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Theory of transient photoconductivity in counter-doped semiconductors

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Abstract. A theory of impurity-related transient photoconductivity in semi-insulating semiconductors is developed. When a photoconductor is illuminated in an applied electric field, the initial sweep-out of carriers generates space charge at the active centres within the crystal. This space charge is neutralised by injection from contacts, but the injected carriers are partially trapped leading to the possibility of current oscillation with frequency determined by a dielectric relaxation time and a trapping time. The theory of this effect is developed for a simple model involving a deep donor and compensating shallow acceptor. Effects of additional traps on the transients are also discussed. If extra traps with large capture cross sections are present near the quasi-Fermi energy, they can damp the oscillations. Such traps can also strongly affect the transient shape, introducing dependence on optical chopping frequency and temperature.

1. Introduction

Deep levels are currently of considerable interest in semiconductor research and a number of experimental techniques are available for their study (Milnes 1973). Photoconductivity is one technique which is particularly useful for optically active centres and a complete photoconductivity transient can contain a wealth of information which is not always easy to interpret. The technique has been reviewed in detail by Ryvkin (1964) who also discusses various analytical models for interpreting the shape of transients.

The literature on the theory of photoconductivity is extensive. It is necessary to set up rate equations for the relevant impurity levels, and the theory of Shockley and Reed (1952) is generally invoked. Analytical solutions of the resulting equations are not possible in general and many papers are devoted to analysing specific level schemes. In the present paper we are particularly concerned with counter-doped semiconductors of the type discussed by Migliorato *et al* (1977) and Elliott (1976). These systems can be typified by a deep donor and a compensating shallow acceptor. The shallow acceptor receives electrons from the donor, leaving the latter in a positive charge state which can be photoneutralised. A simple analytical model for the time dependent photo-response of such a system was given by Migliorato *et al* (1977), and in the present paper we generalise this

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theory to allow for additional trapping levels and space-charge effects. Space-charge effects can be important when the dielectric relaxation time of a sample is comparable with the response time, as occurs for example at very low temperatures with carrier freeze-out, or with excess deep donor, and to allow for this we have used the suggestion by Williams (1969) that under uniform illumination carrier sweep-out is responsible for these effects. Our mathematical formulation of carrier sweep-out and the resulting response from the contacts leads to the prediction of a new mechanism for transient oscillations.

In the small-signal case when the change in carrier concentration (ΔP) is much smaller than the dark carrier concentration (P_0) it is often possible to linearise the response equations and decouple the rate equations for the different levels. When $\Delta P > P_0$, however, a numerical solution is generally called for. An exception occurs when the quasi-Fermi level is distant from all levels except one optically active level and the trapping levels have sufficiently large capture cross sections to be effectively in equilibrium with the valence band. In the present paper we consider detailed analytical and numerical solutions for a model containing one optically active level (a deep donor) with fairly small capture cross section, a shallow compensating acceptor and a deep acceptor as a trap. The deep donor is considered to lie in the lower half of the band gap so that only p-type material is considered.

For such a counter-doped system, the free carrier concentration at low temperatures can be very small. When the sample is illuminated under an applied electric field, the photogenerated carriers are swept out of the system if the transit time is fast compared with trapping times, but the contacts cannot restore charge neutrality in less than a dielectric relaxation time. The resulting space charge couples to the free carriers and can lead to interesting oscillatory phenomena.

Many examples of current oscillation in photoconductors have been reported. If a condition of negative differential mobility is achieved, for example through a field-dependent capture cross section (Ridley 1963) or optic phonon emission (Maksym and Hearn 1979) then dipole domains tend to form which give current oscillations with a frequency determined by the transit time. Oscillations have also been observed which are not transit-time dependent. Moore *et al* (1967) observed oscillations with space-charge-limited currents coupled to traps, Kazarinov *et al* (1973) have discussed wave propagation of trapped space charge, and recently Arrington and Eisenman (1977) published transient photoconductivity data for doped silicon at liquid helium temperatures which show oscillatory behaviour similar to the effect described in this work.

The theory is developed in stages. First the simple model of a deep donor and shallow acceptor is analysed assuming charge neutrality is maintained. In this case analytical solutions for the transients are possible for all values of $\Delta P/P_0$ as long as the quasi-Fermi level is well above the shallow acceptor binding energy. This theory is adequate for the two-level system when the dark carrier concentration is sufficiently high for the dielectric relaxation time to be much shorter than the rise time. This theory is then generalised to analyse the current flow when space-charge neutrality is not maintained. In this case it is shown that the resulting non-linear differential equations have a focus in the phase plane describing damped oscillations. By linearising about the fixed point it is found that the period of oscillation equals the square root of the product of a dielectric relaxation time and a trapping time. The decay time is given by the dielectric relaxation time for the steady-state free carrier concentration. Effects of further trapping levels are then considered and shown to increase the damping of the oscillations and produce interesting effects on the shape of transients. These various effects are illustrated with computer graphs.

2. An analytical model with space-charge neutrality

In this section the transient response is analysed for a two-level system consisting of a deep donor and compensating shallow acceptor. The ratio of optical to capture cross sections is assumed to be much higher for the deep donor. The shallow acceptor, due to its long-range hole-attractive ionisation state, is assumed to have a high hole capture cross section so that it can be considered to maintain equilibrium with the valence band. For simplicity we assume Shockley and Read (1952) kinetics when the rate equation for the population of a level can be written in the form

$$(\mathrm{d}/\mathrm{d}t)(f^-) = Uf^+ - C[f^-P - f^+P_\mathrm{t}]. \tag{1}$$

Here f^- is the probability that a level is occupied by an electron, $f^+ = 1 - f^-$, C is the hole capture cross section (including the mean thermal velocity of free holes), P is the concentration of free holes, P_t is the concentration of free holes obtained if the Fermi level lies at the impurity energy, and Uf^+ denotes the optical transition rate. In the steady state $(\mathrm{d}/\mathrm{d}t)(f^-) = 0$ and equation (1) yields the population probability in the form

$$f^{-\mathrm{e}} = \frac{E + P_\mathrm{t}}{E + P^\mathrm{e} + P_\mathrm{t}}, \qquad E = \frac{U}{C} \tag{2}$$

where a superscript e denotes steady-state values. For simplicity, degeneracy factors are not included explicitly, but if required they can be included by replacing P_t by gP_t, where g is the normal degeneracy factor (Milnes 1973).

To solve equation (1) it is necessary to obtain an expression for P, using charge neutrality. If we use subscripts a and d to denote the shallow acceptor and deep donor respectively, then the charge neutrality condition takes the form

$$P = N_\mathrm{a} f_\mathrm{a}^- - N_\mathrm{d} f_\mathrm{d}^+ \tag{3}$$

where N denotes an impurity concentration. Using (3) with equations (1) and (2) it is clear that in general the rate equations for different levels are coupled, and analytical solutions are not possible. If we assume that for the shallow acceptor

$$P_\mathrm{a} \gg E_\mathrm{a}, \qquad C_\mathrm{a} \gg C_\mathrm{d}, \tag{4}$$

then the population of the shallow level can be approximated to

$$f_\mathrm{a}^- \simeq P_\mathrm{a}/(P + P_\mathrm{a}). \tag{5}$$

If we further assume that the quasi-Fermi level describing the instantaneous free hole population, is always well above the shallow acceptor energy, then (5) simplifies to

$$f_\mathrm{a}^- \simeq 1 - P/P_\mathrm{a}, \qquad P_\mathrm{a} \gg P \tag{6}$$

and the charge neutrality condition (3) reduces to

$$P = \bar{N}_\mathrm{a} - \bar{N}_\mathrm{d} f_\mathrm{d}^+, \qquad \bar{N} = N/(1 + N_\mathrm{a}/P_\mathrm{a}). \tag{7}$$

The rate equation for the deep donor can now be written in the form

$$(\mathrm{d}/\mathrm{d}t)(f_\mathrm{d}^-) = -\alpha(f_\mathrm{d}^-)^2 + \beta f_\mathrm{d}^- + \gamma \tag{8}$$

$$\alpha = C_\mathrm{d}\bar{N}_\mathrm{d}, \qquad \beta = -(U_\mathrm{d} + C_\mathrm{d}P_\mathrm{d}) + C_\mathrm{d}(\bar{N}_\mathrm{d} - \bar{N}_\mathrm{a}),$$

$$\gamma = (U_\mathrm{d} + C_\mathrm{d}P_\mathrm{d}).$$

Equation (8) is a standard integral and the final solution for f_d^- and P takes the form

$$f_d^-(t) = \left(x - y \frac{[f_d^-(0) - x]}{[f_d^-(0) - y]} \exp[-\alpha(x - y)t] \right) \bigg/ \left(1 - \frac{(f_d^-(0) - x)}{(f_d^-(0) - y)} \exp[-\alpha(x - y)t] \right), \tag{9}$$

where x, y are the positive and negative stationary solutions of (8),

$$x = f_d^-(\infty), \qquad y = [\beta - (\beta^2 + 4\alpha\gamma)^{1/2}]/2\alpha.$$

Substitution of (9) in (7) yields the time-dependent free hole concentration. It should be noted that (9) is similar in form to the approximate solution obtained by Migliorato *et al* (1977).

The solution (9) does not have a simple exponential dependence on time. However, all the time dependence is contained in the exponential form $\exp[-\alpha(x - y)t]$ so that we can define a rise time τ by the expression

$$1/\tau = \alpha(x - y) = (\beta^2 + 4\alpha\gamma)^{1/2}. \tag{10}$$

After substituting for α, β, γ, from (8) this reduces to the form

$$(1/\tau)^2 = [U_d + C_d(P_d + \bar{N}_d + \bar{N}_a)]^2 - C_d^2 4\bar{N}_d\bar{N}_a. \tag{11}$$

If $\bar{N}_d \gg \bar{N}_a$ or vice versa, then the last term in (11) is negligible and the rise time reduces to

$$1/\tau \simeq U_d + C_d[P_d + \bar{N}_T^>], \tag{12}$$

where $\bar{N}_T^>$ is the impurity concentration of highest value. It is interesting to note that for exact compensation $N_a = N_d$ and $C_dP_d \ll U_d \ll C_d(\bar{N}_d + \bar{N}_a)$, equation (11) yields a square-root dependence on light intensity

$$1/\tau \to [C_d 2(\bar{N}_d + \bar{N}_a)]^{1/2} U_d^{1/2}. \tag{13}$$

For a deep donor, P_d can be neglected in (11) when

$$(1/\tau)^2 \sim U_d^2 + C_d^2(\bar{N}_a - \bar{N}_d)^2 + 2UC_d(\bar{N}_a + \bar{N}_d). \tag{14}$$

This shows that for high optical excitation $1/\tau \propto U_d$ and as the light intensity falls the time constant becomes longer tending towards the constant value $1/\tau \sim C_d|\bar{N}_d - \bar{N}_a|$.

For large times equation (9) has the form

$$f_d^-(t) \to A - B\exp(-t/\tau) \qquad t \gg \tau \tag{15}$$

so that the time constant can be obtained from the expressions

$$-\frac{1}{\tau}(t) = \frac{\mathrm{d}}{\mathrm{d}t}\ln[f_d^-(\infty) - f_d^-(t)] \qquad \frac{1}{\tau} = \lim_{t\to\infty}\frac{1}{\tau(t)}. \tag{16}$$

If equation (16) is used to define an 'instantaneous' time constant $\tau(t)$ for the transient (9) we obtain

$$\frac{1}{\tau(t)} = \frac{1}{\tau}\left[1 + \frac{S\exp(-t/\tau)}{1 - S\exp(-t/\tau)}\right], \qquad S = \frac{f_d^-(0) - x}{f_d^-(0) - y}. \tag{17}$$

As $t \to \infty$, $\tau(t) \to \tau$ and as $t \to 0$, $(1/\tau(t)) \to (1/\tau)[1 + S/(1 - S)]$. Using equation (10) to express y in terms of x, the expression for S can be simplified to the form

$$S = \frac{1}{1 - 1/\alpha\tau\Delta f_d^-}, \qquad \Delta f_d^- = f_d^-(\infty) - f_d^-(0)$$

$$S/(1 - S) = -\alpha\tau\Delta f_d^- \tag{18}$$

and the initial time constant simplifies to the form

$$1/\tau(0) = (1/\tau)[1 - \alpha\tau\Delta f_{\mathrm{d}}^{-}]. \tag{19}$$

For the rise transient $\Delta f_{\mathrm{d}}^{-} > 0$ and $\tau(0) > \tau$. If τ is approximated by (12), $1/\tau \simeq C_{\mathrm{d}}\bar{N}_{\mathrm{T}}^{>}$, using the expression for α in (8) it follows that $\alpha\tau \simeq \bar{N}_{\mathrm{d}}/\bar{N}_{\mathrm{T}}^{>} \lesssim 1$ for low optical generation rates. For excess deep donor, this becomes $\alpha\tau \sim 1$ and the variation of time constant depends on the change in the population factor for the deep donor.

If the large-time value of $1/\tau(t)$ is observed to be linear in the light intensity and the system is not closely compensated so that equation (12) is valid, then the rise and decay time constant for large time yield the values of U_{d} and $C_{\mathrm{d}}\bar{N}_{\mathrm{T}}^{>}$. The zero time values of $\tau(t)$ then give a value for $\alpha\Delta f_{\mathrm{d}}^{-}$. If the initial and final values of hole concentration P are also measured, then using equations (2) and (3) we obtain five equations for the unknowns U_{d}, N_{a}, N_{d}, C_{d} so that in principle all the unknowns are determined and a consistency condition is also obtained. A further consistency condition is given by the complete time dependence of $\tau(t)$ (17). A more accurate analysis could use the complete expression (11) for τ as this does not involve any additional unknowns.

3. Space-charge effects

The model of §2 assumed space-charge neutrality which is only justified when the dielectric relaxation time τ_{D} is much shorter than the transient time constant τ. For materials at very low temperatures or with the counter-doped material of particular interest in this work having excess deep donor, it is possible to have conditions where $\tau_{\mathrm{D}} \gtrsim \tau$ and space-charge effects can then alter the photoconductivity transient (Williams 1969).

We consider a typical experiment where a photoconductor biased with a constant voltage is subjected to a square wave pulse of radiation and the current monitored. The light creates free carriers in a space-charge neutral state so that it might be expected that the virtual cathode of an ohmic contact would respond instantaneously to replace photoexcited carriers that are swept from the samples by the electric field. This reasoning becomes correct as the constant applied voltage tends to zero but for stronger fields the photoexcited carriers can be swept away as they are created so that the increment in carrier density near the injecting contact due to optical generation is negligible. In this case the band bending near the contact due to continuity with the position of the Fermi level in the bulk is unaffected and the contact can only respond to the space-charge-induced local electric field (Lampert and Rose 1959). As the photoexcited carriers are swept from the sample, immobile space charge is created at the optically active impurity centres. This space charge alters the electric fields at the contacts increasing the field at the injecting contact and reducing the field linearly across the sample consistently with the constant applied voltage, so that more carriers are injected than extracted, giving a driving force to restore space-charge neutrality. As the carrier density builds up in the crystal, the band bending at the ohmic contact is further adjusted to maintain the electric current. The observed transient results from competition between the radiation field generating space charge and the contacts responding to neutralise the sample.

To estimate the increment in carrier density (δp) due to the photogeneration sweep-out current we can solve the continuity equation

$$\partial(\delta p)/\partial t + \partial(\delta j)/\partial x = \bar{U} \tag{20}$$
$$\delta j = \delta p \mu E_0, \qquad \bar{U} = U_{\mathrm{d}} N_{\mathrm{d}} f_{\mathrm{d}}^{+}$$

where μ is mobility, E_0 is applied electric field and δp the increment in free carrier density due to photogeneration (with zero incremental response from the contact). At the steady state the solution to (20) takes the form

$$\delta p = (\bar{U}/\mu E_0)x \qquad 0 < x < L \tag{21}$$

so that if $(\bar{U}/\mu E_0)L \ll P_0$, where P_0 is the dark carrier concentration we can neglect this increment in carrier density and assume that the contact only responds to the local electric field.

As a further approximation we assume that the photoexcited carriers are swept from the sample with negligible trapping. This assumption should be reasonable when the carrier transit time is short compared with the transient time constant τ. It is true that capture at the shallow acceptor, having large capture cross section may be significant, but we assume that this can be allowed for with the trapping factor introduced in equation (7), and neglect any non-uniformity of space charge. Under the condition that δp is negligible (21), trapping on the shallow acceptors is predominantly from the uniform carrier concentration flowing from the injecting contact so that this does not generate non-uniform space charge.

To obtain insight into the small-time response we initially ignore capture at the optically active deep donor, then the space charge generated is $\bar{U}t - (P - P_0)$ where P_0 is the dark hole concentration. Capture at the shallow acceptor can be allowed for by increasing $(P - P_0)$ by the factor $(1 + Na/Pa)$. The total particle current j can be written in the form

$$j(x) = j_i(x) + \bar{U}x, \qquad j_i(x) = \mu p E(x) \tag{22}$$

where we assume that the contact can adjust rapidly to the local electric field on the timescale of the transient under conditions of constant applied voltage. The continuity equation takes the form

$$\frac{\partial P}{\partial t} + \frac{\partial}{\partial x} j(x) = \bar{U}, \tag{23}$$

and solving Poisson's equation for the electric field yields

$$E(x) = E_0 - [\bar{U}t - (P - P_0)](x - L/2)4\pi q/\epsilon, \tag{24}$$

where E_0 is the constant field arising from the applied voltage, L is the sample length, ϵ is the dielectric constant, q is the electron charge and we have assumed that P is independent of x and neglected the time dependence of $\bar{U}$. Substituting $E(x)$ in (23) yields

$$-\frac{\partial}{\partial t} P = \frac{\partial}{\partial x} j_i = -\mu P \frac{4\pi q}{\epsilon} [\bar{U}t - (P - P_0)]. \tag{25}$$

The solution for $P(t)$ can now be obtained in the form

$$P(t) = P_0 \exp\left[\frac{1}{P_0 \tau_D^0}\left(\frac{\bar{U}t^2}{2} + P_0 t\right)\right] \Bigg/ \left\{\frac{1}{\tau_D^0}\int_0^t \exp\left[\frac{1}{P_0 \tau_D^0}\left(\frac{\bar{U}t'^2}{2} + P_0 t'\right)\right] \mathrm{d}t' + 1\right\} \tag{26}$$

where we have introduced a dielectric relaxation time

$$1/\tau_D^0 = 4\pi q \mu P_0/\epsilon. \tag{27}$$

As $\bar{U} \to 0$, $P(t) \to P_0$ as required, and asymptotically as $t \to \infty$, $P(t) \to \bar{U}t$. This large-

time divergence arises, of course, because we have neglected hole capture at the deep donor. Equation (26) does, however, give a useful solution for small times. The initial response has the form

$$P(t) = \frac{P_0 \exp(\bar{U}t^2/2P_0\tau_D^0)}{1 - (\bar{U}/P_0)\{t + \tau_D^0[\exp(-t/\tau_D^0) - 1] - t^2/2\tau_D^0\}} \quad t^2 \ll 2P_0\tau_D^0/\bar{U}. \tag{28}$$

Consequently $(\partial/\partial t)P(t)|_{t=0} = 0$ and there is no appreciable response for $t < \tau_D^0$ under the condition $\bar{U}t \ll 2P_0$. This indicates that at small times the transient is delayed followed by a fast rise. To obtain the complete transient it is necessary to allow for capture at the deep donor. The optical generation rate becomes

$$(\mathrm{d}/\mathrm{d}t)f_d^- = Uf_d^+ - C_d(f_d^-P - f_d^+P_d). \tag{29}$$

The negative space charge Q takes the form

$$Q = (N_a f_a^- - N_d f_d^+ - P)q, \qquad f_a^- = P_a/(P + P_a) \tag{30}$$

and the total particle current becomes

$$j/q = \mu PE + N_d[(\mathrm{d}/\mathrm{d}t)f_d^-]x \tag{31}$$

$$E(x) = E_0 - (4\pi q/\epsilon)Q(x - L/2).$$

Using the continuity equation in the form

$$-\partial Q/\partial t + \partial j/\partial x = 0 \tag{32}$$

we obtain the rate equation for the free carrier density

$$\frac{\mathrm{d}P}{\mathrm{d}t} = \frac{P}{P_0\tau_D^0}\left[N_a\left(\frac{P_a}{P + P_a}\right) - P - N_d f_d^+\right] \bigg/ \left(1 + \frac{N_a P_a}{(P + P_a)^2}\right). \tag{33}$$

Equations (33) and (29) give two coupled non-linear differential equations for $P(t)$ and $f_d^-(t)$ which must be solved numerically. From the expression for the electric field (31) it follows that $(\partial/\partial t)E(x, t) = 0$ for $x = L/2$ and the displacement current vanishes at this point. Consequently the total current measured in the external circuit $J(t)$ can be written as

$$J(t)/q = \mu PE_0 + N_d(L/2)[(\mathrm{d}/\mathrm{d}t)f_d^-]. \tag{34}$$

and in the numerical calculations it is convenient to calculate an effective free carrier concentration ($\bar{p}$)

$$\bar{p} = J(t)/(q\mu E_0). \tag{35}$$

To derive equation (33) we have taken $\partial P/\partial x = 0$. The resulting solution is consistent with this condition but depends on the approximations and assumptions for its validity. It is possible to check the stability of this uniform solution against small perturbations in $P(t)$ and $f_d^-(t)$ of the form $\exp[\mathrm{i}(kx - \omega t)]$ when it is found that such perturbations decay as $\exp(-\gamma t)$ where

$$\gamma = U + CP + (4\pi q\mu/\epsilon)(P - Q) \tag{36}$$

Q = negative space charge.

This stability analysis is very similar to the analysis of Kazarinov *et al* (1973) and shows that damped propagating space-charge waves are possible. In the present analysis, however, we have the additional feature of optical generation of space charge and the expression for the decay constant indicates that if the total negative space-charge density generated in the crystal exceeds the free carrier concentration obtained from the uniform solution, then the latter may become unstable. This instability would probably appear as noisy oscillation. By considering the analytical solution (26) it is easy to prove that for weak optical excitation such that $\bar{U}\tau_{\mathrm{D}}^{0} < P_0$, the decay constant is always positive. As the analytical model neglects hole capture, it overestimates the space charge generated so that this condition gives a lower bound to the critical optical generation rate for stability.

Apart from stability considerations, the main assumptions leading to (33) can be listed as follows:

(i) uniform initial carrier concentration;

(ii) photogenerated carriers are swept from the sample without trapping so that the generated space charge is uniform in space;

(iii) crystal homogeneity;

(iv) the diffusion current at the virtual cathode contact responds instantaneously to the space-charge-induced electric field in an Ohm's law manner.

It is difficult to give a rigorous justification for the contact boundary condition without a very complicated numerical analysis. Williams (1969), used a simple version of the theory developed in this paper and gave strong experimental evidence for the carrier sweep-out origin of dielectric relaxation effects in transient photoconductivity, so that when dielectric relaxation effects are present, we would expect the oscillations to be observable, though details may depend on the contact boundary conditions. The optically generated space charge acts to forward-bias the injecting contact, and calculations by Many and Rakavy (1962) show that the response of an ohmic contact to a voltage pulse under space-charge-limited current conditions can give a current surge due to injected space charge. One may speculate that with low impurity capture cross sections, the contacts could have a super-linear transient response, neutralising the optically generated space charge and damping the oscillations. If we assume fast capture at the shallow acceptor, however, then the fraction of the free carrier increase which is trapped can be obtained from (2) as $N_{\mathrm{a}}P_{\mathrm{a}}/(P_{\mathrm{a}} + P)^2$. If $N_{\mathrm{a}}/P_{\mathrm{a}} \gg 1$, then most of the transient space charge from the contact will be trapped and the free carrier dynamics should behave as though the contact were in the steady state. If this condition does not hold or if the other assumptions break down and the system becomes spatially non-uniform, then it becomes necessary to solve non-linear partial differential equations in both space and time variables, including diffusion. This situation would increase the computational problem enormously and is not explored in the present paper.

4. Transient oscillations

A well known technique for studying non-linear differential equations of the type shown in (29), (33), consists in eliminating the time variable and considering the resulting integral curves (see for example Stoker 1950). The nature of the singular points then determines the character of the solution. In this section we show that under certain conditions the equations for transient response exhibit a focus in the phase plane giving the possibility

of damped oscillation. Using a theorem due to Poincaré, the nature of the singular point can be determined by linearising the equations about the steady state.

If we denote the steady-state expressions with a superscript e, and also consider the situation of excess deep donor where the quasi-Fermi level is much higher than the shallow acceptor level ($P_a \gg P$), the equation (33) can be approximated to

$$\frac{dP_1}{dt} = \frac{1}{\tau_D^e}\left[N_d f_{d_1}^- - \left(1 + \frac{N_a}{P_a}\right)P_1\right]\Big/\left(1 + \frac{N^a}{P_a}\right) \tag{37}$$

$$P = P^e + P_1, \qquad f_d^- = f_d^{e-} + f_{d_1}^-$$

where P_1 and f_{d1}^- denote deviations from the steady-state values, τ_D^e is the dielectric relaxation time corresponding to the steady-state free carrier population and we have linearised in P_1. Similarly equation (29) yields

$$(d/dt)f_{d_1}^- = -[U + C_d(P^e + P_d)]f_{d_1}^- - C_d f_d^{e-} P_1. \tag{38}$$

We can write these linear forms in the standard notation (Stoker 1950) as follows:

$$\frac{d}{dt}P_1 = af_{d_1}^- + bP_1 \qquad \frac{d}{dt}f_{d_1}^- = cf_{d_1}^- + dP_1 \tag{39}$$

where

$$a = -bN_D/[(1 + N_a/P_a)] \qquad b = -1/\tau_D^e$$

$$c = -[U + C_d(P^e + P_d)], \qquad d = -C_d f_d^{e-} \tag{40}$$

(39) shows that the deep donor population and the carrier concentration are coupled, and by considering solutions of the form $\exp(\lambda t)$ we are led to the usual secular determinant with characteristic equation

$$\lambda^2 - \lambda(b + c) - (ad - bc) = 0 \tag{41}$$

having solutions

$$2\lambda = (b + c) \pm [(b - c)^2 + 4ad]^{1/2} \tag{42}$$

a, b, c and d are real quantities so the condition for stable damped oscillation becomes

$$(b - c)^2 + 4ad < 0, \qquad (b + c) < 0. \tag{43}$$

From (40) the stability condition is clearly satisfied and $ad < 0$ so that oscillatory solutions must be considered. The condition (43) takes the form

$$4[\tau_D^e\tau_c(1 + N_a/P_a)]^{-1} > [U + C_d(P^e + P_d) - 1/\tau_D^e]^2 \tag{44}$$

here we have introduced a capture time for the deep donor

$$1/\tau_c = C_d N_d f_d^{e-}. \tag{45}$$

To determine relative magnitudes it is necessary to insert numbers, and typical values in CGS units are $C_d \sim 10^{-8}$ (for a capture cross section $\sim 10^{-15}$ cm^2), $1/P^e\tau_D^e \sim 10^{-5}$ (assuming $\mu \sim 2000$). Consequently at zero light intensity, the right-hand side of (44) can typically be approximated to $(1/\tau_D^e)^2$ and the condition for oscillation reduces to

$$4/[\tau_c(1 + N_a/P_a)] > 1/\tau_D^e. \tag{46}$$

For a sufficiently shallow acceptor $N_a/P_a \leqslant 10$ and this condition is easily satisfied in

semi-insulating material at low optical excitation where τ_D^e can be large. If we neglect N_a/P_a and assume $\tau_c \ll \tau_D^e$ then the oscillation frequency ω and damping K becomes

$$\omega \sim (\tau_c \tau_D^e)^{-1/2} \tag{47}$$

$$K \sim \tfrac{1}{2}(1/\tau_D^e + U + C_d P^e).$$

Consequently the oscillations have a damping time typically less than or of the order of the dielectric relaxation time.

It should be noted that these oscillatory solutions are not expected to be observed in the presence of strong fast trapping. The model has only considered a deep donor

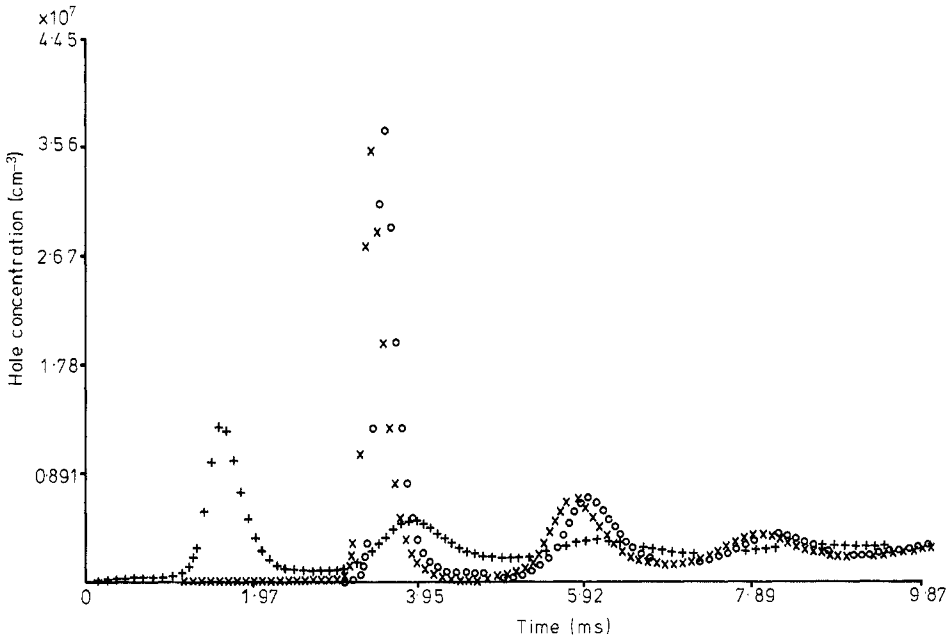

Figure 1. Computer calculation of transient current oscillations. This calculation was for silicon doped with 5×10^{15} cm^{-3} boron and $5{\cdot}4 \times 10^{15}$ cm^{-3} deep donor with energy at 340 meV above the valence band and a capture cross section of 10^{-17} cm^2. The temperature is 80 K and a background photon flux was assumed to set the 'dark' hole concentration at $2{\cdot}7 \times 10^3$ cm^{-3}. Symbols $+$, $\times$, $\circ$ are used to denote the transient obtained after 0, 1, 2 turns of the optical chopper respectively. The chopped light was taken to be a square wave of length 10^{-2} s.

and shallow acceptor for which $N_a/P_a \lesssim 10$. If this latter condition breaks down, or additional fast trapping levels are present, the condition for oscillation may not be satisfied. Under the condition $P_t \ll P^e$ a simple estimate shows that the factor $(1 + N_a/P_a)$ in (46) is replaced by

$$(1 + N_t P_t / P^{e2}) \qquad P_t \ll P^e. \tag{48}$$

If the trapping level is close to the quasi-Fermi level and say $P_t \sim \frac{1}{10} P^e$ for the derivation of (48) to hold, then $N_t P_t / P^{e2}$ can be a large number making oscillatory solutions less favourable.

The formulae for frequency and damping are only valid for small-amplitude oscillations, and to treat the large-amplitude case it is necessary to solve the full non-linear equations numerically. In figure 1 we show a computer solution for the transient under ideal conditions. In a practical experiment crystal inhomogeneities will lead to a spread of frequency ($\omega \propto (N_d f_d^{e-})^{1/2}$) and if two optically active levels are involved the characteristic equation (41) will be replaced by a cubic so that more than one sharp frequency may be superimposed. In an experiment at low temperature, the position of the quasi-Fermi level can be very sensitive to light and temperature, and by using different constant background fluxes and varying the temperature the quasi-Fermi level could have a range of positions relative to the valence band with $\tau_D \gtrsim \tau$. In this way it may be possible to position the quasi-Fermi level well away from any trapping regions and use a second beam to excite oscillations. Under conditions where the transit time is much shorter than the transient time constant τ, the theory of the transient is fairly simple for small signal conditions, and using two beams as described to measure the transient for different positions of the quasi-Fermi level with or without space-charge effects, may provide a useful new technique for the study of imperfections in photoconductors.

5. Additional levels and numerical solutions

With arbitrary additional levels it is necessary to write a rate equation (1) for each level, and use charge neutrality to determine P if space-charge effects are negligible. Under large signal conditions ($\Delta P \gg P_0$) all the levels are coupled and a numerical solution is necessary. Under small signal conditions ($\Delta P \ll P_0$) it is possible to linearise the charge-neutrality condition in ΔP when the steady-state response can be written quite generally as

$$\Delta P = \sum_i \left(\frac{N_i P_0 E_i}{(P_0 + P_i + E_i)(P_0 + P_i)} \right) \Bigg/ \left[1 + \sum_i \left(\frac{N_i (P_i + E_i)}{(P_0 + P_i + E_i)^2} \right) \right] \tag{49}$$

where the index i refers to impurity species, P_0 is the dark hole concentration, $E_i = U_i/C_i$, N_i is the concentration of impurity i and P_i is the free hole concentration when the Fermi level is at the energy level of impurity i. Similarly, the rate equation (1) can be linearised in ΔP and Δf^-

$$(\mathrm{d}/\mathrm{d}t)(\Delta f^-) = U(1 - f^-) - C[f^- \Delta P + P_0 \Delta f^- + P_t \Delta f^-]. \tag{50}$$

If $f^- \Delta P \ll P \Delta f^-$, then in the absence of space-charge effects the solution has the simple exponential form

$$\begin{aligned} \Delta f^- &= A - B \exp(-t/\tau) \\ 1/\tau &= C(E + P_0 + P_t). \end{aligned} \tag{51}$$

In this case the levels become decoupled and the transients are superpositions of simple exponentials.

In the general case there is no alternative to a numerical solution and in this section we discuss the simplest case of the model of §§2 and 3 with one extra level which is assumed to have a large capture cross section so that it can be considered in quasi-equilibrium with the valence band on the timescale of the transient. In this case its electron population has the form $f_t^- = P_t/(P + P_t)$ and gives a correction to the charge-neutrality condition (3). If $P_t \gg P$, i.e. the quasi-Fermi level is well above the trap energy, then the charge-neutrality condition simplifies to the form

$$P = \tilde{N}_a + \tilde{N}_t - \tilde{N}_d f_d^+, \qquad \tilde{N} = N \bigg/ \left(1 + \frac{N_a}{P_a} + \frac{N_t}{P_t}\right), \qquad P_t \gg P, \tag{52}$$

and the extra level can be included in the analytical solution of § 2 as a constant trapping factor.

In the other limit when $P \gg P_t$ and the trap energy is well above the quasi-Fermi level, $f_t^- \sim P_t/P$, the charge-neutrality condition becomes

$$\begin{aligned} P &= \bar{N}_a - \bar{N}_d f_d^+ + \bar{N}_t P_t/P \\ 2P &= (\bar{N}_a - \bar{N}_d f_d^+) + [(\bar{N}_a - \bar{N}_d f_d^+)^2 + 4\bar{N}_t P_t]^{1/2}. \end{aligned} \tag{53}$$

If $\bar{N}_t P_t \gg P^2$ this simplifies to the form

$$P \simeq \tfrac{1}{2}(\bar{N}_a - \bar{N}_d f_d^+) + (\bar{N}_t P_t)^{1/2} \tag{54}$$

and the solution of § 2 again applies with $\bar{N}_d \to \frac{1}{2}\bar{N}_d$ and $\bar{N}_a \to \frac{1}{2}\bar{N}_a + (\bar{N}_t P_t)^{1/2}$. If $\bar{N}_t P_t \ll P$, then the level can simply be neglected.

The difficult region for solution is $\bar{N}_t P_t \sim P^2$, $P_t \lesssim P$, when the solution must be intermediate between the two simplified forms considered above and a detailed numerical solution is required. Physically one can think of the extra trap as introducing p-dependent trapping factors. From the solution for the transient time constant (12) it is clear that strong trapping reduces the value of $\bar{N}_T^>$ and therefore increases τ, slowing down the transient. This implies that in a temperature range where the position of the quasi-Fermi level is sensitive to temperature, this type of trapping can introduce a strong temperature dependence for the transient time constant.

A particularly interesting case arises when the quasi-Fermi level sweeps through the trap energy during the course of the transient. In this case computer solutions can show strong differences between the transient shape obtained from a single shot experiment and from a repeated experiment where complete equilibrium is not achieved between cycles, such as might occur if an optical chopper were used. If the slowing down effect due to trapping is greater than or comparable with the chop time, then the observed transient is obtained from initial trap populations which are disturbed from the dark values. Some of these effects are illustrated in figure 2. The single shot transient shows an initial delay related to space-charge effects and trapping which after one turn of the chopper switches to a different shape. At 80 K the initial and final values of the quasi-Fermi level for the single shot transient were 209 meV and 155 meV so that the trap at 180 meV is swept through. At 90 K the single shot Fermi level positions were 237 meV and 176 meV. In this case the trap at 180 meV is close to the final position of the Fermi level and has the effect of slowing the transient. At higher temperatures the final position of the Fermi level moves further into the gap and the transient becomes faster again as the trapping effect is reduced. The single shot transient at 90 K has a knee. The fast rise below the knee is related to space-charge effects and the sharp slowing of the transient is related to the quasi-Fermi level approaching a fast trapping level. If the trap concentration is increased, the slowing effect near the knee becomes more pronounced. Further calculations with and without space-charge effects showed that fast trapping as the quasi-Fermi level approaches a trap slows the transient and depending on the trap concentration and whether the quasi-Fermi level sweeps through the trap level, can produce a variety of odd shapes for the transients. It should be noted that S-shaped transients have previously been recognised as due to trapping (Ryvkin 1964).

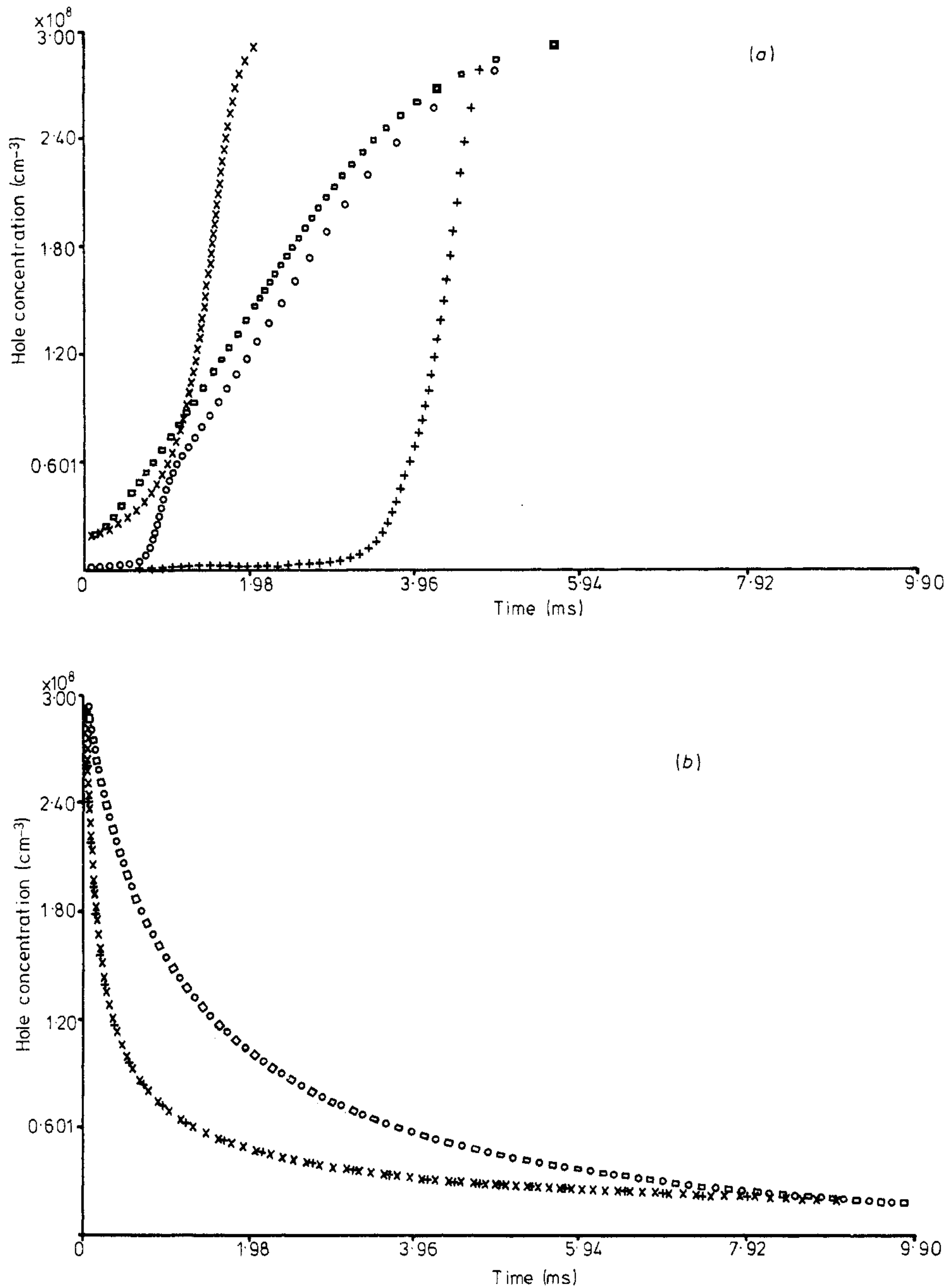

Figure 2. Computer calculation of transients with a fast trap: (*a*) rise transient; (*b*) fall transient. This calculation assumed $N_a = 5 \times 10^{15}$ cm^{-3}, $N_d = 6 \times 10^{15}$ cm^{-3}, $N_t = 10^{11}$ cm^{-3}. The capture cross section for the deep donor is 10^{-17} cm^2 and the additional trap was taken to be in equilibrium with the valence band. The deep donor and trap energies were 340 meV and 180 meV respectively. Symbols +, × refer to 0 and 1 turn of the chopper at temperature 80 K. ○, □ refer to 0 and 1 turn of the chopper at 90 K. A background flux was assumed to set the 'dark' hole concentration at $1{\cdot}2 \times 10^5$ cm^{-3}. The on and off times for the chopper light are both 10^{-2} s.

It would be futile to present computer solutions for all the cases that have been examined theoretically and the value of the technique as an analytical tool must be demonstrated by analysis of experimental data. The method is currently being used to study transients obtained by E Maher and R Humphreys (private communication) for silicon doped with boron and platinum. This system appears to be very complex and the analysis has not yet been completed, though certain features, for example the temperature effects in figure 2, have been observed. Due to the sensitivity of transients to trapping levels close to the quasi-Fermi level it seems that two-beam experiments where one beam is used to position the quasi-Fermi level and the second beam is used to excite the photoconductivity transient could be a powerful tool for studying impurity levels in semiconductors. When the quasi-Fermi level is well away from trapping levels, the model of § 2 applies with modified concentration due to trapping factors, and as the quasi-Fermi level is positioned close to a trapping level, characteristic slowing effects should be observed as the magnitude of the trapping factor changes.

6. Conclusion

A theory of transient photoconductivity has been developed for semi-insulating materials. The prediction of photocurrent oscillations is of particular scientific interest as an example of a non-linear vibration. The physical mechanism for these oscillations is readily understood in terms of carrier sweep-out. The optical flux initially creates trapped space charge in the crystal faster than it can be neutralised by the contacts. When the contacts have injected sufficient free carrier to neutralise this space charge, the ionised deep level concentration is higher than the steady-state value and the trapping rate exceeds the photogeneration rate so that the photocurrent decreases. This mechanism continues until space-charge neutrality is achieved with the steady-state free carrier density. In the example considered here the oscillations are damped due to the decay of photogenerated space charge. For future work it would be interesting to study this type of oscillation in situations where space charge is maintained, for example, in high electric fields with space-charge-limited currents. In fairly simple situations with only a few active trapping levels, the analysis of photoconductivity transients developed in this work could provide a useful tool for studying deep levels.

Counter-doped material contains distributions of positively and negatively charged impurities so that it might be thought that band tailing would have a large effect. This possibility has been examined using the model developed by Herbert *et al* (1975). It was found that with a random charge distribution a large band tail was produced, but when the ionisation state of the impurities was allowed to respond to the large-scale potential fluctuations this band tail was reduced to less than or of the order of kT, having negligible effect. This can be understood when it is noticed that except for very close compensation, the Fermi level will be close to the energy of the dominant impurity species. In the presence of a potential fluctuation, the impurity energy moves with the band edges but the Fermi level remains fixed. Consequently the charge state of the dominant impurity adjusts to screen out the fluctuation. This argument breaks down for very close compensation and in this case large band tails are obtained, but some mechanism of auto-compensation is required to produce such a doping configuration.

If impurity clustering is present (Voronkov *et al* 1979), this could yield a large band tail effect and consequent smearing of the theoretical transient. For samples where in the absence of clustering the transient is well understood, measurements of transient

response in conjunction with annealing experiments could provide an effective way of studying cluster formation.

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