Anomalous Photoconductive Transport Properties of As$_2$Se$_3$ Films

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Amorphous As$_2$Se$_3$ films have been prepared by the thermal evaporation technique. The variation of the photocurrent with the temperature at different illumination intensities showed that the behavior is thermally activated with photocurrent activation energy that increased from 0.18 to 0.3 eV as a function of light intensity. The thermal activation energy of the dark current was found to be 0.86 eV (about half of the band gap of As$_2$Se$_3$). An anomalous behavior has been observed in the photocurrent light intensity as a function of temperature. The photocurrent I_{ph} changes as the light intensity I^α. For low light intensity, $0.58 < \alpha < 0.71$ while at high light intensity the exponent α was found to be greater than unity. On the other hand, the thermal stimulated depolarization current (TSDC) spectrum, under dark and pre-illumination conditions, is measured and the results were correlated with the change of the energy configuration of the defect states in the material under investigation.

Introduction:

Investigation of the transport properties in amorphous semiconductors has been much stimulated by the increasing interest in their potential technological applications. The vitreous arsenic–selenium system, with its wide range of glass formation and relatively well characterized electrical and structural properties, is very suitable for the study of the trapping kinetics in amorphous solids.

Systematic studies of the variation in the photoconductivity, particularly in amorphous and/or crystalline As_2Se_3, with light intensity (white or monochromatic) and / or temperature has been performed in order to extract information on the localized states distribution in the bandgap of these materials [1-5]. The nature of these localized states is very complicated and still open to further investigation [6].

Thermally stimulated depolarization current (TSDC) technique has been successfully used to determine the trap energy distribution of polymer thermoelectrets and still very scarcely in glasses [5-10]. Results reveal the existence of some groups of localized states, which are not detected by the conventional thermal stimulated conductivity spectra (TSC) [3, 5, 11-13].

The aim of the present work is to investigate the photocurrent dependence on both white light intensity and temperature in sufficiently high quality As_2Se_3 films prepared by thermal evaporation technique. Thermally stimulated depolarization current measurements are also reported in order to explore the possibility of finding a suitable explanation for some photocurrent response in relation to the localized states.

Experimental:

A suitable amount of as and Se elements (of purity 99.999; from Alfa products) have been used to obtain As_2Se_3 stoichiometric composition. The mixture is melted in a sealed evacuated quartz tube and continuously rotated to ensure the homogeneity of the resultant product. The temperature of the mixture was raised firstly to 1100 K (higher than the melting temperature of the highest melting constituent). After 8 hours, the temperature was raised to 1320 K for 10 hours, after which the melt is quickly quenched in ice water. Thermal evaporation of the crushed bulk material source has been carried out under vacuum 10^{-5} torr using Edward A 350 coating unit. The quality of the films, of thickness ranging between 3-4 μm, is found to be sufficient to detect TSDC spectra. Corning glasses 7059 have been used as a substrate. Aluminum has been evaporated as an ohmic surface electrode in the form of gap cell. The gap

distance (30 –40μm) is of the order of ten times more than the film thickness, to ensure field homogeneity throughout the film.

Analysis of X- ray diffraction for the samples of the evaporated films, revealed the absence of any crystalline phase. Dark- and photo- current and thermally stimulated depolarization currents of the As_2Se_3 films, under dark and pre-illumination conditions, were measured by a 610 Keithley Electrometer. Measurements of the photocurrent dependence on light intensity were carried out with white light source tungestan lamp (100 mW/cm^2) controlled with different neutral density filters. The temperature of the samples was controlled within the measurements to 0.1^{o}C to assure that the measured photocurrent will not due to the heating of the samples during the illumination process. The dark thermally stimulated depolarization currents (TSDC) measuring procedure can be described as follow: first the samples were polarized by an applied electric field $E_p= 5x10^7$ V/m for a constant time t_p =15 min at constant poling temperature T_p= 393 K. The film after that was cooled to room temperature while the electric field was kept constant. After reaching room temperature, the electric field was switched off and the sample was short-circuited through the Electrometer. The temperature was then raised, at constant rate of heating of about 2 K/min, and thermally stimulated depolarization current is recorded. TSDC spectra under pre-illumination can be obtained as a result of illuminating the sample during the polarization process with 10 V bias voltage, t_p =15 min and T_p= 393 K. After reaching room temperature, the sample was isolated from both illumination and biasing voltage and hence, TSDC spectra is recorded.

Results and Discussion:
A) Dark- and photo-current:

The temperature dependence of the dark and photocurrent for different relative illumination intensities is given in Fig. (1). It is observed that the dark current is thermally activated over many orders of magnitude with an activation energy ~ 0.86 eV in close agreement with half of the As_2Se_3 bandgap Eg ~ 1.8 eV [14]. This activation energy indicates that carriers are thermally activated from the Fermi level to the transport path. The photocurrent– temperature curves are straight line for all light intensities. This shows that photocurrent can be described by the thermally activated process which normaly governs the bimolecular process at low temperature. A maximum in photocurrent, which is a common feature of chalcogenide glasses, was not observed in the temperature range 300 K to 420 K. This behavior is neither similar to the results published earlier for the same materials nor to the standard ones for other chalcogenide semiconductors [5, 15-17]. Where at temperatures higher than 420 K, i.e. near the glass transition temperature of As_2Se_3 (450 K) [18, 19], it was difficult to record the second region related to the

monomolecular process. This can be attributed to the increase in the instability of the dark current associated with higher temperatures, which may leads to non-accurately measured photocurrent. The activation energies (ΔE) of the photocurrent are shown in the inset of Fig (1). It is observed that the thermal activation energy increased as the light intensity increase, between 0.18 eV and 0.3 eV, which represent a contribution of different shallow trap levels having a role in photoconduction transport processes.
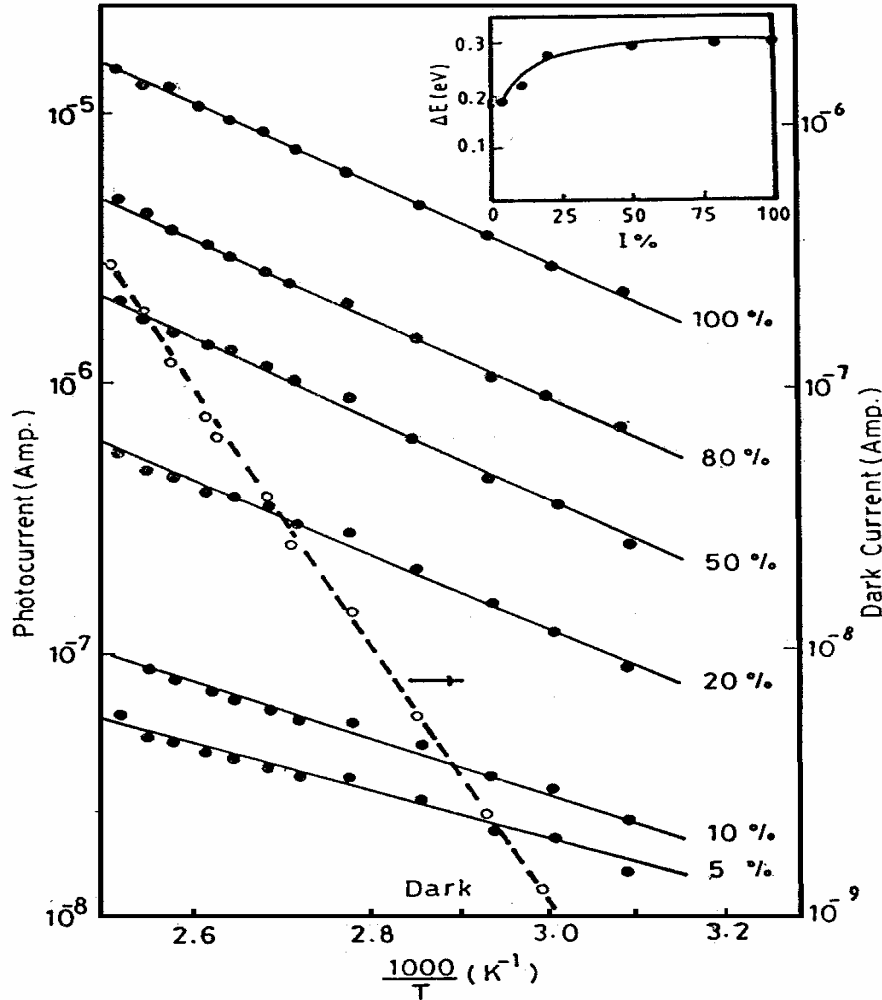

Fig.(1): Temperature dependence of the dark current and steady state photocurrent in As$_2$Se$_3$ film at different light intensities. The inset is the activation energy dependence on the light intensities.

Fig (2) illustrates the variation of the photocurrent of As$_2$Se$_3$ thin films as a function of light intensity, at different temperatures in the range of 300 K to 410K. It is observed that the photocurrent (I_{ph}) varies with light intensity (I)

with a variable fractional power (α), through the whole range of light intensities, according to the relation [5, 6, 20-23]:

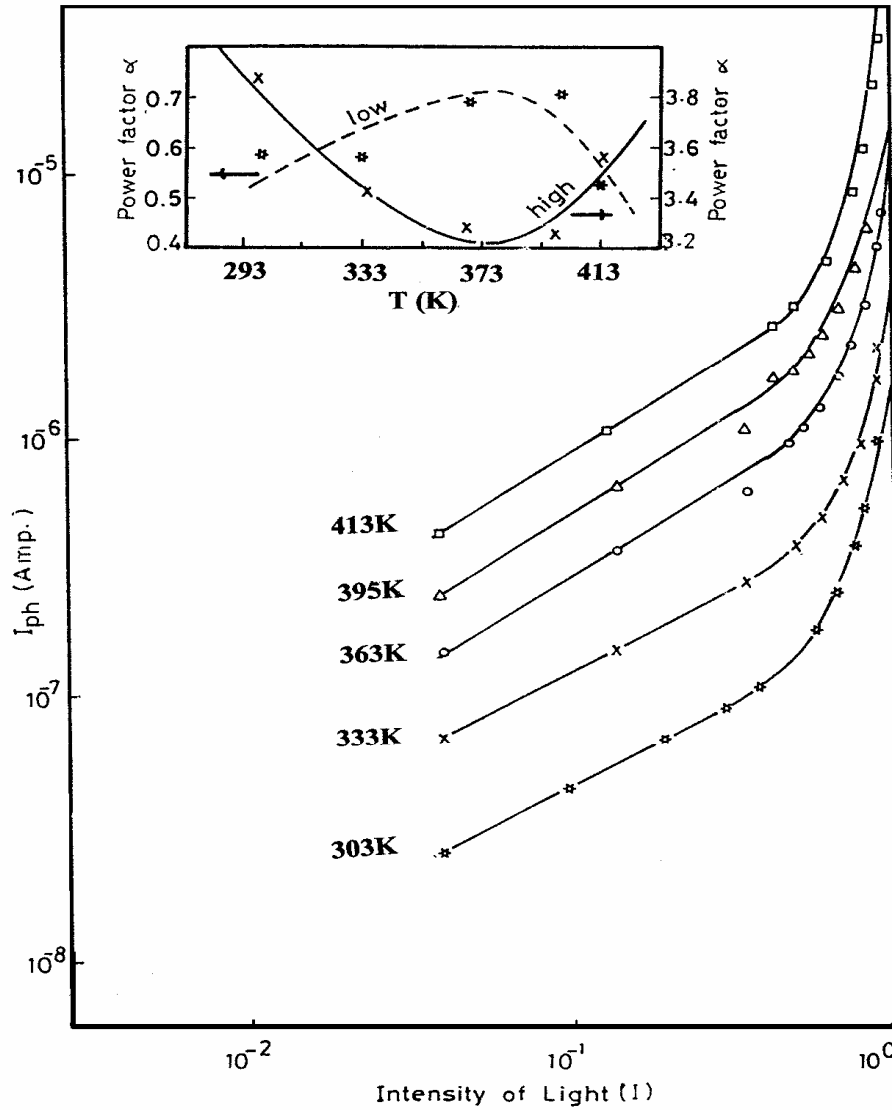$$I_{ph} \sim I^{\alpha} \tag{1}$$

Fig.(2): Light intensity dependence of the photocurrent in As_2Se_3 films at different temperatures. The inset indicates the temperature dependence of the power factor (α) at low (dashed line) and high (solid line) light intensity.

The inset in Fig (2) illustrates the dependence of the power factor (α), for low and high light intensity as a function of temperature. For low excitation intensity, the fractional power (α) has values ranging from 0.58 to 0.71eV. In

single trap level model [6] the values of (α) are close to unity and indicate a monomolecular type of recombination, whereas $\alpha = 0.5$ reflects a bimolecular process. The appearance of the exponent power with $0.5 < \alpha < 1$ is taken as a good argument for the presence of a distribution of traps within the band gap depending on the intensity of light and temperature range [6, 16]. At high light level intensity, the photocurrent increases, in a short intensity domain, tremendously with the fractional power (α) in the range of 3.25 to 3.88 (i.e. $\alpha \gg 1$). The rapid increase of photocurrent following a higher power of illumination ($\alpha \gg 1$) is known as superlinearity dependence [5,16]. The problem of superlinearity has been reported for a long time with fractional power $\alpha \sim 1.38$ and 1.7 for chalcogenide materials and 3 –5 for CdS[5, 16]. The most reasonable explanation of this puzzling phenomenon have been suggested by Rose [16], where the energy distribution of two discrete localized states with different cross-sections have been considered. Till now, there is still no satisfactory understanding of this phenomena.

The tangentional lines of the curves shown in Fig. (2), at each constant temperature, was found to intersect at certain intensity which is found to be independent of the temperature measurements. This point represents the turn over from a sublinear behavior (with $\alpha < 1$) to a superlinear behavior (with $\alpha > 1$). Fig (3) show the temperature dependence of the photocurrent
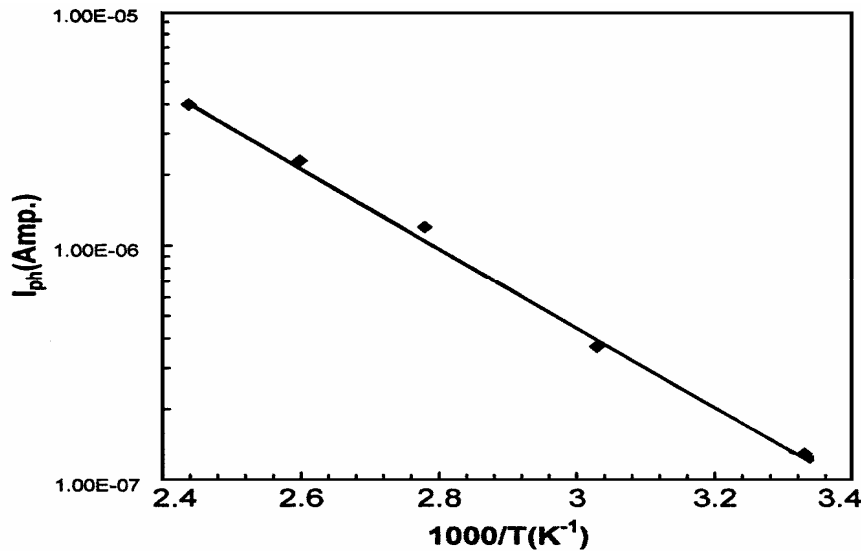

Fig.(3): The temperature dependence of the photocurrent taken at the turn over point.

taken at the turn over point. It is found that the relation is thermally activated with activation energy ~ 0.14 eV representing a predominant shallow trap level corresponding to the appearance of superlinearity phenomenon, which take place at relative light intensity > 70%.

B) Dark- and Photo-Themally stimulated depolarization current.

A typical temperature dependence of TSDC spectrum of As_2Se_3 thin films is illustrated in Fig (4). Under dark conditions (curve a) several TSDC maxima have been observed at 331, 345, 360, 380 and 403 K, which are related to trap energies E_t = 0.3, 0.22, 0.96, 0.54 and 0.53 eV inside the bandgap respectively. These trap energies may be related to different configurations of the defect states.
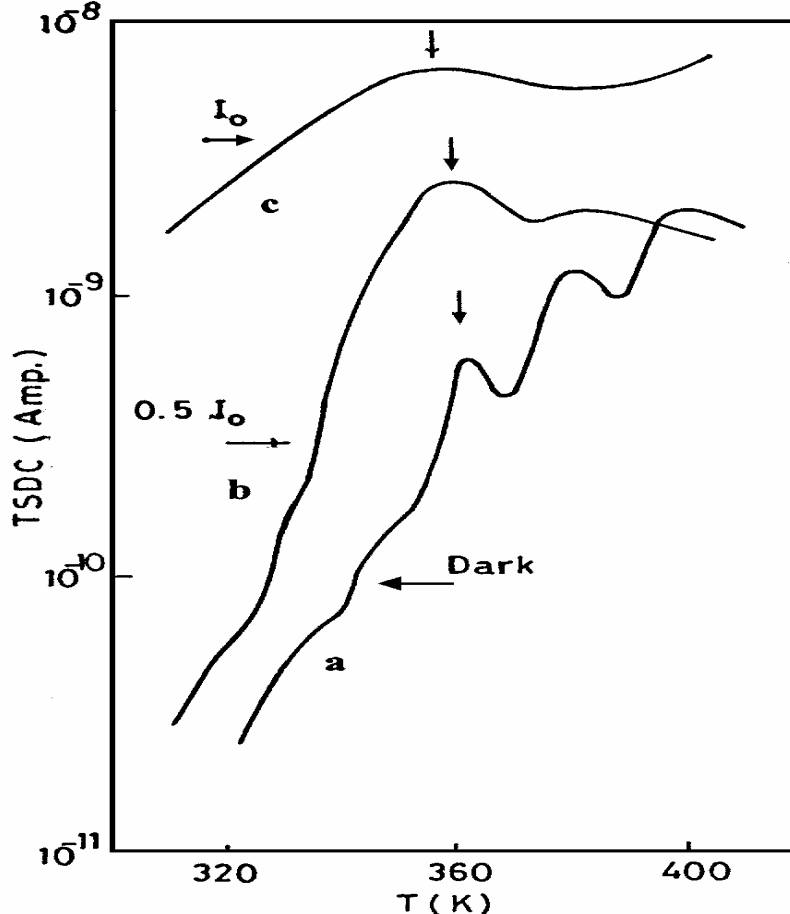

Fig.(4):   Thermally stimulated depolarization current (TSDC) in As_2Se_3 films in dark (a) and under pre-illumination (b) :I=0.5 I_o and (c) :I = I_o, where I_o is the full light intensity.

Another important feature of the TSDC spectrum is its high response to pre-illumination intensity. Curves b and c, in Fig. (4), represent the TSDC spectra for half (b) and full (c) intensities of the incident light. Increasing the pre-illumination intensity is followed by a broadening in the spectrum. The

calculated trap energy E_t, for the samples under pre-illumination, corresponding to both half and full light intensity were found to be 0.61 and 0.17 eV, respectively.

These broadening under pre-illumination, even at room temperature, and the decrease in the activation energies, can be regarded as a significant contribution of multiple shallow traps. This means that as the relative light intensity increased, the localized states move approaching towards their respective band edges and embrace the different shallow localized states and permits a significant redistribution of non-equilibrium charge carriers to take place. This configuration can slow down the recombination processes and increase the life time of the non-equilibrium charge carriers. Such mechanism lead to the enhancement of the photocurrent, as the relative light intensity increased, to take into account the exponent power (α) having values more than unity and may be permit the rationalization of the superlinearity phenomenon.

Conclusion:

Amorphous As_2Se_3 films have been prepared by thermal evaporation technique. The photocurrent–temperature dependence, at different relative light intensities show thermal activated behavior with activation energies ranging between 0.18 and 0.3 eV. Lux-Ampere characteristics showed an exponent power in the range 0.58 to 0.71 for low excitation intensities. At high light intensity the photocurrent increased with a fractional power in the range 3.25 to 3.88 implying the "superlinearity" phenomenon. The activation energy corresponding to the appearance of this phenomenon is found to be ~ 0.14 eV. Results of TSDC spectra, at dark condition, reveals the presence of some trap levels ranging between 0.22 and 0.96 eV within the bandgap. The broadening of the TSDC spectra under pre-illumination implies the contribution of multiple shallow traps (0.61 – 0.17 eV). These shallow trap levels may be playing a significant role for the appearance of superlinearity phenomenon.

Acknowledgments:

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