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The analysis of low-temperature photoconductivity evolution in semi-insulating GaAs

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Abstract. A peculiar slow relaxation of low-temperature photoconductivity in semi-insulating GaAs is analysed. Time evolutions of free electron concentration, n, and free hole concentration, p, are determined from independently measured photoconductivity and current due to the thermoelectric effect. It is shown that during low-temperature illumination the p/n ratio at first rises significantly and then decreases back towards the initial, low value. The same behaviour is obtained from a study of time evolution of photo-Hall mobility, measured independently. Results are analysed and explained in terms of different trapping rates of photogenerated free electrons and holes by deep traps.

1. Introduction

The study of opto-electronic behaviour of semi-insulating (SI) GaAs revealed that illumination at low temperatures generally produces peculiar slow relaxation of photoconductivity (PC), where either a decrease (quenching) [1] or an increase [2], or even combined increase–decrease–increase sequence is observed [3–7]. It was shown recently [6, 7] that this dynamics is connected with deep traps in SI GaAs, other than well known deep level $EL2$ which is assumed to predominantly govern the electric properties. It was also suggested [8] that some of these deep traps are complex defects which might include, as their constituent, the $EL2$ defect, i.e. that $EL2$ could serve as a gettering centre for other native defects and/or impurities. Further investigation of those dynamics might elucidate this mutual relation and even shed more light on $EL2$ itself.

In this paper, we present an analysis of the time evolution of PC and the Hall mobility, μ_H. The Hall constant was measured during low-temperature illumination [9]. These results were combined with the independently measured time evolutions of PC and the current due to the thermoelectric effect (Seebeck effect), I_{TEE}, [10] in order to understand and explain the observed time evolutions of PC and μ_H.

2. Experimental

Good quality liquid encapsulated Chochralski (LEC) SI GaAs samples, and an illumination set-up as previously described [11] were used. The Hall-effect measurements were performed in a standard Wan der Paw configuration [9]. A newly developed method [12] was applied, which enables reasonably accurate determination of the Hall constant even when the measured values of Hall voltage and current through the sample are slowly drifting. However, in order to keep these changes small and smooth, low light intensities were used. The magnetic field was 0.4 T, and the temperature was kept constant at 86 K. PC and TEE measurements were conducted using one pair of the four Hall contacts, in a slightly modified cryostat, as described in [10]. All samples were slightly n-type, with room-temperature free-electron concentration of around 3×10^8 cm^{-3}, and mobility about 5000 cm^2 V^{-1} s^{-1}. The non-ionized $EL2$ concentration was 2×10^{16} cm^{-3} as determined by IR absorption measurement, and at least six other deep levels were observed, acting either as electron or hole deep traps [10]. Their filling rates, i.e. their free-carrier capture cross sections were observed to differ considerably [11].

3. Results

Figure 1(a) depicts a time evolution of photoconductivity current, I_{PC}, during the illumination with above-the-gap photons ($h\nu = 1.55$ eV) at 86 K. Three different curves correspond to various light intensities. It can bee seen that turning on the light causes an abrupt increase in photocurrent, I_{PC}, while further illumination induces gradual additional increase of I_{PC} in two different, successive stages. The Hall mobility, μ_H, shows an interesting time evolution (figure 1(b)); it starts from a relatively high value, then decreases for an order of magnitude, and then again gradually returns to its high value. For all light intensities the onset of the increase of μ_H corresponds to the second stage in I_{PC} evolution. By varying the light intensity the position of a minimum can be adjusted. Whichever process is responsible for this effect, it is linear with the light intensity—doubling the intensity reduces to half the illumination time necessary to achieve minimum in μ_H.

In a previous work [11] we made the assumption that time evolution of I_{PC} is connected with trapping of photogenerated free carriers by electron and hole traps. However, assessing the influence of deep traps on the properties of SI materials is a considerable problem, as capacitance transients methods, like deep level transient spectroscopy (DLTS) are not applicable to SI materials, whereas current transient methods are incapable of determining the type of observed traps. Recently, a new method was proposed, thermoelectric-effect spectroscopy (TEES) [10], which overcomes this problem. Time evolution of the I_{TEE}, is shown in figure 2, along with the I_{PC}. Until the onset of the second step in in I_{PC}, I_{TEE} is positive. Then it starts to diminish ending as a large negative signal. This behaviour is explained as the change in sign of the majority carriers. This conclusion is very important as it reveals which type of carriers predominate at a particular moment, which otherwise can not be distinguished in thermally stimulated currents, I_{TSC}, nor in I_{PC}. Details of TEES measurements and results have been given in [10].

A connection between I_{PC} and deep traps was established in [11]. It has been found that there is a correlation between time evolutions of I_{PC} and the concentration of charge trapped in deep traps. The sign of these deep traps has been determined from TEES measurements; peaks T_1–T_4 resulting from electron traps, T_5 and T_6 being composite peaks of which T_5 is dominated by primarily electrons' and T_6 by primarily holes' traps [10]. The dynamics of deep traps filling, as detected with measurements

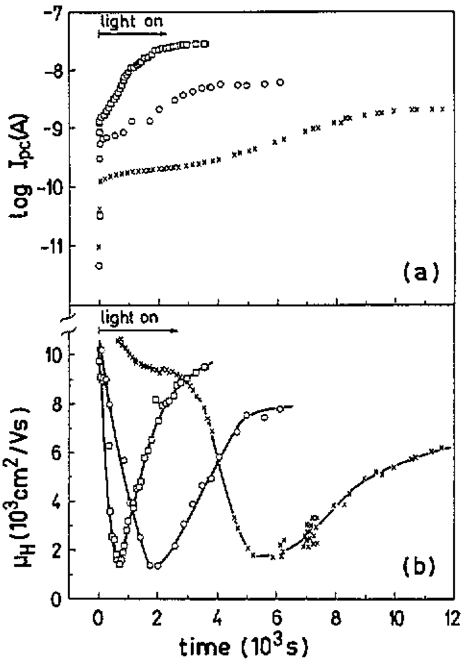

Figure 1. (a) Time evolution of photocurrent, I_{PC}, at 86 K, during illumination with 1.55 eV photons and various flux densities: □, 3×10^{13} cm^{-2} s^{-1}; ○, 6×10^{12} cm^{-2} s^{-1}; ×, 2×10^{12} cm^{-2} s^{-1}. (b) Time evolution of Hall mobility, μ_H, under the same conditions and the same photon flux densities as in part (a).

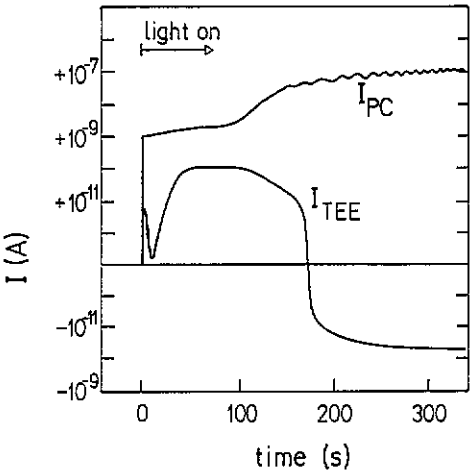

Figure 2. Time evolutions of TEE currents I_{TEE} and photocurrent I_{PC}, during illumination with 1.55 eV photons at 86 K. The photon flux density was 8×10^{13} cm^{-2} s^{-1} [10].

of I_{TSC}, is presented in figure 3. It is obvious that trap filling rates, i.e. their free-carrier capture cross sections, differ significantly; traps T_5 and T_6 being much 'faster' than shallower traps T_1–T_4.

4. Calculations

Standard formulae for a mixed conductivity, σ, and a Hall mobility, μ_{H}, are given [13, 14] by

$$\sigma = e\left(n\mu_{\mathrm{n}} + p\mu_{\mathrm{p}}\right) \tag{1}$$

$$\mu_{\mathrm{H}} = \left|\frac{r_{\mathrm{p}}p\mu_{\mathrm{p}}^2 - r_{\mathrm{n}}n\mu_{\mathrm{n}}^2}{p\mu_{\mathrm{p}} + n\mu_{\mathrm{n}}}\right| \tag{2}$$

where n and p are free electron and hole concentrations, e is elementary charge, and μ_{n} and μ_{p} are electron and hole mobilities, respectively. r_{n} and r_{p} are the Hall factors, which are close to unity. For SI materials value of μ_{n} at 86 K is typically in the 10^4–10^5 cm^2 V^{-1} s^{-1} range, while μ_p is usually 10–20 times lower [13, 15]. For $n = p$, and especially for $n \geqslant p$, electron conductivity prevails and μ_{H} reduces to μ_{n}.

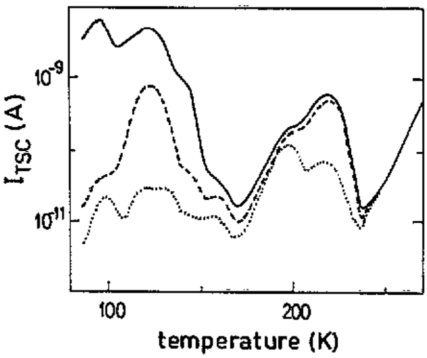

Figure 3. TSC curves after various durations of illumination, t, with 1.55 eV photons of 8×10^{13} cm^{-2} s^{-1} flux density: $t = 10$ s (dotted curve), $t = 80$ s (broken curve), $t = 500$ s (full curve) [10].

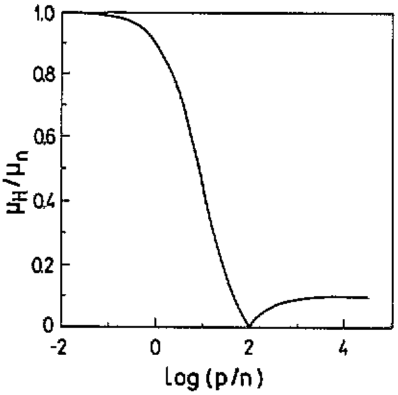

Figure 4. Normalized Hall mobility μ_H/μ_n at low temperature versus free holes, p, over free electrons, n, concentration ratio p/n.

The same equations are valid in describing transport phenomena under illumination, but in that case n and p refer to photogenerated free electrons and holes. In SI GaAs their concentrations are, in general, orders of magnitude larger than dark values, at least at low temperature. Furthermore, during low intensity illumination μ_n and μ_p remain practically unchanged, so any considerable light-induced change in σ or μ_H has to be ascribed to a change in the free carrier concentrations n and/or p [13].

A monotonic rise of I_{PC}, until it reaches its equilibrium value (figure 1(a)) is not very surprising. However, the experimentally observed deep dip in the time evolution of μ_H (figure 1(b)) is more puzzling. To analyse this behaviour we rewrote equation (2), taking $r_n = r_p = 1$:

$$\mu_H = \left| \frac{y/b^2 - 1}{1 + y/b} \right| \tag{3}$$

where $b = \mu_n/\mu_p$ and $y = p/n$. The value of b for undoped, SI GaAs should not be affected considerably by low intensity illumination. Therefore, only changes in y can significantly influence μ_H, as obviously $\mu_H = 0$ for $y/b_2 = 1$, while $\mu_H \approx \mu_n$ for $y/b^2 \ll 1$. The calculated dependence of μ_H/μ_n as a function of y is presented in figure 4 for $b = 10$. (Different values of b would only change the position of a minimum in μ_H ($\mu_H = 0$); all other features of μ_H/μ_n on (p/n) dependence would remain the same.) Comparing the measured time evolution of μ_H (Figure 1(b)) with calculations of μ_H displayed in figure 4 one has to conclude that at the beginning of the low-temperature illumination considerable increase of p/n occurs. Longer illumination, however, seems to reverse this trend and the p/n ratio decreases to a lower value again. In order to confirm this conclusion, derived from the Hall mobility measurements, we calculated the time evolutions of both free electrons and free holes during illumination starting from the results of different experimental methods applied on the same samples. For this calculation we used measured values of I_{PC} and independently measured I_{TEE} (which also depends primarily on n and p and their respective mobilities). The expression for I_{TEE} is derived from the thermopower coefficient, θ, which can be written [13] in the form:

$$\theta = \frac{-k_{\mathrm{B}}}{e} \frac{[\chi_{\mathrm{n}} + \ln(N_{\mathrm{c}}/n)]\, n\mu_{\mathrm{n}} - [\chi_{\mathrm{p}} + \ln(N_{\mathrm{v}}/p)]\, p\mu_{\mathrm{p}}}{n\mu_{\mathrm{n}} + p\mu_{\mathrm{p}}} \tag{4}$$

where the Boltzmann approximation is assumed. N_{c} and N_{v} are the conduction and valence based density of states, respectively, k_{B} is Boltzmann's constant and $\chi_{\mathrm{n}} = 5/2 - s_i$, where $s_i = 1/2, -1/2$ or $-3/2$, depending on free carrier scattering mechanism. For semi-insulating materials, the terms $\ln(N_{\mathrm{c}}/n)$ and $\ln(N_{\mathrm{v}}/p)$ are much larger than the values of χ, so it is not necessary to know the scattering factors χ_{n} and χ_{p} accurately and in further calculations we took $\chi_{\mathrm{n}} = \chi_{\mathrm{p}} = 2$. I_{TEE} is proportional to θ:

$$I_{\mathrm{TEE}} = -C_1 \frac{[2 + \ln(N_{\mathrm{c}}/n)]\, n\mu_{\mathrm{n}} - [2 + \ln(N_{\mathrm{v}}/p)]\, p\mu_{\mathrm{p}}}{n\mu_{\mathrm{n}} + p\mu_{\mathrm{p}}}. \tag{5}$$

For SI GaAs $N_{\mathrm{v}} = 1.5 \times 10^{18}$ cm^{-3} and $N_{\mathrm{c}} = 6.75 \times 10^{16}$ cm^{-3} at 86 K. C_1 is a constant reflecting the sample geometry and applied temperature gradient. Equation (5) can be rewritten as:

$$I_{\mathrm{TEE}} = C_1 C_2\, (C_3 p\mu_{\mathrm{p}} - n\mu_{\mathrm{n}})/(n\mu_{\mathrm{n}} + p\mu_{\mathrm{p}}) \tag{6}$$

where $C_2 = [2 + \ln(N_{\mathrm{c}}/n)]$, and $C_3 = [2 + \ln(N_{\mathrm{v}}/p)]\,/\,[2 + \ln(N_{\mathrm{c}}/n)]$. For example, for $n = p = 10^6\mathrm{cm}^{-3}$, $C_3 = 32/29 = 1.1$. Although C_2 and C_3 are not constants, their dependence on changes in n and p is relatively weak, and in the first approximation they can be regarded as quasi-constant parameters, whose values can be adjusted by iterations during calculation of each point. Electrical conductivity σ is proportional to the current flowing through the sample, I_{PC}. For low temperature illumination of SI GaAs, I_{PC} contains contribution from both photogenerated free electrons and holes. Taking into account equation (2):

$$I_{\mathrm{PC}} = C_4(nb + p) \tag{7}$$

where C_4 is a proportionality constant including μ_{p}, applied voltage and sample geometry. For long enough illumination time, I_{PC} and I_{TEE} tend to saturate (figure 2) reaching constant values, which we denote $I_{\mathrm{PC}}(\infty)$ and $I_{\mathrm{TEE}}(\infty)$. This means that $n(\infty)$ and $p(\infty)$ are also constants, being either equal or differing mutually for a constant factor, δ. As for a long enough illumination μ_{H} regains its high value (figure 1(b)) one can conclude that for $t = \infty$ the ratio p/n approaches unity (figure 4), and the electron conduction prevails due to a larger electron mobility. Therefore $n(\infty)$ can be assessed from simplified equations (1) and (2): $n(\infty) = |\sigma(\infty)/e\mu_{\mathrm{H}}(\infty)|$, while $p(\infty) = n(\infty)(1 + \delta)$. The constants C_4, C_2 and C_1 could in principle be appraised fairly well, but it is also possible to calculate them directly from measurements using equilibrium values for long enough illumination time in equations (6) and (7):

$$C_1 C_2(\infty) = I_{\mathrm{TEE}}(\infty) \frac{1 + \delta + b}{C_3(\infty)(1 + \delta) - b} \tag{8}$$

$$C_4 = \frac{I_{\mathrm{PC}}(\infty)}{n(\infty)} \frac{1}{(b + 1 + \delta)}. \tag{9}$$

Assuming μ_n and μ_p to be constant at a constant temperature and low intensity illumination one can treat equations (6) and (7) as a system of two equations with two unknowns, n and p. Measured values of I_{PC} and I_{TEE}, as presented in figure 2, have been used; experimental points were taken every two seconds. The solution of the system of equations (6) and (7), utilizing C_4 and $C_1C_2(\infty)$ from equations (8) and (9), is:

$$n(t) = \frac{I_{PC}(t)}{I_{PC}(\infty)} \frac{n(\infty)(b+1+\delta)}{b(1+C_3(t))} \left[C_3(t) - \frac{I_{TEE}(t)C_2(\infty)}{I_{TEE}(\infty)C_2(t)} \frac{C_3(\infty)(1+\delta)-b}{b+1+\delta}\right] \quad (10)$$

$$p(t) = \frac{I_{PC}(t)}{I_{PC}(\infty)} \frac{n(\infty)(b+1+\delta)}{1+C_3(t)} \left[1 + \frac{I_{TEE}(t)C_2(\infty)}{I_{TEE}(\infty)C_2(t)} \frac{C_3(\infty)(1+\delta)-b}{b+1+\delta}\right]. \quad (11)$$

If the experimental data for $I_{PC}(t)$ and $I_{TEE}(t)$, shown in figure 2 are inserted in the equations (10) and (11), the time evolutions of n and p can be obtained. Results are displayed in figure 5. For this calculation we assumed $b = 10$ and computed $C_3(t)$ by an iteration method starting with the value $C_3 = 1.1$ to calculate n' and p' from (10) and (11), which would then be used to get the corrected value C_3. This new C_3 was used to calculate $n(t)$ and $p(t)$ as presented in figure 5. The procedure was automatically repeated for each point in the time evolution. In this computation the constant δ remains undetermined. However, an analysis shows that changing δ in any reasonable range influences only the depth of a dip in the calculation of n, but all the main findings and conclusions remain the same.

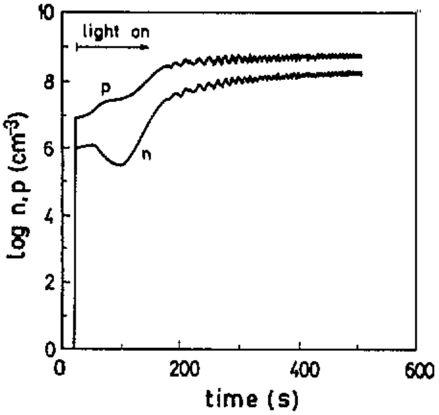

Figure 5. Calculated time evolutions of free hole concentration, p, and free electron concentration, n, during illumination at 86 K.

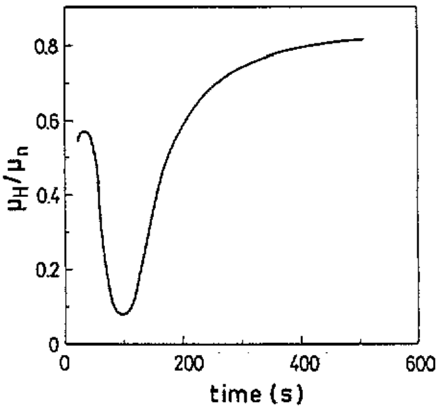

Figure 6. Calculated time evolution of normalized Hall mobility, μ_H/μ_n, during illumination at 86 K.

5. Discussion

The experimental results and performed calculations show that the ratio p/n changes dramatically during illumination. Knowing n and p (obtained by the procedure described in the previous section), one can now calculate μ_H according to equation (2). The result is presented in figure 6. Obviously, the calculation based on independent measurement of TEES and PC predicts the same trend in the time evolution of μ_H as that determined experimentally, by measuring the Hall constant.

Besides confirming the unusual behaviour of μ_H, this result also demonstrates for the first time the usability of a very recently presented spectroscopy [10], TEES, for quantitative calculations of transport properties in SI material. In a similar manner one can insert n and p, calculated from equations (6) and (7) (figure 5), into equation (1) and calculate the time evolution of I_{PC}. Excellent agreement between I_{PC} computed in this way and experimental I_{PC} (figures 1(a) or 3(a)) is obtained, leading to the conclusion that the calculated time evolutions of n and p are realistic.

Now that the time evolutions of n and p, and the subsequent evolution of I_{PC} and μ_H are determined, the question of what is causing this peculiar behaviour still remains. It seems that the observed phenomena are in accordance with the model, proposed previously to explain a time evolution of low-temperature photoconductivity [11], photoconductivity versus temperature experimental results [6], and thermoelectric effect spectra [10], in which all these phenomena have been explained by different filling dynamics of various deep traps in the material. Within the framework of this model, the observed time evolution of the Hall mobility and photoconductivity might be explained as follows. At the beginning of the illumination the trapping of photogenerated electrons and holes by deep levels is the dominant process, limiting free carrier concentration in the material. At first both electrons and holes are trapped, electrons primarily by the fast electron trap T_5, and holes by the hole trap T_6, which is also very fast (figure 3). After the hole traps are filled, the free hole concentration starts to rise, while the electron concentration drops even lower, partly due to trapping by other, more numerous, electron traps (T_1–T_4), and partly due to the increased free hole concentration, which increases the probability, and hence the rate, of electron recombination. The free electron concentration remains relatively low until all of the electron traps are filled, and only then does the electron concentration (as well as I_{PC}) rise up to its high, equilibrium value. At that time, only the recombination of free carriers influences free carrier concentration; the constant, steady state value is an equilibrium between constant generation and constant recombination processes, with no interference from deep traps which are, by now, completely filled. The time evolution of the Hall mobility, as observed experimentally and predicted from calculations, shows a pronounced dip just at the onset of the I_{PC} rise. The value of μ_H decreases as long as p is increasing and n is decreasing, as then p/n is decreasing as well so that $(p/n)/b^2$ is approaching 1. Comparison with figure 4 shows that at the minimum of μ_H, the ratio $p/n \approx 10^2$. Up to that moment all the hole traps and the fastest electron traps are already filled. With further illumination even electron—traps with smaller capture cross sections (which are most numerous in this material see figure 3) gradually become filled as well, trapping fewer and fewer electrons, which are photo generated at a constant rate. When all the traps are filled, they no longer disturb the photo created electrons and holes. Now both free electrons and holes can reach their maximal, equilibrium values, limited only by the recombination processes.

6. Summary

The analysis of peculiar time evolution of low-temperature photoconductivity in SI GaAs is presented, based on the time evolution of photo-Hall mobility, photoconductivity and thermoelectric force induced currents. μ_H was determined experimentally from measurements of the Hall constant during low-temperature illumination with 1.55 eV photons. At first μ_H decreased gradually, dropping almost to zero, but then, during further illumination, it increased back to a high, equilibrium value. Exactly the same behaviour is predicted from calculations of time evolutions of free electron and hole concentrations, derived from the results of independently measured time evolutions of I_{TEE} and I_{PC}. Results are compatible with the model in which the dynamics of trap filling and changes of relative occupancies of traps with different sign are responsible for transient phenomena observed in photoconductivity, Hall mobility and thermoelectric current during low-temperature, low-intensity illumination.

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