The defect responsible for non-radiative recombination in GaAs materials

J C Bourgoin and N De Angelis

Laboratoire des Milieux Désordonnés et Hétérogènes, Université Pierre et Marie Curie
(Paris 6), CNRS, UMR 7603, Tour 22, Case 86, 4 place Jussieu, 75252 Paris Cedex 05, France

E-mail: bourgoin@ccr.jussieu.fr

Abstract
Using electrical techniques (deep-level transient spectroscopy, capacitance and current–voltage measurements) applied to different types of p/n junctions, we correlate the concentration of the EL2 defect with properties directly related to the rate of recombination of minority carriers in a Czochralski-grown material and in epitaxial layers. The results demonstrate that this defect is responsible for minority carrier lifetime in both materials.

1. Introduction

Different GaAs materials are used in micro- and opto-electronics. They are either bulk Czochralski (Cz)- or Bridgman (Bg)- grown materials, or layers obtained by different kinds of epitaxial technique. Because many important characteristics of the devices made with these materials are determined by the minority carrier lifetime, the knowledge of the nature and concentration of the recombination centre they contain is important. Defects have been detected and characterized in these materials (for a review on this question, see [1]) but, up to now, the defect playing the role of the non-radiative recombination centre has not been identified. The influence of each of the detected defects on the minority carrier lifetime has not been recognized because no attempt to correlate the lifetime with the presence of one specific defect has been made. Thermal spectroscopies, such as deep-level transient spectroscopy (DLTS), detect and characterize defects only when they behave as traps and the recombination centre cannot be distinguished from the other, simultaneously detected, traps.

In bulk-grown materials, the concentration of defects is large and the minority carrier lifetime is undoubtedly governed by non-radiative centres. Bg- and Cz-grown materials contain a large concentration (several 10^{16} cm^{-3}) of defects, among which is the defect usually called EL2 (for a review on this defect, see [2]). Because the EL2 defect is characterized by a midgap level, it is commonly assumed that the lifetime is governed by this defect. However, no direct evidence that this is indeed the case has ever been presented, since no correlation between the lifetime and the EL2 concentration has ever been presented. It has only been shown that this defect can play a role in minority carrier recombination [3]. The recent review by Lush *et al* of recombination in GaAs [4] does not even mention the existence of this defect.

In epitaxial layers, grown at conventional (high) temperatures, the defect concentration is low and carrier recombination occurs via the radiative process, as evidenced by the efficiency of light emitting diodes made with these materials. However, at small forward bias, when the density of injected carriers is low, non-radiative recombination still dominates. The reason is that recombination through non-radiative centres is more efficient than the radiative channel and a minimum density of injected carriers is necessary to saturate the non-radiative channel [5]. This can be evidenced by the fact that the current–voltage (I–V) characteristics of light emitting diodes exhibit at low forward bias a linear dependence of log I on V with a slope equal to $q/2kT$, a behaviour characteristic of a Shockley–Read recombination in a space–charge region (see figure 1). As to the radiative recombination process, which corresponds to a linear dependence of log $I(V)$, with a slope q/kT, it dominates only at high enough forward bias. Hence, epitaxial layers also contain non-radiative recombination centres with a lifetime typically of the order of a few nanoseconds at high injection level (see figure 2). In such layers, the EL2 concentration is very small since it cannot be detected (see for instance [6]), and no information on the nature of the recombination centre exists. It is only in the case where the stoichiometry is strongly varied, by the ratio of AsH$_3$ over GaCl in the gas phase, that a defect having characteristics similar to those of EL2 is detected [7]. However, the correlation between the lifetime and the inverse of the defect concentration is not linear, demonstrating that other non-radiative recombination centres are present.

The aim of this paper is to demonstrate that the main recombination centre in the two existing types of GaAs material, i.e. bulk materials and epitaxial layers, is the EL2 defect, and thus that the lifetime in epitaxial materials is still governed by this defect. To achieve this goal, we correlate the
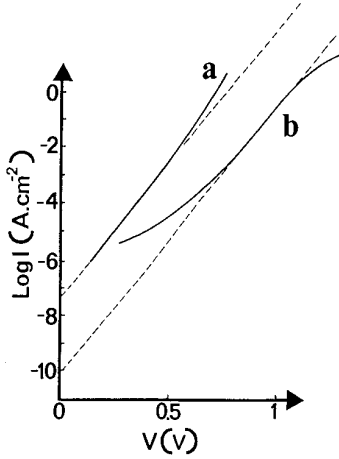
Figure 1. Forward current–voltage characteristics, measured at 300 K, of junctions made on materials 1 (a) and 2 (b). The I_R values are determined from these plots in the voltage range where their slopes are equal to $q/2kT$ (dashed lines).
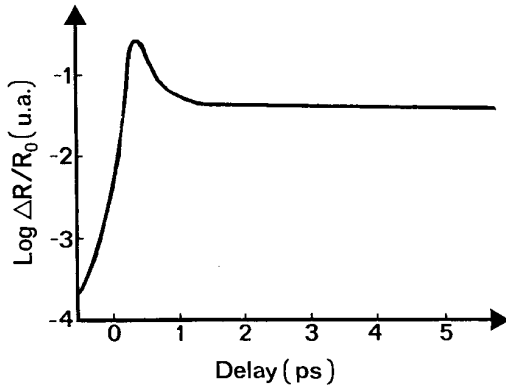

Figure 2. Variation of the reflectivity of a GaAs epitaxial layer (covered by a GaAlAs window) versus the delay between the pulse laser excitation and the beam reflected on the surface of the sample. The first rapid decay is related to electron thermalization. The second, slower, decay is induced by electron recombination. In this case, the corresponding lifetime is 2.5 ns.

concentration of the EL2 defect with a property directly related to the minority carrier lifetime. We also use a specific property of this defect, namely the existence of a metastable state.

2. Experiment

Lifetimes were measured indirectly except in one case for an epitaxial layer (see figure 2). Measurements of recombination currents were made on junctions, the structures used to perform defect spectroscopy by DLTS.

Consider the characteristics of a forward-biased junction. It contains two components associated with the diffusion and recombination currents, respectively. The current at low bias is induced by the so-called Shockley–Read recombination, recognized by the linear dependence of $\log I(V)$ with a slope equal to $q/2kT$. The value of this current, extrapolated to zero voltage [8],

$$I_R = \frac{(\pi/2)\, n_i W kT}{\sqrt{\tau_n \tau_p}\sqrt{V_d}} \quad (1)$$

provides the capture rates, τ_n and τ_p, i.e. the time constants

associated with the capture of electrons and holes on the recombination centre, respectively. For a centre of concentration N, characterized by electron and hole cross sections σ_n and σ_p, these capture rates are given by

$$\tau_{n,p}^{-1} = \sigma_{n,p} v_{n,p} N \quad (2)$$

where $v_{n,p}$ is the electron (hole) thermal velocity. In expression (1), n_i is the intrinsic carrier concentration, V_d the built-in voltage, W the width of the space–charge region and q the electronic charge. Note that extraction of the I_R value is not direct from the extrapolation of the $\log I$ versus V plot to $V = 0$ because the slope of the plot varies as $(V_d - V)^{-1/2}$.

The I_R value is not a measure of the minority carrier lifetime but is proportional to the concentration N of the recombination centres inducing this lifetime. However, this concentration can be measured directly by DLTS, in which case the recombination centres behave as traps. Hence, the role of a given defect as a recombination centre can be recognized by the linear dependence of I_R on N.

Once the recombination current has been extracted from the current–voltage characteristics, the remaining current is the diffusion current. Extrapolation of this diffusion current to zero volts leads to

$$I_D = q n_i^2 N_A^{-1} (D_n/\tau_n)^{1/2} \quad (3)$$

(q is the electronic charge) where D_n is the diffusion length of the minority carriers (assumed here to be electrons in a p-type material doped at the level N_A).

We applied this method to an n-type doped Cz material and to epitaxial layers on which p^+–n junctions were realized by diffusion or epitaxial growth, respectively. Since a recombination centre is intrinsic to the material, the result should not depend on the type of diode used to characterize it. Because the doping is very high on the p side, the recombination current originates from the space–charge region on the n side of the junction and thus this study deals with the recombination in n-type materials.

The different materials we studied are as follows.

(a) *Material 1.* Cz-grown material, n-type doped by Si, at a level of 7.1×10^{16} cm^{-3} during growth. The p^+ side of the junction is realized by Zn diffusion. Mesa diodes of area 2.5×10^{-3} cm^2 are then made by chemical etching and ohmic contacts taken by Au–Ge alloying on the back of the wafer.

(b) *Material 2.* Epitaxial layers grown by metallo-organic chemical vapour deposition (MOCVD) over an n$^+$ wafer through the intermediary of an n$^+$-doped buffer layer. They are n-type doped at a level ranging from 1 to 3×10^{17} cm^{-3}. The junction is realized by the further growth of a p^+ emitter, doped at a level of 10^{18} cm^{-3}. These layers, then covered by a GaAlAs layer preventing surface recombination, are in fact state of the art solar cells from different origins, i.e. grown at slightly different temperatures, with different growth rates (in the range of a few micrometres per hour).

The doping levels n in both types of material are nearly equal so that the space–charge regions W for a given bias have practically the same magnitude, allowing us to compare the I_0 values directly.

DLTS has been performed with the junctions made on materials 1 and 2. In the case of material 1, the concentration

of defects was not negligible in front of the free electron concentration, and a correction had to be made to obtain a correct value of the EL2 concentration (for a description of these corrections, see [9]).

Note finally that epitaxial layers grown by molecular beam epitaxy at low temperature, which are also said to contain EL2-'like' defects, are not considered here. Indeed, the EL2 concentration is then large and impossible to measure accurately. Moreover, the EL2-'like' defects are not identical to EL2 defects since they are not stable at high temperature and do not exhibit the metastable character of EL2 [10].

3. Results

As shown in figure 1, materials 1 and 2 exhibit the current–voltage dependence characteristic of a Shockley–Read recombination, i.e. a linear dependence of $\log I(V)$ with a slope equal to $q/2kT$. The current of the junction made with material 2 contains, at low voltage, a component originating from the GaAs–GaAlAs heterostructure. From the extrapolation of the linear range of this plot towards $V = 0$, once it has been corrected for the $(V_d - V)^{-1/2}$ dependence, we obtain I_R. The values of I_R obtained at 300 K are 5×10^{-8} and 1×10^{-10} A cm^{-2} for materials 1 and 2, respectively.

DLTS spectra recorded on junctions of materials 1 and 2 are given in figure 3. As expected, the diode exhibiting the largest current contains the highest defect concentration. The temperature dependences of the defect emission rates, the so-called signatures (given in figure 4), demonstrate that, in both junctions, the same defect is detected around 400 K. This defect, which exhibits concentrations of 3×10^{16} and 9×10^{13} cm^{-3} in materials 1 and 2, respectively, can be identified by its signature as the EL2 defect classically encountered in Cz materials (11). The signatures of this defect are slightly different in the two materials because the data presented have not been corrected in the case of material 1 to account for the large ratio of the defect concentration to the free carrier concentration. The second peak emitting around 200 K (with a concentration of 3×10^{15} cm^{-3}) in material 1 can be identified with the defect labelled EL6, also classically detected in Cz materials [11]. In material 2 a peak is also observed around 200 K (with a concentration of 9×10^{13} cm^{-3}), associated with a similar activation energy. However, as shown in figure 4, it is different from the EL6 defect since its emission rate at the same temperature is 10^3 times higher. Finally, material 2 exhibits a third peak, whose signature is also reported in figure 4 with a concentration of 2×10^{12} cm^{-3}, which, to our knowledge, has not yet been reported.

4. Discussion

Following section 1, we plot the concentration N of the common defect, i.e. the EL2 defect, detected in materials 1 and 2 versus I_R. As shown in figure 5, $\log N$ versus $\log I_R$ is linear with a unit slope, demonstrating that I_R is proportional to N. Hence, the EL2 defect is the dominant recombination centre in both Cz and epitaxial materials.

The existence of the EL2 defect in MOCVD-grown layers is often questioned because it is difficult to detect by DLTS since its concentration is very low compared to the doping. In order to verify its presence, we take
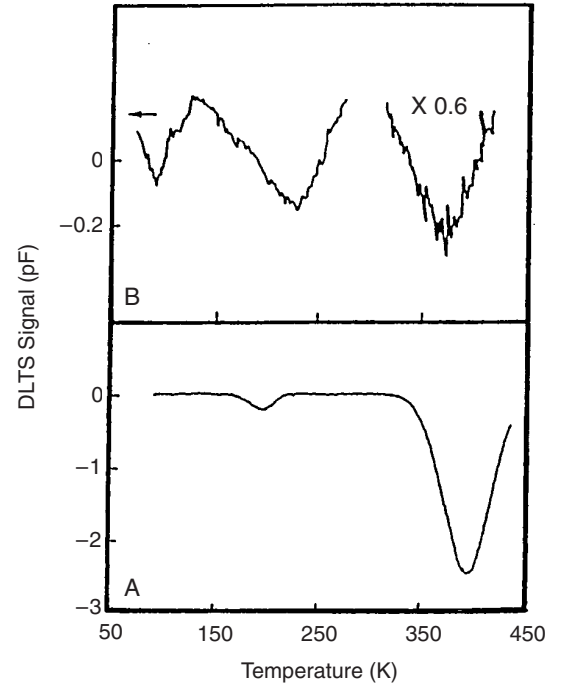

Figure 3. DLTS spectra obtained in materials 1 (*a*) and 2 (*b*). The spectra are recorded with emission rates 2×10^2 s^{-1} and 8×10^3 s^{-1}, respectively. The peak located around 400 K is related to the so-called EL2 defect, while that located around 200 K is another defect already detected and labelled EL6. In order to obtain a measurable capacitance transient in the case of the epitaxial layer, a sample of large area (6 mm^2) is used and the capacitance (1800 pF at zero volt) is strongly compensated, by a value equal to the capacitance (1500 pF) for the chosen reverse bias (3 V).
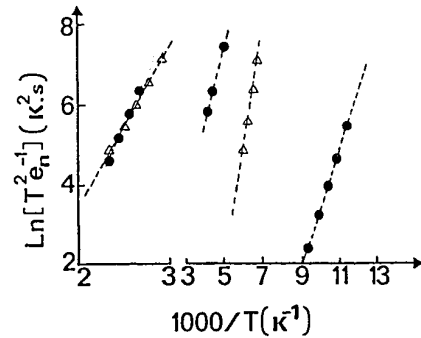

Figure 4. Signatures, i.e. temperature dependences of the electron emission rates, from the various defects observed in materials 1 ($\triangle$) and 2 ($\bullet$). Comparison of the signatures demonstrates that the defects emitting around 400 K are the same in both materials.

advantage of a peculiar property of this defect, namely its metastability. At low temperature, typically below 100 K, the defect transforms into a new state under photo-excitation [1, 2]. The stable to metastable transformation can be monitored by capacitance measurements versus time under photo-excitation, the capacitance of a junction containing the defect increasing first, before decreasing to its original value [12]. The maximum change of capacitance gives the EL2 concentration N directly. When this transformation has taken place the minority carrier lifetime, or equivalently the recombination current, should be modified if the EL2 defect is indeed the main recombination centre.
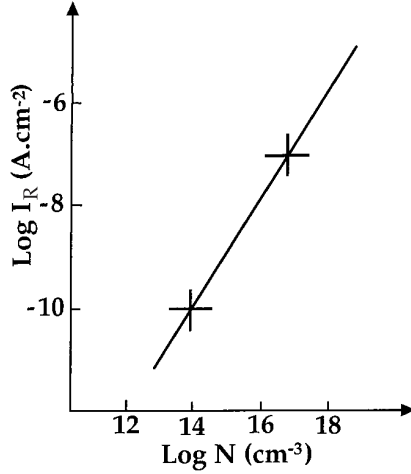
Figure 5. Variation of the recombination current I_R versus the EL2 defect concentration N. The slope of this logarithmic plot is equal to unity (full line), indicating that I_R is proportional to N.
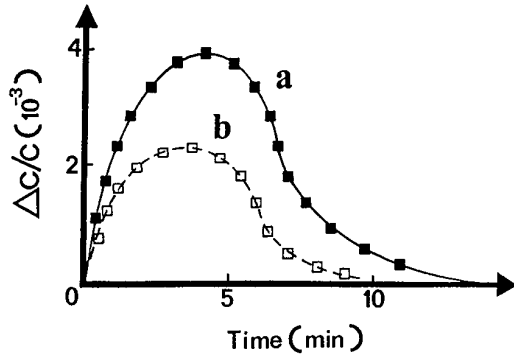

Figure 6. Variation of the capacitance of the junction made on material 2 monitoring the transformation of the EL2 defects into their metastable state versus the time of excitation with white light at 120 K (a). After 1 hour in the dark, at the same temperature, part of the EL2 metastable state anneals and the transformation can be repeated (b).

We perform this experiment on a 1 cm^2, p$^+$–n solar cell made with material 2 (a large area is necessary to obtain a measurable change of capacitance). At zero bias the capacitance C_0 is 67 nF. Following light illumination a capacitance change ΔC is observed (see figure 6), which reaches a maximum value such that $\Delta C/C_0 = 4.0 \times 10^{-3}$ at 80 K. This change corresponds therefore to a value of N such that

$$N/n = 2\Delta C/C_0$$

that is $N = 5.4 \times 10^{14}$ cm^{-3}. This concentration is slightly larger than that measured by DLTS, probably because the layer selected for this study was grown with a higher rate in order to exhibit a higher EL2 concentration (according to [13], the EL2 concentration increases with the growth rate). As illustrated in figure 6, we verified that the capacitance change is indeed induced by the transformation of the EL2 defect into its metastable state by observing the reverse transformation, known to take place above 100 K.

A noticeable change in the forward I–V characteristics is observed when the transformation has taken place (see figure 7). This change corresponds to a decrease of I_R by
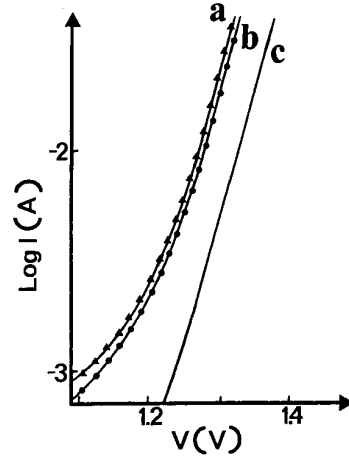

Figure 7. Current–voltage characteristics of material 2 (1 cm^2) measured at 78 K before (a) and after (b) photo-excitation. The difference given by curve c is the variation induced by the transformation of the EL2 defect into its metastable state. The process is reversible after annealing above 150 K.

about 25%, which demonstrates that either the nature, or the concentration, of the recombination centre has been modified. This change presents the same metastable character as the EL2 defect. Because the metastable state of the EL2 defect is expected to be less efficient than the stable state, its associated energy level lying near the conduction band [6], the decrease in the recombination current must be ascribed to a change in the defect nature and not in its concentration.

5. Capture rates

Since the capture rate of electrons τ_n on the EL2 defect has been determined (for a recent review, see [14]), it is possible to obtain the hole capture rate τ_p from the measurement of I_R and I_D using expressions (1) and (2), once the EL2 concentration N is known, which is the case here.

The current–voltage characteristics of some of the solar cells (material 1) clearly exhibited a component related to a diffusion current. In that case, we measured I_D, from which we deduced τ_p, allowing us to obtain $\sigma_p = 2 \times 10^{-13}$ cm^2. In the corresponding material, we also measured the EL2 concentration (2.2×10^{13} cm^{-3}) from the capacitance change induced by light illumination below 100 K. Then, taking the value of σ_n at the same temperature (4×10^{-16} cm^2), we obtain $\sigma_n\sigma_p = 8 \times 10^{-29}$ cm^4. This value is much smaller than the one we derive from I_R (1.2×10^{-24} cm^2). This difference should be ascribed to the fact that the capture rates on the EL2 defect, like the emission rates, are sensitive to the electric field. Indeed, the measurement of I_R is performed in a region of strong electric field while that of I_D is performed in a neutral region. For instance, according to [15], the application of a field of 1×10^5 V cm^{-1} increases e_n and hence σ_n by a factor of 2×10^2 at room temperature. Then, the σ_n value at zero field (4×10^{-16} cm^2) becomes $\sigma'_n = 8 \times 10^{-14}$ cm^2 in the maximum electric field of the junctions considered in this paper (the width of the space–charge region is 1.5×10^{-5} cm for a reverse bias of 1.5 V).

Taking σ'_n for the electron capture rate, the corresponding hole value is $\sigma'_p = 1.5 \times 10^{-11}$ cm^2. Hence, the hole capture

rate is also increased by a factor of 10^2 in the presence of the electric field. We can therefore conclude that the minority carrier lifetime is a strong function of the electric field existing in the region where the capture takes place.

6. Conclusion

From an analysis of the forward current–voltage characteristics, coupled with capacitance and DLTS observations, on diodes made on a Cz-grown material and in MOCVD epitaxial layers, in which the EL2 concentration varies by more than two orders of magnitude, we demonstrate that the recombination current varies linearly with the concentration of the EL2 defect. We also took advantage of the metastable character of the EL2 defect to illustrate that the minority carrier lifetime exhibits the same metastable behaviour. All these observations clearly demonstrate that the EL2 defect is the defect responsible for non-radiative recombination in epitaxial, as well as in bulk materials. Finally, knowing the capture cross section of electrons on the EL2 defect, we deduce the hole capture cross section and we observe that the hole capture rate, and hence the minority carrier lifetime, strongly varies in an electric field.

Acknowledgments

References

[1] Bourgoin J C, von Bardeleben H J and Stievenard D 1988 *J. Appl. Phys.* **64** R65

[2] Martin G M and Makram-Ebeid S 1986 *Deep Centers in Semiconductors* ed S T Pantelides (New York: Gordon and Breach) ch 6

[3] Zaidi M A, Maaref H and Bourgoin J C 1992 *Appl. Phys. Lett.* **61** 2452–4

[4] Lush G B, Melloch M R and Lundstrom M S 1996 *Properties of GaAs* ed M R Brozel and G E Stillman (London: INSPEC) p 135

[5] Ahrenkiel R K, Keyes B M and Dunlavy D J 1991 *Appl. Phys. Lett.* **70** 225

[6] Hasegawa F and Magerfeld A 1975 *Electron. Lett.* **11** 286

[7] Miller M D, Olsen G H and Ettenberg M 1977 *Appl. Phys. Lett.* **31** 538

[8] Sah C T, Moyce R N and Shockley W 1957 *Proc. IRE* **45** 1228

[9] Stievenard D, Lannoo M and Bourgoin J C 1985 *Physica* B **129** 422

[10] Kaminska M, Lilienthal-Weber Z, Weber E R, George T, Kotright J B, Smith F W, Tsain B Y and Calawa A R 1977 *Appl. Phys. Lett.* **31** 538

[11] Martin G M, Mitonneau A and Mircea A 1977 *Electron. Lett.* **13** 191

[12] Bourgoin J C and Neffati T 1997 *J. Appl. Phys.* **82** 4124

[13] Bourgoin J C, Hammadi H, Stellmacher M, Nagle J, Grandidier B, Stievenard D, Nys J P, Delerue C and Lannoo M 1999 *Physica* B **273–4** 725

[14] Neffati T and Bourgoin J C 1997 *Phys. Status Solidi* b **203** 459

[15] Makram-Ebeid S and Lannoo M 1982 *Phys. Rev.* B **25** 6406