Chapter VI
PHOTOCONDUCTIVITY

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I. INTRODUCTION :

Photoconductivity processes involve absorption of energies from electromagnetic radiations (X-rays, γ -rays, UV, visible light, IR) and the excitation of charge carriers from a non-conducting ground state to a higher energy state where they are free to contribute to the electrical conductivity and the return of charge carriers from the conducting states to their ground states. These are structure sensitive phenomena depending on impurity content and structural defects in the material. All semiconductors and insulators are photoconductors. The life time of the free carriers, photosensitivity and capture cross sections are important characteristic parameters of a photoconductor. The conductivity increases upon exposure to suitable radiation. The number of materials, for which the conductivity increases large enough and hence can be useful, is fairly very small. One of the reasons may be the characteristics of a material which determine its sensitivity to radiation are associated with imperfections in the crystal structure. A semiconductor in general exhibits a linear dependence of photocurrent on light intensity and an exponential decay.

Bhatt et al[1] have studied the photoconductivity of SnSe thin films : their dark photocurrent, illuminated photocurrent, response time and effect of temperature. The films used were of thickness about 75 nm prepared by resistive evaporation at 373°K on glass substrates. The deposition and temperature variation studies were done at a pressure of 10^{-5} torr. Aluminium films were used as ohmic electrodes.

Subba Rao and Chaudhari[2] have carried out conductivity, photoconductivity and Hall measurement of SnSe thin films of various thicknesses in the temperature range of 300 K to 800 K. They explained photoconductivity as due to trapping of majority carriers at the grain boundaries.

In the present investigation, study of the photoconductivty of SnSe solid state reacted films[3] was under taken. There areafew reports on photoconductivity of SnSe films directly evaporated from the compound. However, the author has not come across any report on photoconductivity studies on solid state reacted SnSe films.

II. GENERAL DISCUSSION :

When light is absorbed by a material so as to raise electrons to higher energy states several possibilities occur. If the excited electrons are in the conduction band, the conductivity of the material increases as a result of absorption of light and the effect is known as photoconductivity. If the

excited electrons give up their excess energy, when they return to their initial state, in the form of photons, the effect is known as luminescence.

The photocurrent depends on the intensity and wavelength of the illuminating light and the temperature. In this chapter we shall concentrate on those phenomena which are useful in giving us direct information about traps.

Trapping is a fundamental process for energy storage in almost all electronically active solids. This energy storage is accompolished by the spatial location of an electron or hole, in such a way that the electron or hole is prohibited from moving freely through the crystal unless supplied with thermal or optical energy. When the trapped electrons or holes are realeased, they are free to move until captured by a recombination centre or by another trap. Those regions which are able to capture electrons and holes and detain them in a restricted volume are called traps.

Bube[4] has described the following measurements which are useful in giving information about trapping :

1. The growth of luminescence emission or of photoconductivity after the beginning of excitation.
2. Decay of luminescence emission intensity or of photoconductivity after the cessation of excitation.

3. Thermally stimulated trap emptying.

4. Optically stimulated trap emptying.

5. Photoconductivity measurement involving a change in the behaviour of a centre.

6. Space-charge limited current dependence on voltage.

7. Photodielectric effect.

8. Paramagnetic susceptibility and paramagnetic resonance.

The capturing centres may be classified into two groups:

1. **Trapping Centre :**

If the captured carrier has a greater probability of being thermally re-excited to the free state than of recombining with a carrier of opposite sign at the imperfection, the centre is called a trap centre.

2. **Recombination Centre :**

If the captured carrier has a greater probability of recombining with a carrier of opposite sign at the imperfection than of being re-excited to the free state, the centre is called a recombination centre. Although, a centre with an energy level lying near one of the band edges will be more likely to act as a trap than as a recombination centre (and vice versa for centres with levels lying near the middle of the forbidden gap), the distinction between traps and recombination centres is a distinction drawn on the basis of the relative probability of thermal ejection versus recombination i.e., on kinetic conditions, and not on the basis of the intrinsic nature of the

centres themselves. A recombination centre at one condition of light level and temperature may act as a trap at another condition of light level and temperature.

Recombination may also occur, as in the more usual cases, through recombination centres : either an electron being captured by an excited centre containing a hole, or a hole being captured by an excited centre containing an electron. Photosensitivity means photoconductivity per unit excitation intensity i.e. the change in conductivity caused by excitation divided by the excitation intensity.

When light of appropriate wavelength is incident on a photoconductor free electrons and holes are generated at identical rates and recombine via the discrete states (impurity levels). On physical grounds it can be stated that there are states (A) near the conduction band such that the electrons falling into these states are rapidly re-excited thermally into the conduction band. These states which are in thermal equilibrium with the electrons in the conduction band are known as shallow trapping states. It is also clear that the electron falling into deeper lying states (B) will not be thermally re-excited for a long time. Before thermal re-excitation takes place, such an electron is more likely to capture a free hole. These deeper lying states are known as ground states (recombination centres). The electrons and holes falling into

these states have completed their life history. The occupancy of ground states by electrons or holes is determined by purely kinetic processes of recombination. The occupancy of shallow trapping states is determined by the condition of being in thermal equilibrium with the electrons in the conduction band or the holes in the filled band.

Bube[5] has conveniently defined the location of a demarcation level, separating the trapping and the recombination levels in the following ways : When an electron (hole) is located at the electron (hole) demaraction level, it has equal probability of recombining with a free hole (electron) and of being thermally ejected to the conduction (valence) band. The occupation of a level lying above the electron demaraction level is determined by the conditions of thermal equilibrium between the levels and the conduction band. Similarly, the occupation of a level lying below the hole demarcation level is determined by the condition of thermal equilibrium between the levels and the valence band. The occupation of levels lying between the electron demarcation level and the hole demarcation level is determined by the recombination kinetics of the material. Figure - 1 shows schematically the relationship between the demarcation levels and the steady state Fermi levels for a semiconductor. The thermally excited density of free carriers is greater than the optically excited density. With reference to the above figure, levels are distributed into four

categories : levels located in region I are electron traps ; region II extends from the Fermi level to the demarcation level, region III having collapsed to a line at the demarcation level.

When the recombination or capture process terminating or interrupting photoconductivity is radiative, luminescence emission results. Thus measurements of luminescence provide useful information about critical steps in the mechanism of photoconductivity.

According to the Scharnhorst model[6] the temperature dependence of photoconductivity is through

$$\Delta\sigma(T) \quad \propto \quad \mu_0 n_0(T) = \mu \Delta n \qquad \ldots\ldots 1$$

The maxima in $\Delta\sigma(T)$ will be observed regardless of the magnitude of the fixed intensity of illumination, (where n is the excess electron density, n_0 is the equilibrium electron density, μ is the carrier mobility and $\Delta\sigma$ photoconductivity).

Rose[7] explained the photoconductivity dependence on intensity and temperature on the basis of the concept of demarcation levels. The recombination velocity is governed by the discrete states lying between these two decmarcation levels. Discrete states lying outside the two demarcation lines have a negligible effect on recombination. The positions of

demarcation lines usually coincide almost exactly with steady state Fermi levels or the quasi-Fermi levels, the portions of which in turn determine the electron and hole densities in the bands. When the rate of generation of non-equilibrium carriers increases, their densities in the band increases and the quasi-Fermi levels are displaced towards the band edges. Consequently, the levels which have acted as traps under weak excitation now become recombination centres. Conversely, when the generation of non-equilibrium carriers is reduced, their density decreases and the quasi-Fermi levels approach one another coming close to the equilibrium position. Then the levels which have acted as recombination levels under intense excitation become traps.

In the case of weak excitation, when the free carrier densities are low compared to the densities of band electrons and holes, the total densities of bound carriers remain practically constant. However, the localized electrons and holes are re-distributed between recombination and trapping levels by intermediate transitions to the bands and from bands to these levels.

III. EXPERIMENTAL RESULTS :

Films having rectangular geometry were deposited on glass substrates. The thickness and substrates temperature were varied and the photoconductivity was studied. Also

photoconductivity was measured at different temperatures. On top of these films deposited on glass substrates, Aluminium electrodes having finger shaped geometry were deposited as shown in Figure - 2. This particular geometry of the electrode enables a large sensitivity area to be employed between closely spaced electrodes and hence increases the sensitivity. A halogen lamp of 100 W was used as the light source and the intensity was measured by a foot candle-meter.

Variation of Photocurrent with intensity :

The illuminating intensity was varied from 25mW/cm² to 100 mW/cm² and a plot of $\log \Delta\sigma$ vs log intensity was obtained (Figure - 3). It is seen that the plot is linear in agreement with the power law $\Delta\sigma \propto L^n$ where n is the slope. However, above 60 mW/cm² the slope changes. The change in the slope (from 1 to 0.6) is indicative of the trap centre changing over to behave as a recombination centre with increase in intensity. If the electron Fermi level in a photoconductor is raised, by increasing light intensity or lowering temperature so as to include levels formally acting as electron trapping levels, the increased recombination due to these levels causes a decrease in photosensitivity. This decrease in the photosensitivity manifests itself by a decrease in n. However, in the present case this decrease has been observed to occur at a higher intensity, viz., beyond 60 mW/cm², than the change-over intensity, viz. 20 mW/cm², observed in the case of the directly evaporated films[1]. The decrease in photosensitivity is known

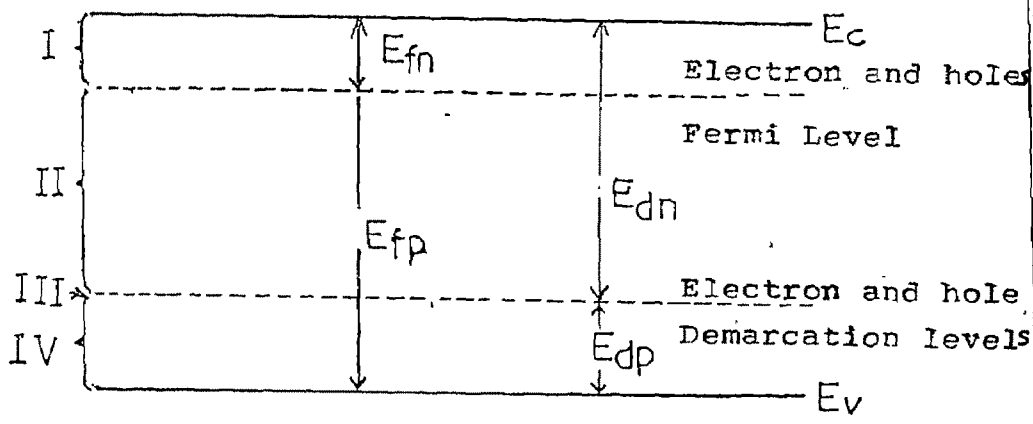

Figure - 1 : Fermi levels and demarcation levels for a semiconductor.

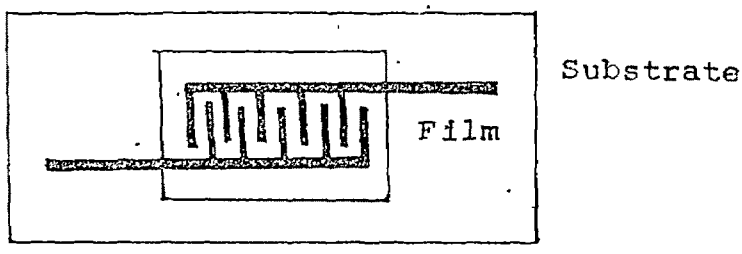

Figure - 2 : Comb-shaped electrodes on the film for photoconductivity measurements.

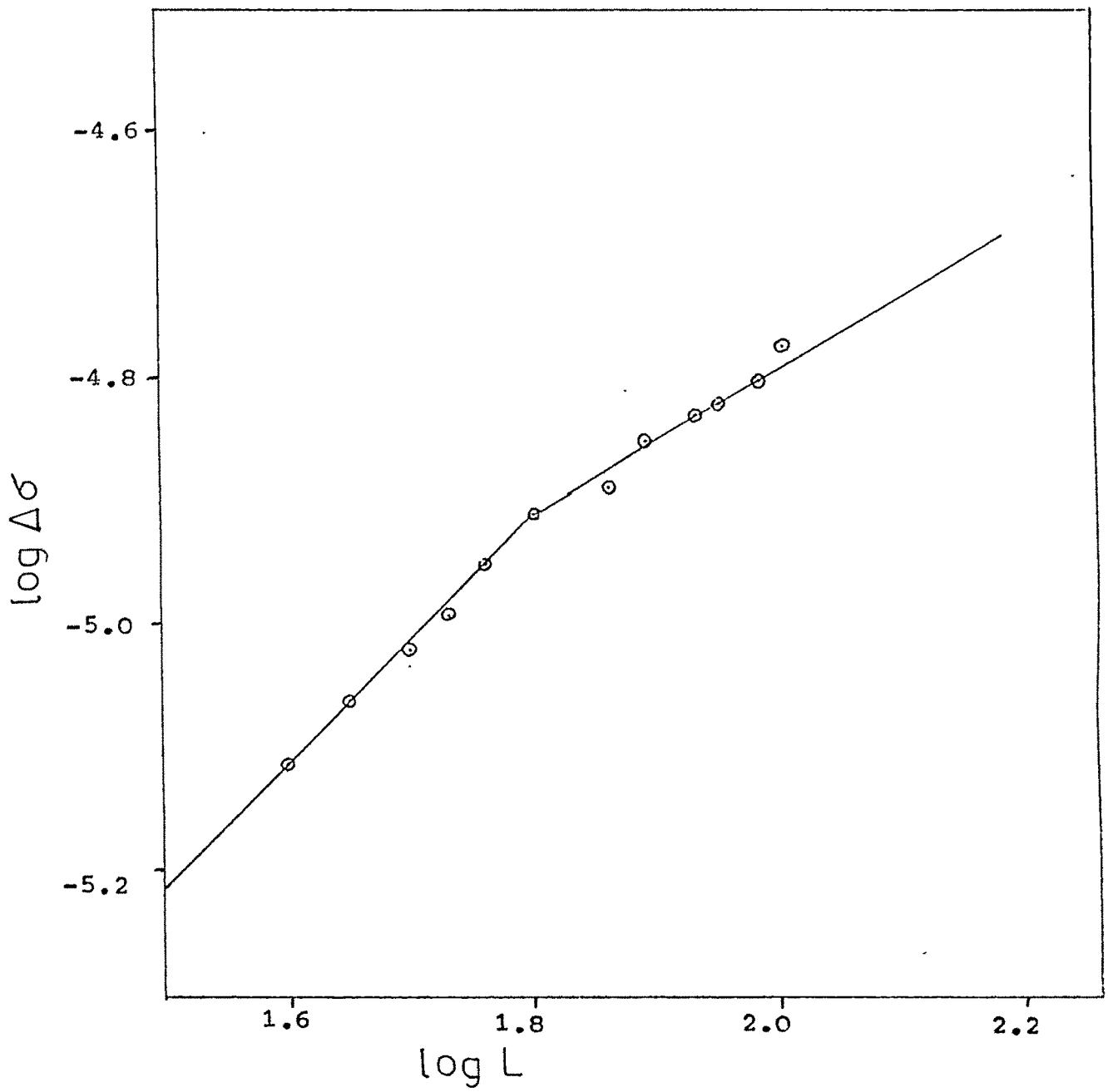

Figure - 3 : Plot of log $\Delta\sigma$ vs log L ; solid state reacted SnSe film.

to set in fairly suddenly if trapping levels involved are reasonably monoenergetic[8-10].

For all intensities of illumination used, the photocurrent was found to increase with illumination time reaching a saturation at around 120 sec. Therefore after illumination for 120 sec., the source was switched off and the measurements were continued for further 200 sec. The rise and decay curve of photocurrent as a function of time is shown in Figure - 4. The photocurrent during decay will be proportional to the rate at which carriers are thermally freed from traps, multiplied by the appropriate life time for the freed carriers. Those traps which have been filled during the excitation of the material will become empty[12] when the excitation is removed, at a rate depending on their capture cross section and their ionization energy. If it is assumed that re-trapping of the carriers freed from traps is negligible, an exponential decay is expected. If many different traps are present with different capture cross sections and ionization energies, as seems to be frequently the case, the decay curve has time dependence which can be expressed generally as $I = I_0 t^{-n}$ where t is the time, I_0 is the initial carrier concentration, I is the carrier concentration at time t and n may varry in different ranges of t.

The illumination time for saturation of photogeneration in the case of directly evaporated films was found to be about

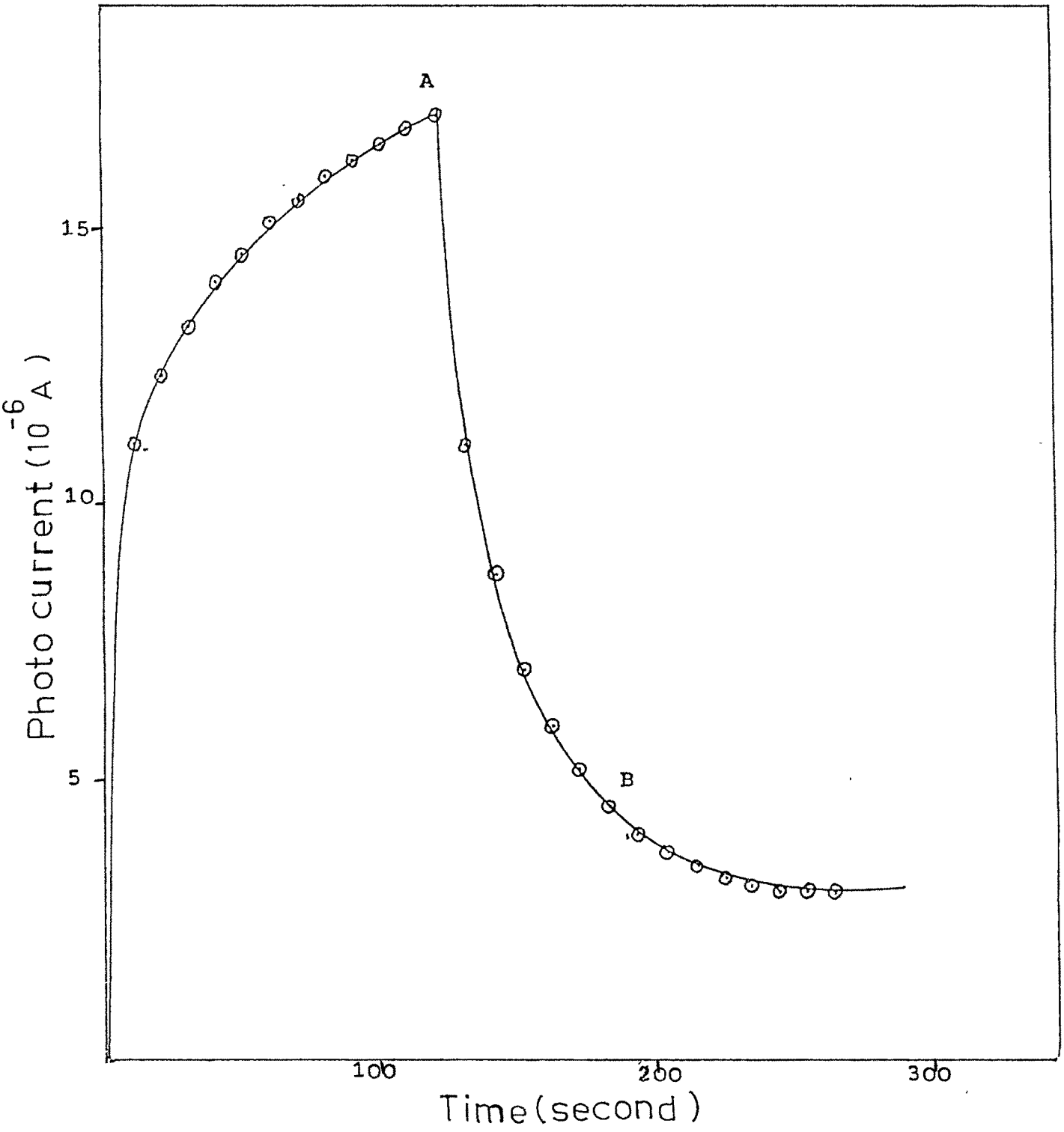

Figure - 4 : Rise and decay curve of photo current of solid state reacted SnSe film.
(Intensity 100 mW/cm²)

60 seconds[14] while it is twice in the present case. This may be interpreted to indicate the life time of the carriers in these films is twice that of the carriers in directly evaporated SnSe films. After switching off the illumination, there is a sudden drop in the photoconductivity, by about 75 % within 60 seconds of the switching off (from A to B in Figure - 4). This is also in contrast with the directly evaporated films in which case the corresponding drop of photoconductivity is found to be only about 40 %. The rise and decay curves for intensities upto 40 mW/cm² displayed similar characterisitcs.

Variation of photocurrent with temperature :

The temperature of the sample under illumination was varied from room temperature to about 400 K and the photocurrent was measured. The plot of photocurrent vs temperature is shown in Figure - 5 for a constant illumination intensity of 100 mW/cm². The heating rate was about 1°C/min. The peak is observed at about 350°K, indicating that the traps filled by excitons are emptied beyond this temperature. The sharp maximum gives a clear indication of the single trap depth. The increase of thermally stimulated conductivity is proportional to the rate of trap emptying multplied by the appropriate life time[15,16].

To study the effect of crystallinity, films (of thickness 1200 Å) were deposited at room temperature and at

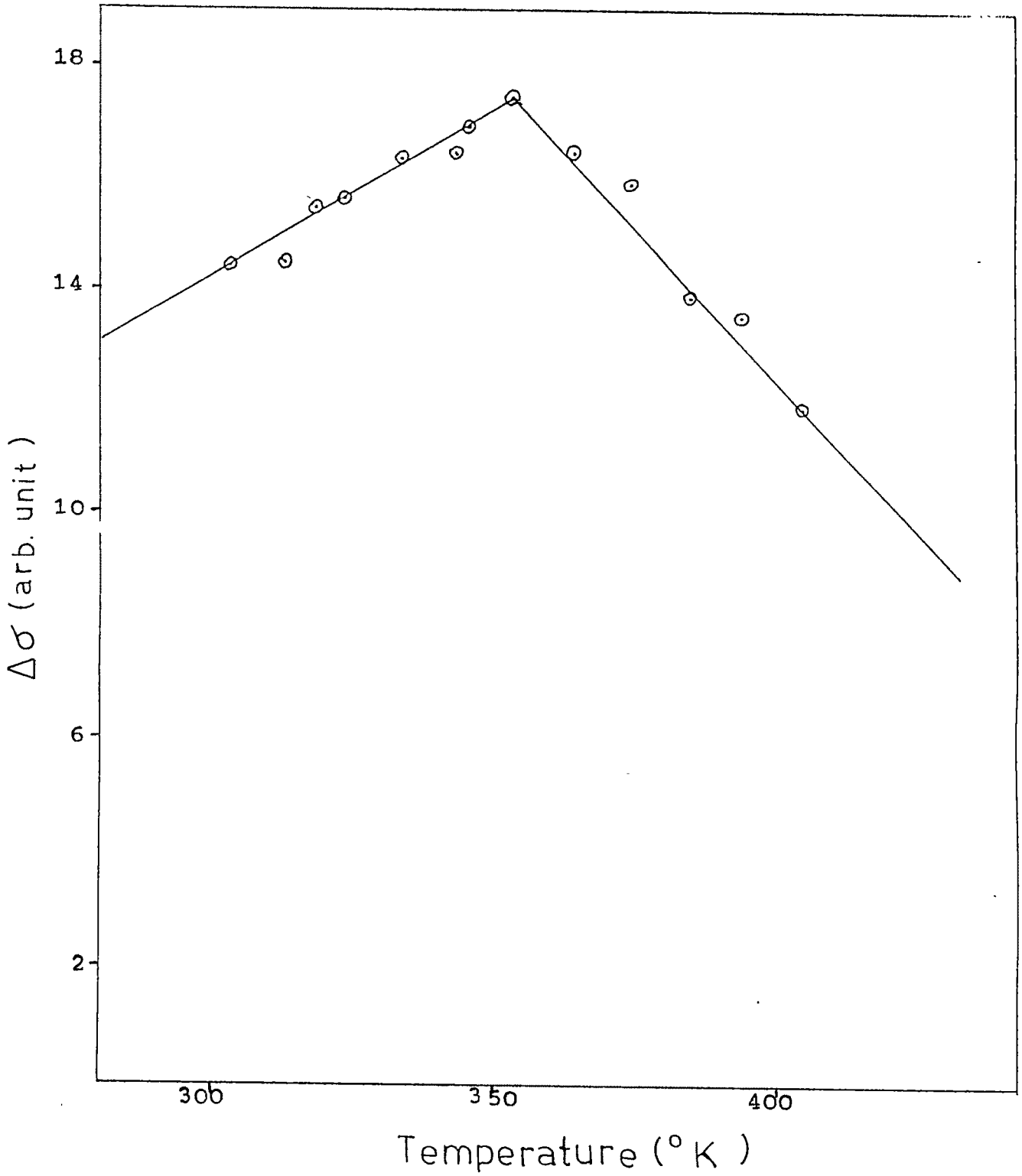

Figure - 5 : Plot of $\Delta\sigma$ vs Temperature ; SnSe solid state reacted film.
(Intensity 100 mW/cm²)

100°C. The graphs of log photocurrent vs log intensity, obtained for these films are shown in Figure - 6. It can be seen from these plots that the films obtained at 100°C substrate temperature exhibit higher photoconductivity than the room-tempeature deposited films. It is known that the crystallinity improves due to increased grain size in the films obtained at a higher substrate temperature. This results into increased effective mobility and life time of photogenerated carriers. This probably explains the increased photosensitivity.

Photoconductivity measurements were also made on the $SnSe_2$ films and the films obtained by evaporating SnSe-$SnSe_2$ eutectic compound. No measurable difference in dark conductivity and conductivity under illumination was observed. This may be due to quite low electrical conductivity of these films (Chapter - 4). Thus it may be concluded that $SnSe_2$ and SnSe-$SnSe_2$ films are practically not photoconductors.

CONCLUSIONS :

1. The photocurrent variation with illumination intensity follows the power law theoritically predicted and experimentally observed by previous workers. The change over of the trap centre to recombination centre occurs at a relatively higher intensity (about 3 times) than corresponding intensity observed in the case of directly evaporated SnSe films.

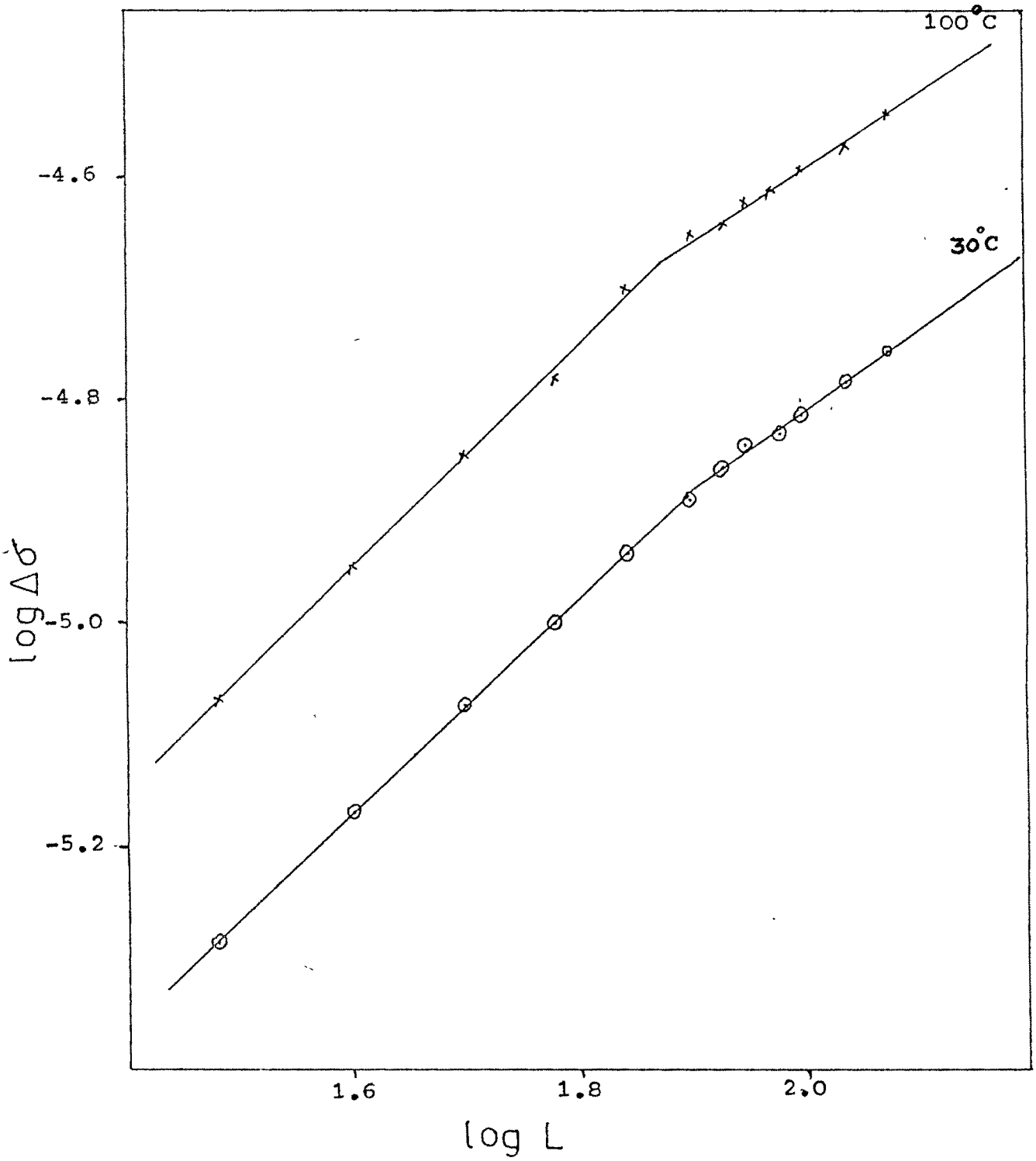

Figure - 6 : Plot of log $\Delta\sigma$ vs log L ; SnSe solid state reacted films deposited at room temperature and at 100°C substrate temperature.

2. The temperature dependence of the photoconductivity of the solid state reacted SnSe films indicates a single trap depth and trap emptying to occur beyond 350 K.

3. In the films of $SnSe_2$ and SnSe-$SnSe_2$ no photoducting effect has been observed which may be due to high electrical resistivity of the films.

4. SnSe films prepared by solid state reaction have a far improved photosensitivity in comparison to the films obtained by direct evaporation of the compound material.

5. The illumination time for saturation of photogeneration in the case of directly evaporated SnSe films was found to be about 60 second while it is twice in the preset case. This indicates, the life time of the carriers in directly evaporated SnSe films may be half of that inthe solid state reacted films.

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