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Optically induced recharging of titanium in semi-insulating GaAs

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Abstract. Semi-insulating GaAs: Ti was investigated by thermally detected (TD) EPR and TD optical absorption. The resonance at $g = 1.935$ and the absorption spectrum with ZPL at 566.0 meV are assigned to Ti_{Ga}^{3+}. The spectral dependence of their intensities upon illumination indicates the photoinduced recharging $Ti_{Ga}^{3+} \rightarrow Ti_{Ga}^{2+}$ with the preceding photoexcitation of the donor electron from $EL2^0$.

Substitutional titanium in GaAs has been investigated in recent years by capacitance spectroscopy (DLTS, DLOS) [1–3], optical absorption (OA) [3–5], photoluminescence (PL) [5], Zeeman effect [5, 6] and by electron paramagnetic resonance (EPR) [7, 8]. These experiments have revealed the existence of the Ti^{2+}/Ti^{3+} acceptor level at $E_c - 0.20$ eV and the Ti^{3+}/Ti^{4+} donor level at $E_v + 0.6$ eV within the gap, and an assignment of several spectroscopic features to the impurities Ti_{Ga}^{2+} and Ti_{Ga}^{3+} could be made with some certainty. However, the behaviour of Ti_{Ga} in GaAs is not yet fully understood, especially the correlation of the titanium related features measured by different experiments and the electron–phonon coupling of the electronic states of Ti_{Ga}^{2+} and Ti_{Ga}^{3+}.

This paper presents the results of thermally detected EPR (TDEPR) and thermally detected optical absorption (TDOA) experiments on semi-insulating (SI) GaAs: Ti. The advantages of these techniques, especially for studying phonon-coupled impurities in semiconductors, have been described elsewhere [9–11]. Using these techniques, the change in the intensities of the Ti_{Ga}^{3+} and Ti_{Ga}^{2+} features upon sub-bandgap illumination is monitored and permits a correlation between them as well as suggestions for the optically induced recharging mechanisms in SI GaAs: Ti.

The samples were cut from a LEC-grown boule (50 mm in diameter, 130 mm long) doped with 1 mg Ti per 1 g GaAs. The entire boule (5ISTW 1) is semi-insulating ($\rho \simeq 10^7\ \Omega$ cm at $T = 300$ K) with its electrical properties similar to that of undoped SI GaAs (but with a lower mobility, $\mu_H \simeq 2 \times 10^3\ cm^2\ V^{-1}\ s^{-1}$), i.e. the Fermi level is pinned by the $EL2^0/EL2^+$ level and not by the Ti^{3+}/Ti^{4+} level as has been checked by temperature-dependent Hall effect and optical absorption studies. The Ti content in the tail end (samples EO) is about $1.5 \times 10^{16}\ cm^{-3}$ from spectrochemical analysis in accordance with

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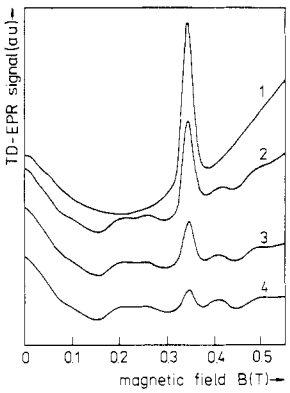

Figure 1. TDEPR spectra of SI GaAs:Ti (sample EO) measured at 9.3 GHz and $T \simeq 5$ K. Curve 1: after cooling in the dark; curves 2 to 4: after illumination with $h\nu_{exc} = 0.79$ eV, 1.03 eV and 1.38 eV, respectively.

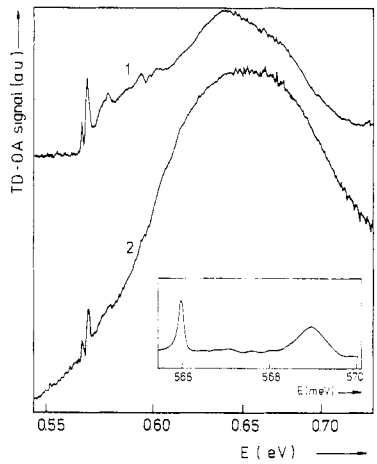

Figure 2. Thermally detected optical absorption (TDOA) spectra of SI GaAs:Ti (EO) measured at $T = 1.7$ K. Curve 1: after cooling in the dark; curve 2: after illumination with $h\nu_{exc} = 1.24$ eV. The inset shows the TDOA spectrum in the region of the two sharp lines measured with high resolution.

the distribution coefficient $k_{eff} \simeq 3 \times 10^{-5}$ [3] of Ti in GaAs. The experiments described here were carried out on EO samples because of their higher Ti-content. The same results have been observed on seed end samples, though less pronounced. The dimensions of the samples were $6 \times 7 \times 15$ mm^3 with the 15 mm side $\|\langle 110 \rangle$ direction, and all faces were polished. In the TDOA studies, the absorbing thickness was 6 mm. The equipment used for the TDEPR and TDOA studies are those described in [9, 10].

Curve 1 in figure 1 shows the TDEPR spectrum of a SI GaAs: Ti sample (EO) measured at $T \simeq 5$ K after cooling in the dark. It consists of one intense isotropic resonance line. Its position was measured as a function of the microwave frequency between 8.0 GHz and 12.4 GHz and gives $g = 1.9353 \pm 0.0012$. Since in this SI GaAs:Ti, all the Ti is in the Ti^{3+} charge state and the g-value coincides with that of the isotropic signal assigned to Ti^{3+}_{Ga} in the conventional EPR spectrum [7], we interpret the TDEPR line as due to Ti^{3+}_{Ga}. This is supported by the result that this signal is not saturated. Such a behaviour is expected for a d^1 impurity with a ^2E ground state because of its short spin–lattice relaxation time. Curves 2 to 4 in figure 1 are measured after illumination (the light of a tungsten lamp filtered by metal interference filters was guided to the sample in the resonator with an optical fibre). For photon energies $h\nu_{exc} > 0.7$ eV the Ti^{3+} signal drastically decreases and a new spectrum appears.

Curve 1 in figure 2 is the TDOA spectrum of the same sample measured at $T = 1.7$ K after cooling in the dark. The sharp lines at 566 and 569 meV, the phonon sidebands, and the overall bandshape coincide exactly with those measured by conventional OA on GaAs: Ti and are assigned to the $^2E \rightarrow {}^2T_2$ transition of Ti^{3+}_{Ga} (see figure 11 in [3]). After illumination with $h\nu_{exc} > 0.7$ eV (see curve 2 in figure 2) the intensity of the sharp lines and of the phonon replica of the Ti^{3+}_{Ga} spectrum are strongly decreased indicating a change of the Ti_{Ga} charge state. On the other hand, the absorption in the region of the broad band between 0.55 eV and 0.75 eV is considerably enhanced and can be explained

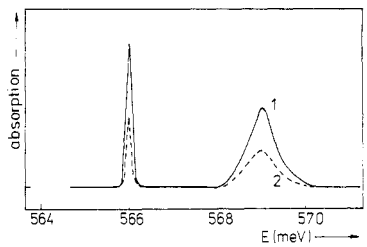

Figure 3. Conventional optical absorption spectra of SI GaAs:Ti (EO) measured at $T = 5$ K with high resolution. Curve 1: after cooling in the dark; curve 2: after illumination with $h\nu_{exc} = 1.3$ eV.

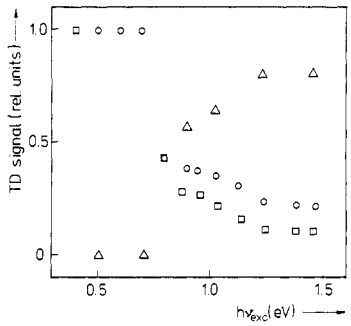

Figure 4. Dependence of the photoinduced changes on light energy $h\nu_{exc}$ measured on SI GaAs:Ti (EO): □, TDEPR signal intensity of Ti^{3+}_{Ga}; ○, intensity of the 566 meV line of Ti^{3+}_{Ga} measured by TDOA (close to the data points of the 569 meV line); △, intensity of the $^3A_2 \rightarrow {}^3T_1(F)$ absorption band of Ti^{2+}_{Ga} derived from the TDOA spectra.

as follows. Simultaneously with the decrease of the broad Ti^{3+} absorption band, a new broad band appears with a maximum at 0.66 eV which has to be assigned to the $^3A_2 \rightarrow {}^3T_1(F)$ transition of Ti^{2+}_{Ga} (see figure 12 in [3] and figure 1 in [5]). The inset in figure 2 shows the sharp lines measured by TDOA with higher resolution. Both the halfwidth of the lines and the ratio of their intensities are the same as those measured by conventional optical absorption (cooled PbS detector) using the same spectral resolution (see figure 3).

The photoinduced change of the spectroscopic features described above, assigned to Ti^{3+}_{Ga} and Ti^{2+}_{Ga}, with the light energy $h\nu_{exc}$ is shown in figure 4. It can be seen that with the onset at $h\nu_{exc} \simeq 0.7$ eV both the TDEPR signal and the 566 meV ZPL (zero phonon line) of Ti^{3+}_{Ga} decrease with very similar spectral dependence whereas the $^3A_2 \rightarrow {}^3T_1(F)$ absorption band of Ti^{2+}_{Ga} increases analogously. The lineshape of the Ti^{2+} band for the different $h\nu_{exc}$ was obtained by subtracting the lineshape of the Ti^{3+}_{Ga} band, reduced by a factor taken from the decrease of the 566 meV line, from the measured band. The slow decay in the dark of the photoinduced changes, as observed for several photoinduced rechargings involving transition metal impurities in GaAs and GaP [12], was not detectable in the present experiments.

TDOA as well as OA measurements in the region 0.8 to 1.5 eV show the well known broad absorption due to $EL2^0$ with the ZPL at 1.039 eV. This $EL2^0$ absorption decreases under illumination with light $1.0 \text{ eV} < h\nu_{exc} < 1.40$ eV because of the transformation $EL2^0 \rightarrow EL2^*$ into the metastable state of EL2 [13]. This transformation does not occur in undoped SI GaAs for $h\nu_{exc} > 1.40$ eV. However, illumination of the SI GaAs:Ti samples with $h\nu_{exc} = 1.46$ eV reduces the 1.039 eV ZPL intensity to about 0.5 of the dark value. Therefore, this reduction, not explicable by the $EL2^0 \rightarrow EL2^*$ transformation, should be related to the Ti_{Ga} recharging.

These experiments strongly suggest that the EPR signal at $g = 1.953$ (curve 1 of figure 1) and the optical spectrum with ZPL at 566 meV (curve 1 of figure 2) belong to the same Ti^{3+}_{Ga} centre and that illumination with $h\nu_{exc} > 0.7$ eV effects a recharging of $Ti^{3+}_{Ga} \rightarrow Ti^{2+}_{Ga}$. Consequently, the recharging mechanism most probably occurring is

$$EL2^0 + h\nu_{exc} \rightarrow EL2^+ + e_{CB} \quad (1)$$

$$Ti_{Ga}^{3+} + e_{CB} \rightarrow Ti_{Ga}^{2+}. \quad (2)$$

This means that an electron from the filled deep-donor $EL2^0$ is excited by illumination into the conduction band (e_{CB}) and afterwards this e_{CB} can be captured by Ti_{Ga}^{3+} forming Ti_{Ga}^{2+}. Additional excitation processes can contribute to (2) at higher h_{exc} (see the onset at 1.0 eV in figure 4), e.g. $EL2^+ + h\nu_{exc} \rightarrow EL2^{++} + e_{CB}$, $Ti_{Ga}^{3+} + h\nu_{exc} \rightarrow Ti_{Ga}^{4+} + e_{CB}$.

The new TDEPR lines appearing together with this recharging cannot be identified at present. Their interpretation as being due to Ti_{Ga}^{2+} ($^3A_2$ orbital singlet ground state) or $EL2^+$ can be unequivocally excluded. Although the paramagnetic centres $EL2^+$ exist (with a concentration $< 1 \times 10^{16}$ cm^{-3}) after illumination, according to (1) and (2), their lines are small and masked by the unidentified spectrum so that they cannot be detected. The dependence on microwave frequency of this new photoinduced TDEPR spectrum is very similar to that of the V^{2+}(II) spectrum in GaAs [14]. However, there are no arguments at all in favour of the presence of vanadium in the samples, except we assume this V^{2+}(II) centre being extremely strongly phonon-coupled, so that already about 10^{14} centres per cm^3 can give rise to a detectable spectrum. The presence of such a small amount of V cannot be excluded.

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