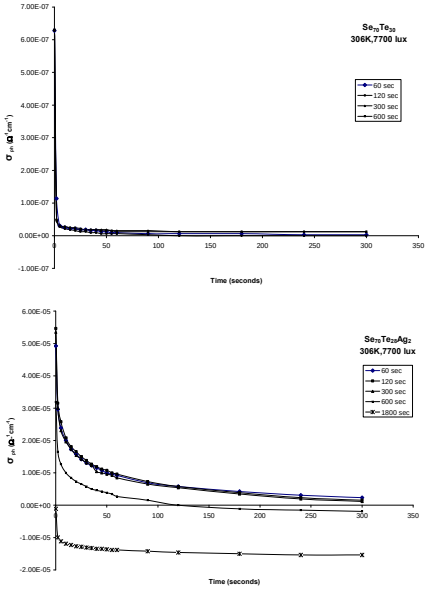

Fig. 8. Rise of photoconductivity at different temperatures in amorphous $Se_{70}Te_{30}$ and $Se_{70}Te_{28}Ag_2$ thin films.

4. Discussion

When Ag is added into the Se-based glasses, Ag–Se ionic bonds are formed. This has been confirmed in several structural studies [34,35]. In Ag-rich chalcogenide glasses, $\mu_h > \mu_{Ag}^+$ and $\mu_h >> \mu_e$, where μ_h, μ_{Ag}^+ and μ_e are mobilities of the hole, Ag^+ ion and electron [36].

When a film is connected to an external voltage source and light is shone on it, photoexcited holes may flow from the positive electrode to the negative electrode. Ag^+ ions may not influence hole flow if the distribution of Ag^+ ions is uniform. Furthermore, photoexcited electrons will not contribute to the photo-current, since their mobility is negligibly small. Therefore, the photocurrent may be considered to be due only to hole flow. In the present case, the photoconductivity rises with time, reaches its maximum value within a few minutes from the start of illumination and then decreases under illumination, as shown in Figs. 5.

In Ag-rich chalcogenide glasses, upon illumination, a negative Dember photovoltage is reported [36], with a time constant of 10^3 s and then it decays slowly. The response after terminating illumination is also slow, continuing for hours and days. The reason for such a Dember voltage is given in terms of the diffusion of holes towards the back electrode, as holes are more mobile than electrons in silver rich glasses [36]. Hence, the front electrode will provide negative photovoltage. Based on the above experimental results regarding Ag doped glasses, the anomalous behaviour in rise and decay of photocurrent can be explained as follows:

In the present case, first, the bulk of photoconduction may occur where photocurrent rises to the maximum value; and then due to the appearance of Dember voltage, photocurrent starts decreasing, and may also be negative at very high temperatures where Ag^+ becomes more mobile.

When the 1ight is switched off, the photocurrent reaches zero slowly, and takes a few hours or a few days as the Dember voltage approaches zero. It is interesting to note that the fall-off of photoconductivity from its maximum is faster as the temperature is increased (Fig. 5), due to more rapid movement of silver ions at high temperatures. The decay curves at different temperatures, (Fig. 6), indicate that the photocurrent approaches zero at a faster rate at higher temperatures. This is also expected to be due to rapid movement of Ag^+ ions at higher temperatures.

5. Conclusions

Temperature dependence of dark conductivity is studied in vacuum-evaporated thin films of amorphous $Se_{70}Te_{30-x}Ag_{x,}$ where x is varied from 0 to 8. The values of ΔE, $\sigma_{d,}$ σ_o and $\sigma_{ph/}$ σ_d are calculated. The results of these calculation show that σ_d increases while ΔE and $\sigma_{ph/}$ σ_d decreases with silver incorporation.

The rise and decay of photoconductivity have also been studied in the above series at various intensities, illumination times and temperatures. It has been observed that in silver doped samples, under certain experimental conditions, the rise and decay of photoconductivity show anomalous behaviour. When light is shone, photoconductivity first increases, attains a maxima and then decreases under illumination and becomes negative in some cases. When light is turned off, the photoconductivity decays from negative value, and then levels off to zero value after a very long time. The anomalous effect is found to be greater at longer illumination times and higher temperatures. The above results indicate that the anomalous behaviour is due to Ag impurity in $Se_{70}Te_{30}$ system. The resu1ts are explained on the basis of the interaction between photoexcited holes and Ag^+ ions.

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