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Prominent thermally stimulated current trap in low-temperature-grown molecular beam epitaxial GaAs

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By far, the largest thermally stimulated current trap in molecular beam epitaxial GaAs grown at 200–250 °C is \( T_5 \), with an activation energy of 0.27 eV and most likely related to \( V_{Ga} \). After an anneal at 300–350 °C, another trap \( T'_{5} \) appears, with an activation energy of 0.14 eV and closely identified with \( V_{As} \) or the complex, \( V_{As} - As_{Ga} \). Proposed defect reactions in this As-rich material include \( V_{Ga} + As_{Ga} \rightarrow V_{As} - As_{Ga} \), and \( V_{Ga} + As_{Ga} \rightarrow V_{Ga} - As_{Ga} \).

Molecular beam epitaxial (MBE) GaAs grown at low substrate temperatures (LT), 200–400 °C, has been shown to be uniquely useful in several device applications. Compared with the usual MBE GaAs, grown at 580–600 °C, the only major difference is a large concentration \( (10^{19} - 10^{20} \text{ cm}^{-3}) \) of point defects in the as-grown LT material, and smaller concentrations \( (10^{18} \text{ cm}^{-3}) \) of point defects along with large As precipitates after annealing at 550–600 °C. Because LT GaAs is known to be very As rich (1%–2% for \( T_G = 200 °C \)), the expected point defects are \( As_{Ga} \), \( As_{i} \), and \( V_{Ga} \), and indeed the \( As_{Ga} \) has been positively identified and there is good evidence for \( As_{i} \) or at least \( As \)_dimers. With all the point defects in the layers, it would be expected that abundant deep traps would be seen by the usual methods, i.e., deep level transient spectroscopy (DLTS) or thermally stimulated current (TSC) spectroscopy. In fact, however, DLTS is difficult because good Schottky barriers are nearly impossible to form, and TSC spectroscopy suffers from a high dark current due to hopping conduction.

The situation is illustrated in Fig. 1 which compares semi-insulating (SI) liquid-encapsulated Czochralski (LEC) substrate material with 2-μm-thick LT-MBE GaAs layers grown at 250 °C in a modified Varian 360 system and annealed at 300, 400, and 600 °C. The samples were irradiated with strong 1.46 eV laser light for 5 min at 82 K and then the temperature was swept upward. The LEC sample shows TSC peaks due to several deep traps, \( T_6 \), \( T_5 \), \( T_4 \), \( T_3 \), and \( T_2 \) before the dark current, controlled by \( EL_2 \) at \( E_C = 0.76 \pm 0.01 \text{ eV} \), takes over at about 250 K. The LT layers, on the other hand, show a much higher conductivity at low temperatures, due to hopping conduction among the \( As_{Ga} \) centers, but then an actual decrease in the dark current (negative TSC) below 140 K for the samples annealed at 400 and 600 °C. This decrease is now well understood and is due to the quenching of the \( As_{Ga} \) centers, which leads to the quenching of the hopping conduction; thus, the light which is used in the TSC experiment to fill the traps (1.46 eV laser light in this case) actually causes the dark current to decrease. However, the quenching does not take place for the as-grown sample or the one annealed at only 300 °C (shown in Fig. 1), so that it is possible to see a positive TSC current due to traps in these samples. Indeed, the peak known as \( T_5 \) \( (R = 0.27 \pm 0.02 \text{ eV}) \) appears strongly at 140 K and there is also some trap activity in the region around 80–90 K. Thus, it could be said that \( T_5 \) is the dominant trap (other than the \( As_{Ga} \)-related center at 0.64 ± 0.01 eV which is obscured by the dark current) in LT GaAs. It is also important to point out that the layers discussed here were separated from their respective substrates by a technique described earlier. We and others have seen several traps in LT layers which were not separated, but it is not always clear in such cases which traps are coming from the substrate and which from the layer of interest. The separation process itself does not produce any new traps, as found from other studies.

We have shown in an earlier work that the peak \( T_5 \) in LEC GaAs quenches with IR light and thermally recovers with nearly the same kinetics as those of \( EL_2 \), assuming that the \( EL_2 \) quenching can be represented by the IR photocurrent quenching. Thus, in that work we argued that \( T_5 \) either has a microscopic structure similar to that of \( EL_2 \), or else has its trapping process controlled by \( EL_2 \). For LT GaAs, the dominant donor (\( As_{Ga} \)-related but not \( EL_2 \))
also quenches in much the same manner as does the LEC EL2,11 but we do not know if the $T_5$ kinetics in LT GaAs are identical to those of the As$_{Ga_{3}}$-related donor in LT GaAs. In this study we have attempted to avoid quenching so that the concentrations of $T_5$ could be followed as a function of annealing temperature $T_A$. The photocurrent (PC) vs time responses associated with two different annealing temperatures are shown as a function of laser power in Fig. 2. In this experiment, of course, the light is left on during the measurement. Although we will not analyze these curves in detail in this letter, we note that at high illumination power the PC quenches quickly, and even the dark current can be quenched to some extent because the 0.65 eV donors are being transformed to their metastable states. However, if the illumination intensity is kept low (top curve in Fig. 2, $1 \times 10^{14}$ photons/cm$^2$s), then significant PC can be observed and $T_5$ trap filling can take place without significant quenching, at least over the first 30 s.

To accurately characterize the trap $T_5$, as it appears in the top curve of Fig. 1 and at other annealing temperatures, we must subtract the large dark current (mainly due to hopping conduction). The quantity $I_{PC} - I_{dark}$ is plotted vs $T$ for several annealing temperatures in Fig. 3. For as-grown layers ($T_G = 250$ °C), or layers grown at 250 °C and annealed at 300 °C or below, a strong $T_5$ peak appears at 140 K, as seen in Fig. 3(a). For $T_A = 350$ °C, a new peak $T_6^+$ appears at about 96 K. From previous studies, it is known that $T_6^+$ has an activation energy of 0.14 eV, and is by far the fastest growing center during 1 MeV electron irradiation of SI GaAs. Thus, $T_6^+$ is almost certainly the same as the center E2 observed by DLTS and Hall-effect measurements in n-type GaAs and generally agreed to be the As vacancy, $V_{As}$.$^{12}$ The peak current values of $T_5$ and $T_6^+$ are plotted vs $T_A$ in Fig. 4 along with the values of $I_{dark}$ and the peak values of $I_{ph}$ vs time for an illumination intensity $1 \times 10^{14}$ photons/cm$^2$s (cf. Fig. 2). The similar shapes of these curves cannot be simply due to carrier lifetime variations which, of course, would affect the TSC and photocurrent, because $I_{dark}$ is an equilibrium parameter which does not depend on lifetime. Further, the acceptor concentration $N_A$, measured by the Hall effect, goes through a strong dip at $T_A = 400$ °C, as evidenced by a strong peak in mobility; thus, $T_5$ seems to behave much like the dominant acceptor. Note also that the concentration ratio $[T_6^+]/[T_5]$ increases strongly for $300 < T_A < 400$ °C and then remains relatively constant.

Although the microscopic identification of $T_5$ is not certain, it must involve $V_{Ga}$ because of the three point defects expected in very As-rich stoichiometry ($As_{2}$, $As_{Ga_{3}}$, and $V_{Ga}$) only $V_{Ga}$ is expected to have acceptor levels below midgap. This assignment would be consistent with the low annealing temperature of the acceptor (350 °C), because it is known$^{12}$ that all of the defects created by 1 MeV electron irradiation, which would include the vacancies $V_{As}$ and $V_{Ga}$, have annealing stages at or below 350 °C. Thus, e.g., this low annealing temperature would rule out the acceptor defect Ga$_{As}$, although such a defect...
would not be expected in heavily As-rich stoichiometry anyway. Other independent studies also postulate the existence of high $V_{Ga}$ concentrations in LT GaAs.\textsuperscript{13,14}

If the $V_{Ga}$ defects begin to move and disappear at 300–350°C, then several possible defect reactions can be taking place:

\begin{align}
V_{Ga} + As_{Ga} &\rightarrow V_{As} + As_{Ga} \quad (1) \\
V_{Ga} + As_{Ga} &\rightarrow V_{Ga} + As_{Ga}^* \quad (2) \\
V_{Ga} + As_{I} &\rightarrow As_{Ga} \quad (3) \\
V_{Ga} + As_{I} &\rightarrow V_{Ga} + As_{I} \quad (4)
\end{align}

Reaction (1) denotes a simple nearest-neighbor hop and has been thoroughly investigated from a theoretical standpoint,\textsuperscript{15} and also invoked on several occasions to explain experimental results. The fact that we see $T_0^*$ ($V_{As}$ related) form as $T_0$ ($V_{Ga}$ related) begins to decrease is consistent with reaction (1). However, reaction (2) is also quite probable from 350–400°C because it is known that both $N_A$ (or at least the total acceptor charge) and $[As_{Ga}]$ decrease in this temperature range.\textsuperscript{3} Further, there would be a Coulomb attraction between $V_{Ga}$ and $As_{Ga}$. The donor/acceptor nature of the complex $V_{Ga}As_{Ga}$ is unknown, but it might well have a single acceptor transition below midgap. If so, and if $V_{Ga}$ alone has a triple negative charge, as postulated when $E_F$ is near midgap,\textsuperscript{16} then reaction (2) could be written

\begin{align}
V_{Ga} + As_{Ga}^* &\rightarrow (V_{Ga}As_{Ga})^- + e^- \quad (5)
\end{align}

which reduces the total acceptor charge, as observed. To complete the discussion of the reactions listed above we note that reaction (3) would increase the $As_{Ga}$ concentra-

tion, which is sometimes (but not always) observed between 300 and 350°C, and reaction (4) would form a complex with properties perhaps similar to that of $V_{As}As_{Ga}$ complex.

We next must explain the interesting observation that $N_A$ (or the total acceptor charge) tends to increase between 400 and 450 or 500°C, while $[As_{Ga}]$ continues to decrease. An obvious candidate to explain this phenomenon would be the inverse of reaction (3):

\begin{align}
As_{Ga} &\rightarrow V_{Ga} + As_{I} \quad (6)
\end{align}

which would also provide more $V_{As}As_{Ga}$ complexes through reaction (1) and help supply the $As$ for the $As$ precipitates which are forming. Finally, for $T > 450$ or 500°C, $[As_{Ga}]$ and $N_A$ along with $T_0$ and $T_0^*$ all decrease, with the $V_{Ga}$ perhaps aggregating to provide space for the $As$ precipitates. Thus, in this model, we would identify $T_5$ with $V_{Ga}$ and $T_0^*$ with the complex $V_{As}As_{Ga}$. However, for this latter assignment to be correct, the complex $V_{As}As_{Ga}$ would have to possess a donor transition near $E_c-0.14$ eV, the same as that of the isolated $V_{As}$. Such a near energy equivalence is reasonable. It may also be true that the isolated $V_{Ga}$ and the complex $V_{Ga}As_{Ga}$ both have a transition near $E_F+0.27$ eV. Thus, the $T_5$ observed in LEC GaAs, which has experienced high temperatures during growth, may be $V_{Ga}As_{Ga}$, rather than $V_{Ga}$, because isolated $V_{Ga}$ would not be expected to exist in the LEC material.

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