Deep electron traps in organometallic vapor phase grown $Al_xGa_{1-x}As$

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Deep electron traps have been studied by means of deep level transient spectroscopy in *n*-type nominally undoped and intentionally Te-doped $Al_xGa_{1-x}As$ epitaxial layers which were grown by vapor phase epitaxy from organometallic compounds (OMVPE). Three main deep electron levels are present in undoped material: a trap with an activation energy of 0.8 eV, which is also found in GaAs grown by conventional VPE, and two levels specific to OMVPE with activation energies of 0.32 and 0.38 eV, respectively. The concentration of the 0.8 eV level is found to be independent of the aluminum content x, supporting the assumption that it is not related to substitutional oxygen. The other levels, however, exhibit a very strong dependence of concentration on the composition, varying by four orders of magnitude in the range of $0 \leqslant x \leqslant 0.35$. In Te-doped samples, a level with an activation energy of 0.23 eV has been identified, which is thought to be related to an IR emission found in photoluminescence in OMVPE as well as in liquid phase epitaxial material.

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INTRODUCTION

The recent progress in the technology of vapor phase epitaxial growth of aluminum gallium arsenide from organometallic compounds (OMVPE) allows the growth of high quality epitaxial layers,[1] which have electron transport properties and radiative recombination efficiences comparable with liquid phase (LPE) grown layers. These achievements make the OMVPE technology applicable for the growth of device structures such as for light emitting devices, i.e., double heterostructure layers and LED's, and for solar cells and FET structures. In fact, good performance DH lasers have been reported fabricated by this technology,[2,3] making it competitive to the LPE process used conventionally.

The ability to grow material suitable for device application increases the interest in the electron transport properties and in the physical processes controlling them. Beside the characterization of shallow impurity identity[4] and carrier concentration and mobility,[5-7] the characterization of deep level (DL) properties is an important indicator of the material quality, since DL's may control minority-carrier lifetime and hence radiative recombination efficiency, which is important for optoelectronic device performance.

Using deep level transient spectroscopy (DLTS),[8] DL's have been thoroughly investigated in GaAs grown by various methods such as liquid phase epitaxy (LPE),[9] molecular beam epitaxy (MBE),[10] and VPE, both the conventional chloride process[11] and the OMVPE technique.[12] The results show some common features, such as the electron trap with an activation energy of 0.8 eV,[13] but some levels seem to be a characteristic of the particular technology used for epitaxy, e.g., Battacharya *et al.*[12] report an electron trap with ~ 0.36 eV activation energy which has been found only in OMVPE-grown GaAs, and not in material grown by other methods.

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In this paper we report on the investigation of deep electron traps in $Al_xGa_{1-x}As$ grown by the organometallic technique for aluminum concentrations between 0 (GaAs) and 0.35, the range of greatest interest for optoelectronic device structures. We also report the DLTS results for tellurium-doped $Al_xGa_{1-x}As$ and compare the results with those from investigations on Te-doped LPE material.

EXPERIMENTAL

The epitaxial layers were grown on Si-doped n^+ or on Cr-doped semi-insulating GaAs substrates oriented (100) to within $\pm 0.5°$. The growth was performed at 750 °C under inductive heating of a SiC-coated graphite pedestal in a vertical reactor.[1] Trimethylgallium (TMG) and trimethylaluminum (TMA) were used as the sources for gallium and aluminum, together with arsine. Hydrogen was used as the diluent gas. For intentional *n*-type doping, diethyltelluride (DeTe) was added. The ratio of As to the sum of the group III elements (V/III ratio) was in the range between 5 and 15. The DLTS results quoted in this report have been obtained from growth runs with various sources of arsine and TMG,[14] and proved to be independent of the gas supplier.

In order to obtain high-quality $Al_xGa_{1-x}As$, graphite baffles have been used which presumably lower the oxygen contamination of the gas stream.[1] Typical growth rates are about 0.15 μm/min and the thicknesses of the layers investigated were between 3 and 5 μm. The morphology of the layers was excellent, though they exhibit a low density of unique mesa-type defects[15]

Schottky contacts were fabricated by gold evaporation, and only diodes with good I/V characteristics were used for the DL analysis. The DL investigations were carried out using an automated DLTS system,[16] which provides a high resolution in both time and capacitance (5 μsec and 0.002 pF, respectively). Because of the ease and speed of the measurements, a large number of samples could be evaluated. The analysis of each sample was based on 16 or more spectra.

The majority-carrier (electron) traps are filled by the

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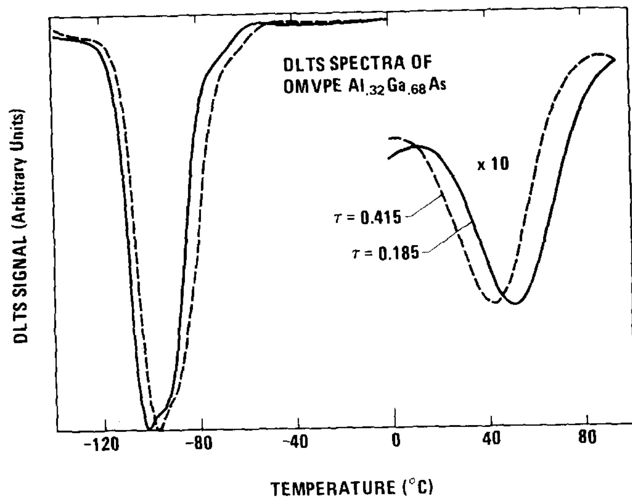

FIG. 1. Typical DLTS spectra of $Al_xGa_{1-x}As$ layers with $x = 0.32$. The spectra are for time constants of 0.185 ms (solid line) and 0.415 ms (dashed line), showing the signal of levels 1 and 2 between $-100\,^\circ$ and $-90\,^\circ$C, and of level 3 at approximately 45 °C.

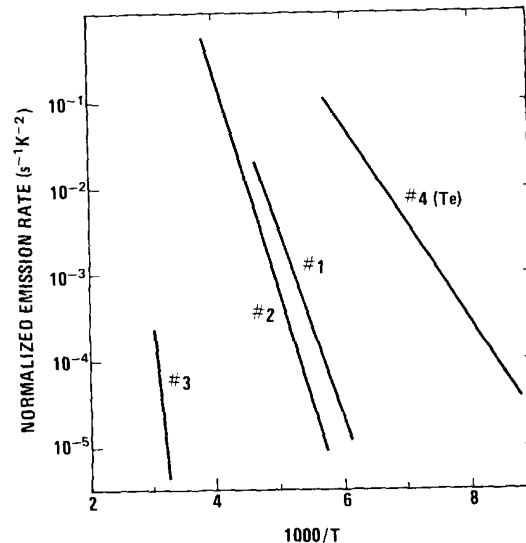

FIG. 2. Arrhenius plot of the normalized emission rate e/T^2 vs $1/T$ for the levels found in unintentionally doped (1–3) and in Te-doped (4) $Al_xGa_{1-x}As$.

application of a 1-ms pulse of zero voltage to the devices, and the capacitance transients are analyzed under reverse bias well below the diode breakdown voltage. The capacitance transients are due to the change of the depletion layer width which is caused by the thermal emission of electrons from the DL into the conduction band,

$$\Delta C = C(0)\exp(-t/\tau). \tag{1}$$

The emission rate e, equal to $1/\tau$, may be written

$$e = \sigma\langle v\rangle N_c \exp(-E_T/KT), \tag{2}$$

where σ is the DL cross section, $\langle v\rangle$ is the thermal velocity, and N_c is the conduction-band density of states. The data are analyzed in the manner developed for conventional DLTS measurements.[17] The capacitance change between times t_1 and t_2 (the DLTS signal) is plotted versus temperature. The value of T at which the maximum occurs is determined for several values of e, where experimentally

$$e = 1/\tau = \frac{\ln(t_1/t_2)}{t_1 - t_2}. \tag{3}$$

Since the pre-exponential term in Eq. (2) is proportional to T^2, the data are analyzed using an Arrhenius plot of e/T^2 versus reciprocal temperature. The slope yields the activation energy E_T and the $1/T = 0$ intercept yields σ.

Using the approximation that the DL concentration is much smaller than the shallow level concentration (which holds true in the most cases for our investigation, as is shown below), the concentration of the DL can be obtained as

$$N_T = 2(N_D - N_A)\,[\Delta C(0)/C], \tag{4}$$

where $\Delta C(0)/C$ is the ratio of the amplitude of the capacitance transient, immediately after the filling pulse, to the equilibrium capacitance.

TABLE I. Characteristics of electron traps observed in OMVPE $Al_xGa_{1-x}As$.

Level	Activation energy (eV)	Capture cross section (cm^{-2})
1	0.32	1.1×10^{-14}
2	0.38	3.8×10^{-14}
3	0.84	2.4×10^{-13}
4(Te)	0.23	6.1×10^{-15}

RESULTS AND DISCUSSION

Deep electron traps have been found in all the samples

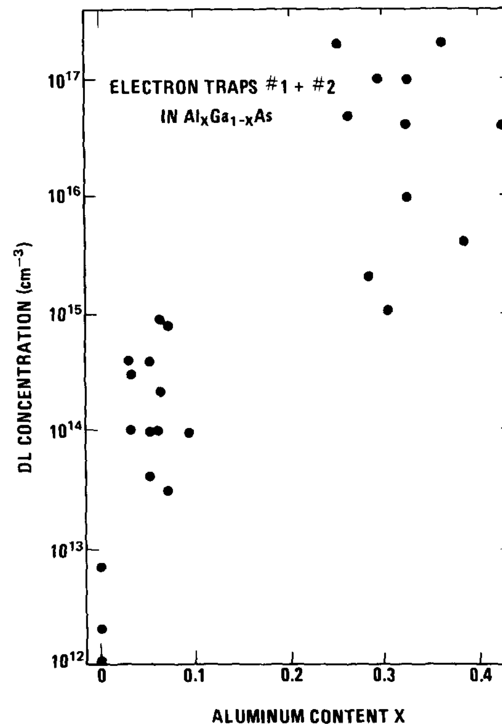

FIG. 3. Dependence of the concentration of electron levels 1 and 2 on the Al content in $Al_xGa_{1-x}As$.

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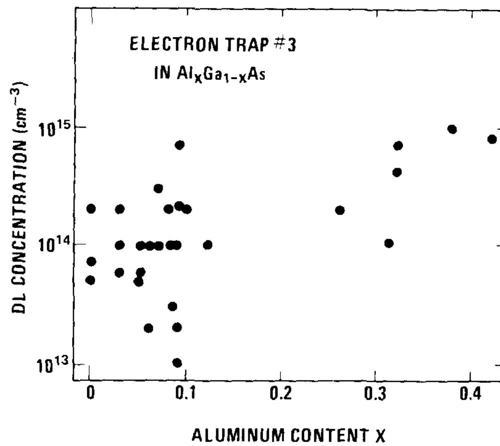

FIG. 4. Dependence of the concentration of electron level 3 on the Al content in $Al_xGa_{1-x}As$.

investigated. More than ten different electron traps were identified in OMVPE material. This report concentrates, however, on the investigation of three main electron levels, labeled by numbers 1–3, which have been found in all the samples, and a level 4 characteristic of Te-doped samples.

Figure 1 shows a typical DLTS spectrum of a nominally undoped sample with $x = 0.06$. In Fig. 2, the data points obtained from the DLTS spectra are plotted for the three main deep levels, as well as the Te related deep electron trap. The physical quantities obtained from the analysis of these data for levels 1–4 are given in Table I.

The most significant result of this investigation is the very strong composition dependence of the concentration of the two levels 1 and 2, located at ~ 0.32 and ~ 0.38 eV below the conduction band. In our experiments the two levels could not in all cases be distinguished unambiguously, since in the DLTS spectra the minima are very close together. This configuration, in general, can cause problems in the determination of the activation energy[18] and the concentration, and therefore we quote only concentration values which we determined from the peak height of the sum of both levels, representing approximately the sum of the two concentrations.

As can be seen from Fig. 3, the concentration of these levels is low, in the range of 10^{12}–10^{13} cm^{-3} for GaAs, but increases to 10^{16} or 10^{17} cm^{-3} as x increases to 0.35. Figure 3 illustrates this trend. The actual values, however, are less accurate in the high-concentration range, as the approximation of low DL concentration is no longer valid.

These two electron traps have been reported in GaAs grown by OMVPE, where a DL with 0.38 eV activation energy was found in two samples, and a 0.34 eV level in one sample.[12] The values are very close to our results, so it seems likely that the levels are the same as found here in GaAs and $Al_xGa_{1-x}As$. The chemical origin of these levels is still in question. From the results shown in Fig. 3, however, it is obvious that they are strongly related to the aluminum content. The fact that the levels can even be observed in GaAs might be explained by slight amounts of TMA unintentionally present in the system, since both the systems, ours and the one referred to in Ref. 12, were used for the deposition of both GaAs and $Al_xGa_{1-x}As$ epitaxial layers. From Fig. 3 one can see that the incorporation of the levels is superlinear with regard to the Al content being roughly proportional to x squared. This would mean that the DL concentration is related to a complex consisting of two defects which are induced by the TMA itself or by impurities carried with it. For the GaAs samples this would mean an unintentional Al content of less than $\sim 0.5\%$, a value which would not be detectable by the photoluminescence measurements used to determine x.

In contrast to the levels discussed above, the concentration of the third level which is found in all OMVPE samples is independent of the Al content. This can be seen from Fig. 4, which shows the concentration vs aluminum content. The defect is a deep electron trap with an activation energy of ~ 0.84 eV (nearly independent of x in the range 0–0.35) and a capture cross section of 2.4×10^{-13} cm^2. This level, labeled A, has been reported in the literature several times[11-13] and is the dominant electron trap found in GaAs grown by LPE and by conventional VPE. It was originally attributed to oxygen on an arsenic site, but in addition to earlier doubts a recent study[19] shows that this assignment is incorrect. The complete lack of dependence of the concentration of this level on the aluminum content would also strongly contradict the assignment to oxygen, as the main concern in VPE growth of $Al_xGa_{1-x}As$ is indeed the contamination with oxygen.[1] Another possible assignment of the 0.8 eV level is a gallium vacancy (or related complex), a hypothesis which could explain some other findings reported in the literature. For OMVPE,[12] as well as for chlorine-VPE GaAs,[11] an increase of the 0.8 eV concentration with increasing arsine partial pressure is reported, a finding which would be consistent with the assignment of the defect to a gallium vacancy or a complex containing a gallium vacancy. We attempted to verify the results of Ref. 12 on $Al_xGa_{1-x}As$ and found an increase of the concentration of the electron trap with the V/III ratio,[3] although the sample-to-sample scattering was higher than that reported in the GaAs study.[12]

Despite the analysis of a large number of samples with varying aluminum content, no composition dependence of the activation energies of levels 1–3 could be observed in excess of the sample-to-sample scattering of approximately ± 30 meV. This means that all the three electron traps are

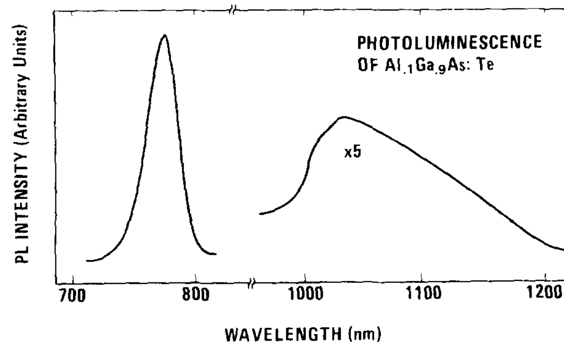

FIG. 5. Typical room-temperature photoluminescence spectrum of a Te-doped OMVPE $Al_{0.1}Ga_{0.9}As$ sample with a carrier concentration of 4×10^{18} cm^{-3}.

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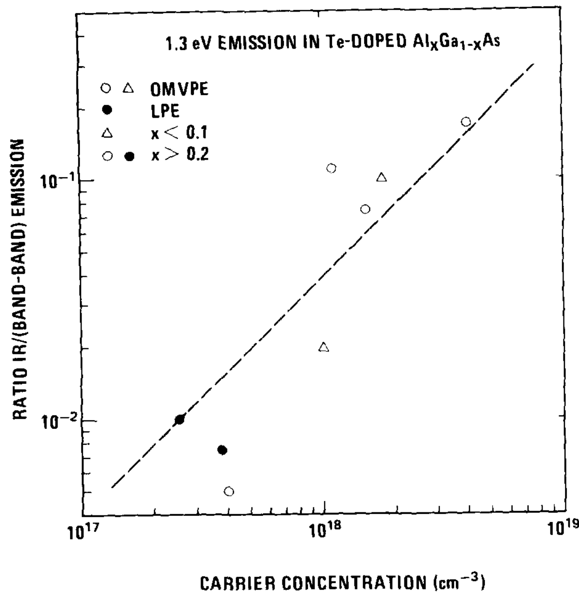

FIG. 6. Intensity ratio of the infrared to band-band emission of Te-doped samples as a function of the carrier concentration for both OMVPE and LPE $Al_xGa_{1-x}As$ layers.

tightly bound to the conduction band, as the band gap varies by 400 meV between $x = 0$ and $x = 0.35$.

n-type doping with tellurium introduces a characteristic level which is clearly distinct from those identified in unintentionally doped layers. The level 4 associated with Te has an activation energy of 0.23 eV and a capture cross section of 6.1×10^{-15} cm^2. It occurs in all Te-doped samples with a concentration between 0.005 and 0.015 times the doping concentration. Photoluminescence experiments on these samples reveal a characteristic emission in the infrared at around 950 nm. Figure 5 shows a typical photoluminescence spectrum of a Te-doped sample with a carrier concentration of 4×10^{18} cm^{-3}. The relative infrared emission intensity, as compared with the band-to-band recombination intensity, is related to the doping level, as shown in Fig. 6. For comparison, we investigated Te-doped epitaxial layers grown by LPE where we also found the IR emission (c.f. Fig. 6). The data were consistent with our OMVPE results. The IR peak shows a characteristic shift towards higher energies with increasing doping level, from 1.2 to 1.35 eV with n increasing from 4×10^{17} to 3×10^{18} cm^{-3}.

In summary, we have identified three main electron levels which are present in all samples of $Al_xGa_{1-x}As$ grown by OMVPE technique. An 0.8 eV electron trap, also found in GaAs grown by other techniques and reported to be related to either an oxygen impurity or a gallium vacancy, is incorporated in the crystal in concentrations around 10^{14} cm^{-3}, independent of alloy composition. The concentrations of two other levels with 0.32 and 0.38 eV activation energies exhibit a very strong dependence on the aluminum content x, increasing from 10^{12} to 10^{16} cm^{-3} between $x = 0$ (GaAs) and $x = 0.35$.

These latter levels have not been detected in GaAs or $Al_xGa_{1-x}As$ grown by methods other than OMVPE. A fourth level at 0.23 eV is reported which is related to the dopant Te. It could also be identified in LPE $Al_xGa_{1-x}As$.

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