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Time-resolved measurements on $^2T_2 \rightarrow {}^2E$ photoluminescence of Ti^{3+} in GaP

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The time dependence of the $^2T_2 \rightarrow {}^2E$ photoluminescence transition of $\mathrm{Ti_{Ga}}^{3+}$ in GaP has been measured on semi-insulating, *p*-type conducting, and *n*-type conducting samples. A decay time $\tau_0 = 2.0$ μs was obtained at $T = 10$ K. The temperature dependence of the decay time in the conducting samples is found to be affected by the capture of free carriers by $\mathrm{Ti_{Ga}}^{3+}$ in the excited state whereas the results on *p*-type conducting samples suggest hole localization at the $\mathrm{Ti_{Ga}}^{3+}$.

I. INTRODUCTION

Titanium, as an impurity in GaP, has been extensively studied. It is known to introduce a donor level ($\mathrm{Ti_{Ga}}^{3+}/\mathrm{Ti_{Ga}}^{4+}$) at $E_v + 0.93$ eV (Ref. 1) and an acceptor level ($\mathrm{Ti_{Ga}}^{2+}/\mathrm{Ti_{Ga}}^{3+}$) at $E_c - 0.50$ eV (Refs. 1–3). An intense photoluminescence band with zero-phonon lines (ZPL) at 604.1 and 604.6 meV has been identified as the $^2T_2 \rightarrow {}^2E$ internal luminescence transition of $\mathrm{Ti_{Ga}}^{3+}$ (see Fig. 4 in Ref. 4). Zeeman spectroscopy experiments are found to be consistent with this assignment.[5] Photoluminescence excitation (PLE) spectra of this transition were investigated to clarify the different excitation processes terminating in the $^2T_2$ excited state of $\mathrm{Ti_{Ga}}^{3+}$.[6] In this paper we report time-resolved measurements performed on the $^2T_2 \rightarrow {}^2E$ internal luminescence of $\mathrm{Ti_{Ga}}^{3+}$ in GaP. These are complementary experiments to the PLE ones and allow one to analyze the deexcitation mechanisms.

II. EXPERIMENTAL DETAILS

The samples investigated in this paper were cut from liquid-encapsulated-Czochralski (LEC)-grown GaP:Ti and GaP:Ti:Zn boules investigated in earlier studies; their electrical properties are given by Ulrici *et al.*[4] In the *n*-type conducting sample (NA1), all the Ti impurities are in the Ti^{2+} charge state, whereas in the *n*-type semi-insulating sample (NE) the Fermi level is pinned by the $\mathrm{Ti_{Ga}}^{2+}/\mathrm{Ti_{Ga}}^{3+}$ level and both charge states are present. The *p*-type conducting PM1 sample contains Ti only in the Ti^{4+} charge state in thermal equilibrium, and temperature-dependent Hall measurements reveal an activation energy of 50 meV caused by the Zn acceptors.

In Fig. 1 the experimental setup for the time-resolved photoluminescence (PL) experiments is shown. The excitation is performed by a pulsed yttrium aluminum garnet (YAG):Nd laser coupled with a dye laser and a Raman shifter that allows one to cover the excitation range from the visible region up to 2 μm in the near-infrared range. The 15-ns pulse has an energy of 900 mJ at 1.06 μm. A cooled InSb detector is used to measure the PL signal integrated with a bandpass optical filter that fits the $\mathrm{Ti_{Ga}}^{3+}$ internal emission band.

The electrical signal is amplified and recorded with a digital oscilloscope. The decay time of the detector after a laser pulse is 800 ns. As detailed in Ref. 7, this explains the rise time of about 400 ns observed in all measured transients.

III. RESULTS

The *n*-type semi-insulating *NE* sample has been excited with photon energies corresponding to two different excitation mechanisms already analyzed by Roura *et al.*[6]

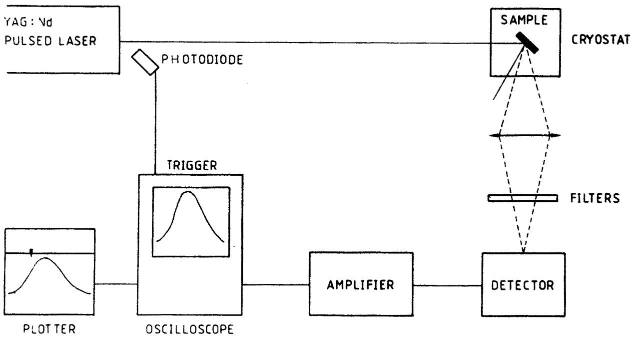

FIG. 1. Schematics of the experimental setup.

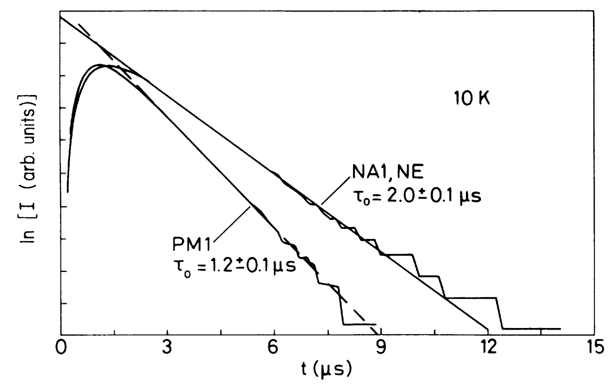

FIG. 2. Photoluminescence transients measured at $T = 10$ K after excitation with a laser pulse in the samples *NE* (*n*-type semi-insulating), *NA*1 (*n*-type conducting), and *PM*1 (*p*-type conducting). The straight line fits the exponential decay. The rise time is due to the detector response time.

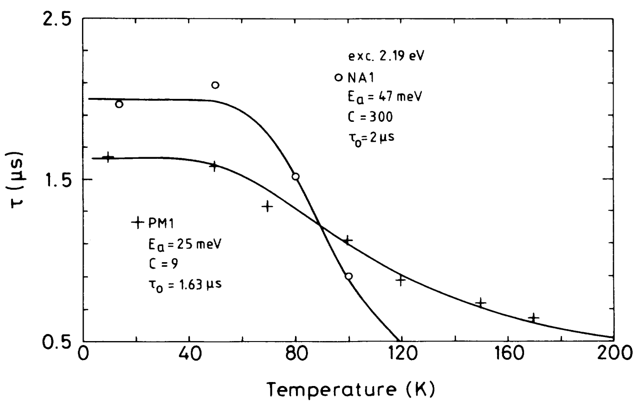

FIG. 4. Temperature dependence of the decay-time constant of the *n*-type conducting *NA*1 and *p*-type conducting *PM*1 samples with the excitation energy 2.19 eV. The solid curves are the fit with relation (1) and the given parameters.

The Ti^{3+} intracenter excitation is performed with photons of 0.73 eV, whereas the more subtle Ti^{2+} photoneutralization, which leaves the Ti^{3+} in its excited state

$$\mathrm{Ti}^{2+} + h\nu \rightarrow (\mathrm{Ti}^{3+})^* + e_{cb} \quad (A \text{ mechanism})$$

is carried out with photons of 2.19 and 1.7 eV. Figure 2 shows the PL transient measured after the laser pulse at $T = 10$ K. The time dependence is exactly the same for all mentioned excitation energies. After the rise time due to the detector response, the PL intensity decreases with a time constant $\tau_0 = 2.0 \pm 0.1$ μs. No deviations from the exponential behavior have been observed before the signal has been reduced by a factor of 50. In Fig. 3 the temperature dependence of the decay time τ is shown. The experimental points are fitted with the standard model[8] that supposes a competing multiphonon decay process with the time constant

$$\tau_{nr} = \tau_\infty \exp(-E_a/kT) \; .$$

The overall decay time is

$$\tau(T) = \tau_0 / [1 + C \exp(-E_a/kT)] \; . \qquad (1)$$

The parameters $E_a = 158$ meV and $C = \tau_0/\tau_\infty = 10^3$ are obtained from the fit.

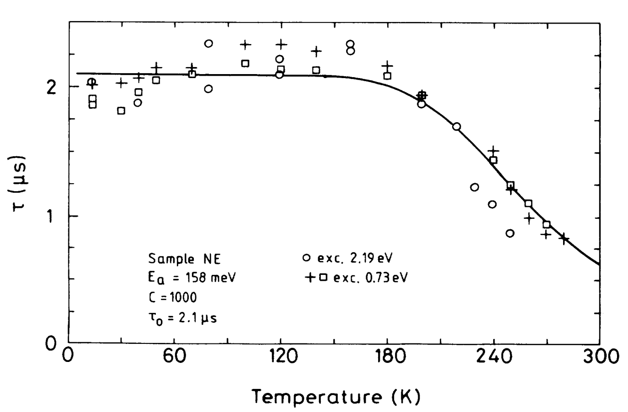

FIG. 3. Temperature dependence of the decay-time constant of the *NE* sample for the two excitation energies 0.73 and 2.19 eV. The solid curve is the fit with relation (1) and the given parameters.

The samples *NA*1 and *PM*1 (*n*- and *p*-type conductors) have been excited with 2.19-eV photons. In the case of the *NA*1 sample, this corresponds to the excitation by the *A* mechanism described above. At $T = 10$ K a transient very similar to that of the *NE* sample is measured. However, above 50 K the transients became faster as shown in Fig. 4. Fitting with relation (1) gives $E_a = 47$ meV and $\tau_0/\tau_\infty = 300$.

In the case of the *PM*1 sample the excitation mechanism involved is the photoneutralization of Ti^{4+}, which leaves the Ti^{3+} in its excited state

$$\mathrm{Ti}^{4+} + h\nu \rightarrow (\mathrm{Ti}^{3+})^* + \mathrm{hole}_{\mathrm{VB}} \quad (B \text{ mechanism}) \; .$$

Surprisingly, the PL transient is already at $T = 10$ K faster than in the other samples (see Fig. 2), giving $\tau_0 = 1.6$ μs. Figure 4 shows the temperature dependence fitted with the parameter $E_a = 25$ meV and $\tau_0/\tau_\infty = 9$.

IV. DISCUSSION

A. The lifetime of the excited $^2T_2$ state

The identical decay behavior for different excitation energies (see Fig. 3), together with the PLE results[6] of the *NE* sample, indicate that we investigate the decay of the $^2T_2 \rightarrow {}^2E$ PL of $\mathrm{Ti_{Ga}}^{3+}$. The lifetime $\tau_0 = 2.0 \pm 0.1$ μs measured at low temperature is for the same order of magnitude as those found for other symmetry-allowed electric-dipole $T_2 \leftrightarrow E$ transitions of transition-metal impurities on group-sites in III-V semiconductors. Examples are the $^5T_2 \rightarrow {}^5E$ transitions of Fe^{2+} in GaAs ($\tau_0 = 10$ μs), GaP ($\tau_0 = 15$ μs), InP ($\tau_0 = 11$ μs), and the $^2E \rightarrow {}^2T_2$ transitions of Ni^+ in GaAs ($\tau_0 = 4$ μs) and GaP ($\tau_0 = 9$ μs).[9,10]

These τ_0 values measured at low temperature ($T < 20$ K) are usually interpreted as due to pure radiative transitions with the transition probability

$$\tau_r^{-1} \sim |\langle T|r|E\rangle|^2 . \tag{2}$$

As for GaP:Ti^{3+}, the ZPL's at 604.1 and 604.6 meV have been found also by thermally detected optical absorption (TD-OA),[11] we have to conclude that a certain part of the electrons excited optically into the $^2T_2$ state recombine nonradiatively. TD-OA or calorimetric absorption spectroscopy (CAS) (Ref. 12) detects only that part of the absorbed light which is transformed to heat and detected by a thermometer. The ZPL's have been measured by TFD-OA experiments also for the $^2T_2 \rightarrow {}^2E$ transition of GaP:Ni$^+$ (Ref. 13) and the $^5E \rightarrow {}^2T_2$ transition of GaP:Fe^{2+}.[14]

For a quantitative evaluation of the nonradiative recombinations, measurements could be carried out comparing the total absorbed light by the $^2E \rightarrow {}^2T_2$ transition (e.g., by Fourier-transform absorption spectroscopy) and that part of the absorbed light transformed to heat by nonradiative recombination (by TD-OA). Since thermally detected absorption is a very sensitive method, the nonradiative part may be quite small.[12] However, such a quantitative evaluation is considerably restricted as, by reabsorption of the PL light together with multiple reflections within the sample, the thermally detected part is strongly enhanced and a correction using theoretical models is not very accurate.

For an estimation we calculate the radiative lifetime τ_{ZPL} connected with the ZPL's at 604.1 and 604.6 meV (Ref. 15)

$$\tau_{\mathrm{ZPL}}^{-1} = \frac{8\pi n^2 \nu^2}{c^2} \frac{g_1}{g_u} \int \sigma(\nu) d\nu \tag{3}$$

using the measured absorption cross section $\int \sigma(\nu) d\nu$ of the ZPL's given by Ulrici *et al.*[4] and the degeneracies of the ground state $g_1 = 4$ and the excited state $g_u = 6$;[16] n is the refraction index. A value of $\tau_{\mathrm{ZPL}}^{-1} = (2.3 \pm 1) \times 10^4\ \mathrm{s}^{-1}$ is obtained. This can be compared with the experimental value $\tau_{\mathrm{ZPL}}^{-1} = 2.5 \pm 0.5 \times 10^4\ \mathrm{s}^{-1}$ derived from the measured $\tau_0 / \tau_{\mathrm{ZPL}} = I_{\mathrm{ZPL}} / I_b$, where $I_b / I_{\mathrm{ZPL}} = 20$ is the ratio of the integrated PL intensities of the phonon side-band spectrum and the ZPL's. As can be seen, the large uncertainties on τ_{ZPL}^{-1} do not allow one to evaluate the nonradiative part of the recombination.

B. Free-carrier capture by the $^2T_2$ excited state

In both the n- and p-type conducting samples the transients become thermally activated at much lower temperatures than the semi-insulating *NE* sample. Therefore, a competing deexcitation process different from the multiphonon decay must be effective in order to explain this behavior. In the following, arguments are given that the transients become faster in conducting GaP:Ti samples due to free-carrier capture by Ti^{3+} in its excited $^2T_2$ state.

In the conducting samples, Ti^{3+} is not present without excitation and it disappears after the laser pulse. Thus, Ti^{3+} in its excited state (Ti^{3+})* can reach the ground state not only by the recombination within the Ti^{3+} but it can alternatively capture a free carrier (an electron from the conduction band or a hole from the valence band in the *NA* or *PM* samples, respectively). In the case of the p-type conducting *PM*1 sample this capture process is

$$(\mathrm{Ti}^{3+})^* + (\mathrm{hole})_{VB} \rightarrow \mathrm{Ti}^{4+} . \tag{4}$$

If the hole concentration p is much higher than the Ti^{3+} concentration so that it remains constant during the PL decay, the capture will be exponential with the probability

$$\tau_p^{-1} = p \sigma_p^* v_p , \tag{5}$$

where $v_p \sim T^{1/2}$ is the thermal velocity of the holes, $\sigma_p^* = \sigma_{p\infty}^* \exp(-\Delta E / kT)$ is the hole cross section of the (Ti^{3+})*, and $p \sim T^{3/2} \exp(-E_H / kT)$ the hole concentration with $E_H = 50$ meV and p (300 K) $\approx 2 \times 10^{17}\ \mathrm{cm}^{-3}$ from Hall measurements. Therefore, the temperature dependence of τ_p^{-1} is given by

$$\tau_p^{-1} \sim T^2 \exp[-(E_H + \Delta E)/kT] . \tag{6}$$

Considering this hole-capture process, the time constant of the PL transient will be

$$\tau^{-1} = \tau_0^{-1} + \tau_p^{-1} . \tag{7}$$

Therefore, from the different τ values measured on the *NE* and *PM*1 samples (Figs. 3 and 4), the τ_p values at the different temperatures can be calculated from a

$$\ln(\tau_p T^2)^{-1} = f(1/T)$$

plot according to relation (6). An activation energy of 4 meV is derived. This results in an unreasonable negative activation energy ΔE of the hole-capture cross section. Moreover, at $T = 10$ K, the PL decay is also exponential (see Fig. 2), whereas the hole concentration at this temperature is too low and cannot be considered to be constant during the capture transient. Furthermore, at $T = 150$ K all acceptors are ionized and σ_p^* can be calculated according to relation (5) with the derived τ_p^{-1} after (7). This gives a value of about $10^{-18}\ \mathrm{cm}^2$, whereas typical values of the capture cross section for neutral deep impurities are 10^{-15} to $10^{-16}\ \mathrm{cm}^2$.

These results require modification of the hole capture process, proposing that it takes place in two steps: (i) in a very short time the hole will be bound to the (Ti^{3+})* center; (ii) this bound hole recombines, forming Ti^{4+} and τ_p is the lifetime of the bound hole. The overall process is exponential as measured because the slower step (ii) is always exponential, independently of the hole concentration. At $T = 10$ K the lifetime of the bound hole is $\tau_p = 7.5\ \mu\mathrm{s}$.

A similar model was used to explain the PL transients of the $^5T_2 \rightarrow {}^5E$ transition of $\mathrm{Fe_{Ga}}^{2+}$ in GaP.[18] For this system the hole was assumed to be bound to the $\mathrm{Fe_{Ga}}^{2+}$ by the Coulomb potential and a lifetime of 12 μs was found. In the case of neutral $\mathrm{Ti_{Ga}}^{3+}$ the hole can be bound by the defect polarization potential.[19] For the n-type conducting sample the data points are not sufficient to discuss it in detail, but also in this case any kind of free-carrier capture seems to affect the time dependence of the $^2T_2 \to {}^2E$ PL transients.

V. CONCLUSIONS

Time-resolved PL measurements on *n*-type semi-insulating GaP:Ti reveal, at low temperature, a decay time $\tau_0 = 2.0 \pm 0.1$ μs for the $^2T_2 \to {}^2E$ transition of $\mathrm{Ti_{Ga}}^{3+}$. This value is of the same order of magnitude as that found for other $T_2 \leftrightarrow E$ transitions of transition-metal impurities in III-V semiconductors. A nonradiative part of the $^2T_2 \to {}^2E$ recombination is obviously also present at very low temperatures, but its quantity is difficult to evaluate. From the comparison of the temperature dependence of the decay time measured for semi-insulating and conducting (*p* as well as *n*) GaP:Ti samples, it is derived that a decay process additional to the multiphonon decay is effective in the conducting samples. It is suggested that this process is connected with the capture of free carriers by $\mathrm{Ti_{Ga}}^{3+}$ in its excited $^2T_2$ state. The proposed model for *p*-type conducting samples with the hole localized at the excited $\mathrm{Ti_{Ga}}^{3+}$ explains the available results but has to be verified by experiments on samples with different hole concentrations.

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[1] P. Roura, G. Brémond, A. Nouailhat, G. Guillot, and W. Ulrici, Appl. Phys. Lett. **51**, 1696 (1987).

[2] G. Brémond, P. Roura, G. Guillot, and W. Ulrici, Semicond. Sci. Technol. **6**, 85 (1991).

[3] P. Roura, J. R. Morante, G. Brémond, T. Benyattou, G. Guillot, and W. Ulrici, Appl. Surf. Sci. **50**, 496 (1991).

[4] W. Ulrici, K. Friedland, L. Eaves, D. P. Halliday, and C. A. Payling, Phys. Status Solidi B **150**, 177 (1988).

[5] D. P. Halliday, C. A. Payling, M. K. Saker, M. S. Skolnick, W. Ulrici, and L. Eaves, Semicond. Sci. Technol. **2**, 679 (1987).

[6] P. Roura, G. Guillot, T. Benyattou, and W. Ulrici, Semicond. Sci. Technol. **6**, 36 (1991).

[7] P. Roura, T. Benyattou, G. Guillot, R. Moncorge, and W. Ulrici, Semicond. Sci. Technol. **4**, 943 (1989).

[8] R. Renz and H. J. Schultz, J. Phys. C **16**, 4117 (1983).

[9] J. Crasemann and H. J. Schultz, in *Defects in Semiconductors*, edited by H. J. von Bardeleben, Vols. **10-12** of Mater. Sci. Forum (Trans Tech, Aedermannsdorf, Switzerland, 1986), p. 693.

[10] P. B. Klein, J. E. Furneaux and R. L. Henry, Phys. Rev. B **29**, 1947 (1984).

[11] A. M. Vasson (private communication).

[12] A. Juhl and D. Bimberg, J. Appl. Phys. **64**, 303 (1988).

[13] A. Erramli, M.S.G. Al-Ahmadi, W. Ulrici, N. Tebbal, J. Kreissl, A. M. Vasson, A. Vasson, and C. A. Bates, J. Phys. Condens. Matter **3**, 6345 (1991).

[14] T. Wolf, D. Bimberg, and W. Ulrici, Phys. Rev. B **43**, 10 004 (1991).

[15] B. Di Bartolo, *Optical Interaction in Solids* (Wiley, New York, 1968).

[16] By uniaxial stress experiments on the sharp absorption lines at 604.1, 604.6, and 607.9 meV of GaP:Ti^{3+} it has been unequivocally shown that the 604.1-meV line has to be assigned to the $^2E(\Gamma_8) \to {}^2T_2(\Gamma_8)$ transition and the 604.6-meV line to the $^2E(\Gamma_8) \to {}^2E_2(\Gamma_7)$ transition (Ref. 17); this means the Jahn-Teller reduced spin-orbit splitting of the $^2T_2$ state amounts to only about 0.5 meV and the 607.9-meV line is of vibronic origin.

[17] B. Clerjaud *et al.* (unpublished).

[18] P. B. Klein and K. Weiser, Solid State Commun. **41**, 365 (1982).

[19] M. Lax, Phys. Rev. **119**, 1502 (1960).