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PHOTOCONDUCTIVITY AND HIGH FIELD EFFECTS IN AMORPHOUS $Se_{75}In_{10}Sb_{15}$ THIN FILM

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This paper shows that $Se_{75}In_{10}Sb_{15}$ thin film can be prepared by thermal evaporation technique. Current–voltage (I-V) characteristics and photoconductivity measurements have been obtained. Coplanar indium electrodes were used. At low electric field, the behavior of the current suggests ohmic conductivity. However, at high electric fields ($E \sim 10^4$V/cm), non ohmic behavior is observed. An analysis of the experimental data confirms the presence of space charge limited conduction (SCLC) in the glassy material studied in the present case. From the fitting of the data to the theory of SCLC, the density of defect states (DOS) near Fermi level is calculated. Temperature dependence of steady state and transient photoconductivity measurements in the aforesaid thin film at different temperature and intensity has been obtained. Temperature dependence of conductivity in dark as well as in presence of light shows that conduction is through a thermally activated process in both the cases. The activation energy is found to decrease with the increase in light intensity. This indicates the shift of Fermi level with intensity. Transient photoconductivity measurements at different temperatures indicate that the decay of photoconductivity is quite slow which is found to be non-exponential in the present case indicating the presence of continuous distribution of defect states in the aforesaid glassy alloys.

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1. Introduction

The phenomenon related with electronic conduction in amorphous chalcogenides semiconductors has attracted a great deal of scientific attention since the discovery of electrical switching in chalcogenides glasses in 1968 [1]. Selenium is selected because of its wide commercial applications. In pure state this Se has disadvantages because of its short lifetime and low sensitivity. To overcome these difficulties, certain additives are used e.g. Sb, In, Te, Ge etc. and binary and ternary alloys are formed [2].

Since, network connectivity, rigidity and nature of bonding do play important roles in electronic conduction process [3] and hence in order to understand the conduction phenomena, a great deal of experimental data is required. Many workers have carried out the investigations of electrical and optical properties of binary and ternary chalcogenides glasses [4-7].

Glassy Se-In alloys have drawn great attention because of their potential application in solar cells [8-9]. The effect of incorporation of third element in binary chalcogenide glassy alloys has always been an interesting problem in getting relatively stable glassy alloys as well as to change the conduction type from p to n as most of these glasses show p type conduction only. In Ge - Se and Se - In systems, some metallic additives have been found [10-15] to change conduction from p type to n type and hence these binary systems are of great importance.

Though the electrical and optical properties of these glasses have been studied by various workers the photo-conducting properties of these glasses have not been studied in detail. Since the

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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. From application point of view also photoconductive properties are important.

As high field effects are most readily observed in these materials because of their low conductivity (Joule heating is negligibly small at moderate temperatures) and have been studied by various groups working in this field [16-25]. The result of these workers have been interpreted in terms of heating effect, space charge limited conduction (SCLC) and high field conduction due to the Poole - Frenkel effect. This indicates that the interpretation of the high field data is highly intriguing in these materials and much has to be done in this field.

Keeping this fact in mind, we report in this paper, the high field conduction and photoconductivity measurements in glassy $Se_{75}In_{10}Sb_{15}$ thin film. The experimental data fits well with the theory of space charge limited conduction (SCLC) in the high electric field region. From the fitting of the data, the density of defect states (DOS) near Fermi level is calculated.

Temperature dependence of steady state photoconductivity is also studied at different light intensities. Intensity dependence of photoconductivity is studied at different fixed temperatures. Transient photoconductivity measurements at different temperatures have also been obtained. Section 2 describes the experimental details. The results have been presented and discussed in section 3. The conclusions have been presented in the last section.

2. Experimental technique

2.1 Sample preparation

Glassy alloy of $Se_{75}In_{10}Sb_{15}$ system was prepared by melt quenched technique. High purity elements (99.999 %pure), selenium, indium and antimony were weighed by electronic balance according to their atomic percentages .The properly weighed materials were put into clean quartz ampoule (length ~ 5 cm and internal diameter ~ 8 mm) and then sealed under vacuum of 1.3×10^{-3} Pa. This sealed ampoule was heated in electric furnace up to 1000°C and kept at that temperature for 10 - 12 hours. The temperature of the furnace was raised slowly at a rate of 3-4 °C/min. During the heating process ampoule was constantly rocked, by rotating a ceramic rod to which the ampoule was tucked away in the furnace. This was done to obtain homogenous glassy alloy.

After rocking for about 10 hours, the obtained molten materials ampoule rapidly quenched by removing the ampoule from the furnace and dropping into ice-cooled water. The quenched samples of the glassy alloy was taken out by breaking the quartz ampoule. The amorphous nature of sample was confirmed by the absence of any sharp peak in the X-ray diffraction pattern. Compositional analysis was performed using electron probe micro- analysis (EPMA) technique.

2.2 Preparation of thin films

Thin film of glassy alloy of $Se_{75}In_{10}Sb_{15}$ was prepared by vacuum evaporation technique keeping glass substrate at room temperature. Vacuum evaporated indium electrodes at bottom were used for the electrical contact. The thickness of the film is ~ 500 nm. The co-planar structure (length ~ 1.2 cm and electrode separation ~ 0.12 mm and 0.5 mm) is used for the present measurements. A vacuum ~ 1.3 Pa was maintained in the entire temperature range (300K to 340K).

2.3 Procedure of measurements

The thin film was kept in the deposition chamber in the dark for 24 hours before mounting that in the sample holder. This was done to allow sufficient annealing at room temperature so that a metastable thermodynamic equilibrium may be attained in the sample as suggested by Abkowitz [26]. Before measuring the d. c. conductivity, the film was first annealed at 340K (below their glass transition temperature, T_g) for one hour in a vacuum ~ 1.3 Pa.

As co-planar structure of the film is used for the present measurements, a d. c. voltage was applied across the electrodes to measure I-V characteristics and found to be linear and symmetric up to 10 V. The present measurements are, however, made by applying a voltage up to 300 V across the films. The resulting current is measured by a digital Pico-Ammeter. The heating rate was kept quite small (0.5 K/min) for these measurements. Thin film sample was mounted in a specially designed sample holder. A vacuum ~ 1.3 Pa was maintained throughout the measurements. The temperature of the film was controlled by mounting a heater inside the sample holder, and measured by a calibrated copper- constantan thermocouple mounted very near to the film.

The dark and photo-conductivity of the amorphous film was studied by mounting that in a specially designed metallic sample holder in which illumination could be achieved through a transparent window. The light source used for these measurements was a 200 W tungsten lamp. Light intensity was measured by a digital lux meter (Testron, model LX-101). The photocurrent (I_{ph}) was obtained after subtracting the dark current (I_d) from the current measured in the presence of light.

3. Results and discussions

3.1 High field conduction measurements

Results of I -V characteristics at different temperature shows that in the glassy sample studied here, ohmic behavior is observed at low voltages, i.e., up to 10 V. However, at higher voltages ($E \sim 10^4$ V/cm), a super-ohmic behavior is observed in the sample. Here, ln I/V vs. V curves are found to be straight lines. Fig.1 shows such curves in case of $Se_{75}In_{10}Sb_{15}$glassy alloy. According to the theory of SCLC, in the case of a uniform distribution of localized states having density g_0, the current (I) at a particular voltage (V) is given by [27]:

$$I = (2\ e\ A\ \mu\ n_0 V/\ d) \quad [\exp (SV)] \tag{1}$$

Here, e is the electronic charge, A is the cross sectional area of the film, n_o is the density of free charge carriers, d is the electrode spacing and S is given by:

$$S = 2\ \varepsilon_r\ \varepsilon_0 / e\ g_0\ k\ T\ d^2 \tag{2}$$

Where ε_r is the static value of the dielectric constant, ε_0 is the permittivity of free space, g_0 is the density of traps near the Fermi level and k is Boltzmann's constant.

It should be noted that eq. 1 is not an exact solution of SCLC equation, but is a very good approximation of the one carrier space charge limited current under the condition of a uniform distribution of traps. In the present case, the one carrier assumption is justified as these glasses are known to behave as p- type material. As present measurements scan a very limited range of energy near the Fermi level, the assumption of uniform distribution of traps is also not unjustified.

According to eq.1, ln I/V vs. V curves should be straight lines whose slope should decrease with increase in temperature as evident from eq.2. It is clear from Fig. 1that the slope (S) of ln I/V vs. V curves is not the same at all the measuring temperatures. The value of these slopes is plotted as a function of temperature in Fig.2 for the glassy system used in the present study. It is clear from this figure that the slope decreases linearly with the increase in temperature. These results indicate the presence of SCLC in the present samples.

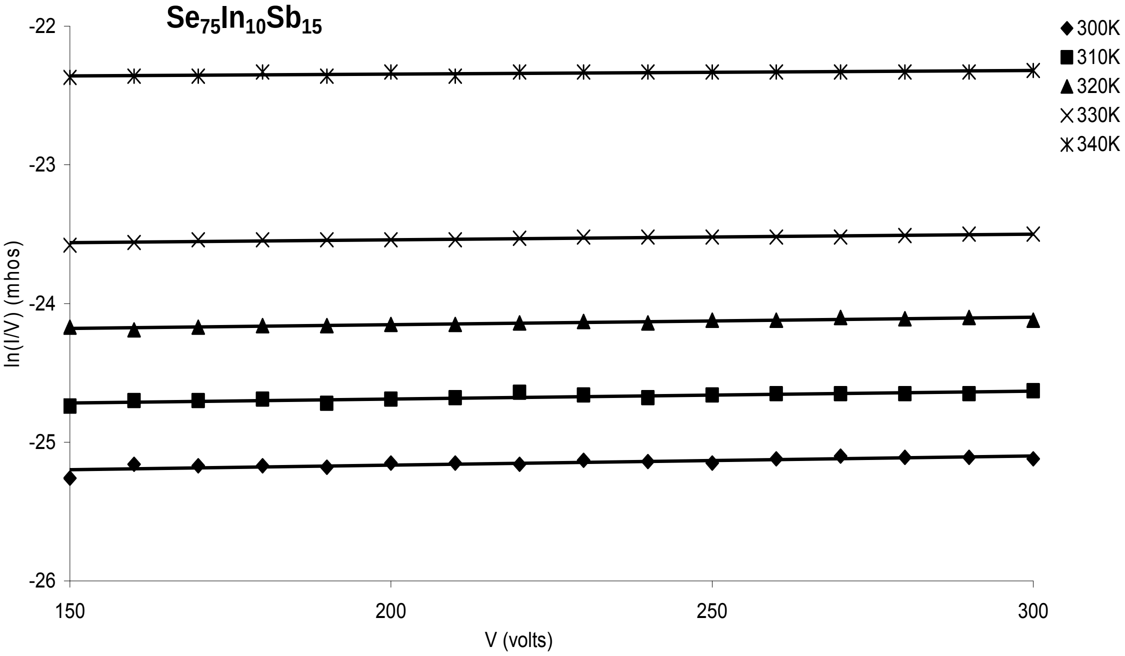

Fig.1. Plot of ln(I/V) vs V curves for $Se_{75}In_{10}Sb_{15}$ at different temperatures.

Using eqn. 2, we have calculated the density of localized states from the slope of Fig. 2. The value of the relative dielectric constant ε_r is measured by using capacitance measuring assembly model "Hioki 3532-50 LCR Hi TESTER", employing the four terminal techniques. The results of these calculations are given in Table 1.

Table 1. Density of localized states (g_0) in $Se_{75}In_{10}Sb_{15}$ glassy system.

Glassy alloy	Slope of S vs. 1000/T curves	ε_r (at 120 Hz, 305 K)	g_0 ($eV^{-1}cm^{-3}$)
$Se_{75}In_{10}Sb_{15}$	1.02×10^{-3}	17.92	1.56×10^{15}

3.2 Temperature and intensity dependence of dark and photo conductivity

Fig.3 shows the temperature dependence of dark conductivity and steady state photoconductivity at different intensities (F). It is clear from Fig.3 that ln σ vs.1000/T curves are straight lines having single slope indicating that the dark conductivity as well as photoconductivity is due to an activated process having single activation energy in the present range of temperature. The conductivity can, therefore, be written as

$$\sigma = \sigma_0 \exp(-\Delta E / k T) \quad (3)$$

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

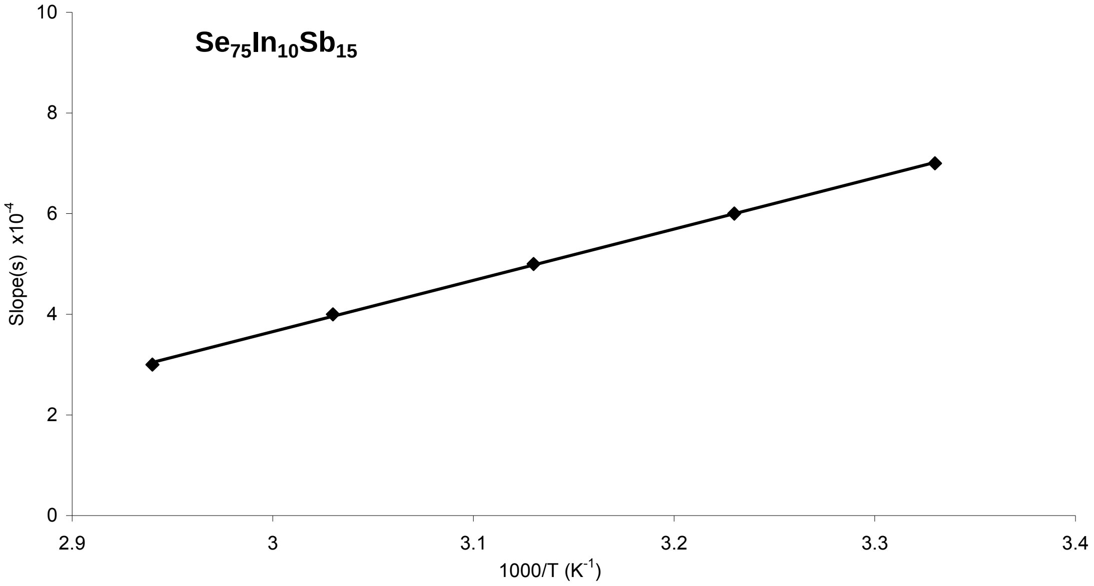

Fig.2. Plots of S vs. 1000/T curve for $Se_{75}In_{10}Sb_{15}$ glassy system.

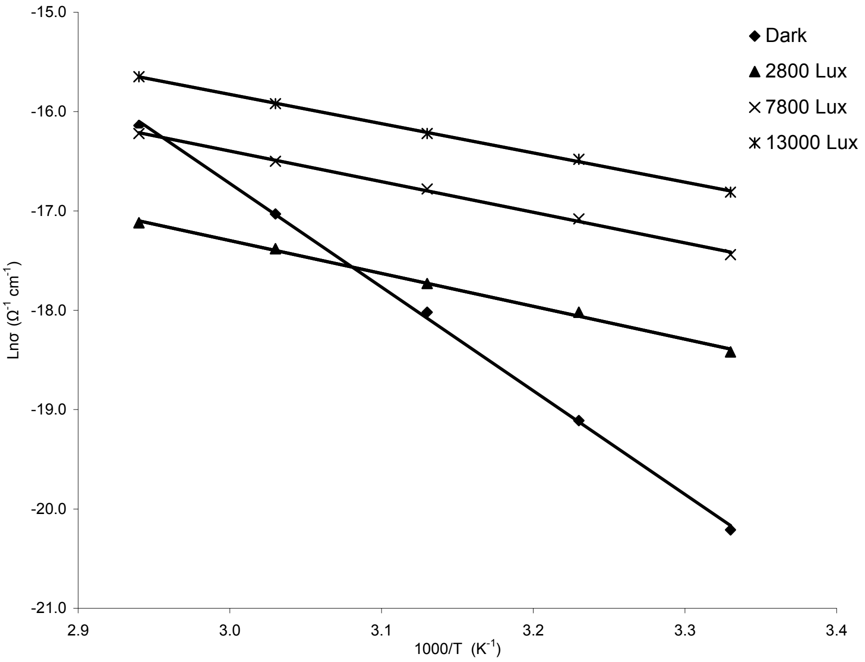

Fig.3. Temperature dependence of dark and photoconductivity at different intensities in$Se_{75}In_{10}Sb_{15}$ thin film.

The values of ΔE are calculated using the slope of Fig.3 and Eq.3.The results of these calculations are given in table 2.

Table 2. Dark and photoconductivity along with activation energy at various intensities in $Se_{75}In_{10}Sb_{15}$ glassy system.

S.No.	Intensities (Lux)	$\sigma(\Omega^{-1}\ cm^{-1})$ at 300K	ΔE (eV)
1.	Dark	1.67×10^{-9}	0.90
2.	2800	1.00×10^{-8}	0.29
3.	7800	2.67×10^{-8}	0.27
4.	13000	5.00×10^{-8}	0.25

It is clear from this table that the activation energy decreases at different intensities of light and is much smaller than the activation energy in dark. Hence the activation energy in this case depends on the light intensity which clearly indicates the shift of Fermi level with intensity..

Intensity (F) dependence of photoconductivity (σ_{ph}) is studied at different temperatures. The results for $Se_{75}In_{10}Sb_{15}$glassy alloy are shown in Fig. 4. It is clear from Fig. 4 that, at all temperatures, ln σ_{ph} vs. ln F curves are nearly straight lines which indicates that photoconductivity follows a power law with intensity ($\sigma_{ph} \propto F^{\gamma}$). The power γ is found to vary between 0.5 and 1.0 for all the glassy alloys studied here. Rose [28] has pointed out that the power γ between 0.5 and 1.0 can not be understood by assuming a set of discrete trap levels but demands the existence of continuous distribution of traps. In the present case also γ is between 0.5 and 1.0 which indicates that a continuous distribution of localized states exists in the mobility gap of the present glassy system.

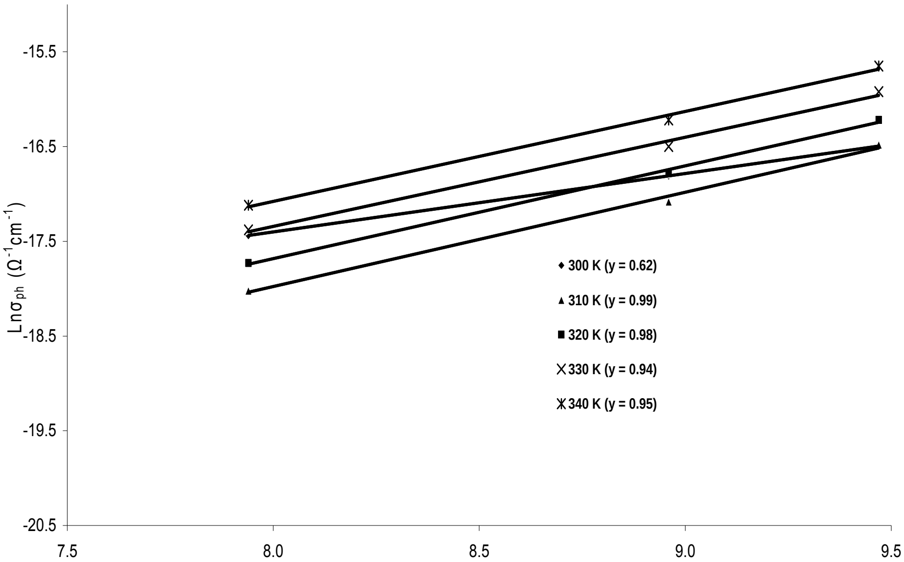

Figure. 4. Intensity dependence of photoconductivity at different temperatures in$Se_{75}In_{10}Sb_{15}$ thin film.

In single trap analysis [29], the value $\gamma = 1$ corresponds to the case of monomolecular recombination and $\gamma = 0.5$ to bimolecular recombination. However, in the case of a continuous distribution of traps, the value of γ may be anywhere between 0.5 and 1.0, depending upon the intensity and temperature range [28]. These results can be explained on the basis of a model proposed by Simmons and Taylor [30]. In the SCLC mechanism pointed above, we have also assumed the same.

3.3 Transient photoconductivity measurements

To measure the rise and decay of photoconductivity with time, thin film sample was mounted in the same metallic sample holder and light of desired wavelength 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 photoconductivity during decay.

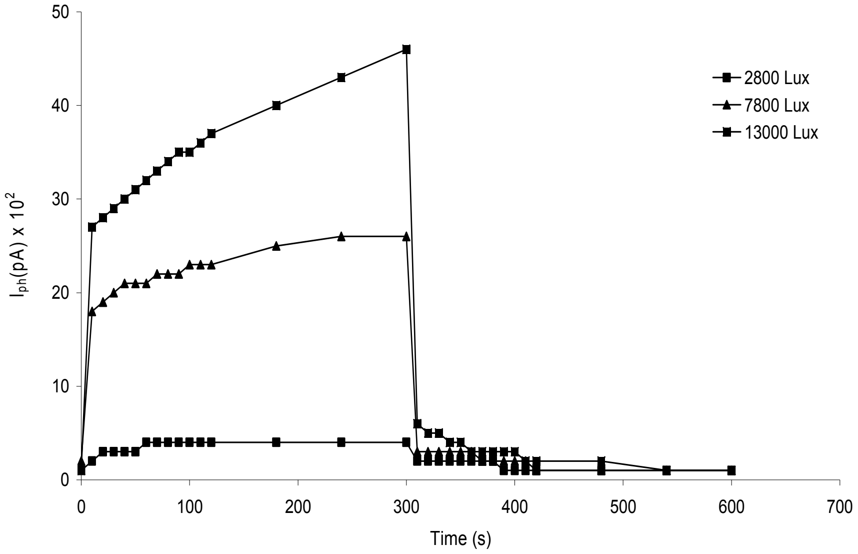

Fig.5. Time dependence of photocurrent at different intensities during rise and decay at 300 K in $Se_{75}In_{10}Sb_{15}$ thin film.

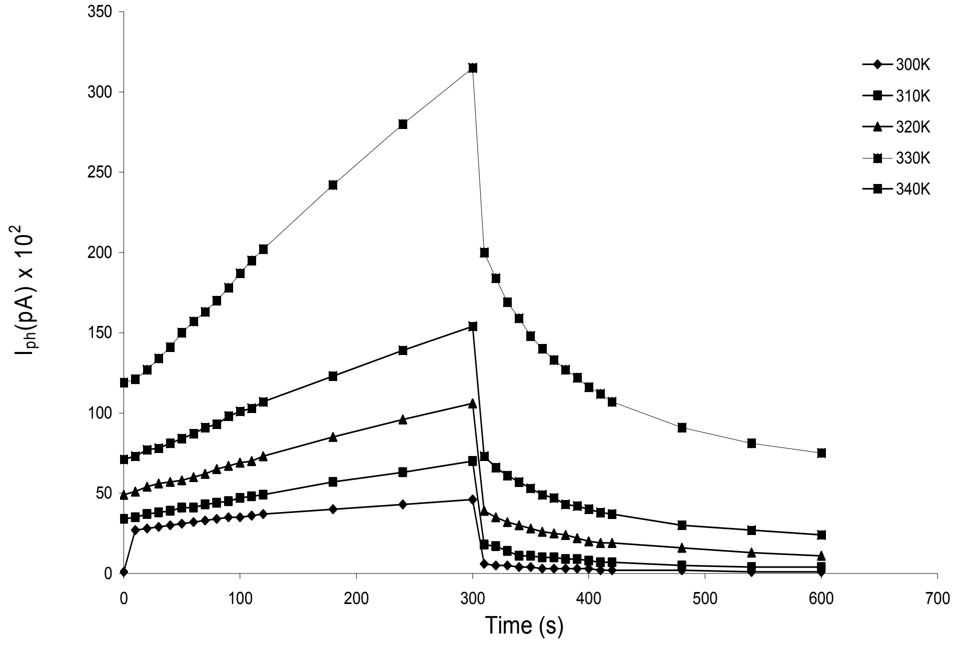

Fig.6.Time dependence of photocurrent at different temperatures during rise and decay in $Se_{75}In_{10}Sb_{15}$ thin film at light intensity 13000 Lux .

Figs. 5-6 show the results of the transient photoconductivity measurements at different intensity and temperature in the sample studied at present. It is clear from these figures that the rise and decay of photocurrent is quite slow. A persistent photocurrent (the asymptotic value of the current in the decay curve) was also observed. This type of decay of photocurrent was observed [31-32] 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 non-exponential even after subtracting the persistent photocurrent.

4. Conclusions

High field conduction and photoconductivity measurements in glassy $Se_{75}In_{10}Sb_{15}$ thin film have been obtained. The experimental data fits well with the theory of space charge limited conduction (SCLC) in the high electric field region. From the fitting of the data, the density of defect states (DOS) near Fermi level is calculated.

Temperature dependence of steady state photoconductivity is also studied at different light intensities. Intensity dependence of photoconductivity is studied at different fixed temperatures. Temperature dependence of photoconductivity measurements at different intensities indicates that photoconductivity is also thermally activated in the above temperature. The value of γ in between 0.5 and 1.0 indicates a continuous distribution of localized states in the mobility gap of the present glassy system.

Transient photoconductivity measurements at different temperatures and intensities indicate that the decay of photoconductivity has two components, initially; it is little faster and then become quite slow. This component is found to be non exponential in the present case indicating the presence of continuous distribution of defect states. A persistent photoconductivity is also observed, which increases at higher intensities. This is attributed to light induced effect in this material.

Acknowledgements

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