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Electrical and photo-electrical properties of a chalcopyrite semiconductor $AgInSe_2$

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Abstract. In this paper we report the electrical and photoelectrical properties of $AgInSe_2$. Nyquist plots for $AgInSe_2$, obtained at different temperatures, are perfect arcs of a semicircle with their centres lying below the abscissa at an angle α. Finite values of α (the distribution parameter) clearly indicate a multirelaxation behaviour. Transient and steady state photoconductivity of $AgInSe_2$ has been studied at different temperatures and illumination levels. The ln I_{ph} vs ln F curves at different temperatures follow the empirical relation: $I_{ph} \propto F^{\gamma}$. Values of γ are close to 0·5 at all the temperatures, suggesting a bimolecular recombination. Decay of the photocurrent, when the illumination is switched off, shows that during decay, photocurrent has two components, i.e. a fast decay in the beginning and a slow decay thereafter. Decay time constant for slow decay process decreases with increasing temperature, suggesting that recombination is a thermally activated process in the temperature range studied.

Keywords. Electrical property; photoelectrical property; chalcopyrite semiconductors; transient photoconductivity; steady state photoconductivity.

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1. Introduction

In recent years, the ternary chalcopyrite semiconductors have been receiving considerable attention because of their adaptability, as an absorber component, in thin-film solar cells. They are of technological interest because they show promise for applications in visible and infrared LED's, infrared detectors, optical parametric oscillators and upconverters [1,2]. It has been discovered that several ternary compounds can be converted to *p*-type or *n*-type materials by just changing their composition [1].

Although Cu-III-VI_2 and Ag-Ga-VI_2 compounds have been studied extensively, information on Ag-In-VI_2 compounds is rather scarce. $AgInSe_2$ is a material of special interest since it is a ternary analog of CdS which has been used for a number of electronic devices [3,4]. $AgInSe_2$ is a direct gap, *n* type [5] semiconductor with an energy gap of 1·19 eV and melting point $\simeq$ 770°C. Only dc resistivity of $AgInSe_2$ has been reported by Patel *et al* [6].

The present paper reports some new results on electrical properties of $AgInSe_2$ over a wide range of frequencies (5 Hz to 100 kHz). These measurements provide a useful information about the conduction mechanism in the material. The author also reports a study of photo-electrical properties of $AgInSe_2$. These measurements show that $AgInSe_2$ is quite sensitive to optical and thermal stresses. An analysis of results indicates that this sensitivity may be due to the existence of distribution of defect states.

2. Experimental

2.1 *Preparation of material and samples*

$AgInSe_2$ was prepared by sealing the desired quantity of constituent elements (99·99% pure) in an evacuated quartz ampoule which was heat treated in a rocking furnace. The temperature was gradually increased and kept constant for about six hours near the melting point of each element. The temperature was finally maintained around 1050°C for about 24 h. The ingots of the alloy were finally obtained by quenching the homogeneous melt in ice cold water.

Elemental EDAX analysis of the prepared material was made on Kevex Delta system. The results of the analysis are: Ag = 24·982 At. %, In = 25·014 At. %, Se = 50·004 At. %. X-ray diffraction pattern of the sample is as shown in figure 1. This figure clearly indicated that the material is polycrystalline in nature.

The samples, in the form of thin pellets, were prepared by finely grounding the ingots and then compressing the powder in a die under hydraulic pressure. All the samples were annealed at a temperature of 80°C for about 24 h. Measurements were made on two different sample-configurations, i.e. (i) pellets coated with gold on both the faces for bulk measurements (ii) sheet measurements on a planar configuration by exposing a narrow slit of the material in between two electrodes obtained by coating a conducting silver paste on one face of the pellet. Both the samples displayed identical behaviour, ruling out the possibility of any electrode migration.

2.2 *Measurements*

Measurements of impedance parameters were made on a modular a.c. impedance system (Models 368 EG & G, PARC, USA) [7]. Measurements of real and imaginary parts of the impedance were made over a frequency range of 5 Hz to 100 kHz on a.c. impedance system using dual lock-in amplifier. The impedance system also has a facility to obtain $I-V$ (current vs voltage) and $I-T$ (current vs time) characteristics. These characteristics have been used for the study of photoconductivity. Ealing (UK)

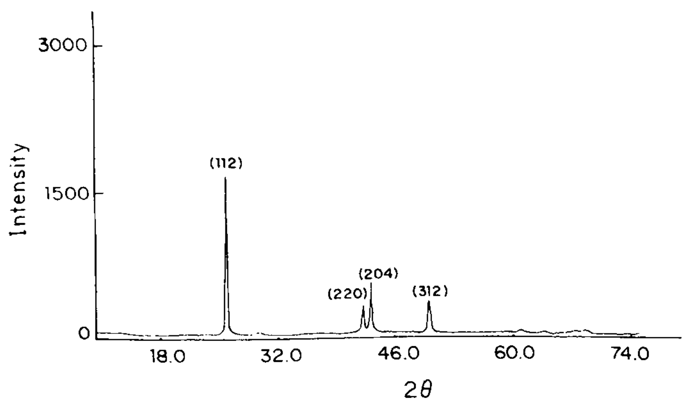

Figure 1. X-ray diffraction pattern for $AgInSe_2$ powder.

fibre optics illumination set, with a light source of variable intensity (tungsten-halogen, Sylvania lamp, 150 W) was used to illuminate the sample with the help of a fibre bundle.

3. Results and discussion

3.1 *Study of complex impedance and admittance*

Nyquist plots for $AgInSe_2$ were obtained at different temperatures and over a wide range of frequencies (5 Hz to 100 kHz) by using the computer assisted a.c. impedance system. The results are shown in figures 2(a, b, c, d). As evident from the figure, the plots are perfect arcs of a semicircle with their centres lying below the abscissa at an angle α. Incidentally, α (the distribution parameter) displays a temperature independent behaviour, because it remains almost unchanged over the temperature range studied. A finite value of α and a depressed semi-circular arc clearly indicate a multirelaxation behaviour for $AgInSe_2$. The inversion of Nyquist plots in admittance plane is shown in figure 3. The figure shows plots of real and imaginary components of $Y(Y'$ and $Y'')$ at different temperatures. It is clear from the figure that the angle of inclination $(s\pi/2)$ remains the same at all the temperatures. Figures 2 and 3 clearly indicate that the frequency exponent s is temperature independent.

The above mentioned behaviour of complex impedance for $AgInSe_2$ (figure 2) can be explained even by a simple R–C equivalent network. The value of Z' at lower

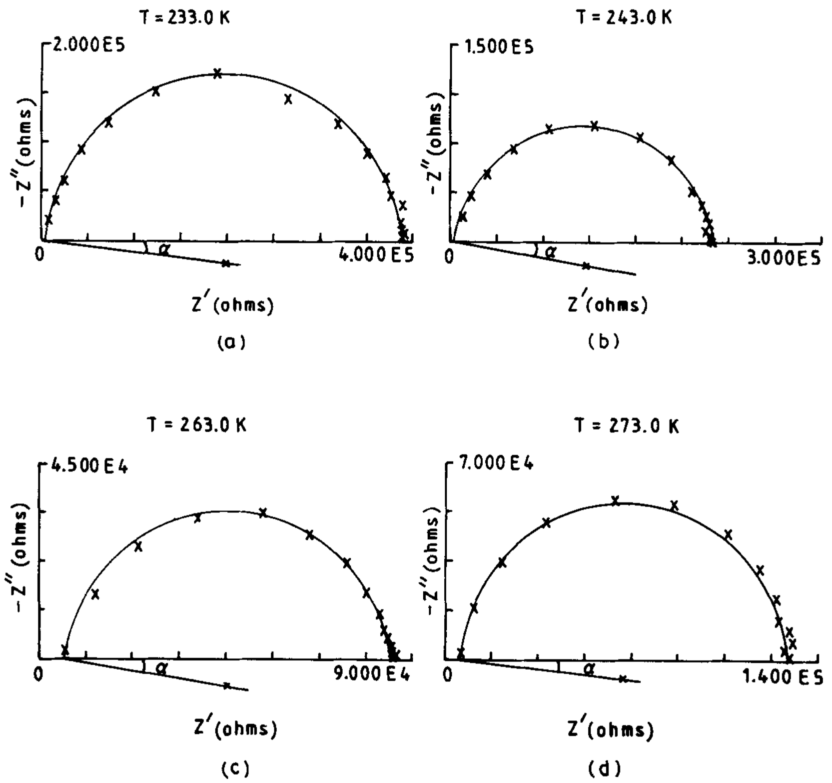

Figure 2. Nyquist plots at different temperatures for $AgInSe_2$.

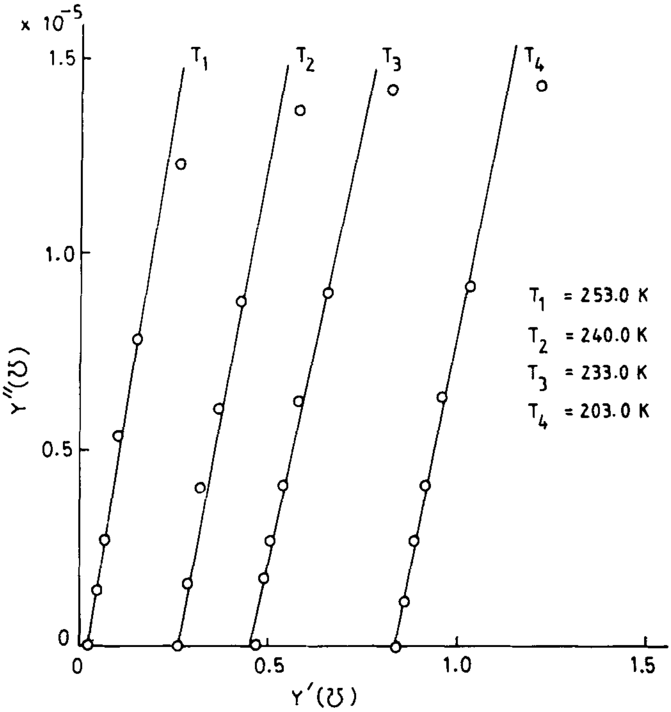

Figure 3. Y' vs Y'' plots at different temperatures for $AgInSe_2$.

frequency (the point where semicircle cuts abscissa) gives us in idea of d.c. resistivity. Patel *et al* [6] studied the d.c. resistivity of $AgInSe_2$ films deposited at different substrate temperatures (150°C to 250°C) and the resistivity value varied between 10^2–10^4 ohm-cm at room temperature. The value observed by us (10^3 ohm-cm) lies in the same range.

3.2 *Steady state photoconductivity*

Figure 4 shows the temperature dependence of dark current and photocurrent [8] at different illumination levels (F_1, F_2, F_3). Values of activation energy (ΔE), indicated in the figure, show that ΔE gets reduced when the sample is illuminated. Figure 5 shows the variation of photocurrent (I_{Ph}) with illumination level F (arbitrary units, A.U.) at different temperatures. Linear behaviour of $\ln(I_{Ph})$ vs $\ln F$ plots indicate that $AgInSe_2$ follows the power law, i.e.

$$I_{Ph} \propto F^{\gamma} \tag{1}$$

Identical behaviour has been reported recently for $AgInTe_2$ from this laboratory by Shukla *et al* [7]. The exponent γ in (1) determines whether the recombination process is monomolecular or bimolecular. It is equal to 0·5 for a bimolecular and is equal to 1·0 for monomolecular recombination [9]. The slopes of $\ln I_{ph}$ vs $\ln F$ plots provide the values of γ, which has been found to lie between 0·55 and 0·48 at all temperatures for $AgInSe_2$. This clearly indicates that the recombination process is bimolecular in $AgInSe_2$.

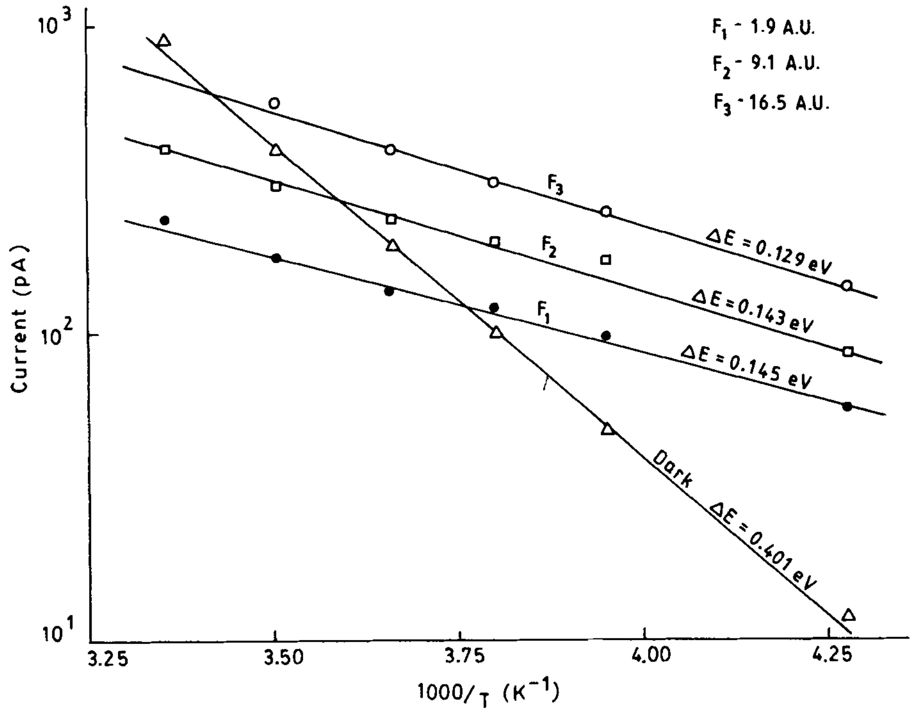

Figure 4. Temperature dependence of dark current and photocurrent at different levels of illumination.

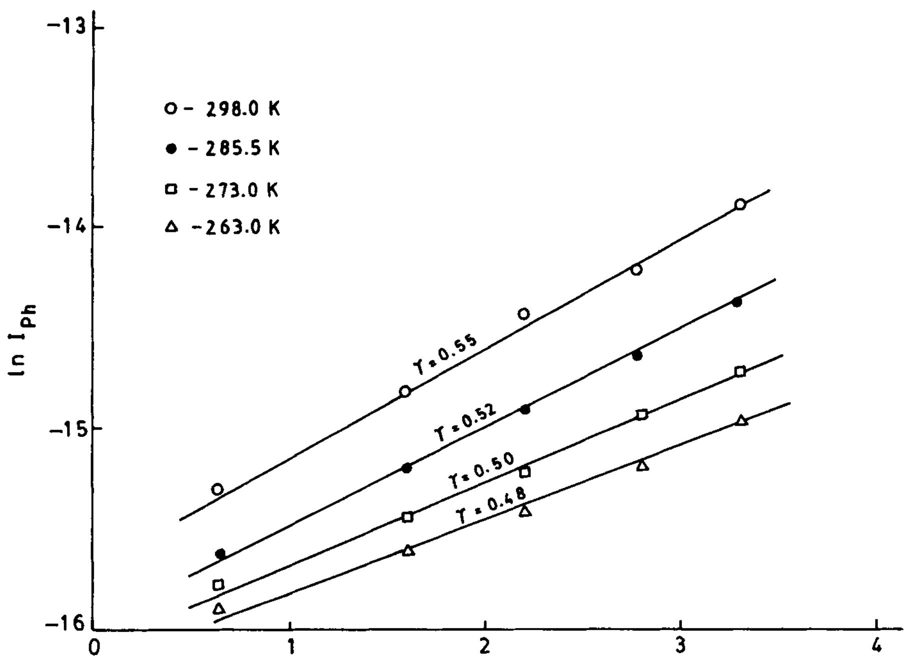

Figure 5. Variation of photocurrent with illumination level.

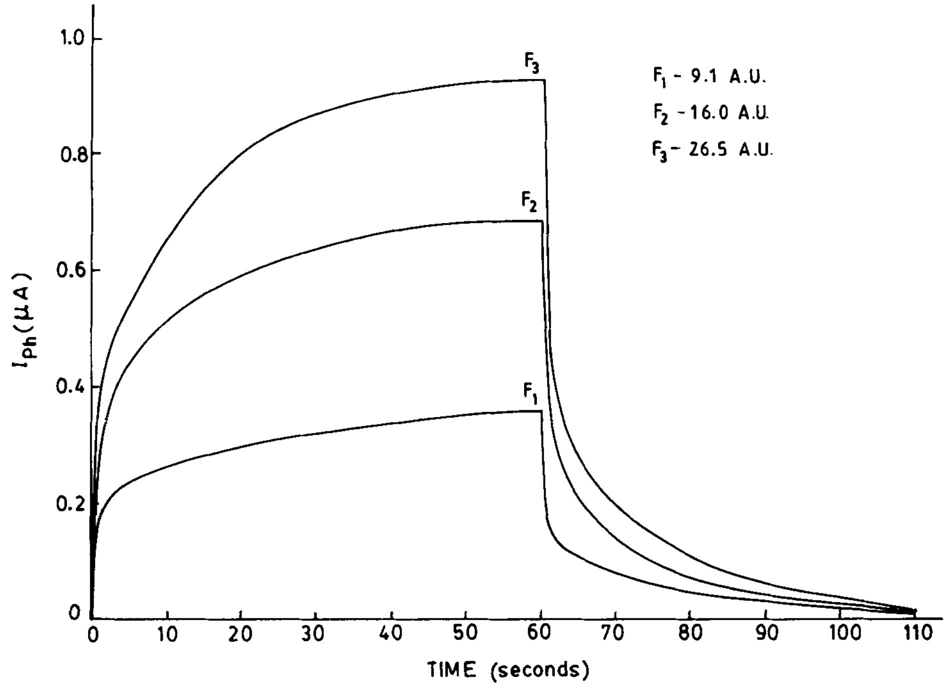

Figure 6. I_{ph} vs time plots at different levels of illumination for $AgInSe_2$.

3.3 *Transient photoconductivity*

To study transient photoconductivity, the sample was exposed to light radiations and d.c. current was recorded simultaneously for a given period. Thereafter the light was switched off and the current decay was recorded. The photocurrent (I_{Ph}) was obtained by subtracting the dark current from total current. Figure 6 shows the I_{Ph} vs time plots, obtained at a given temperature for different illumination levels (F). Similar behaviour was observed at other temperatures. It is evident from figure 6 that the initial rise and decay of current is rapid and thereafter the process becomes slow. Figure 6 further shows that the initial rate of rise/decay of photocurrent (dI_{Ph}/dt) increases with increasing [10] F. Figure 7 shows a similar trend, when the temperature is increased at a given level of illumination.

Rapid rise/decay of photocurrent is often attributed to localized-localized recombination mechanism according to which the trapped carriers recombine directly with carriers of opposite sign [10, 7]. Shukla *et al* [7] have made an attempt to show that rapid process can be analyzed through a simple R–C (resistance-capacitance) equivalent of the sample-system. As indicated by them the value of R–C time constant (τ) represents the rate of recombination/generation of charge carriers (i.e higher the rate, lesser would be the value of τ). The experimental results obtained here for $AgInSe_2$ further support the investigations reported by Shukla *et al* for $AgInTe_2$.

The mechanism of slow decay process has been reported [12, 13] to be due to the presence of deep-level traps and explained by using the concept of differential life time τ_d (often written as decay time constant). For an exponential decay, it is not a function of time and is given by

$$\tau_d = \frac{d\ln(I_{Ph})}{dt}. \tag{2}$$

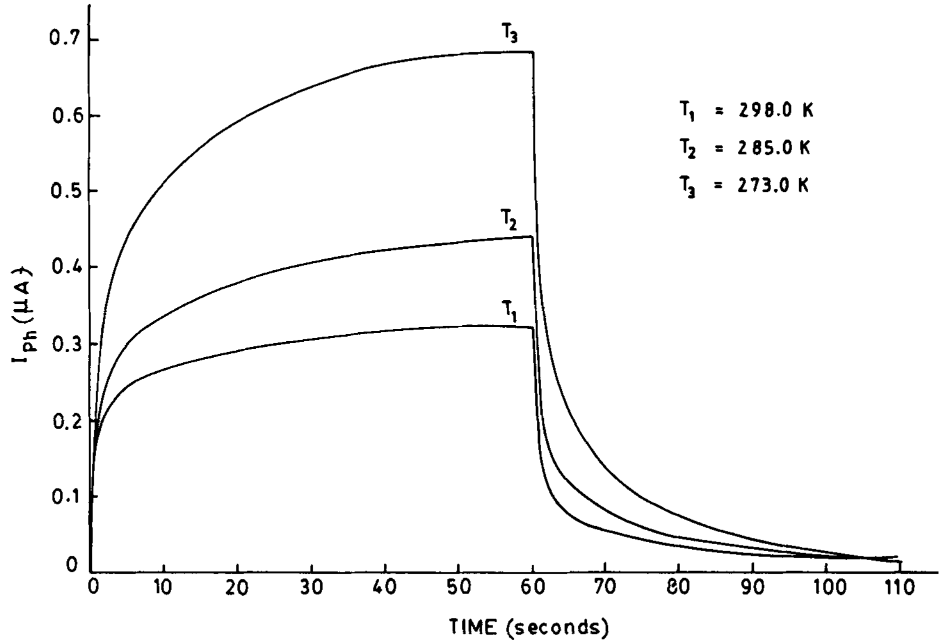

Figure 7. I_{ph} vs time plots at different temperatures for $AgInSe_2$.

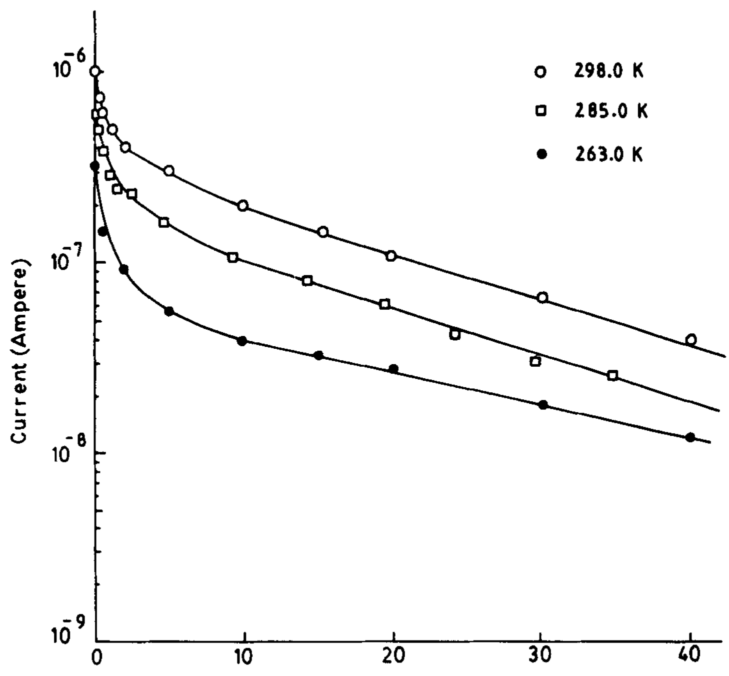

Figure 8. Photo-current vs time plots at different temperatures for $AgInSe_2$.

This type of decay is expected for materials having monoenergetic traps with negligible retrapping probability [9]. But if there are traps of different kinds, then the resulting decay will be a sum of many exponentials, each corresponding to a different set and the plot of ln I_{Ph} vs T will be a combination of different slopes.

Figure 8 shows the behaviour of photocurrent with respect to time at different temperatures for a fixed level of illumination. Whereas figure 9 shows the decay of photocurrent at a fixed tempeature and at three different levels of illumination. Both these figures indicate that, during decay, the photocurrent has two components, i.e, a fast decay in the beginning and slow decay thereafter, with different values of decay time constant. It seems to follow the relation:

$$I(t) \simeq I_{01}\exp(-t/\tau_{d1}) + I_{02}\exp(-t/\tau_{d2}) \quad (3)$$

where I_{01} and I_{02} are the pre-exponential factors and τ_{d1} and τ_{d2} are decay time constants for fast and slow processes respectively. Using the data plotted in figures 8 and 9 for different temperatures and illumination levels, values of τ_{d2} (decay time constant for slow process) were computed and are listed in table 1. It is clear from table 1 that the value of decay time constant τ_{d2} decreases with increasing temperature. This is probably due to the fact that recombination process is thermally activated.

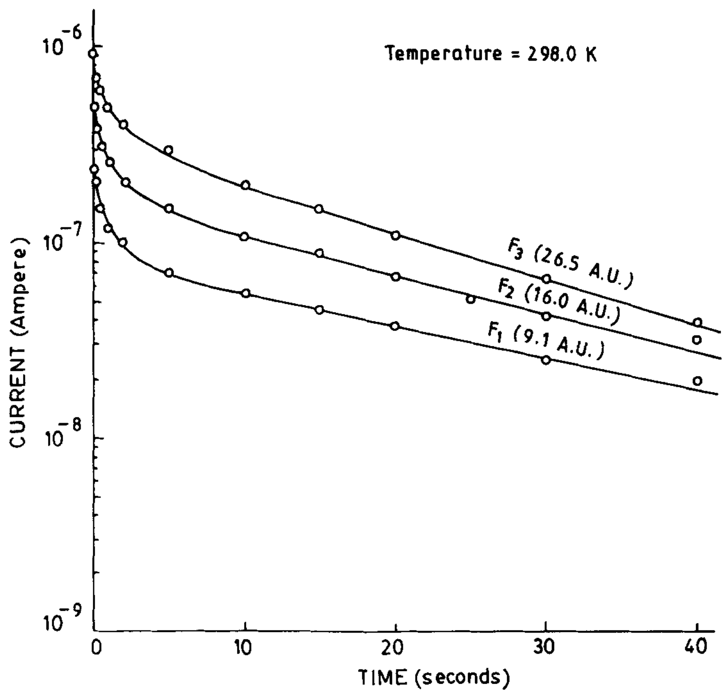

Figure 9. Photo-current vs time plots at different illumination levels for $AgInSe_2$.

Table 1. Values of τ_{d2} (slow decay time constant) at different temperatures and different illumination levels.

Temperature (K)	τ_{d2}(s) F_3(26·5 A.U)	F_2(16·0 A.U)	F_1(9·1 A.U)
298·0	17·9	18·2	18·4
285·0	18·0	19·1	19·5
273·0	20·05	20·2	24·0
265·0	25·33	25·3	27·2

When the electron traps are thermally emptied via conduction band, recombination is much enhanced and recombination rate is determined by the excitation of trapped carriers to the conduction band, leading to the temperature dependence of decay time as $\tau \approx \exp(E_c - E_f)/kT$. Trap depth so obtained is of the order of 0·1 eV.

4. Conclusions

$AgInSe_2$ displays a sensitivity to optical and thermal stresses. a.c. conductivity of $AgInSe_2$ displays the behaviour $\sigma_{ac} \propto \omega^s$, where frequency exponent x is temperature independent. Photo induced changes in conductance are rapid in the beginning, followed by a slow process of rise/decay which indicates the existence of gap states.

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