# Absorption spectra of Ti-doped GaAs

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We observed the $3d^1$ intracenter transition $^2E \rightarrow {}^2T_2$ in semiconductor crystals having a tetrahedral crystal field. The absorption was measured in Ti-doped melt-grown GaAs crystals. The spectrum consists of two sharp zero-phonon lines at 0.566 and 0.569 eV and of some broad phonon features with a maximum at 0.64 eV. The $Ti^{3+}(3d^1)$ spectrum can only be observed in high-resistivity GaAs crystals. In $n$-type conducting crystals the compensation of titanium acceptors leads to the appearance of the $Ti^{2+}(3d^2)$ intracenter transitions at 0.66 and 1.01 eV. The corresponding single-acceptor level $Ti^{3+}/Ti^{2+}$ was identified to be at $0.23 \pm 0.01$ eV below the conduction band on the basis of deep-level transient spectroscopy and capacitance transient measurements.

The optical spectra of substitutional titanium in II-VI semiconductors have been known for some time (see, for example, Refs. 1 and 2). In contrast, there is very little knowledge concerning the behavior of titanium in III-V compounds.[3] Bekmuratov and Murygin[4] have found a titanium-related acceptor level at $E_c - 0.45$ eV from Hall-effect measurements on Ti-doped GaAs grown by the liquid encapsulated Czochralski (LEC) technique. They have also reported some features in the photoconductivity and absorption spectra at 1.04 and 0.7 eV, which they have interpreted as titanium-related levels. On the other hand, it has been suggested by Stevenson, Ketrush, Chand, and Borchewesky[5] that titanium does not compensate donor impurities but removes them during crystal growth. These authors studied layers of Ti-doped GaAs obtained by the liquid-phase epitaxy (LPE) technique. They have also identified a deep level at $E_v + 0.64$ eV in their crystals from Hall-effect measurements of $p$-type layers. A few papers have reported some luminescence spectra of Ti-doped GaAs and GaP.[6-8] Most of these results were obtained on implanted samples[7,8] where the observed spectra can depend upon the post-implantation annealing,[9] making their interpretation rather difficult. Very recently, Ulrici, Eaves, Friedland, and Halliday[10] presented the first absorption spectrum of titanium in GaAs. However, as will be shown in this paper, they observed a composite of different absorption spectra which was erroneously attributed to only one of the titanium charge states $[Ti^{2+}(3d^2)]$.

In this paper two different absorption spectra of substitutional titanium in GaAs are reported for the first time. These spectra were observed separately for Fermi-level positions above and below the titanium-related acceptor, which was found to be located at 0.23 eV below the conduction-band minimum by means of deep-level transient spectroscopy (DLTS) and Hall-effect measurements.

Three types of Ti-doped GaAs crystals grown in our laboratory were studied. Melt-grown crystals were prepared by the LEC and the horizontal Bridgman (HB) techniques, while solution-grown crystals were obtained using liquid-phase electroepitaxy (LPEE).[11] Some of the crystals were additionally doped with selenium or silicon to facilitate electrical characterization.

From the Hall-effect measurements, we have found that titanium doping decreases the concentation of free electrons. Furthermore, the 77-K electron mobility values were consistently lower than those at 300 K. This behavior is similar to that of GaAs doped with vanadium,[12] and it indicates that titanium also introduces an acceptor level.

This level was found in all three types of GaAs crystals by means of DLTS and detailed capacitance transient measurements. From a standard thermal activation plot of the electron emission rate (Fig. 1), the energy of this trap was found to be $0.23 \pm 0.01$ eV below the conduction-band minimum with an electron-capture cross section $\sigma_n$ of about
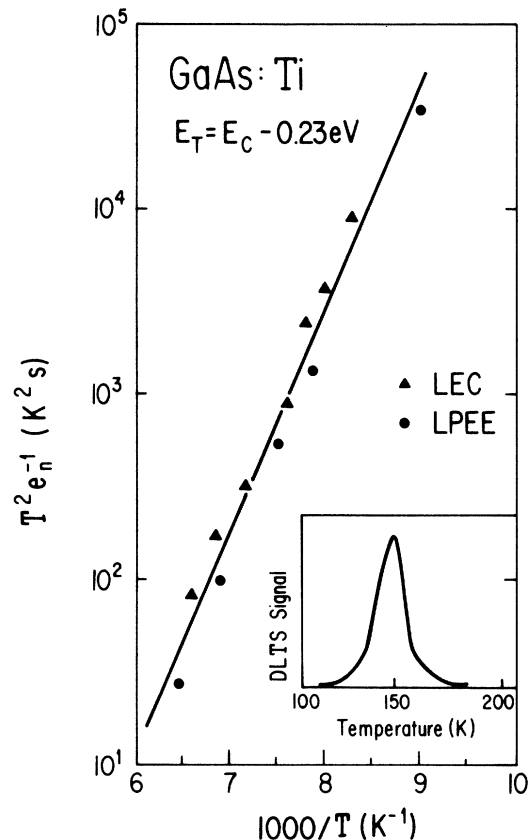


FIG. 1. Emission-rate thermal activation plot $T^2 e_n^{-1}$ vs $10^3/T$ for titanium-related trap in LPEE- and LEC-grown GaAs. (Inset: DLTS spectrum of this trap in arbitrary units, bias: $-5$ V, filling pulse amplitude 6 V, $t_1/t_2 = 5$ ms/10 ms.)

$4 \times 10^{-14}$ cm$^2$. By carrying out precise measurements of this cross section as a function of temperature (using short-duration filling pulses) we determined the ratio $\sigma_n(80$ K)$/\sigma_n(160$ K) to be about 0.6. Consequently, the electron-capture cross section activation energy, which could introduce an uncertainty in the obtained value of the binding energy, was found to be smaller than our experimental error (0.01 eV).

The assignment of this level to titanium is based on the following arguments: (1) The 0.23-eV trap is present in Ti-doped LPEE samples, which otherwise do not contain any electron traps. (2) An electron trap with this energy and capture cross section is not present in over 100 LEC and HB GaAs titanium-free crystals grown in this laboratory. (3) The intensity of the corresponding DLTS peak in different crystals is well correlated with the intensity of the titanium absorption bands shown in Fig. 3. (4) Two different titanium absorption spectra (shown in Figs. 2 and 3) are observed for the Fermi-level positions above and below the 0.23-eV level. (5) The concentration of the electron traps in the melt-grown crystals is on the order of $10^{16}$ cm$^{-3}$, which corresponds to the Ti concentration estimated from these absorption spectra.

Features 1–5 cannot be attributed to any known impurity in GaAs. Thus, they should be related to titanium rather than to contaminants introduced during Ti doping.

The absorption measurements were performed at 5 K on all our Ti-doped GaAs crystals. In the case of the LPEE crystals, the Ti concentration obtained from DLTS is on the order of $10^{14}$ cm$^{-3}$, making absorption measurements difficult.

An absorption spectrum of a melt-grown crystal is shown in Fig. 2. One can see two sharp zero-phonon lines (ZPL's) at 0.566 and 0.569 eV (4567 and 4591 cm$^{-1}$—values corrected to the vacuum) followed by some broad phonon features with a maximum at 0.64 eV. From the temperature dependence of the ZPL's, it can be deduced that both correspond to transitions from a ground state to a two-level excited state. Furthermore, an additional broad absorption band between 1.25 and 1.5 eV has also been observed. The
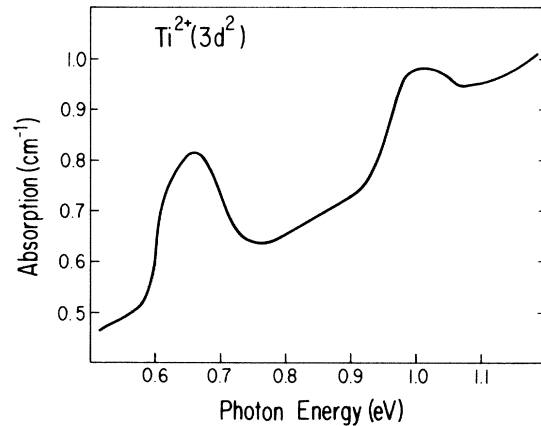


FIG. 3. Optical-absorption spectrum of Ti- and Se-doped GaAs at 5 K.

intensity of this higher-energy absorption is correlated with the ZPL's intensity in all of our samples.

All of the above absorption features disappear in $n$-type Ti-doped GaAs, where Ti is compensated with Se or Si doping, and new bands appear. As shown in Fig. 3, the new absorption spectrum consists of two broad, structureless bands at 0.66 and 1.01 eV, respectively. Their relative intensities remain at a ratio of approximately 2:1 in all our crystals. Both bands are superimposed on a monotonically increasing absorption background, which starts at about 0.3 eV. The shapes and energy widths of the 0.64- (Fig. 2), 0.66-, and 1.01-eV (Fig. 3) bands are typical for intracenter transitions within the $3d^n$ shell of the substitutional Ti.[1-3] The remaining broad absorptions correspond, most likely, to photoionizing band-to-level transitions. From the intensities of these absorption spectra, one can estimate the concentration of the absorbing centers as being on the order of $10^{16}$ cm$^{-3}$. It should also be mentioned that both spectra presented in Figs. 2 and 3 were partially obscured by the well-known $EL2$ absorption band,[13] which was photoquenched by white light illumination at liquid-helium temperature.

These arguments prove clearly that we observed the absorption spectra of two different charge states of the substitutional titanium acceptor level in GaAs located at $E_c - 0.23$ eV. The remaining problem is their identification. In principle, the level in question could be either the Ti$^{3+}(3d^1)$/Ti$^{2+}(3d^2)$ single-acceptor level or the Ti$^{2+}(3d^2)$/Ti$^{1+}(3d^3)$ double-acceptor level. Several arguments, however, favor the single-acceptor assignment. For the Ti$^{3+}(3d^1)$ electronic configuration, one can expect to observe only one intracenter absorption transition ($^2E \rightarrow {}^2T_2$) with the ZPL's due to a spin-orbit splitting of the excited $^2T_2$ triplet (Fig. 4). This splitting should be on the order of a few millielectronvolts.[14] All of these elements correspond exactly to the experimental results. One could also expect to observe an emission transition ($^2T_2 \rightarrow {}^2E$) corresponding to the same Ti$^{3+}(3d^1)$ absorption. In this case, however, there should be only one ZPL observed (Fig. 4). Such a luminescence band with a ZPL at 0.566 eV was reported by Ulrici, Eaves, Friedland, and Halliday[10] for Ti-doped GaAs. Furthermore, for the Ti$^{2+}(3d^2)$ electronic configurations one can expect two strong intracenter absorption bands [$^3A_2 \rightarrow {}^3T_1(F)$ and $^3A_2 \rightarrow {}^3T_1(P)$]
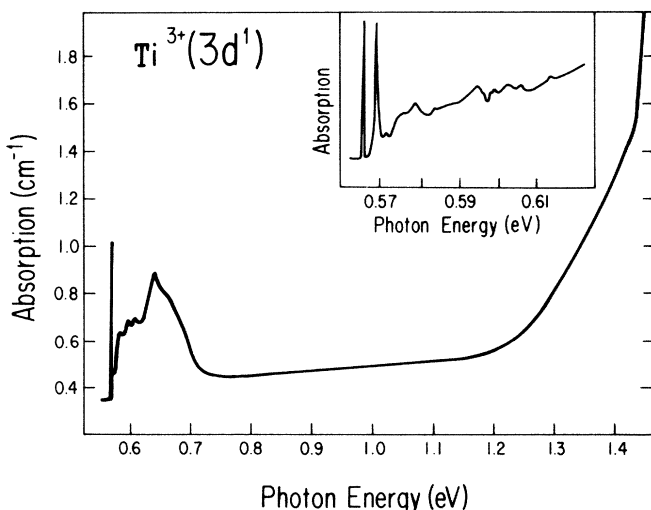


FIG. 2. Optical-absorption spectrum of Ti-doped GaAs at 5 K. (Inset: low-energy part of the spectrum shown with higher resolution.)
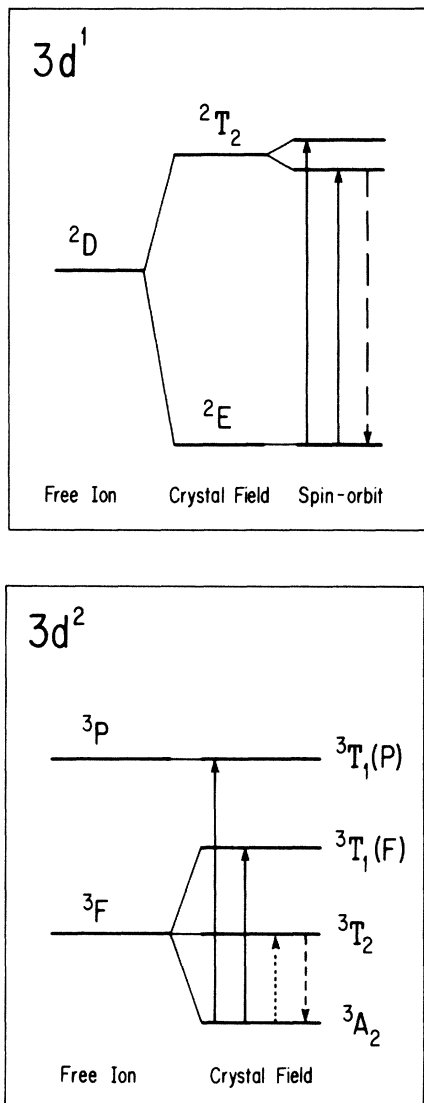
FIG. 4. Energy-level scheme for the $3d^1$ and $3d^2$ electronic configurations in a tetrahedral crystal field. Solid lines, absorption; dotted line, forbidden absorption; dashed lines, emission (not to scale).

as is observed in the II-VI compounds[1,2] (Fig. 4). This fact again corresponds very well with our experimental results.

Predictions in the literature[15-17] place the Ti double-acceptor level in the GaAs-conduction band, and the Ti single-acceptor level $Ti^{3+}/Ti^{2+}$ deeper in the energy gap than the V single-acceptor level $V^{3+}/V^{2+}$, located at $E_c - 0.15$ eV.[12]

If one were to consider the double-acceptor hypothesis, an important difficulty is soon apparent. The absorption band with the ZPL's presented in Fig. 2 should be interpreted as the $^3A_2 \rightarrow {}^3T_1(F)$ transition of the $Ti^{2+}(3d^2)$ charge state (Fig. 4). This was the case for the $V^{3+}(3d^2)$ charge state in GaAs and other III-V compounds,[3] where the second $^3A_2 \rightarrow {}^3T_1(P)$ transition is covered by the absorption edge of GaAs. Consequently, the corresponding luminescence spectrum with a ZPL at 0.566 eV observed by Ulrici, Eaves, Friedland, and Halliday[10] must be interpreted as the $^3T_1(F) \rightarrow {}^3A_2$ transition, in complete disagreement with the entire $V^{3+}(3d^2)$ energy scheme.[3] The luminescence of the $V^{3+}$ charge state in the III-V compounds is, indeed, observed from the lowest $^3T_2$ excited state. This state is difficult to observe in absorption, since the $^3A_2 \rightarrow {}^3T_2$ transition is symmetry forbidden. We therefore cannot account for the optical spectra of Ti in GaAs using the double-acceptor state hypothesis. Furthermore, we have recently identified the Ti donor level $Ti^{4+}/Ti^{3+}$ at $E_c - 1.0$ eV, which will be published elsewhere.[18]

In conclusion, we attribute the new absorption spectra of Ti in GaAs as due to the intracenter transition of the $Ti^{3+}(3d^1)$ charge state (the ZPL's and the low-energy band in Fig. 2) and the $Ti^{2+}(3d^2)$ charge state (both bands in Fig. 3). Consequently, the observed electron trap at $E_c - 0.23$ eV is attributed to the $Ti^{3+}/Ti^{2+}$ single-acceptor level. In addition, the broad absorption band at 1.25 V (Fig. 2) corresponds to the transition from the valence band to the empty acceptor level

$$Ti^{3+}(3d^1) + h\nu + e_{\overline{VB}} \rightarrow Ti^{2+}(3d^2) \ ,$$
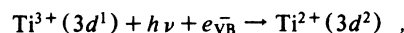
and the continuous absorption background in Fig. 3 most probably corresponds to the reverse transition

$$Ti^{2+}(3d^2) + h\nu \rightarrow Ti^{3+}(3d^1) + e_{\overline{CB}} \ .$$
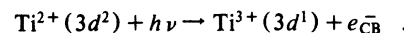
Using this model, we can explain some of the results of Bekmuratov and Murygin[4] (the indicated level $E_c - 0.45$ eV was not observed in the present study). Both excited states of the $Ti^{2+}(3d^2)$ are degenerate with the conduction band of GaAs, in which case the intracenter transitions can also be observed in photoconductivity due to the autoionization effect.[3] The $^3T_2$ excited state is probably also degenerate with the conduction band, and the emission $^3T_2 \rightarrow {}^3A_2$ cannot be observed. A luminescence band with a ZPL at 0.655 eV observed in $n$-type implanted samples[7,8] is, therefore, more likely associated with Ti-related complexes than with isolated titanium impurities due to its annealing characteristics.

To the best of our knowledge, this paper presents the first observation and positive interpretation of the $3d^1$ intracenter transition in semiconductor crystals with a tetrahedral crystal field.

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