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On the mechanism of long-term relaxation in polycrystalline cadmium telluride and zinc telluride films

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Abstract. Photoconductivity and photoconductive relaxation measurements have been carried out on vacuum-evaporated, air-exposed CdTe and ZnTe films in the temperature range 330–130 K to probe into the mechanism of photoconduction in the films. An analysis is made of the long-term photoconductivity as a function of temperature and light intensity in the cases where drift and recombination are governed by the same or different barriers. It is shown that the experimental results can be interpreted in the light of our analysis by assuming a recombination barrier different from the drift barrier, the height of which is not modulated under illumination. It is observed that both the recombination and drift barrier heights vary with the thickness of the film. The average value of the recombination and drift barrier heights are of the order of 0.22 eV and 0.70 eV for ZnTe, 0.04 eV and 0.45 eV for CdTe films respectively.

1. Introduction

The phenomenon of long-term photoconductivity decay has attracted widespread attention (Shienkman and Shik 1976, Varfolomeev *et al* 1985). In recent years a gradual consensus has developed towards a qualitative view of this phenomenon and it is now fairly well accepted that the observed slow photodecay is due to the presence of macroscopic potential barriers called the recombination barriers (Shienkman and Shik 1976, Sinkkonen 1981). It is also well known that the transport of majority carriers and hence the conductivity of a polycrystalline semiconductor is governed by the grain-boundary barriers called drift barriers (Seto 1975, Shienkman and Shik 1976). However, depending on the structure and physical properties of the semiconductor, the recombination and drift barriers may or may not be the same. This work analyses the photodecay characteristics in both cases, and it is shown that the experimental results of photodecay can be effectively employed to determine whether or not the same barrier is responsible for the recombination and drift of charge carriers. This analysis has also been employed to study the mechanism of the photoconductivity and field effect, long-term relaxation phenomena in CdTe, ZnTe and PbTe thin films.

2. Experimental details

Polycrystalline powders of the samples (i.e. CdTe, ZnTe and PbTe) were obtained after a direct synthesis of the respective components of 99.999 % purity in an evacuated quartz ampoule ($\sim 10^{-4}$ Pa). Films of CdTe, ZnTe and PbTe were deposited on glass substrates in a vacuum of the order of 10^{-4} Pa at room temperature with the help of a Hind High Vacuum Coating Unit (Model 12-A4). The thickness of the films is measured with a Surfometer (SF 101).

The electrical conductivity and photoconductivity measurements were carried out for these films at different temperatures by a conventional method described elsewhere (Datta *et al* 1978). The number of optical energies used for photoexcitation was measured with an Eppley calibrated thermopile. The source of white light was a tungsten–halogen lamp (600 W, 230 V) fed by a constant voltage supply. The light intensities were of the order of 400 W m^{-2} and 1400 W m^{-2} for low and moderate intensities respectively. Relaxation of conductivity after cessation of photoexcitation was recorded by an Omniscribe stripchart recorder (Model no 5000).

DC field-effect measurements were carried out in air using a mica spacer with a thickness of the order of a few

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micrometres placed between the film and the field electrode brass plate of approximate dimensions 1.0 × 1.0 cm^2. The applied DC voltage ranged between 300–700 V. The relaxation of conductivity after removal of the field was monitored by the stripchart recorder.

3. Theoretical consideration

The slow photoconducting decay is attributed here to the reconstruction of the recombination barrier which has spatially separated the photogenerated electron–hole pairs by trapping minority carriers. The dark conductivity is established only after equilibrium filling of the recombination barrier states, the process being self-hampering because it involves the barrier being overcome by majority carriers. Therefore, considering a p-type semiconductor, we can write down the kinetics of the decay of excess photogenerated carriers after the cessation of illumination as (Datta 1986, Subba Rao and Chaudhuri 1986)

$$\frac{d}{dt}(n_r) = -S_p n_r (P_g + \Delta P_g)\exp(-q\phi_r/kT) \qquad (1)$$

where n_r is the density of trapped electrons in the recombination centres (per unit area) at the grain boundary under illumination, T is the absolute temperature, ΔP_g is the excess hole concentration in the grains, ϕ_r is the recombination barrier height under illumination, S_p is the capture coefficient for holes at the grain boundary and P_g is the hole concentration in the dark. The charge neutrality condition in this case (Datta 1986, Subba Rao and Chaudhuri 1986) is given by

$$L\,\Delta P_g = n_r \qquad (2)$$

where L is the grain size.

The recombination barrier height (ϕ_r) under illumination can be written as (Seto 1975)

$$\phi_r = \frac{q(N_r - n_r)^2}{8\varepsilon N_A}$$

where N_r is the density of recombination centres per unit area, N_A is the acceptor state density per unit volume and ε is the dielectric constant. Using equation (2) we obtain an expression for ϕ_r as a function of ΔP_g (Datta 1986):

$$\phi_r = \phi_{r0}\left(1 - \frac{L\Delta P_g}{N_r}\right)^2 \qquad (3)$$

where $\phi_{r0}(= qN_r^2/8\varepsilon N_A)$ is the barrier height in the dark. Using equations (2) and (3), equation (1) can be expressed as

$$\frac{d}{dt}(\Delta P_g) = -S_p \Delta P_g (P_g + \Delta P_g) \times \exp\left[-\left(\frac{q\phi_{r0}}{kT}\right)\left(1 - \frac{L\Delta P_g}{N_r}\right)^2\right] \qquad (4)$$

which in the general case can only be solved numerically. However, for weak illumination intensities where $\Delta P_g \ll P_g$ and $\phi_r \approx \phi_{r0}$, the solution of equation (4) leads to the well known expression of an exponential decay given by

$$\Delta P_g = (\Delta P_g)_0 \exp(-t/\tau_{r0}) \qquad (5)$$

where

$$\tau_{r0} = \frac{1}{S_p N_v}\exp\left(\frac{q\phi_{r0} + (E_F - E_v)}{kT}\right). \qquad (5a)$$

E_F and E_v are the Fermi level and the top of the valence band respectively and $N_v = (2\pi m^* kT/h^2)^{3/2}$.

For moderate illumination intensities where $\Delta P_g < P_g$ and the change in recombination barrier height under illumination is small enough such that the approximation

$$\left(1 - \frac{L\Delta P_g}{N_r}\right)^2 \simeq 1 - \frac{2L\Delta P_g}{N_r}$$

holds good, equation (4) can be solved assuming $\alpha\Delta P_g > 1$ where $\alpha = (2L/N_r)(q\phi_{r0}/kT)$ and we obtain

$$\frac{\exp(-\alpha\Delta P_g)}{\alpha\Delta P_g} = \frac{t}{\tau_{r0}} + \frac{\exp[-\alpha(\Delta P_g)_0]}{\alpha(\Delta P_g)_0}. \qquad (6)$$

Noting that $\exp(-\alpha\Delta P_g)$ varies much more rapidly than $\alpha\Delta P_g$, equation (6) can be further simplified to the following form for $t > \tau_B$:

$$(\Delta P_g)_t = (\Delta P_g)_0 - \frac{1}{\alpha}\ln(t/\tau_B) \qquad (7)$$

when

$$\tau_B = [\tau_{r0}/\alpha(\Delta P_g)_0]\exp[\alpha(\Delta P_g)_0].$$

Equation (7) indicates that ΔP_g should vary as the logarithm of time t, for such large values of t not violating the conditions $\alpha\Delta P_g > 1$ and $\tau_B < t < \tau_{r0}$.

Before going into the calculations of excess conductivity as a function of time after the cessation of illumination, we note that the conductivity of a polycrystalline semiconductor is given by (Datta 1986)

$$\sigma = AN_v \exp\left(-\frac{q\phi_d + (E_F - E_v)}{kT}\right) \qquad (8)$$

where

$$A = Lq^2/(8\pi m^* kT)^{1/2}.$$

ϕ_d is the drift barrier height, and m^* is the effective mass of holes.

We shall now consider the photoconductivity decay in the following two cases.

Case I. When the recombination barrier and drift barrier are one and the same (i.e. $\phi_d = \phi_{r0}$).

From equation (8) we obtain an expression for excess conductivity given by

$$\Delta\sigma = A\left[(P_g + \Delta P_g)\exp\left(-\frac{q\phi_d'}{kT}\right) - P_g \exp\left(-\frac{q\phi_d}{kT}\right)\right] \qquad (9)$$

where $\phi_d'(= \phi_r)$ is the barrier height under illumination.

For weak illumination intensities no significant change in barrier height will occur ($\phi_d' \simeq \phi_d = \phi_{r0}$), hence equa-

tion (9) takes the form

$$\Delta\sigma = A\Delta P_g \exp(-q\phi_{r0}/kT). \quad (9a)$$

Putting equation (5) in equation (9*a*), we get

$$(\Delta\sigma)_t = A(\Delta P_g)_0 \exp\left(-\frac{q\phi_{r0}}{kT}\right)\exp\left(-\frac{t}{\tau_{r0}}\right) \quad (10)$$

since for weak illumination $(\Delta P_g)_0 = (g/S_pP_g)$ $\exp(q\phi_{r0}/kT)$ (Subba Rao and Chaudhuri 1985), where g is the photogeneration rate. Equation (10) can be written as

$$(\Delta\sigma)_t = \frac{Ag}{S_pN_v}\exp\{[(E_F - E_v)/kT]\exp(-t/\tau_{r0})\}. \quad (10a)$$

For moderate illumination intensities, using the approximations previously stated and substituting the value of ΔP_g from equation (7) we get

$$(\Delta\sigma)_t = AP_g \exp(-q\phi_d/kT)\left(\frac{T_B\exp[\alpha(\Delta P_g)_0]}{t} - 1\right) \quad (11)$$

Case II. When recombination and drift barriers are different (i.e. $\phi_d \neq \phi_{r0}$) and no modulation of drift barrier occurs under weak illumination. In this case, the expression for $\Delta\sigma$ (equation (9)) takes the form

$$(\Delta\sigma)_t = (Ag/S_pN_v) \times \exp\left(-\frac{q(\phi_d - \phi_{r0}) - (E_F - E_v)}{kT}\right)\exp(-t/\tau_{r0}) \quad (12)$$

indicating an exponential decay for weak illumination intensities. Again at $t = 0$, the excess photoconductance ΔG can be expressed as

$$\Delta G = B\exp\{-[q(\phi_d - \phi_{r0}) - (E_F - E_v)]/kT\} \quad (13)$$

where B is a constant.

For moderate illumination intensities $\Delta\sigma$ varies as

$$(\Delta\sigma)_t = A\exp\left(-\frac{q\phi_d}{kT}\right)\left[(\Delta P_g)_0 - \frac{1}{\alpha}\ln\left(\frac{t}{\tau_B}\right)\right]. \quad (14)$$

Therefore, it can easily be seen from equations (10) and (12) that for weak illumination intensities which have practically no effect on the recombination barrier height, the photoconductive decay varies exponentially with time in both the cases. However, for moderate illumination intensities, the photoconductivity decay obeys laws (equations (11) and (14)) which are slower than those for weak illumination, and its nature depends on whether the same barrier governs the recombination and drift of charge or not.

4. Results and discussion

The films CdTe and ZnTe deposited in vacuum and exposed to the atmosphere after deposition are found to be p-type and the films of PbTe are found to be n-type as determined by thermoelectric measurements. X-ray and electron diffraction studies have revealed that the films were polycrystalline and consist of crystallites of size ranging from 6 nm to 68 nm (Saha *et al* 1988, Pal *et al* 1989, Sinha *et al* 1976). Figures 1(*a*) and (*b*) show the photorelaxation curves ($\ln \Delta\sigma \sim t$) of CdTe and ZnTe thin films at different temperatures for weak photoexcitation (400 W m^{-2}). It is observed that the photorelaxation curves follow an exponential decay for weak illumination intensity which is in accordance with the equation (12) (figures 1(*a*) and (*b*)). Increase of slope with increase of temperature indicates that the value of photorelaxation time constant (τ_{r0}) decreases with an increase of temperature. But for moderate intensity (1400 W m^{-2}) photorelaxation is observed to follow a non-exponential decay (figures 2(*a*) and (*b*)). Photocon-

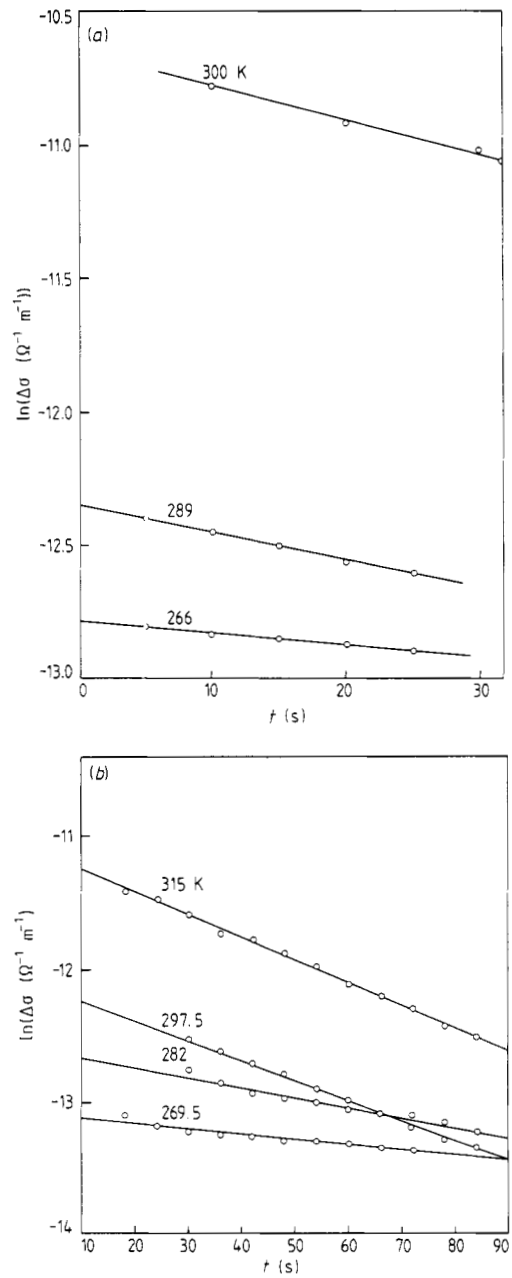

Figure 1. Plots of ln $\Delta\sigma$ versus t at different temperatures for (*a*) CdTe (0.40 μm) and (*b*) ZnTe (0.63 μm) films for weak illumination (400 W m^{-2}).

ductivity decay follows a linear relationship with ln t which is in accordance with the equation (14). Fuhs and Stuke (1968) have also observed similar variation of photoconductivity decay with time in Se. Assuming the variation of E_F with temperature is very small, the values of $\phi_d - [\phi_{r0} + (E_F - E_v)]$ are estimated from the temperature variation of excess conductance (ΔG) following equation (13) (figures 3(*a*) and (*b*)) and given in table 1. Photorelaxation time constants of stable CdTe and ZnTe films are estimated from the photorelaxation curves at different temperatures (figures 1(*a*) and (*b*)) using equation (12) (Subba Rao and Chaudhuri 1986). Figures 4(*a*) and (*b*) show the temperature variation of the photorelaxation time constant (τ_{r0}) for films of different thickness. The photorelaxation time constant was found to increase with decreasing temperature. The values of $\phi_{r0} + (E_F - E_v)$ estimated from these (figures 4(*a*) and (*b*)) curves using equation (5*a*) for CdTe and ZnTe films are shown in table 1.

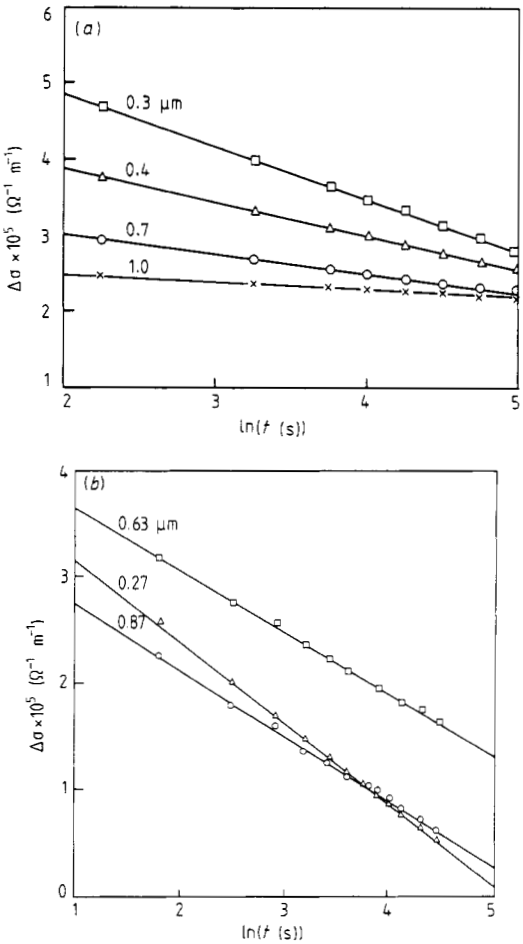

Figure 2. Plots of $\Delta\sigma$ versus ln t for different thicknesses of (*a*) CdTe and (*b*) ZnTe film at a moderate intensity of illumination (1400 W m^{-2}).

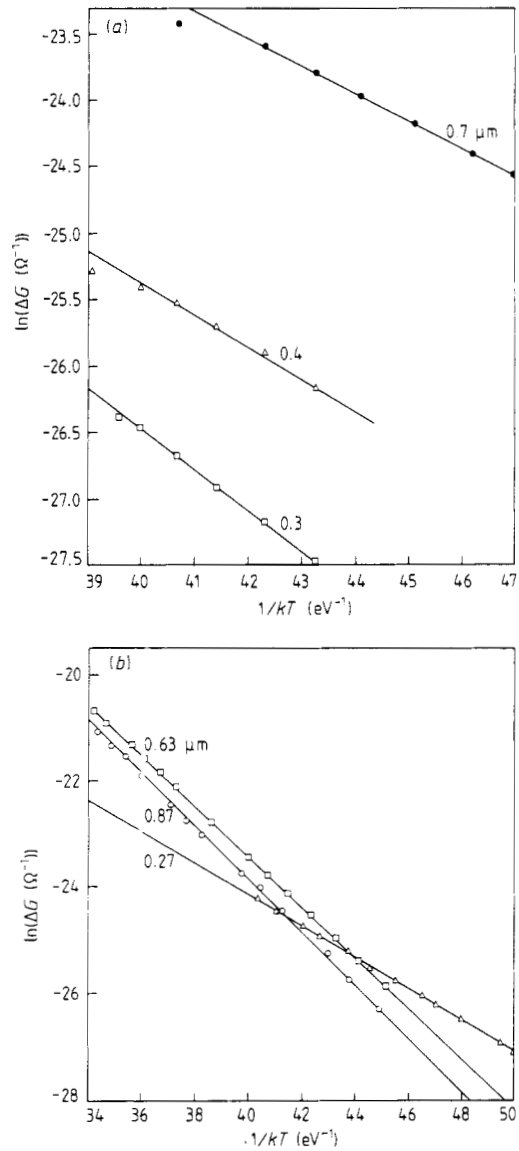

Figure 3. Plots of ln ΔG versus $1/kT$ for different thicknesses of (a) CdTe and (*b*) ZnTe films under weak illumination (400 W m^{-2}).

Table 1. Variation of different electrical parameters of ZnTe and CdTe films.

Sample	Thickness (μm)	$\phi_d + (E_F - E_v)$ (eV)	$\phi_d - (\phi_{r0} + E_F - E_v)$ (eV)	$\phi_{r0} + E_F - E_v$ (eV)	ϕ_d (eV)	$E_F - E_v$ (eV)	ϕ_{r0} (eV)
ZnTe	0.42	0.51	0.32	0.13	0.45	0.06	0.07
	0.63	0.80	0.45	0.30	0.75	0.05	0.25
	0.87	0.95	0.50	0.40	0.90	0.05	0.35
CdTe	0.30	0.75	0.30	0.27	0.57	0.18	0.09
	0.40	0.62	0.24	0.20	0.44	0.18	0.02
	0.70	0.48	0.20	0.15	0.35	0.13	0.02

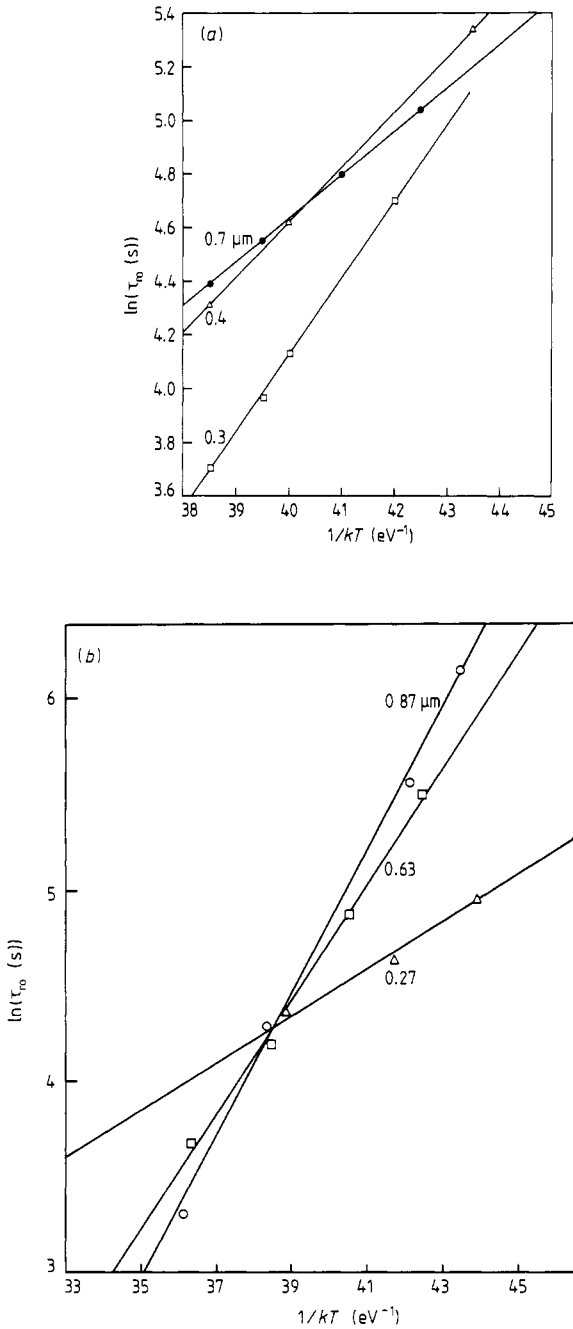

Figure 4. Plots of ln τ_{r0} versus $1/kT$ for different thicknesses of (*a*) CdTe and (*b*) ZnTe films.

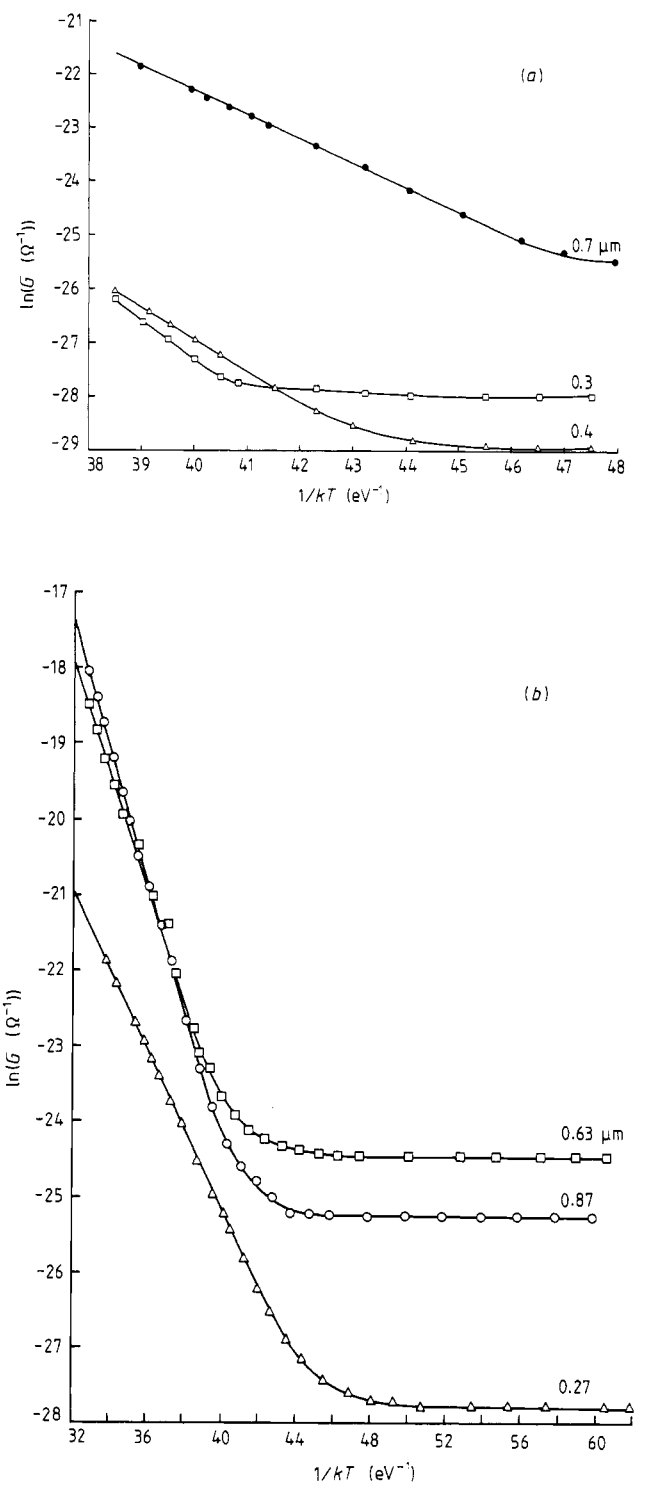

Figure 5. Variation of dark conductance (G_d) with temperature of (*a*) CdTe and (*b*) ZnTe films of different thicknesses.

The dark conductance of the films can be expressed as (Bube 1975, Kumar 1982)

$$G = G_0 \exp\{-[\phi_d + (E_F - E_v)]/kT\} \qquad (15)$$

where G_0 is a constant. The values of $\phi_d + (E_F - E_v)$ have also been calculated from the temperature variation of dark conductance of the CdTe and ZnTe films (figures 5(*a*) and (*b*)).

The values of drift barrier heights (ϕ_d), recombination barrier heights (ϕ_{r0}) and activation energies ($E_F - E_v$) are calculated by manipulating the values obtained for $\phi_d - [\phi_{r0} + (E_F - E_v)]$, $\phi_{r0} + (E_F - E_v)$ and $\phi_d + (E_F - E_v)$ shown in table 1. From this table it is clear that the recombination and drift barriers are not the same for CdTe and ZnTe films. Figure 6 shows the field-induced conductivity versus ln*t* plots for a typical PbTe film (Sinha 1976, Bose *et al* 1977). This variation is found to be in accordance with equation (14). In our model

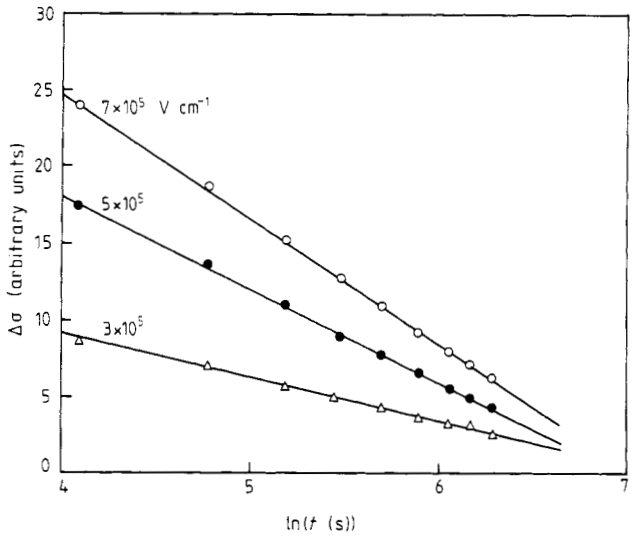

Figure 6. Plots of $\Delta\sigma$ versus ln t of PbTe film (0.20 μm) for different field intensities.

recombination barriers are assumed to be formed at the grain-boundary region. This field-effect relaxation phenomenon can be accommodated in our model if we assume that the recombination barriers are formed in this case on the free surface of the grains due to surface band bending instead of at the grain boundary. The free-surface barrier height is altered by an applied transverse field changing the value of τ_{r0} (equation (14)), but the drift of carriers is hindered by grain-boundary barriers. So it seems that the same model can be applied to explain both the photo- and field-effect relaxation phenomena.

5. Conclusions

A theoretical analysis has been made for the phenomenon of long-term photoconductivity decay in terms of the 'recombination barrier' and the 'drift barrier'. The derived expressions show that the model of decay under weak and moderate illumination intensities will be different and the decay process is very sensitive to the temperature.

Experimental results presented here show that the recombination barrier is different from the grain-boundary drift barrier, the height of which is assumed not to be modulated under illumination.

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