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Comparison of deep centers in semi-insulating liquid-encapsulated Czochralski and vertical-gradient freeze GaAs

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Three-inch, semi-insulating (SI) GaAs, grown by the vertical gradient freeze (VGF) technique, has been studied by IR absorption, temperature-dependent dark current and Hall-effect, thermally stimulated current (TSC), and photoinduced current transient spectroscopy and has been compared with undoped, SI GaAs, both As-rich and Ga-rich, grown by the high-pressure liquid-encapsulated Czochralski method. The results clearly indicate that (1) the VGF GaAs contains less EL2, which suggests a less As-rich crystal stoichiometry; (2) in some VGF samples activation energies of 0.43 or 0.46 eV are deduced from temperature-dependent carrier concentration or resistivity measurements, respectively, and (3) VGF samples often show a thermal quenching behavior in the TSC peak $T_5$.

I. INTRODUCTION

In order to reduce dislocation density and improve uniformity, a vertical gradient freeze (VGF) growth technique has been successfully developed to grow 2 and 3-in. semi-insulating (SI) GaAs. Improved uniformity of 3-in. VGF SI-GaAs has been demonstrated in etch-pit density (EPD), deep donor density (EL2), resistivity $\rho$, mobility $\mu$, and carrier concentration $n$, which shows the material to be quite promising for GaAs MESFET applications.

However, a comparison study of Si-donor activation efficiency and implant uniformity using SI-GaAs materials prepared by a variety of growth methods, including liquid-encapsulated Czochralski (LEC), horizontal gradient freeze (HGF), and vertical gradient freeze (VGF), indicated that the undoped LEC GaAs material yielded the best implant activation, distribution and uniformity and suggested that point defects in SI-GaAs materials have a significant impact on the donor implant activation processes. To study the deep centers in SI-GaAs we have employed two techniques: photoinduced current transient spectroscopy (PICTS) and thermally stimulated current spectroscopy (TSC), using samples with small Schottky contacts. Earlier we compared various LEC SI-GaAs samples with low-temperature, As-rich molecular-beam epitaxial (MBE) GaAs and showed that the relative concentrations of the main electron and hole traps, which are believed to be due to point defects, were closely related to crystal stoichiometry.

In this paper, a comparison study of deep centers in SI LEC and VGF GaAs has been performed by a variety of measurements. They are IR (1.1 $\mu$m) absorption for the EL2 concentration, temperature-dependent dark current and Hall effect for the activation energies of the resistivity and carrier concentration, and PICTS and TSC for the deep trap energies. The results indicate: (i) VGF GaAs contains less EL2 but more of the other main electron traps such as EL5 and EL6 and is, in fact, quite similar to Ga-rich LEC GaAs; (ii) samples taken from the middle and the tail of a VGF GaAs ingot show an activation energy of 0.43 eV rather than the usual 0.74 eV for LEC samples, which further confirms that some VGF materials are not dominated by EL2; and (iii) VGF samples often show a thermal quenching behavior in their TSC signal at a temperature around 140 K, resulting in a reduction of the TSC peak $T_5$, which is a hole trap in As-rich LEC GaAs and is possibly related to the gallium vacancy ($E_g + 0.27$ eV).

II. EXPERIMENT

The three LEC SI-GaAs samples (L113, L059, and L189) used in this study were taken from ingot-annealed crystals grown at Spectrum Technology, Inc. (Holliston, MA) by the high pressure LEC technique (approximately 20 atmospheres), using pyrolytic boron nitride (PBN) crucibles and different melt stoichiometries. Sample L113 was cut from the middle of an As-rich LEC SI-GaAs ingot. Sample L059 was cut from the middle of a Ga-rich LEC SI-GaAs ingot, and sample L189 from the tail of the same ingot. Therefore, sample L189 should be even more Ga-rich than sample L059. The carbon concentrations in these samples are in the range $10^{14}$-$10^{15}$ cm$^{-3}$, i.e., $<3 \times 10^{14}$ cm$^{-3}$, $1 \times 10^{15}$ cm$^{-3}$, and $7.4 \times 10^{14}$ cm$^{-3}$ for samples L113, L059, and L189, respectively. The four VGF SI-GaAs samples (V005, V032, V063, and V123) discussed in this study were taken from a 3-in. ingot grown at AT&T Engineering Research Center. The average dislocation density, as measured by etch-pit counting, is about $2-3 \times 10^3$ cm$^{-2}$, more than one order of magnitude lower than that usually found in LEC GaAs wafers. The room-temperature data of carrier concentration, mobility, and resistivity for all samples used in this study are summarized in Table I. For detailed information concerning the crystal growth, such as crucible material, encapsulant, arsenic pressure, and carbon incorporation, for both the VGF technique (AT&T Engineering Research Center) and the LEC technique (Spectrum Technology, Inc.) readers can refer to the Refs. 1, 5, and 6, respectively.

The EL2 patterns were measured by means of an automated absorption apparatus, using a wavelength of 1.1
TABLE I. Sample properties at 300 K.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Growth</th>
<th>Resistivity</th>
<th>Mobility</th>
<th>Carrier concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(10^2 cm)</td>
<td>(10^2 cm²/V·s)</td>
<td>(10^15 cm⁻³)</td>
</tr>
<tr>
<td>L113</td>
<td>HP-LEC-from</td>
<td>2.0</td>
<td>7.8</td>
<td>4.0</td>
</tr>
<tr>
<td>L059</td>
<td>HP-LEC-from</td>
<td>8.2</td>
<td>6.7</td>
<td>1.1</td>
</tr>
<tr>
<td>L189</td>
<td>HP-LEC-from</td>
<td>41</td>
<td>3.1</td>
<td>0.49</td>
</tr>
<tr>
<td>V005</td>
<td>VGF (near seed)</td>
<td>16</td>
<td>5.3</td>
<td>0.72</td>
</tr>
<tr>
<td>V032</td>
<td>VGF (in upper middle)</td>
<td>16</td>
<td>6.3</td>
<td>0.62</td>
</tr>
<tr>
<td>V063</td>
<td>VGF (in the middle)</td>
<td>2.0</td>
<td>4.0</td>
<td>7.5</td>
</tr>
<tr>
<td>V125</td>
<td>VGF (near tail)</td>
<td>3.5</td>
<td>4.0</td>
<td>4.4</td>
</tr>
</tbody>
</table>

μm, which is strongly absorbed by neutral EL2, i.e., EL2'.

Temperature-dependent dark currents were measured on rectangular samples with dimensions of 2.5×10×0.7 mm³, which were also used for the TSC study. Temperature-dependent Hall-effect measurements were performed on square samples measuring 7×7×0.7 mm³. Indium contacts, alloyed at 450 °C for a few minutes in N₂ flow, were used as ohmic contacts in both dark current and Hall-effect measurements. In the TSC measurements, 1-min light excitation at 90 K was provided by a 1.46 eV, 100 mW GaAs laser diode and the thermally stimulated currents were then measured by an electrometer (Keithley 616) upon warming the samples with a heating rate of 0.2 K/s. For the PICTS measurements, samples with Ti-Au or Au Schottky contacts (diameter of 0.5 or 0.7 mm) on the front side and silver paint on the back side were used and the transient currents were amplified by a current amplifier (Keithley 427), then fed to a commercial DLTS apparatus (Polaron DL 4600) for spectral analysis using the dual-gate technique.

III. RESULTS

The EL2 patterns measured on wafer V033, which was adjacent in the boule to sample V032, are shown in Fig. 1. As seen in Fig. 1(b), the median value of [EL2'], about 2×10¹⁵ cm⁻³, is significantly lower than that usually found in As-rich LEC SI-GaAs. From the gray-scale map and 7.5 mm horizontal and vertical slices for [EL2'] no obvious fourfold symmetry or W patterns, which are typical for LEC crystals, can be found. However, a fourfold pattern is seen for sample V005 (not shown). The EL2 concentrations in the three LEC samples are 1.1×10¹⁶ cm⁻³, 7.4×10¹⁵ cm⁻³, and 4.0×10¹⁴ cm⁻³, respectively, corresponding to crystal stoichiometry ranging from As-rich to Ga-rich.

The temperature-dependent dark currents, plotted as log I₆ vs 1000/T, for three LEC and four VGF samples, are shown in Fig. 2. From the plots it can be seen that all of the LEC samples, either As-rich or Ga-rich, and one of the VGF samples (V032) show an activation energy of 0.78 eV. Sample V005 has an activation energy of 0.72 eV, whereas the other two VGF samples taken from the middle and the tail of the ingot show an activation energy of 0.46 eV, in the temperature range from 250 to 360 K. To determine if the carrier mobility involved in the dark current measurements has any effect on the measured slopes, temperature-dependent Hall-effect measurements were carried out on one LEC sample (L113) and two VGF samples (V005 and V063). The plots of log (n T⁻³/²) vs 1000/T, shown in Fig. 3, present an activation energy of 0.74 eV for samples L113 and V005, and 0.43 eV for sample V063. Therefore, the results indicate that, unlike the LEC SI-GaAs crystals, about half of the VGF boule is not dominated by the deep donor EL2 (Eₓ = -0.75 eV), but by a shallower donor, near Eₓ = -0.43 eV, probably EL5 (usually given as Eₓ = -0.42 eV).

The TSC spectra for three LEC samples with ohmic contacts are presented in Fig. 4. Similar to the TSC spectra for the same samples measured earlier but using Schottky contacts, the main traps observed in LEC SI-GaAs are still T₂, T₃, T₄, T₅, and T₆. Owing to the different sample
structures (large sample with In ohmic contacts versus small Au Schottky dots) some spectral variations can be found in the TSC spectra with the ohmic contacts, i.e., (i) generally higher intensities of the TSC peaks, (ii) higher relative peak heights of the TSC peaks at lower temperatures ($T < 160$ K), and (iii) the observation of new features ($T_6$ and $T_7$). However, the variations of the main TSC peaks with stoichiometry are the same as before; i.e., the stoichiometry transition from Ga-rich to As-rich favors the occurrence of traps $T_2$ and $T_3$ or an increase in the ratios $T_2/T_3$ and $T_5/T_6$.

For purposes of comparison, a TSC spectrum of VGF sample V032 is presented with two TSC spectra of LEC samples L113 (As-rich) and L059 (Ga-rich) in Fig. 5. In the VGF sample, the same major TSC peaks, i.e., $T_1$, $T_5$, $T_3$, and $T_5$, as those in the two LEC samples can be observed but with a peculiar behavior in $T_5$, i.e., a thermal quenching of the TSC signal at around 140 K. Here the thermal quenching is defined as a sudden drop of thermally stimulated current just past the peak position of trap $T_5$. Without this quenching behavior the whole TSC peak of $T_5$ would be observed. The ratio of $T_2/T_3$ in the VGF sample is quite close to that in Ga-rich LEC GaAs, which
FIG. 6. Thermally stimulated current spectra of four adjacent samples taken from VGF GaAs wafer V032, showing nonuniformity of the thermal quenching behavior in $T_5$.

means that the VGF crystal is, more or less, similar to a Ga-rich LEC crystal from a stoichiometry point of view. The thermal quenching behavior of peak $T_5$ was also examined on four adjacent samples taken from wafer V032, as shown in Fig. 6. In spite of nearly identical spectra for peaks $T_2$ and $T_3$, the spectrum for peak $T_5$, including its thermal quenching, varies considerably from piece to piece, which indicates nonuniformity. Considering a relative variation of $\pm 25\%$ for [EL2] on wafer V033 (Fig. 1), this nonuniformity might be related to the major defect EL2. A possible explanation for the peculiar thermal quenching behavior will be given later.

The PICTS spectra under positive bias for three LEC samples with different crystal stoichiometries, and a VGF sample (V032) are shown in Figs. 7(a) and 7(b), respectively. From Fig. 7(a), as pointed out previously, very interesting trends in the variation of peak height for traps can be found; i.e., when the crystal stoichiometry is changed from Ga-rich to As-rich, $C_3$ and $C_5$ in the high-temperature portion of the spectra are reduced, while in the low-temperature portion, $C_4$ and $C_6$ are increased, but $C_6$ and $C_7$ are also reduced. Another interesting observation is that the peak height and position of $C_5$ and $C_4$ vary with crystal stoichiometry and $C_6$ and $C_7$ seem to be anti-correlated with each other (i.e., an increase in one trap causes a decrease in the other). Further comparisons of Figs. 7(a) and 7(b) confirm that the VGF crystal is indeed like a Ga-rich LEC crystal, except for the higher relative peak heights of $C_5$ and $C_6$. From an earlier discussion about the possible identities of traps, it was suggested that Ga-rich crystal stoichiometry results in more electron traps, such as EL3 and EL6.

IV. DISCUSSION

It is well known that the electrical properties of undoped LEC SI-GaAs grown by using PBN crucibles can be controlled by the melt composition. There exists a critical melt composition, $f_5 = 0.475$ for the fraction of arsenic atoms in the melt, above which GaAs is semi-insulating with EL2 the dominant deep donor and below which it is distinctly $p$-type, with $C_{As}$ and/or $Ga_{As}$ the dominant acceptors. The densities of two major point defects, EL2 (with $As_{Ga}$ as a core) and $Ga_{As}$ are evidently determined by the crystal stoichiometry, as determined by IR absorption and photoluminescence. In addition to these two antisite defects, there also exist a number of other point defects, such as $V_{Ga}$, $V_{As}$, and their related defect complexes, which are believed to play an important role in the semi-insulating/semi-conducting reversibility of undoped GaAs crystals and the activation efficiency of Si, implanted into undoped SI-GaAs with different stoichiometries. Usually, the vacancy-related defects are very difficult to measure directly. Although the positron annihilation technique has been used to characterize the vacancy or divacancy in various types of bulk materials, the large scatter in the results and sometimes conflicting results clearly show that the application of this technique in semiconductors is far more complicated than in metals. However, several reasons lead us to believe that the main
traps observed by TSC and PICTS techniques are due to point defects. These reasons are: (i) by applying the equation 
\[ N_t = Q/eV \mathrm{G}^{16,12} \]
where \( N_t \) is the trap density, \( Q \) the total electrical charge of a TSC peak, \( e \) the electronic charge, \( V \) the effective excited volume of the sample, and \( G \) the gain or the current collection factor (usually \( G < 1 \)). The estimated trap densities for \( T_3 \) and \( T_2 \) in sample L113 and \( T_4 \) in sample L189, are at least \( 3 \times 10^{17} \text{ cm}^{-3} \), \( 1.8 \times 10^{16} \text{ cm}^{-3} \), and \( 3 \times 10^{17} \text{ cm}^{-3} \), respectively; (ii) in the undoped LEC SI-GaAs samples the main impurities are carbon and boron with concentrations of \( 10^{14} - 10^{15} \text{ cm}^{-3} \) and \( 10^{15} - 10^{16} \text{ cm}^{-3} \), respectively, which are certainly less than the observed trap densities. The concentrations of transition metals such as Cu, Fe, and Mn are typically 0.01, 0.02, and 0.005 ppma, respectively, for present day undoped LEC SI-GaAs crystals; (iii) the clear stoichiometry association of the main traps found in both TSC and PICTS spectra cannot reasonably be attributed to any impurities, but must be associated with native defects (most probably, \( T_3 \) and \( T_5 \), which thrive under As-rich stoichiometry, are related to \( \text{As}_n \) and \( \text{V}_{\text{Ga}} \), and \( T_3 \) and \( T_6 \), which are favored by Ga-rich stoichiometry, are related to \( \text{V}_{\text{As}} \) and \( \text{Ga}_{\alpha} \)); and (iv) the peak height of \( T_5 \) is highly dependent on the illumination time and the excitation light intensity at 90 K which was previously reported for the sample with a Schottky contact structure, but using 1.96 eV light.\(^{17} \) The same phenomenon can be repeated on the sample with In contacts using 1.46 eV light. As we discussed before, the phenomenon cannot be explained by a simple trap filling mechanism; instead, a photoinduced defect reaction or a photoinduced rearrangement of the atomic configuration for the \( T_5 \) related defect should be considered to help explain the development of the huge peak \( T_5 \).

In temperature-dependent Hall-effect measurements on undoped or O-doped high-resistivity GaAs, a dominant activation energy of 0.43 eV, rather than the usual 0.75 eV in SI-GaAs, has been reported many times.\(^{18-21} \) Thomas et al. reported an activation energy of 0.45 eV, without \( T_5 \) correction, on LEC GaAs, grown in a gallium-rich melt, provided that boron concentrations were kept low.\(^{18} \) According to Pearson et al. as-grown LEC GaAs grown in a Ga-rich melt, but with a low carbon concentration \(( \text{IC} < 3 \times 10^{14} \text{ cm}^{-3} )\) shows a dominant activation energy of 0.43 eV. However, when subjected to a thermal treatment at 950 °C, the material becomes dominated by a EL2-like center with an activation energy of 0.72 eV.\(^{19} \) Alt also reported an activation energy of 0.43 eV in a low-pressure LEC GaAs sample with an extremely low carbon concentration of \( 1 \times 10^{14} \text{ cm}^{-3} \), as measured by the 582 cm\(^{-1} \) local vibrational mode (LVM) absorption; he associated the center with two oxygen related LVM absorption bands, \( \text{band A at 730 cm}^{-1} \) and \( \text{band B at 714 cm}^{-1} \).\(^{20} \) However, Look et al. studied the \( E_c \) — 0.43 eV center in undoped and O-doped GaAs by a combination of temperature-dependent Hall-effect measurements, spark-source mass spectroscopy, and secondary-ion mass spectroscopy and concluded that neither oxygen nor any other impurity could account for the 0.43 eV center, which had a concentration of \( 2 \times 10^{16} \text{ cm}^{-3} \); therefore it had to a pure defect.\(^{21} \) In the present work, once again, an activation energy of 0.43 eV has been found in sample V063, taken from the middle of a VGF GaAs ingot. As we pointed out above, VGF GaAs has a Ga-rich crystal stoichiometry in comparison with As-rich LEC GaAs. Furthermore, the carbon concentration versus fraction solidified \( g \) in VGF GaAs, reported by Clemans et al.,\(^{1} \) indicates an effective segregation coefficient \( K_{\text{eff}} \) of 2.1 ± 0.6 for carbon, and low carbon concentrations \(( < 1 \times 10^{15} \text{ cm}^{-3} )\) for \( g > 0.5 \). Thus, some VGF samples meet the two necessary conditions for the 0.43 eV dominancy in the dark current or Hall-effect measurements; i.e., Ga-rich (or less As-rich) crystal stoichiometry, and low carbon concentration, which could result in a higher density of arsenic vacancies in the crystal. Thus, the deep donor with an activation energy of 0.43 eV might be a \( \text{V}_{\text{As}} \) related point defect; note also that it is close to the electron trap EL5 at \( E_c \) — 0.42 eV, which is often observed in DLTS investigations of \( n \)-type LEC GaAs.\(^{32,34} \) Oxygen doping in GaAs crystal growth mainly plays a metallurgical role in the suppression of C and Si contamination. Simultaneous observations of the oxygen related LVM absorption lines and the 0.43 eV center may not necessarily imply that the oxygen is involved in a 0.43 eV deep donor, but that both of them are related to \( \text{V}_{\text{As}} \) (for further discussion on the postulated \( \text{V}_{\text{As}} \) — O center, see Ref. 25).

To our knowledge, the thermal quenching behavior observed in the present TSC study has never been reported before. To further study this phenomenon, a TSC study, by using IR \(( \text{hv} < 1.12 \text{ eV} )\) light obtained from a strong tungsten lamp through a Si-wafer filter, has been performed on the LEC sample L113. It was found that TSC peak \( T_5 \) was suppressed when the illumination time, \( t_{\text{illum}} \), at 90 K was increased from 1 to 60 s and a thermal quenching behavior of \( T_5 \) was observed as an intermediate stage when \( t_{\text{illum}} \approx 30 \text{ s} \). When \( t_{\text{illum}} \) was further increased to longer than 2 min, \( T_5 \) was not observed at all. The IR photocurrent \(( \text{or photoconductivity} )\) quenching has been well explained by a transition from the normal state to the metastable state of EL2 accompanied by a change in the atomic configuration. No matter what the microscopic configuration of EL2, our results suggest that there might exist an intermediate state during both the quenching and thermal recovery processes. If so, this intermediate state may play a role in the sudden reduction of either the lifetime or the mobility of the carrier, since thermally stimulated currents are directly dependent on the trap density, the carrier lifetime, and the mobility. It is not likely, from the trap densities involved, that the mobility could be strongly affected.

We have also observed the thermal quenching of \( T_5 \) on an as-grown LEC GaAs sample with the 0.43 eV dominancy mentioned above and a sample cut from the ring \(( \text{low EL2} )\) region of LEC GaAs wafer 113. It seems that there may exist a certain correlation between the thermal quenching of \( T_5 \) and the 0.43-eV deep donor dominancy. A detailed study of the thermal quenching behavior of \( T_5 \) is in progress and will be published later.
V. CONCLUSIONS

The deep centers in VGF GaAs, which are believed to be mainly due to point defects in the crystal, have been studied by a combination of temperature-dependent dark current and Hall effect, IR absorption, TSC, and PICTS measurements, and have been compared to those in LEC GaAs with different stoichiometries. The results clearly indicate that: (1) VGF GaAs contains less EL2, but more of the shallower electron traps such as EL5 and EL6, which suggests that its crystal stoichiometry is less As-rich; (2) samples taken from the middle and the tail of the VGF GaAs ingot show an activation energy of 0.43 eV, rather than the usual 0.74 - 0.78 eV, in the plot of log \((nT^{-3/2})\) versus \(1/T\); and (3) VGF samples often show a thermal quenching behavior in TSC peak \(T_s\) (most probably, a \(V_{Ga}\) related defect) which needs to be further studied.

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