Activation energies of the EL6 trap and of the 0.15 eV donor and their correlation in GaAs

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Abstract. In the understanding of properties of deep levels in undoped bulk GaAs there are still considerable deficiencies and obscurities. One example is the activation energy of the electron level EL6, which is present in undoped bulk GaAs mostly in a relatively high concentration. There are indications that its activation energy by deep-level transient spectroscopy (DLTS) differs clearly from the impurity-to-band activation energy. Temperature-dependent Hall effect and DLTS measurements performed on the same sample confirmed the hypothesis of the identity of EL6 with the 0.15 eV donor. The difference between the two energies was found to arise from thermally activated carrier capture with an unusually high value of the barrier energy ($E_\sigma = 0.14$ eV).

1. Introduction

The most essential electrical methods used for the investigation of deep levels in GaAs are the temperature-dependent Hall effect (TDH), deep-level transient spectroscopy (DLTS), thermally stimulated currents (TSC) and photo-induced current transient spectroscopy (PICTS). TDH is only applicable if the corresponding level is not completely compensated. DLTS allows the investigation of deep levels in semiconducting materials, whereas TSC and PICTS are suitable for the detection of medium deep and deep levels in high-resistivity material.

Deep-level investigations by DLTS on undoped GaAs grown by the liquid-encapsulated Czochralski (LEC) method and by the Bridgman technique (horizontal or vertical) show in general the same spectrum: electron traps with activation energies of about 0.82 (EL2), 0.56 (EL3) and 0.35 eV (EL6) dominate [2–4] (defects labelled according to Martin *et al* [1]). In semi-insulating (SI-) GaAs besides the main donor EL2 deep levels with activation energies of about 0.60 (T2), 0.52 (T3), 0.34 (T5) and 0.15 eV (T6*) (labels after Fang and Look [5]) were measured by TSC [5–7] and by PICTS [8].

For the midgap level EL2, an intrinsic defect related to the As_{Ga} antisite, TDH yields a thermal activation energy of $(0.75, \dots, 0.78)$ eV for SI-GaAs. Since TDH is based on thermodynamic equilibrium this activation energy corresponds to the level position in the gap (at $T = 0$ K). On the other hand, the non-equilibrium method DLTS gives an activation energy of $E_a = 0.82$ eV influenced by the emission process. This latter value contains the impurity-to-band activation energy ΔE_{DD} and an activation energy $E_\sigma \approx 70$ meV of the capture cross section which appears in the emission process as barrier energy for carrier capture.

Moreover, the threshold for photoionization measured by infrared absorption and photoconductivity, respectively, can be described consistently in the framework of a configuration coordinate model [9].

Such a clear and reliable picture exists only for the deep level EL2, because the other deep and medium deep levels in GaAs have drawn much less attention. However, the concentration of the EL6 defect sometimes amounts to a value equal to or higher than those of residual donor and acceptor impurities. In this case EL6 plays an important role for the free carrier density. Especially, in SI-GaAs EL6 (assuming it to be a donor-like trap) must be additionally compensated by acceptors. If the EL6 concentration is higher than the effective acceptor concentration the material deviates from semi-insulating behaviour. The Fermi level is shifted towards shallower levels, the activation energy of free carriers (TDH) is lowered (compared to SI-GaAs) and the carrier density increases, resulting in n-type conductive GaAs.

The activation energy of EL6 by DLTS is about 0.35 eV. When using TDH measurements no donor with this energy was observed. However, activation energies of 0.42 and 0.15 $(0.13, \dots, 0.20)$ eV have often been measured in undoped GaAs [10,11]. Since the value of 0.42 eV is near to the DLTS energy, in [10] it was assumed that both energies belong to the same defect centre. On the other hand, there are indications that the electron level EL6 should be identical with the so-called '0.15 eV donor' (TDH), although the activation energy of the latter $(E_D = 0.13, \dots, 0.20$ eV) deviates considerably from the DLTS energy [3,12,13]. This hypothesis is supported by results of Zhao *et al* [14], that in the case of EL6 the DLTS activation energy E_a is composed of the impurity-to-band activation energy ΔE_{EL6} and of an

unusually high value of the activation energy of the capture cross section E_σ (0.200 ± 0.025 eV).

The aim of this paper is to reveal the validity of the hypothesis that the 0.15 eV donor is identical with the electron trap EL6. For this purpose the determination of all three relevant activation energies should be carried out on the same sample, because the activation energies reported in the literature show a considerable range (TDH—0.13, ..., 0.20 eV [10, 11], DLTS—mostly 0.32, ..., 0.35 eV [1], but also 0.27 eV [3] and 0.42 eV [15]). The determination of the activation energy for carrier capture is performed similarly as described by Zhao *et al* [14]. Reliable values for E_σ are obtained analysing the DLTS spectra in terms of the fast and the slow part of carrier capture [16] as well as of the high trap density.

2. Evaluation procedures

2.1. TDH measurements

An n-type GaAs sample is considered which contains a shallow donor (N_{SD}), a medium deep donor (N_{DD}) and acceptors (N_A). In the temperature range of investigation the shallow donor is fully ionized. The medium deep donor is treated as a single-charged state with the energy level E_{DD}. The existence of further deep levels (deeper than the regarded one) does not influence the following considerations.

At sufficiently low temperatures the medium deep donor is totally filled so the free carrier concentration n reveals the net concentration $N_S = N_{SD} - N_A$ of the shallow donors. At higher temperatures the medium deep donor emits its electrons to the conduction band, and it is partially positively ionized:

$$N_{DD}^+ = \frac{N_{DD}}{(g_1/g_0)\exp[(E_F - E_{DD})/(kT)] + 1} \quad (1)$$

where (g_1/g_0) is the degeneracy factor. The charge balance equation yields the free carrier concentration [18]

$$n(T) = N_S + \frac{N_{DD}}{1 + n/\Phi(T)} \quad (2)$$

with

$$\Phi(T) = (g_0/g_1)N_C\exp[-(E_C - E_{DD})/(kT)] \quad (2a)$$

where N_C is the effective density of conduction band states.

However, because of a possible temperature dependence of the donor activation energy according to

$$\Delta E_{DD}(T) = \Delta E_{DD0} - \alpha_{DD}T \quad (2b)$$

by TDH analysis, the value of ΔE_{DD0} is obtained. Then for equation (2) it is valid:

$$\Phi(T) = (g_0/g_1)\exp(\alpha_{DD}/k)N_C\exp[-\Delta E_{DD0}/(kT)]. \quad (2c)$$

From equation (2a) results a quadratic equation in the free carrier concentration n, the solution of which is

$$n(T) = 0.5\left[N_S - \Phi + \sqrt{(N_S - \Phi)^2 + 4(N_S + N_{DD})\Phi}\right] \quad (3)$$

2.2. Analysis of DLTS

First a numerical evaluation procedure of the DLTS spectra is given. Describing the capture kinetics of the medium deep electron trap on the basis of the Shockley–Reed–Hall (SRH) model the capture coefficient, c_n (usually related to the capture cross section, σ_n, of the deep trap by $c_n = \sigma_n\bar{v}_n$), the emission rate, e_n, and the mean thermal velocity in the conduction band, $\bar{v}_n$, are introduced. The medium deep trap investigated has its level much closer to the conduction band than to the valence band. Hence the interaction of such a trap with the valence band can be neglected. From the SRH model follows

$$\frac{dN_T^+(x, t)}{dt} = e_n[N_T - N_T^+(x, t)] - c_n n(x, t)N_T^+(x, t) \quad (4)$$

where $n(x, t)$ is the carrier concentration in the conduction band and N_T^+ the concentration of the ionized part of the deep centre.

Considering a thermally activated capture process with

$$\sigma_n(T) = \sigma_\infty\exp[-E_\sigma/(kT)] \quad (5)$$

the emission rate e_n is given by

$$e_n(T) = (g_0/g_1)\sigma_\infty\bar{v}_n(T)N_C(T)$$
$$\times \exp[-(\Delta E_T + E_\sigma)/(kT)] \quad (6)$$

with the impurity-to-band activation energy, ΔE_T, of the trap and the barrier energy, E_σ, for carrier capture.

The standard evaluation of DLTS yields the activation energy $E_a = \Delta E_T + E_\sigma$ and the apparent capture cross section σ_a

$$\sigma_a = (g_0/g_1)\sigma_\infty \quad (6a)$$

as the 'trap signature' of the Arrhenius plot of (T^2/e_n).

If ΔE_T is temperature dependent ($\Delta E_T = \Delta E_{T0} - \alpha_T T$), then the Arrhenius plot yields analogously to the TDH analysis the value $E_{a0} = \Delta E_{T0} + E_\sigma$ and σ_a includes the factor $\exp(\sigma_T/k)$:

$$\sigma_a = (g_0/g_1)\sigma_\infty\exp(\alpha_T/k). \quad (6b)$$

In the case of a large trap concentration the DLTS analysis is rendered more difficult, because of the following factors.

(1) The refilling kinetics of the deep trap causes a non-exponential capture of carriers by the trap, because there is a non-negligible change of carrier concentration in the region of fast capture. In this region charge neutrality exists, and the carrier concentration is the sum of the net concentration of the shallow donors and of the ionized fraction of the traps according to equation (4):

$$n(x, t) = N_S + N_T^+(x, t). \quad (7)$$

(2) During refilling of the deep traps there is a time-dependent local distribution of the carrier density, particularly in the region of slow capture. In contrast, in the case of a negligible trap concentration there exists a time-independent distribution of n.

(3) Due to the high trap concentration the width of the space–charge region changes considerably during the refilling and the emptying of the deep trap. This feature causes non-exponential capacitance transients during electron emission of the deep trap.

These conditions lead to a non-exponential behaviour not only in the emission, but also in the refilling process. For this reason, the commonly used DLTS procedure with variation of the filling pulse duration, t_p, after Lang [19] is not possible particularly when determining the capture parameters of the deep trap.

To account for these problems the authors have chosen a numerical self-consistent treatment of the capture kinetics of the deep trap in a way analogous to Pons [16]: the shape of the electrostatic potential is computed solving Poisson's equation for a metal–semiconductor contact with $x = 0$ at the metal/semiconductor interface

$$\frac{d^2 V(x, t)}{dx^2} = -\frac{q}{\varepsilon}[N_S + N_T^+(x, t) - n(x, t)] \qquad (8)$$

with the limits $V(x = 0) = V_0 + V_{bi}$; $V_1 + V_{bi}$ and $V(x = \infty) = 0$ and where

$$n(x, t) = N_C \exp[-(E_C - qV - E_{F,n})/(kT)]. \qquad (9)$$

The potential V at the contact results from the external voltages V_0 or V_1 and the built-in voltage V_{bi} of the diode. In the case of thermal equilibrium the ionized trap concentration is expressed by equation (1). To calculate the kinetics of the trap the solution of Poisson's equation (8) is obtained keeping the ionized trap concentration $N_T^+(n, t)$ constant. The relation for free carrier concentration $n(x, t)$, equation (9), includes the band bending $-qV$. $E_{F,n}$ is the quasi-Fermi level for electrons. As by other authors, it was assumed that the approximation of a constant quasi-Fermi level over nearly the whole space–charge region is valid. At large distances from the contact the quasi-Fermi level coincides with the Fermi level of the bulk semiconductor, which can be derived from the net concentration of the shallow donor and the trap concentration at a given temperature.

It was assumed that prior to the pulse applied to the diode an equilibrium distribution of charge density exists over the space–charge region at the bias voltage V_0. Due to the pulse there is an abrupt change of the potential at the contact from the bias voltage $V(x = 0) = V_0 + V_{bi}$ to the pulse voltage $V(x = 0) = V_1 + V_{bi}$. The electrical potential V is evaluated by equation (8) using a self-consistent treatment. This treatment is extended to the emission regime of the deep trap. The integration of Poisson's equation according to Zhao et al [14] and Pons [16] yields

$$V_0 + V_{bi} = -\frac{q}{\varepsilon}\left[\int_{x=0}^{W} N_S x \, dx + \int_{x=0}^{l} N_T^+(x, t)x \, dx\right] \qquad (10)$$

assuming a totally ionized shallow donor (with the net concentration N_S) between the metal/semiconductor interface and the depletion edge W. The concentration $N_T^+(x, t)$ of the ionized deep trap is taken from the numerical solution of Poisson's equation at a point $x = l$ in the bulk of the semiconductor, where electrical neutrality prevails during

the whole experiment. In the temperature range from 160 to 190 K, where DLTS is performed, the deep trap is only very weakly ionized in the bulk of the semiconductor. The integration of the ionized trap density in equation (10) is extended to the point $x = l$ [16].

The capacitance is measured by a small RF voltage on top of the external voltage:

$$C_{HF}(t) = \frac{dQ}{dV} = \frac{\varepsilon A}{W(t)} \qquad (11)$$

where the width of the space–charge region, $W(t)$,

$$W(t) = \sqrt{2}\sqrt{-\frac{\varepsilon V_0}{q N_S} - \frac{1}{N_S}\int_{x=0}^{l} N_T^+(x, t)x \, dx} \qquad (12)$$

results from equation (10).

If the emission rate of the deep trap is comparable to the pulse repetition rate the assumption of an equilibrium charge density as a starting point of the self-consistent treatment of the DLTS spectra is not longer justified. In this case the above numerical algorithm is extended over some pulse excitations until the calculated DLTS signal approaches a constant value.

3. Experiment

For DLTS measurements on n-type GaAs using Schottky diodes, besides the medium deep level of interest, shallow donors must be present which yield about 1×10^{14} cm^{-3} free carriers in the temperature region of interest. This is necessary for the RF capacitance measurements ($f = 1$ MHz) to hold the series resistance of the sample at a low level.

For the TDH measurements the concentration of the medium deep level must be equal to or higher than the effective shallow donor concentration. This means, on the other hand, that the DLTS investigations have to take place under the condition of a large trap concentration, which requires a more difficult analysis (see above) than the standard DLTS with a low trap concentration. Due to these requirements the sample selection is strongly restricted. Only few suitable samples were found.

For TDH and DLTS investigations LEC-GaAs samples were used with a carrier concentration of about 2×10^{15} cm^{-3} at room temperature and with a clear single EL6 peak in the DLTS spectrum. The samples with dimensions of $(5 \times 5 \times 0.6)$ mm^3 were alloyed with Sn contacts for TDH measurements after Van der Pauw (magnetic field $B = 0.57$ T). For DLTS an electrolytically deposited Ni–Schottky contact and an alloyed Sn ohmic back-contact were prepared. The quality of these contacts was checked at a typical temperature for DLTS experiments ($T = 160$ K) by forward and reverse $I–V$ characteristics with the following results: barrier height of 0.89 eV (built-in voltage $V_{bi} = 0.83$ V), diode ideality factor $n = 1.2$ (at 300 K: $n = 1.04$) for the Ni–Schottky contact and an ohmic series resistance of approximately 50 Ω. The DLTS measurements were carried out with a SULA apparatus which works with modified boxcar window technique†.

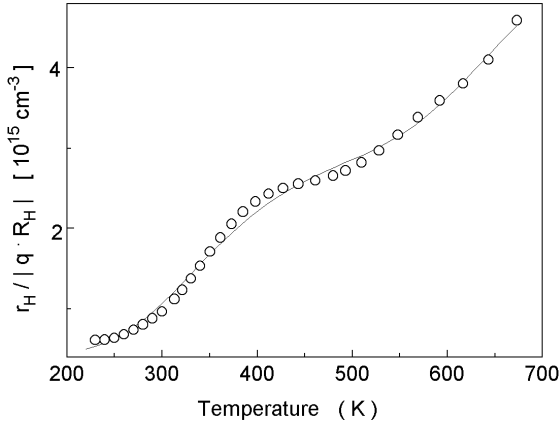† The emission rate is correlated to the initial delay t_i by $e_n = 0.232 t_i$.

Figure 1. Temperature dependence of carrier concentration as determined by Hall effect measurements in an n-type LEC GaAs sample. The solid curve is the theoretical fit.

4. Results

Figure 1 shows the $n(T)$ dependence as measured by TDH on an n-type GaAs sample in the temperature range between 200 and 680 K. The free carrier concentration n was taken from the well known relationship $n = -r_H/(qR_H)$, with the Hall coefficient, R_H, and the Hall scattering factor, r_H. The Hall scattering factor r_H was estimated in a way as described by Look *et al* [18]. Its value is nearly one and shows only a small change ($r_H = 1.06, \ldots, 1.14$) in the relevant temperature range. Then the carrier density $n(T)$ was fitted by a computer least-squares method considering that the $n–T$ curve at temperatures $T \geqslant 550$ K is influenced by a further deep level. Fit parameters of the interesting donor are N_{DD} and ΔE_{DD0}. The parameter $(g_0/g_1)\exp(\alpha_{DD}/k)$ can also be fitted; however, the fit is insensitive for the estimation of this parameter since only a limited range of $n–T$ values is influenced by the analysed defect level. For this reason we have used the value $(g_0/g_1)\exp(\alpha_{DD}/k) = 1.6$ obtained by fitting as average in [18]. The results of the fit are $N_S = 2.3 \times 10^{15}$ cm^{-3}, $N_{DD} = 1.3 \times 10^{15}$ cm^{-3} and $\Delta E_{DD0} = 178$ meV. The concentration error was estimated at $\pm 0.3 \times 10^{15}$ cm^{-3} and the error of activation energy at ± 10 meV.

Figure 2 shows the measured DLTS spectra as a function of the rate window. With a shorter initial delay t_i the emission rates at the negative peak increase and, as usual, the peak is shifted to higher temperatures. It has been noted that there was an increase of the negative peak height with rising peak temperature, which is a result of a high activation energy of the capture cross section: with rising peak temperature (decreasing initial delay) the capture cross section increases. According to the SRH model, equation (4), the fraction of occupied medium deep traps increases. This results in a more pronounced DLTS peak. This behaviour of the DLTS peak is used to determine the activation energy E_σ of the capture cross section. The DLTS activation energy E_{a0} of the medium deep trap was taken from the temperature shift of the DLTS peak with initial delay. The inset of figure 2 shows the Arrhenius plot of $(t_i T^2)$ yielding $E_{a0} = 0.328$ meV after standard DLTS evaluation. In the numerical simulation of the DLTS spectra the values of the net concentration of shallow donors, N_S, and the concentration of the medium deep
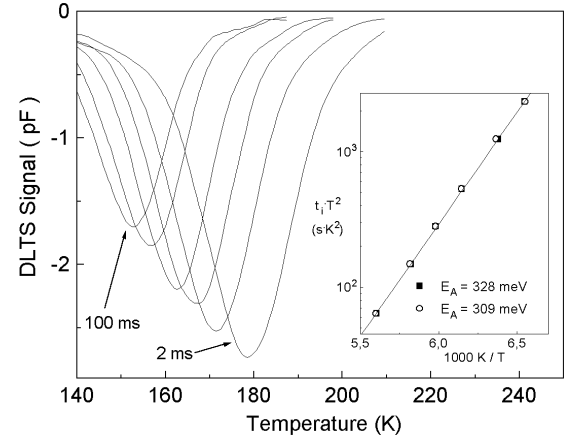

Figure 2. DLTS curves of EL6 measured on n-type GaAs with pulse width $t_p = 50$ μs, bias voltage $V_0 = -6$ V, pulse voltage $V_1 = -1$ V. The initial delays are $t_i = 2, 5, 10, 50$ and 100 ms, respectively. Inset: corresponding Arrhenius plot; squares—standard evaluation, circles—simulation procedure.

trap, N_{DD}, as obtained by TDH measurements, were used. However, it should be noted that deviations from the used trap concentration have only a negligible influence on the determination of E_σ [14]. The pulse parameters (filling time, t_p, repetition time, pulse voltage, V_1, and the bias voltage, V_0) are arbitrarily chosen parameters of the DLTS apparatus. The parameters E_σ and σ_a are unknown. The numerical algorithm for the determination of the activation energy E_σ of the capture cross section is given in the following.

(1) All peaks $\Delta C(t_i)$ of the measured DLTS curves and the calculated ones are normalized to that of the highest value belonging to the shortest initial delay $t_{i,min}$ (see figure 3). This procedure corresponds to the graphical estimation of the capture cross section activation energy E_σ by Zhao *et al* [14] and excludes the area of the Schottky contact as a source of error.

(2) In the numerical calculations of the DLTS spectra the parameters E_σ and σ_a are the remaining undetermined parameters. From the temperature dependence of the spectra σ_a can be determined for a given E_σ. This E_σ allows the calculation of the normalized peak heights as a function of emission rate e_n, which is correlated to the initial delay t_i (see figure 3).

(3) The above calculation is repeated for different values of E_σ. The comparison of the experimental normalized DLTS peak heights with the calculated curves gives an estimation of the activation energy E_σ of the capture cross section.

In figure 3 the calculated DLTS peak heights of the normalized spectra are plotted versus the initial delay t_i, e.g. for a pulse width of $t_p = 50$ μs. The comparison of the experimental data with the theoretical curves indicates a capture cross section activation energy $E_\sigma = (135 \pm 5)$ meV.

Five series of DLTS measurements were performed for different sets of pulse width ($t_p = 50$ or 100 μs), bias voltage ($V_0 = -6$ or -10 V) and pulse voltage ($V_1 = -1, \ldots, -4$ V), varying the initial delay between $t_i = (2, \ldots, 100)$ ms for each parameter set. Therefore, as a result
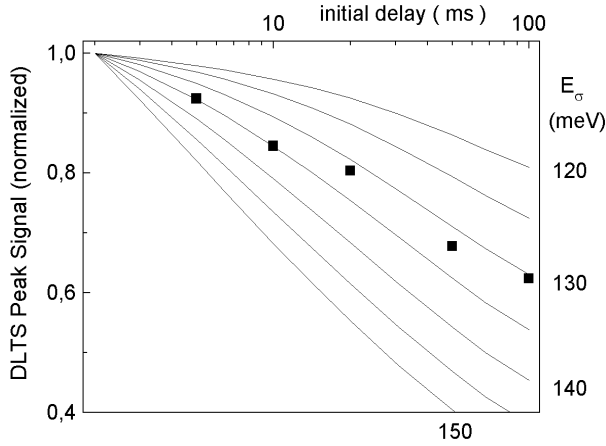
Figure 3. Peak height of calculated DLTS spectra versus initial delay t_i (curves) with DLTS parameters as in figure 2. Squares: experimental points for EL6 from figure 2.
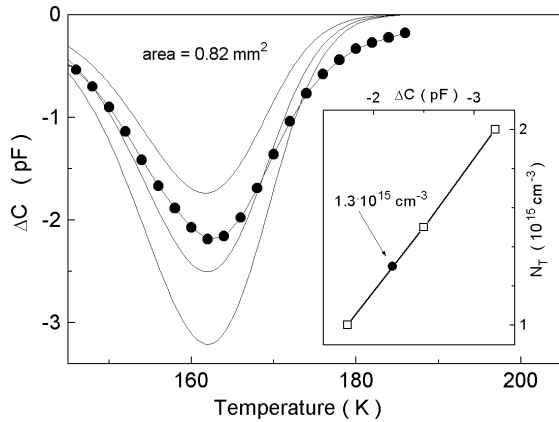

Figure 4. DLTS peaks calculated for different trap concentrations (curves). Dots: experimental results for EL6. Inset: evaluation of the trap concentration.

$E_\sigma = (135 \pm 10)$ meV and $\sigma_\infty = (2, \dots, 5) \times 10^{-15}$ cm^2 were obtained. The DLTS activation energy E_{a0} determined by the standard evaluation is only an approximation, because the emission transient is non-exponential. The described simulation procedure regarding the non-exponential transient also allows the determination of the emission rate e_n (for the peak temperature) and of a correct value of activation energy $E_{a0} = (305 \pm 15)$ meV (see figure 2).

Due to the non-exponential behaviour of the emission transient caused by the large trap density the commonly used method for the determination of the concentration by standard DLTS is not suitable. Therefore the concentration of EL6 was determined by comparing the measured DLTS curve with corresponding simulated curves (see evaluation procedure) taking into account the energy values and the area A of the investigated Schottky contact (figure 4). A value of $N_{EL6} = (1.3 \pm 0.3) \times 10^{15}$ cm^{-3} was obtained.

A field dependence of the emission rate of a defect (e.g. by the Poole–Frenkel effect) can influence the carrier emission from this defect and can also give rise to a non-exponential emission transient. However, our measurements performed under different bias conditions do not show such an effect and consequently a field dependence was not considered.

5. Discussion

Despite the large spread of the reported results [1, 3, 10, 11, 15] the consistency of the relevant values found in this investigation is remarkable. All measurements were carried out on the same sample, which is characterized by a clear dominant single DLTS peak of the electron trap EL6 (see figure 2). In other contemporary literature the simultaneous presence of different energetically neighbouring electron levels (EL6 group) [20] was often reported for bulk n-type GaAs.

Comparing the activation energy, $\Delta E_{DD0} = (178 \pm 10)$ meV as obtained by TDH with the equivalent quantity ΔE_{T0} resulting from DLTS experiments as the difference $E_{a0} - E_\sigma = \Delta E_{T0} = (170 \pm 20)$ meV, a good agreement can be stated. Thus, the hypothesis that the '0.15 eV donor' is identical with the medium deep electron trap EL6 is supported. The strong difference between the TDH and the DLTS activation energy is due to the unusually high value of the activation energy of the capture cross section.

In addition, it should be stressed that both defects are dominant in TDH and DLTS (besides EL2) and that the concentration of EL6 and of the 0.15 eV donor coincides very well quantitatively.

Both the agreement of the activation energies and of the concentrations of the two defects obtained by the different methods can be regarded as evidence for their identity.

Of course, the two levels must have the same temperature dependence ($\alpha_T = \alpha_{DD}$), if they are identical. Therefore, deducing the capture cross section σ_∞ according to equation (6b) $(g_0/g_1) \exp(\alpha_T/k)$ was replaced by the value $(g_0/g_1) \exp(\alpha_{DD}/k) = 1.6$ used in the TDH analysis. Considering this temperature dependence no remarkable change in the value of the capture cross section σ_∞ results.

The value of σ_∞ is only a rough estimation under the assumption that the temperature dependence of σ used in the model calculation (equation (5)) is valid. Nevertheless, this value is in the range of those reported by other authors [1, 2, 4, 14]. Moreover, the high value of σ_∞, including the strong temperature dependence, may explain the unusual behaviour of the trap kinetics known for the EL6: action as an effective recombination centre in n-type bulk GaAs [2], a slow carrier capture kinetics in TSC [21, 22] and DLTS [20] experiments, a large Frank–Condon shift [9], a remarkable metastable behaviour of the T5 defect (EL6) [22] and of the 0.15 eV donor (TDH) [23, 24].

As a matter of fact, the microscopic structure of defects cannot be identified by electrical measurements. In the literature different models exist. Some authors correlate EL6 and also the 0.15 eV donor (TDH) with an As-vacancy complex [24, 25]. An As vacancy as a constituent of the EL6 defect has been clearly proved by positron annihilation [25].

Acknowledgments

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