PRECISE DETERMINATION OF THE MULTIPHONON AND PHOTON CARRIER GENERATION PROPERTIES USING THE IMPURITY PHOTOVOLTAIC EFFECT IN SEMICONDUCTORS*

C. T. Sah

Departments of Electrical Engineering and Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois

and

A. F. Tasch, Jr. Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois (Received 29 May 1967)

The electronic properties (energy levels and electron- and hole-capture or -emission cross sections) of the deep energy-level impurity or defect centers in semiconductors have been measured by the Hall effect and photoconductivity decay.¹ The energy-level determination from Hall effect versus temperature measurement has an accuracy of about $\pm kT$; however, the numerical results of cross-section measurements at one temperature (usually 77 and 300°K) may vary as much as one or two orders of magnitudes from different laboratories for a given impurity in silicon or germanium.² Thus, a detailed and precise experimental-theoretical correlation has not been possible, although a semiquantitative understanding of the magnitude of the cross sections has been obtained by Lax² based on a multiphonon cascade process. The large inconsistency comes in part from the determination of the impurity concentration of the defect, an appropriate decay time constant in the nonexponential time dependence of the photoconductivity for large signal, and the steady-state carrier concentration in the small signal case where the transient is exponential.³ In this Letter we explore a new method for the precise determination of these carrier generation properties using the previously unexplored impurity photovoltaic effect in semiconductor junction depletion regions, which suffers none of these inaccuracies.

In Figure 1, a schematic diagram and the energy levels are shown for a p-n junction, under reverse bias, which contains a uniformly distributed deep energy-level defect or impurity center. The nonlinearity of the kinetics of the trapped electron concentration n_T at the defect level comes from the two carrier-capture processes (a) and (c) whose rates are proportional to the carrier concentrations.^{3,4} Thus, the nonlinear terms are removed in the junction depletion region under reverse bias since the carriers are swept out and depleted by the presence of the large static electric field.

We first consider the physical result of a sample exposed to a chopped light flux with sufficiently long duration. The time constant of the turn-on transient of n_T (trapped electron concentration) would be the reciprocal of the sum of the electron and hole emission rates from the defect level due to both the multiphonon (Shockley-Read-Hall-Lax model) and the photon processes. However, the turn-off transient is governed by the multiphonon process only. Thus, the photocurrent transient in the junction gives information on electron and hole emission-capture cross sections from the defect level for both of these processes.

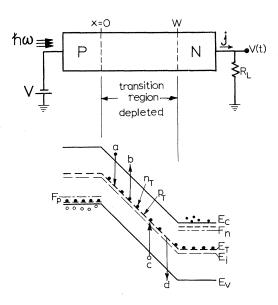


FIG. 1. The schematic diagram of the p-n junction and associated circuit, and the energy-band diagram showing the four Shockley-Read-Hall multiphonon-transition processes labeled by a, b, c, and d. Photoexcitations of electrons from E_T to E_C and from E_V to E_T are also present but not shown.

The kinetics is governed by

$$-\partial n_{T} / \partial t = (c_{n} + e_{n} + c_{p} p + e_{p}) n_{T} - (c_{n} + e_{p}) N_{TT} + g_{N} - g_{P}$$
(1)

$$\cong (e_{n} + e_{n}^{o} + e_{p} + e_{p}^{o})n_{T} - (e_{p} + e_{p}^{o})N_{TT},$$
(2)

where in (2) use is made of the depletion condition, n = p = 0, and the relationships $g_N = e_n^{\ o} n_T$ and $g_P = e_p^{\ o} p_T = e_p^{\ o} (N_{TT} - n_T)$ for the optical generation rate of electrons and holes, respectively, from the defect level. The notation used here follows the common usage.^{3,4} Thus,

$$\begin{split} c_{n}n_{1} = e_{n} = \sigma_{n}\theta_{n}n_{1} = \sigma_{n}\theta_{n}N_{C} \exp[(E_{T} - E_{C})/kT], \quad c_{p}\theta_{1} = e_{p} = \sigma_{p}\theta_{p}h_{1} = \sigma_{p}\theta_{p}N_{V} \exp[(E_{V} - E_{T})/kT], \\ N_{C} = 2(kTm_{N}/2\pi\hbar^{2})^{3/2}, \quad N_{V} = 2(kTm_{P}/2\pi\hbar^{2})^{2/3}, \quad e_{n}^{o} = \sigma_{n}^{o}cI = \sigma_{n}^{o}\Phi, \end{split}$$

and

$$e_p^{\ o} = \sigma_p^{\ o} cI = \sigma_p^{\ o} \Phi.$$

Here, N_{TT} is the total concentration of the defect or impurity center in number per cm³; θ_n and θ_p are the thermal velocities of electrons and holes, respectively; m_N and m_P are the density-of-state effective masses; c is the velocity of light; I is the photon concentration; Φ is the photon flux (photon per cm² per sec); $\sigma_n, \sigma_n^0, \sigma_p$, and σ_p^0 are, respectively, the multiphonon and optical cross sections for electrons and holes. The photo cross sections are light-frequency dependent⁵ while the photon flux is spatially dependent due to this and other optical-absorption processes. The solution of (2) for a chopped light source of zero rise and fall time and sufficiently long duration may be readily obtained. Assuming that the chopped light is turned on at t=0 and turned off at t=T which is large, then

$$n_{T}(x,t)/N_{TT} = [e_{p}/(e_{n}+e_{p})] \exp(-t/\tau_{on}) + [(e_{p}+e_{p}^{o})/(e_{n}+e_{n}^{o}+e_{p}+e_{p}^{o})][1-\exp(-t/\tau_{on})],$$

$$\tau_{on} = 1/(e_{n}+e_{n}^{o}+e_{p}+e_{p}^{o})$$
(3)

for the turn-on transient, and

$$n_{T}(x,t)/N_{TT} = [(e_{p} + e_{p}^{o})/(e_{n} + e_{n}^{o} + e_{p} + e_{p}^{o})] \exp(-t/\tau_{\text{off}}) + [e_{p}/(e_{p} + e_{n})][1 - \exp(-t/\tau_{\text{off}})],$$

$$\tau_{\text{off}} = 1/(e_{n} + e_{p})$$
(4)

for the turn-off transient where t is measured from T.

A sketch of three possible cases is shown in Fig. 2, for the conditions of e_n^{o}/e_n greater than, equal to, or less than e_p^{o}/e_p . It is evident that negative-impurity photovoltaic effect may be observed if $e_n^{o}/e_n < e_p^{o}/e_p$. The dashed lines show the effect of higher light intensity or photon flux which speeds up the turn-on transient.

The photocurrent and the static current flowing in the external circuit shown in Fig. 1 can be readily obtained from the continuity equation with $\partial n/\partial t$ set to 0 in the depletion region. This gives

$$-j = -\int_{0}^{W} dj_{n} = q \int_{0}^{W} (e_{n}n_{T} + g_{N}) dx = q \int_{0}^{W} (e_{n} + e_{n}^{O}) n_{T}(x, t) dx$$
(5)

$$\cong q \left(e_n + e_n^{O} \right) n_T W.$$
(6)

In the approximation in (6), we have assumed that all the quantities are spatially constant; however, for large absorption and incomplete depletion near the edge of the depletion-transition region of the junction, $e_n^{\ o}$, $e_b^{\ o}$, and Φ are all position dependent and e_n and e_p must be replaced by $e_n + c_n n$

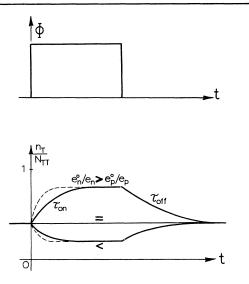


FIG. 2. The chopped-light photon flux (upper figure) and the transient response of the trapped electron concentration, $n_T(t)$, for the three conditions $e_n{}^{o}/e_n$ greater than, equal to, or less than $e_p{}^{o}/e_p$. The dashed curves are for a higher light intensity or photon flux.

and $e_p + c_p p$, respectively, which become spatially dependent.

The solution just obtained shows the following possible experiments on the determination of the parameters of the defect or impurity centers. (1) τ_{off} versus temperature provides σ_n , σ_p , $E_T - E_V$, and $E_C - E_T$ or E_G . (2) $\tau_{\text{on}}^{-1} - \tau_{\text{off}}^{-1}$ versus temperature and photon energy gives the temperature and photon-frequency dependences⁵ of the photo cross sections, $\sigma_n^O(T, \omega)$ and $\sigma_p^O(T, \omega)$. In addition, it provides the data of the photocurrent threshold which may be used to determine the optical-defect level, $E_T - E_V$ or $E_C - E_T$ or both, precisely. (3) By varying the dc reverse bias in a p-*i*-*n* structure where the depletion layer width Wis independent of voltage, the cross sections may be obtained as a function of the electric field strength. Since the photocurrent is independent of surface leakage, the surface would have little effect on the results.

There are a number of obvious applications of the impurity photovoltaic effect for lightintensity modulation (varying W by modulating the applied junction voltage) and for light detection. In the following Letter, some experimental results are presented to illustrate this effect.

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RECOMBINATION PROPERTIES OF THE GOLD ACCEPTOR LEVEL IN SILICON USING THE IMPURITY PHOTOVOLTAIC EFFECT*

C. T. Sah

Departments of Electrical Engineering and Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois

and

A. F. Tasch, Jr.

Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois

and

D. K. Schroder

Department of Electrical Engineering and Materials Research Laboratory, University of Illinois, Urbana, Illinois (Received 29 May 1967)

The method proposed in the preceding Letter¹ is demonstrated in several experiments described below using the gold acceptor level in silicon which is located at $E_C - E_T = 0.55$ eV or $E_T - E_V = 0.57$ eV in the band gap.² This is the only active level in the depletion region of the p-n junction due to the relative values of electron and hole emission rates,³ although it is well known that the gold impurity also has a donor level located below the midgap