Spectral distribution of photomagnetoelectric and photoconductivity currents in n-GaSe single crystals: Theory and experiment

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A model is presented by which the various transport parameters (ambipolar diffusion length, hole and electron lifetimes, and surface recombination velocities) are obtained directly by fitting the experimental photomagnetoelectric and photoconductivity spectral distributions. The model improves the one introduced by Gärtner, since it allows for different hole and electron lifetimes and for anisotropy of mobilities. An experimental application to n-GaSe is presented, and the results are discussed and compared with previous ones.

I. INTRODUCTION

The photomagnetoelectric (PME) effect has been largely used together with photoconductivity (PC) measurements in order to analyze some transport properties of several semiconductor materials.[1-4] In these measurements, the short-circuit current or the open-circuit voltage of the PME effect has been measured as a function of different parameters, such as magnetic field, intensity, and wavelength of the incident light. In this paper we tried a different approach which was suggested theoretically by Gärtner,[5] and which has never been used experimentally. In this approach, spectral responses of the PME and of the PC effect are analyzed as a function of wavelength, in order to evaluate the transport parameters by a best-fit procedure. This procedure has been applied to some n-GaSe samples.

The experimental spectra have been analyzed using theoretical relations[5] suitably modified in order to account for the different lifetimes of the minority and majority carriers, and for the mobility anisotropy of GaSe. The experimental data have been fitted with theoretical curves, by using the minority-carrier diffusion length, the hole-electron lifetime ratio, and the recombination velocity of the illuminated surface as parameters. From the obtained values of the parameters, the electron and hole lifetimes were determined.

II. EXPERIMENTAL

The GaSe samples used in the present work have been grown in our laboratory, from the vapor phase, by using iodine as transporting agent.[6] As grown samples, with surface area of about 0.5 cm^2 and thickness ranging between 17 and 50 μm, were used in the measurements. The samples were always n type, with electron concentration, at room temperature, of about 10^{11} cm^{-3}.[7]

Indium contacts were deposited by evaporation, under a vacuum of about 2×10^{-6} Torr. In order to improve the contact quality, a thermal treatment at 300 °C under N_2 atmosphere was carried out in an infrared oven for few minutes. The samples were placed in a magnetic field of 1.0 T, supplied by a Bruker BM-8 electromagnet. They were illuminated by a high-intensity Bausch-Lomb monochromator equipped with a tungsten lamp. The light beam was continuously monitored during the measurements, by using an achromatic beam splitter and a photodiode. The whole optical system was calibrated, as a function of wavelength, with a Spectra Physics power meter. The sample contacts were suitably masked in order to avoid photovoltaic effects. The PME and PC currents were measured with a Keithley model 417 picoammeter.

III. THEORY

The spectral distribution of the photomagnetoelectric effect and the photoconductivity, has been theoretically calculated by Gärtner[5] under the following assumptions: (i) conditions of nondegeneracy; (ii) absence of magnetoresistance; (iii) local charge neutrality; (iv) absence of boundary effects, i.e., the semiconductor slab was taken as infinite in both the x and z directions, x being the direction of the PME and PC currents, y the direction of the incident light, and z the direction of the magnetic field; (v) steady-state conditions; (vi) small-Hall-angle condition; (vii) small injection level; (viii) constant lifetime; and (ix) dependence of the bulk generation rate on the y coordinate only.

For many semiconductors, the local charge neutrality condition seemed too restrictive and some authors have generalized the PME theory, introducing an unrestricted charge neutrality condi-

tion.[8-10] For GaSe we have evidenced the presence of trapping effects in the photoelectronic properties[11]: then, the unrestricted charge neutrality condition must be used in the spectral distribution analysis. Furthermore, since GaSe is a typical layered semiconductor, it displays anisotropic transport properties and therefore, the equations of the PME effect must be modified in order to take into account this feature.[12,13] We have calculated the PME short-circuit current and the photoconductance spectral dependence, using the same assumptions of Ref. 5, but introducing the anisotropy of the carriers mobility along and perpendicular to the c axis, and the unrestricted charge neutrality condition. Furthermore, in order to take properly into account the presence of trapping phenomena, the following relationship has been used:

$$\Delta p = \Gamma \Delta n^{\alpha} \tag{1}$$

which was deduced from a charge-balance equation (see Ref. 14). In this equation Δn and Δp are the excess electron and hole concentrations. In cases of small injection, as the present one, one can take $\alpha = 1$. Since in steady-state conditions

$$\Delta p/\tau_p = \Delta n/\tau_n , \tag{2}$$

Γ clearly assumes the meaning of hole-electron lifetime ratio and τ_p and τ_n are the electron and hole lifetimes.

Taking into account the geometry used in this experiment (light incident along the c axis, PC or PME current direction and magnetic field direction mutually perpendicular), the continuity equation for electrons in steady-state conditions can be written as follows[5,12]:

$$\frac{d^2\Delta n}{dy^2} - \frac{\Delta n}{\tau_n D_{\parallel}} = -\frac{1}{D_{\parallel}} g(y) , \tag{3}$$

where $g(y)$ is the bulk generation rate and $D_{\parallel}$ is defined as follows:

$$D_{\parallel} = D_{n\parallel}(n_0\Gamma + p_0)/(n_0 b_{\parallel} + p_0) , \tag{4}$$

where n_0 and p_0 are the electron and hole concentrations at thermal equilibrium, $b_{\parallel}$ is the ratio of electron and hole mobilities along the c axis, and $D_{n\parallel}$ is the electron diffusion coefficient along the c axis. With a newly defined $L_{\parallel} = (D_{\parallel}\tau_n)^{1/2}$, Eq. (3) is formally equivalent to the standard differential equation in absence of trapping effects.[5] Clearly, $L_{\parallel}$ is the minority-carrier diffusion length when the majority-carrier concentration largely exceeds the minority one. By applying the usual boundary conditions,[5] in which the new definition of $D_{\parallel}$ has been used, assuming the bulk generation rate to be given by $g(y) = Ike^{-ky}$, where k is the optical-absorption coefficient and I is the incident flux density per second ($cm^{-2}\,sec^{-1}$), and the generation rates on the front and back surface to be zero, the following solution can be obtained for Eq. (3):

$$\Delta n = \frac{wI}{D_{\parallel}} \frac{K}{W^2 - K^2} \left(\frac{(K-S_2)(W+S_1)e^{-K} - (W-S_2)(K+S_1)e^{-W}}{(W+S_2)(W+S_1)e^{W} - (W-S_2)(W-S_1)e^{-W}} e^{Y} \right.$$
$$\left. + \frac{(K-S_2)(W-S_1)e^{-K} - (W+S_2)(K+S_1)e^{W}}{(W+S_2)(W+S_1)e^{W} - (W-S_2)(W-S_1)e^{-W}} e^{-Y} + e^{-(K/W)Y} \right) , \tag{5}$$

where the following dimensionless quantities have been used: $W = w/L_{\parallel}$, $Y = y/L_{\parallel}$, $K = kw$, $S_1 = s_1 w/D_{\parallel}$, and $S_2 = s_2 w/D_{\parallel}$, w being the sample thickness, s_1 and s_2 the surface recombination velocity at the illuminated and back surfaces, respectively. The solution for the case $K = 1/L_{\parallel}$, in which expression (5) assumes an indeterminate form 0/0, is given in Ref. 5. The short-circuit PME current per unit width (A/cm)

$$I_{sc} = -qD_{\parallel}(\mu_{n\perp} + \mu_{p\perp}) B[\Delta n(w) - \Delta n(0)] , \tag{6}$$

$\mu_{n\perp}$ and $\mu_{p\perp}$ being the electron and hole mobilities perpendicular to c-axis, can be written by using Eq. (5)

$$I_{sc} = qB(\mu_{n\perp} + \mu_{p\perp}) wI \frac{K}{W^2 - K^2} \left(\frac{(K-S_2)(W+S_1)(1-e^{W})e^{-K} + (K+S_1)(W-S_2)(1-e^{-W})}{(W+S_2)(W+S_1)e^{W} - (W-S_2)(W-S_1)e^{-W}} \right.$$
$$\left. + \frac{(K-S_2)(W-S_1)(1-e^{-W})e^{-K} + (K+S_1)(W+S_2)(1-e^{W})}{(W+S_2)(W+S_1)e^{W} - (W-S_2)(W-S_1)e^{-W}} + 1 - e^{-K} \right) . \tag{7}$$

The photoconductance, per unit width to length ratio (mho), ΔG, can be evaluated as follows:

$$\Delta G = q \int_0^w (\Delta n\, \mu_{n\perp} + \Delta p\, \mu_{p\perp})\, dy = q(\mu_{n\perp} + \Gamma \mu_{p\perp}) \int_0^w \Delta n\, dy \tag{8}$$

and therefore, by using Eq. (5),

$$\Delta G = \frac{q(\mu_{n\perp} + \Gamma \mu_{p\perp}) w^2 I}{D_{\parallel}} \frac{K}{(W^2 - K^2)W} \left(\frac{(K - S_2)(W + S_1)(e^{W} - 1)e^{-K} + (W - S_2)(K + S_1)(e^{-W} - 1)}{(W + S_2)(W + S_1)e^{W} - (W - S_2)(W - S_1)e^{-W}} \right.$$

$$\left. - \frac{(K - S_2)(W - S_1)(e^{-W} - 1)e^{-K} + (K + S_1)(W + S_2)(e^{W} - 1)}{(W + S_2)(W + S_1)e^{W} - (W - S_2)(W - S_1)e^{-W}} + \frac{W}{K}(1 - e^{-K}) \right). \tag{9}$$

It can be noted that, while the expression for I_{SC} is formally equivalent to the standard one in the case of charge neutrality, ΔG depends explicitly on Γ.

Moreover, in the case $K \gg 1$, $W \gg 1$, $s_1 = s_2 = 0$, the expressions for I_{SC} and ΔG (or I_{PC}) are equal to those reported in Ref. 8. However, the use of two different lifetimes τ_{PME} and τ_{PC}, as in Ref. 8, is not suitable for the analysis of the spectral distributions of PC and PME effects.

IV. RESULTS AND DISCUSSION

Figure 1 shows the experimental spectra of short-circuit PME current and photoconductance for sample 1. These spectra are similar to those obtained from the other samples. The experimental data were fitted with Eqs. 7 and 9, respectively, by using a high-convergence minimization procedure based on the χ^2 method.[15] The parameters used in the fit are W and S_1 for I_{SC} and only $D_1 = (\mu_{n\perp} + \Gamma \mu_{p\perp})/D_{\parallel}$ for ΔG, since in this last case W and S_1 were extracted from the previous fit. It was also assumed S_2 equal to zero, since it was realized[5] that our I_{SC} curves were practically independent of S_2 and that also ΔG curves were compatible with this assumption. Moreover, the values quoted in the literature have been used for the absorption coefficient,[16] the reflectivity,[17] and for mobilities perpendicular to the c axis.[18]

The analysis has been carried out in the 5200–6200-Å wavelength range: in fact below 5200 Å, the small injection condition is no longer fulfilled, because the light is strongly absorbed in a thin region near the surface. Above 6200 Å, the absorption coefficient starts to be dependent on the impurity content of our samples.

In Table I, the values of the parameters directly obtained from the fits both on I_{SC} and ΔG, are reported together with errors and confidence levels. From these data, the physical parameters $L_{\parallel}$, Γ, τ_p, τ_n, and s_1 have been calculated as follows. The

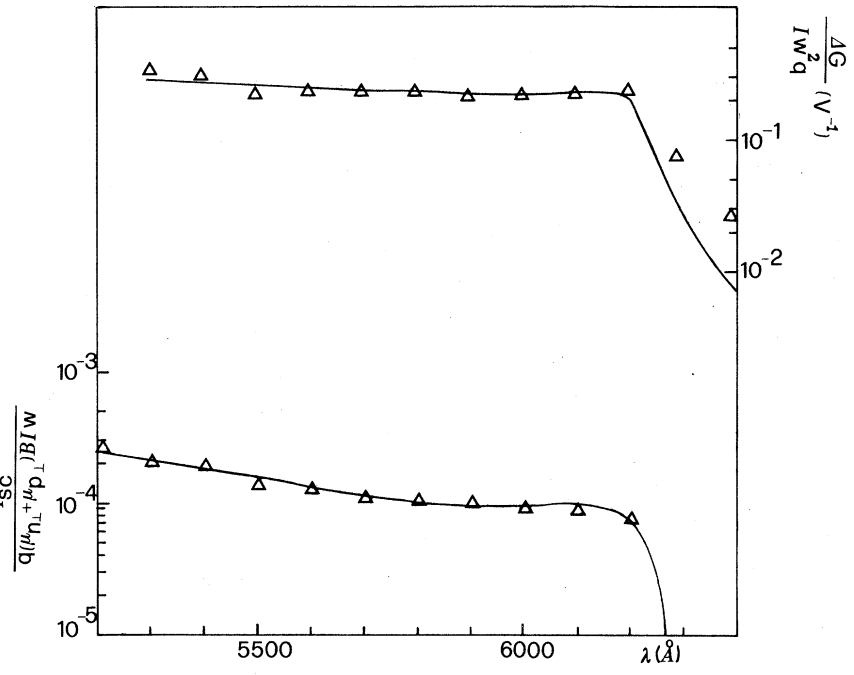

FIG. 1. Experimental behavior of the dimensionless quantity $I_{SC}/q(\mu_{n\perp}+\mu_{p\perp})BIw$ and of the quantity $\Delta G/qw^2I$ as function of the wavelength λ. Full lines represent the best fit of the experimental points, obtained by using Eqs. (7) and (9), respectively.

TABLE I. Values of the parameters obtained from the best fit of the experimental spectra of I_{SC} and ΔG. The confidence levels (CL) of the fits are also listed.

Sample	Photomagnetoelectric			Photoconductivity	
	W	S_1	Confidence levels	D_1 (V^{-1})	Confidence levels
1	75.1 ± 0.8	14.8 ± 1.8	90%	1899 ± 144	99%
2	91.3 ± 3.5	301 ± 31	60%	1210 ± 44	99%
3	87.0 ± 0.9	2.73 ± 0.4	65%	343 ± 8	30%
4	26.1 ± 1.1	12.7 ± 1.2	85%	273 ± 7	30%

value of $L_{\parallel}$ has been evaluated directly from W. The value of Γ has been obtained from the parameter D_1, since in our samples $n_0 \simeq 10^{11}$ cm$^{-3} \gg p_0$ and therefore from Eq. (4) $D_{\parallel} \simeq D_{p\parallel}\Gamma$, where $D_{p\parallel}$ is the hole diffusion coefficient along the c axis. In this case, the Einstein relationship has been used and $\mu_{p\parallel} = 215$ cm^{2}V^{-1}sec^{-1}.[16] Because $L_{\parallel} \simeq (D_{p\parallel}\tau_p)^{1/2}$, τ_n and τ_p may be directly evaluated. Finally, use has been made of the relationship $s_1 = S_1 D_{\parallel}/w$ in order to calculate the surface recombination velocity.

Table II shows the values of $L_{\parallel}$, Γ, τ_p, τ_n, and s_1 calculated for various samples. A first observation is that $L_{\parallel}$ varies from sample to sample and in all cases it is very short in comparison with the sample thickness. This result is clearly consistent with the previous hypothesis that back-surface recombination velocity does not play a significant role in the spectral distribution of the PME effect. Secondly, also the value of Γ varies considerably from sample to sample, and in any case $\Gamma \ll 1$ (while for local charge neutrality $\Gamma = 1$). This result supports the conclusion that it is necessary to introduce different hole and electron lifetimes in order to analyze the PME effect in GaSe.

The values of the electron and hole lifetimes, even measured in relatively different physical conditions, can be successfully compared with the values of trapping times measured on the same samples with nuclear techniques.[19] In fact, in these measurements, the hole trapping times were much lower than electron trapping times which were of the same order of magnitude as those reported in Table II. It is not completely clear why our results are compatible only with time-of-flight values for the mobilities, but it is possible that light could destroy the potential barriers which, in the dark, are responsible for low and field-dependent values of the mobilities.

Finally, also the surface recombination velocity varies from sample to sample, being its average value relatively low, comparable with previous measurements,[12] and probably caused by the layer structure of GaSe itself, which gives a large resistance to adsorption contamination.

As a last remark, an interesting correlation may be found between the PME results and growth or doping conditions of the investigated samples. Essentially, the former two samples were grown with an I_2 concentration of 4 mg/cm^3 in the ampoule, while the other two samples were grown with an I_2 concentration of 3 mg/cm^3. The sharp difference between the Γ values is clearly correlated with I_2 concentration, probably because the iodine introduces a greater concentration of minority-carrier trapping or recombination centers.

Clearly, a detailed expression for Γ could be obtained if the parameters for the recombination and trapping centers were exactly known.[10] More systematic analyses of these points are in progress.

V. CONCLUSIONS

A theoretical and experimental analysis of PME and PC measurements in n-GaSe is presented for

TABLE II. Values of $L_{\parallel}$, Γ, τ_p, τ_n, and s_1 calculated for the investigated samples.

Sample	$L_{\parallel}$ (cm)	Γ	τ_p (sec)	τ_n (sec)	s_1 (cm/sec)
1	$(0.226 \pm 0.002) \times 10^{-4}$	0.024 ± 0.002	$(9.2 \pm 1.5) \times 10^{-11}$	$(3.9 \pm 0.4) \times 10^{-9}$	$(1.15 \pm 0.24) \times 10^{3}$
2	$(0.471 \pm 0.018) \times 10^{-4}$	0.037 ± 0.001	$(4.0 \pm 0.6) \times 10^{-10}$	$(1.07 \pm 0.12) \times 10^{-8}$	$(1.46 \pm 0.26) \times 10^{4}$
3	$(0.679 \pm 0.007) \times 10^{-4}$	0.135 ± 0.003	$(8.3 \pm 0.5) \times 10^{-10}$	$(6.2 \pm 0.3) \times 10^{-9}$	$(3.5 \pm 0.5) \times 10^{2}$
4	$(1.76 \pm 0.07) \times 10^{-4}$	0.171 ± 0.005	$(5.6 \pm 0.7) \times 10^{-9}$	$(3.3 \pm 0.3) \times 10^{-8}$	$(2.62 \pm 0.43) \times 10^{3}$

the first time, in which the various parameters (ambipolar diffusion length, hole and electron lifetimes, surface recombination velocities) are determined directly by fitting the experimental spectral distribution. The method displays some interesting features, since (i) it takes into account trapping effects, allowing for different lifetimes for electrons and holes; (ii) the small-injection condition can be maintained in the whole measurement, thus avoiding the need for measuring PME and PC effects as a function of light intensity; (iii) the method is inherently much more reliable than previous ones[12,20] in which the extrapolation of I_{SC}^{-1} and/or ΔG^{-1} as a function of K^{-1} was too much dependent on the exact behavior of the absorption coefficient, particularly at short wavelengths.

The results obtained for n-GaSe, even if in fair agreement with previous ones, indicate clearly that the ambipolar diffusion length and the carrier lifetimes vary from sample to sample, being correlated with the conditions under which the samples were grown. A certain agreement has been found with the results obtained by nuclear techniques.[19] A more systematic work, both theoretical and experimental, is in progress, in order to develop a general theory by overcoming the small-injection condition and introducing a variable carrier lifetime.

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