

Signature of the gallium-oxygen-gallium defect in GaAs by deep level transient spectroscopy measurements

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Experimental results of deep level transient spectroscopy (DLTS) and Fourier transform infrared spectroscopy (FTIR) on oxygen-doped GaAs crystals are presented. A positive identification of the DLTS signature of the Ga-O-Ga defect (tentatively identified as an oxygen-arsenic vacancy complex) is made through correlation with FTIR measurements. The energy level for the two-electron state of the defect is found to be located at 0.55 eV below the conduction band, and direct proof is given that this center is actually a negative U center. A calibration factor for local vibrational mode absorption is calculated to be $8 \times 10^{16} \text{ cm}^{-1}$.

The role of oxygen in GaAs has been investigated since it was discovered that doping with oxygen caused GaAs to turn semi-insulating (SI).¹ It was thought that oxygen was a component of the major deep donor level EL2, but evidence against this assignment was presented by Huber *et al.*² The primary effect of oxygen was found to be the suppression of the Si concentration (with deposition of SiO₂ on the crucible walls) causing the formation of SI GaAs.³ Later it was proposed that oxygen could constitute a part of another mid gap level designated by either ELO⁴ or EL2O.⁵ This center has an activation energy very close to EL2, but a capture cross section about four times greater than EL2. The uncertainty caused by difficulties in interpretation of deep level transient spectroscopy (DLTS) spectra in heavily compensated samples proved this assignment inconclusive.⁶

The recent identification of local vibrational modes (LVMs) due to oxygen⁷ has once again increased the interest in identifying whether there are deep levels due to oxygen in GaAs. Two different defect centers have been discovered using infrared spectroscopy: an isolated interstitial oxygen (O_i), and a Ga-O-Ga defect which appears to be analogous to the A center in Si.⁸ The isolated interstitial is not electrically active, a behavior that is similar to the oxygen interstitial in Si, subsequently the position of its LVM lines is not affected by the position of the Fermi level or illumination. The LVMs of the Ga-O-Ga center, however, are photosensitive and three distinct groups of lines have been observed under optical excitation.⁹ The center can exist in three different charge states being occupied by zero, one, or two electrons. The location of corresponding levels was determined by thermal deactivation of optically populated Ga-O-Ga levels in SI GaAs. The thermal ionization energy of the first electron ionization energy was found to be 0.14 eV and that of the second to be 0.57 eV providing a strong argument that the center exhibits a negative U property.¹⁰ In this letter we present identification of the DLTS signature of oxygen-induced defects in GaAs.

The growth part of this study has been performed by

the Electronic Materials Group at Massachusetts Institute of Technology utilizing a horizontal Bridgman (HB) system with a quartz boat. A total of six ingots intentionally doped with oxygen have been grown using two different doping methods: Ga₂O₃ added to the melt, or the growth ampoule was filled with an oxygen overpressure. These crystals were then either slowly cooled to room temperature or quenched rapidly after growth. The major difficulty in growing crystals for this study is the very narrow window for oxygen and doping concentrations which must be achieved. The oxygen detection limit for optical absorption measurements is $2 \times 10^{15} \text{ cm}^{-3}$ (see discussion). The carrier concentration, though, must be at least several times that amount to allow for DLTS interpretation, yet lower than $2 \times 10^{16} \text{ cm}^{-3}$ in order to keep the free-carrier absorption from obscuring the LVM lines. A number of crystals were either too resistive or had too high a carrier concentration, limiting the number of acceptable samples. The two high oxygen crystals in Fig. 3 came from crystals that were doped with oxygen by using an overpressure of ¹⁸O₂ in the ampoule (240 Torr at room temperature) and quenching after growth. These samples came from the seed and tail portions of the crystal used by Schneider *et al.*,⁷ and had $(N_D - N_A) = 1.2\text{--}0.8 \times 10^{16} \text{ cm}^{-3}$ measured at $T = 200 \text{ K}$. It is interesting to note that we observe the free-electron concentration decreasing in going from the seed to the tail end, with the very end turning *p* type (the *p* type portions were not used in our study). DLTS measurements gave an EL2 concentration of $1.4\text{--}1.0 \times 10^{16} \text{ cm}^{-3}$, which is a typical concentration of this defect in HB GaAs. There were quite a few samples with oxygen concentrations below the detection limit for Fourier transform infrared spectroscopy (FTIR) measurements and accordingly low trap concentrations as detected by DLTS.

High-resolution FTIR measurements were made on the samples at liquid nitrogen temperatures with a long pass filter ($\lambda_{\text{cutoff}} = 1400 \text{ cm}^{-1}$) in front of the sample. For both samples, the LVM bands occurring at 845 cm^{-1} (O_i) and at 715 cm^{-1} (Ga-O-Ga) were present, as well as

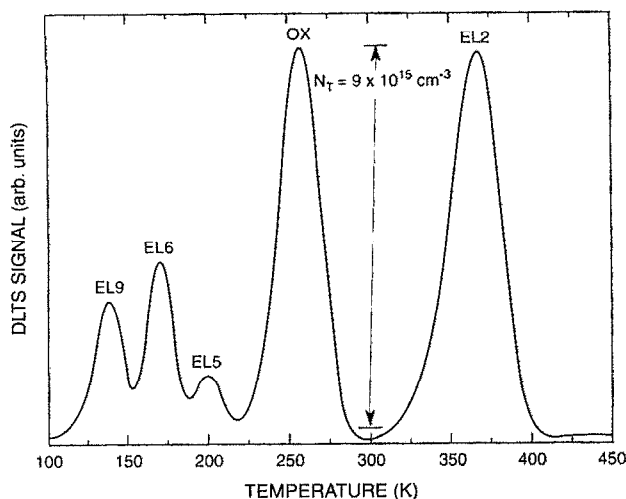


FIG. 1. DLTS spectrum of horizontal Bridgman grown GaAs doped with oxygen.

bands at 802 cm^{-1} (O_i) and 679 cm^{-1} (Ga-O-Ga) in the ^{18}O doped samples. The fact that only the 715 cm^{-1} line was present in our samples indicated that the Fermi level was close to the conduction band, and that the samples were n type. No other peaks due to oxygen were observable in the range from 1400 to 600 cm^{-1} . All samples showed a characteristic broadband absorption due to free carriers and the intensity of this background agreed well with the carrier concentration as measured by capacitance-voltage measurements.

The samples for the transient capacitance measurements were prepared by alloying InSn (50-50) to the polished surface to make ohmic contacts, and evaporating Au to make Schottky diodes. The current-voltage characteristics were tested to ensure that the diodes had a leakage current below 10^{-7} A/cm^2 at the applied reverse bias. Transient capacitance measurements were performed using both a standard DLTS method and by recording and an-

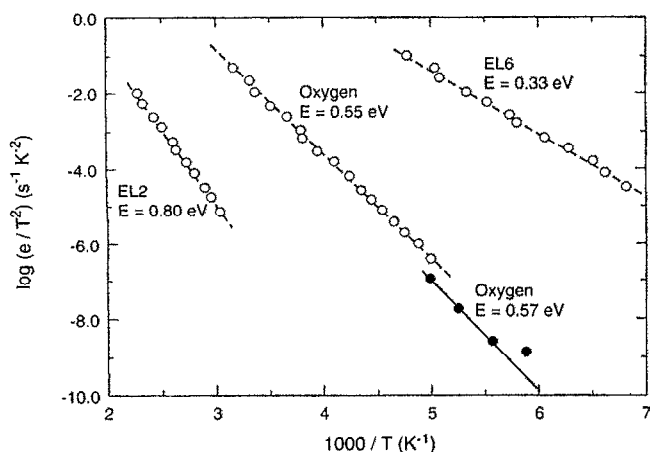


FIG. 2. Arrhenius plot of transient capacitance (open circles and broken lines) and FTIR (closed circles and solid line) measurements. Trap energies are given in electron volts below the conduction band edge.

TABLE I. DLTS peak temperatures, activation energies, and tentative assignments for spectrum shown in Fig. 1.

Peak temperature (K)	Activation energy ^a (eV)	Assignment ^b	Activation energy ^b (eV)
375	0.80	EL2	0.825
255	0.55	EL3	0.575
200	0.43	EL5	0.42
170	0.33	EL6	0.35
140	0.23	EL9	0.225

^aThis experiment.

^bReference 11.

alyzing whole transients.

Figure 1 shows a DLTS spectrum obtained on the seed end of the oxygen-doped crystal using a rate window of 50 s^{-1} , and a reverse bias of -5 V . Five peaks were observed with activation energies listed in Table I. Comparing the data in Table I to values catalogued by Martin *et al.*,¹¹ tentative assignments were made and are shown in Fig. 1. In addition to the activation energy, the capture cross section for the 255 K peak was calculated and found to be $1.3 \times 10^{-13}\text{ cm}^2$. This value is within the range for the capture cross section of EL3 ($0.8\text{--}1.7 \times 10^{-13}\text{ cm}^2$) as given by Martin *et al.*¹¹ Two major peaks are located at 375 and 255 K , with the high temperature peak due to the well known EL2 defect. Arrhenius plots were used to determine the activation energies of the traps, and some of these are shown in Fig. 2 (open circles and dashed lines). The peak located at 255 K in Fig. 1 (designated OX) has an activation energy of about 0.55 eV , which is close to that observed by Skowronski *et al.*¹⁰ for the ionization energy of the second electron from the Ga-O-Ga center by optical measurements. Their data are also shown in Fig. 2 (closed circles and solid line). The emission rates and activation energies are within experimental error considering the entirely different experimental setups used. Therefore we propose that the observed DLTS peak labeled OX in Fig. 1 is due to the ionization of the Ga-O-Ga center. Schneider *et al.*⁷ estimated the concentration of the Ga-O-Ga center in a sample from the same ingot to be $6.4 \times 10^{15}\text{ cm}^{-3}$, based

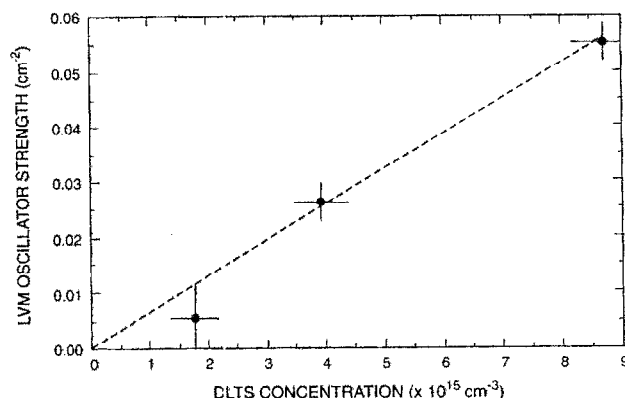


FIG. 3. Plot of the correlation between the 715 cm^{-1} LVM band oscillator strength and the DLTS concentration for the Ga-O-Ga defect.

on an assumed value of the effective charge η . This estimate is in the same range as the concentration of the OX center from DLTS spectra.

There were two previous reports on DLTS measurements on vapor phase epitaxy layers intentionally doped with oxygen.^{12,13} Both reported a peak located at approximately the same position, but no positive assignments were made at that time.

In order to confirm that the OX trap is due to the Ga-O-Ga defect, a correlation was made between the concentration given by DLTS and the LVM oscillator strength (integrated absorption) given by FTIR measurements. This correlation is shown in Fig. 3. The two points with the higher concentration came from the ^{18}O -doped sample, and include the LVM strength from both isotopes. The other point is from a sample which had an oxygen content close to the detection limit for FTIR measurements. It appears that there is a direct correlation between the two measurements of the defect which supports the identification of the DLTS peak as being due to the Ga-O-Ga center.

Additional support for this assignment comes from preliminary studies of the effects of annealing. Two samples underwent rapid thermal annealing at 1000 °C for 30 s. Both the absorption line intensity and the DLTS peak of the Ga-O-Ga defect decreased by about a factor of 3, indicating that these are due to the same defect center.

Lastly, one should discuss the negative U property of the center. If this were a center with two charge states in the usual order (positive U) in the band gap, then as the sample was heated one electron should be ionized first at a low temperature, and then at a higher temperature a second electron should also be ionized. In DLTS spectra this would correspond to two peaks of equal height at two different temperatures, since the trap would emit the same number of electrons at each temperature. With the activation energies known from optical measurements to be 0.14 and 0.55 eV, it is clear that no pair of peaks is observed. For a negative U center the energy required to ionize the second electron on the center is higher than that of the first electron, and therefore the temperature at which the second electron is emitted is also high enough to cause the first electron to be emitted immediately afterwards. The characteristic of this in DLTS measurements is a single peak at the temperature required to ionize the second electron with its height being twice the concentration of the center. Therefore, the lack of a DLTS peak with an acti-

vation energy of 0.14 eV provides proof that the Ga-O-Ga defect is a negative U center.

As stated before, the ionization energy derived from the Arrhenius plot is within the expected error of the ionization energy derived from earlier FTIR experiments. With this being a negative U center, the trap concentration recorded in Figs. 1 and 3 would actually be twice the true concentration. This would give concentrations of $4.4 \times 10^{15} \text{ cm}^{-3}$ for the seed end and $2.0 \times 10^{15} \text{ cm}^{-3}$ for the tail end samples. Both of these concentrations are lower than those given by Schneider *et al.*, but in their letter, they imply that their estimate is probably the upper limit of the concentration and could be lower if the value of η is greater as it is in the case of oxygen in silicon. From this observation and Fig. 3, one can obtain a calibration factor for the LVM oscillator strength of $8 \pm 1 \times 10^{16} \text{ cm}^{-1}$.

In conclusion, results of LVM absorption and DLTS measurements on the same samples have been correlated and a positive identification was made of the DLTS signature of Ga-O-Ga in GaAs. This level is located at 0.55 eV below the conduction band and corresponds to the two-electron state of the center. The DLTS measurements provide definite proof of the center's negative U property. Finally, the calibration factor for LVM absorption is found to be $8 \times 10^{16} \text{ cm}^{-1}$.

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