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Photoluminescence in electrically reversible (semiconducting to semi-insulating) bulk GaAs

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A photoluminescence study has been made of electrically reversible, bulk, liquid-encapsulated Czochralski GaAs at temperatures 2–300 K. The reversibility from the semiconducting to the semi-insulating state is made by slow or fast cooling, respectively, following a 5-h, 950 °C heat treatment in an evacuated quartz ampoule. A donor level at \( E_D = -0.13 \) eV and two acceptor levels at \( E_A + 0.069 \) eV and \( E_A + 0.174 \) eV are produced after the heat treatment. Only the acceptor levels were detected by photoluminescence. A tentative model assigning the acceptor to the intrinsic defect pair \( V_{Ga} \)-\( Ga_{As} \) is discussed.

I. INTRODUCTION

Intrinsic defects in GaAs have been the subject of intensive research. The research has been motivated primarily by the need to understand the effects of these defects on the material properties. Bulk GaAs crystals grown by the liquid-encapsulated Czochralski (LEC) technique can be made \( n \)-type, semi-insulating (SI), or \( p \)-type conducting by forcing the stoichiometry toward the As-rich or Ga-rich side, respectively, which results in the formation of the As-antisite related defect \( \text{EL2} \) or Ga-antisite double acceptor \( \text{Ga}_{antisite} \) as the center controlling the compensation mechanism between donors and acceptors. The formation of undoped SI material is generally considered to be due to a balance between a shallow donor \( \text{SiGa} \), a shallow acceptor \( \text{CAs} \), and a deep donor \( \text{EL2} \). Recently, we showed \( \text{J} \) that (i) the bulk crystals can be grown with \( \text{C} \) and \( \text{Si} \) \( < 5 \times 10^{14} \) cm\(^{-3} \) by the low-pressure, liquid-encapsulated Czochralski technique (LP-LEC), (ii) the ingot can be reversibly changed from a semi-insulating to a conducting state by a heat treatment, and (iii) the electrical properties are controlled by a small change of the relative concentration of intrinsic donors and acceptors produced by heat treatment. In this work we report a study on the photoluminescence properties of such electrically reversible crystals.

II. EXPERIMENT

A. Crystals

The GaAs crystals were grown in a low-pressure (2 atm, \( \text{N}_2 \)) LEC reactor, with PbN crucibles under near-stoichiometric conditions. The ingots were 2.5–3 in. in diameter and 2–5 in. long. The as-grown ingots, in general, were not uniformly semi-insulating from top to bottom. However, the ingots became electrically uniform by heat treatments. A conducting state (\( \sim 1 \) cm\(^{-1} \)) was produced after slow cooling from a 5-h, 950 °C soak in an evacuated quartz ampoule by turning off the furnace and a SI state (\( \sim 10^7 \) Ω cm) after rapid quenching from the 950 °C soak by removing the ampoule from the furnace.

Table I shows the reversibility of the conducting and SI states for an ingot. Here, 950 °C-Q means the sample was quenched whereas 950 °C-A means the sample was slowly cooled (annealed) after the 950 °C soak as described above. It is evident that the electrical properties can be cycled between the two states. Table I also shows the main level controlling the conduction properties as determined by a fit to the absorption.

B. Photoluminescence measurements

Photoluminescence (PL) measurements were made using the 647.1-nm line of a continuous Kr-ion laser as an excitation source. The intensity was varied between \( 10^{-4} \) and 10 W/cm\(^2 \). PL signals were detected using a cooled Ge detector or a S-1 response photomultiplier tube. The signal

<table>
<thead>
<tr>
<th>Treatment</th>
<th>( \rho ) (Ω cm)</th>
<th>( n ) (cm(^{-3} ))</th>
<th>Major level (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As grown</td>
<td>2.5</td>
<td>( 4.7 \times 10^{14} )</td>
<td>( E_D = -0.003 )</td>
</tr>
<tr>
<td>950 °C-Q</td>
<td>9.4 \times 10^6</td>
<td>1.3 \times 10^8</td>
<td>( E_D = -0.77 )</td>
</tr>
<tr>
<td>950 °C-A</td>
<td>7.8</td>
<td>( 1.7 \times 10^{14} )</td>
<td>( E_D = -0.13 )</td>
</tr>
<tr>
<td>950 °C-Q</td>
<td>9.6 \times 10^6</td>
<td>1.3 \times 10^8</td>
<td>( E_D = -0.77 )</td>
</tr>
<tr>
<td>950 °C-A</td>
<td>3.3</td>
<td>( 2.7 \times 10^{14} )</td>
<td>( E_D = -0.13 )</td>
</tr>
<tr>
<td>950 °C-Q</td>
<td>2.7 \times 10^7</td>
<td>3.4 \times 10^7</td>
<td>( E_D = -0.77 )</td>
</tr>
</tbody>
</table>
and two-LO-phonon transitions. The acceptors involved are CAs and ZnGa in the as-grown sample, whereas the appearance of SiAs-related bands is clear in addition to ZnGa and CAs for both the annealed and quenched crystals. The emission due to SiAs is not clear in the as-grown crystal. Another feature in the heat-treated samples is the presence of two sharp peaks at 1.508 eV (X2) and 1.510 eV (X1).

**FIG. 1.** 2-K photoluminescence characteristics of (a) as-grown, (b) annealed, and (c) quenched crystals. NI means near-intrinsic transitions and SA indicates the shallow-acceptor-related bands. The A1 and A2 bands are, respectively, at 1.45 and 1.34 eV at $T = 2$ K. Their longitudinal optical phonons are indicated by 1LO and 2LO.

**FIG. 2.** Detailed photoluminescence spectra of the near-intrinsic and shallow-acceptor-related transitions of (a) as-grown and (b) quenched crystals. The near-intrinsic transitions consist of the free exciton ($X$), donor-bound exciton ($D^0X$), and acceptor-bound exciton ($A^0X$) transitions. The X1 and X2 transitions are at 1.510 and 1.508 eV, respectively. $D^0A^0$ and $e^-A^0$ mean the neutral donor-acceptor pair and the conduction-band-electron to neutral-acceptor transitions, respectively.
Figure 3 shows the temperature-dependent PL characteristics of a quenched crystal. The shallow-acceptor-related transition quenches down rapidly with an increase of temperature above $T = 25$ K. The A1 transition becomes a dominant transition near $T = 40$ K as shown in Fig. 3(b). With a further increase of temperature the PL intensity of the A1 transition decreases. Around $T = 75$ K, the A2 transition begins to dominate the PL spectra. Figure 4 shows the transition energy versus temperature relation for the A1 and A2 transitions. The solid lines represent the theoretical $e-A^0$ transition energies for the A1 and A2 PL bands with the assumption that the centers responsible for A1 and A2 bands are due to two acceptor levels. The peak energies are given\(^6\) by

$$E = E_g - E_a + (kT/2),$$  \((2)\)

where the symbols have their usual meanings. The temperature dependence of the energy gap $E_g(T)$ is taken as\(^7\)

$$E_g(T) = E_g(0) - [\alpha T^2/(T + \beta)],$$  \((3)\)

with $\alpha = 5.8 \times 10^{-4}$, $\beta = 300$, and $E_g(0) = 1.5196$ eV. An excellent agreement between experiment and theoretical lines is obtained by taking $E_g = 69 \pm 3$ and $174 \pm 5$ meV for the A1 and A2 centers at temperatures higher than $\sim 30$ K. In this temperature range, the A1 and A2 bands are due to the $e-A^0$ transitions. At temperatures lower than $\sim 30$ K the $D^0-A^0$ transitions dominate over the $e-A^0$ transitions. A shift to lower energies for the A1 and A2 transitions with decreasing temperature is expected in the case where the $D^0-A^0$ transition becomes dominant over the $e-A^0$ transition at low temperatures. This evidently shows that the donor participating in the $D^0-A^0$ transition of the A1 and A2 PL bands is the shallow effective-mass donor at $E_D = 5.7$ meV. The $D^0-A^0$ and $e-A^0$ transitions are clearly resolved, at $T = 2$ K, for the shallow-acceptor transitions as shown in Fig. 2. However, the resolution is not clear for the A1 and A2 bands, the dominant transition being due to the $D^0-A^0$ pair type.

Figure 5 shows the relative PL intensity $\ln I$-vs-$10^3/T$ relation for the shallow-acceptor (SA), A1, and A2 transitions. Activation energies of $E_a = 70 \pm 7$ and $170 \pm 15$ meV are obtained from the $\ln I$-vs-$10^3/T$ relation by using the simple following relationship:

$$I(T) = I_0 \exp(E_a/kT),$$  \((4)\)

where the symbols have their usual meanings. The decrease of the PL intensities is due to the thermal release of the respective acceptor centers. These values are in good agreement with those obtained from the temperature-dependent transition-energy measurements.

Both the temperature dependence of energy and intensity for the A1 and A2 PL transitions clearly show that the centers involved in the transitions are located at $E_a = 0.069$ eV and $E_a = 0.174$ eV and act as acceptors. The deep nature of the centers is also consistent with the determined value of the average number of phonons $\bar{N}$ involved in the hole-phonon interaction as discussed earlier. Heat treatments, both quenching and annealing, produce two acceptor levels.

With this we now turn our attention to the 1.508- and 1.510-eV lines in Fig. 2, which show in both quenched and annealed crystals. Previously, several sharp-line PL transitions in the energy range of 1.508-1.515 eV from vapor-phase-epitaxy GaAs were observed.\(^8\) These transitions were understood in terms of excitons bound to donor-acceptor-type complexes. Possibilities of deep double donor or accep-
and 1.510-eV lines in heat-treated crystals are due to Ga AS
ble acceptor BAs was observed from both as-grown 10 and
...J
Other concentrations of other impurities other experiment a sharp line at
...J
FIG. 5. Photoluminescence intensity vs
...J
IV. SUMMARY
We have described the photoluminescence characteristics of electrically reversible LEC GaAs. Two photoluminescence bands at 1.34 and 1.45 eV were observed after a 950 °C heat treatment. The photoluminescence bands were attributed mainly to the neutral donor-acceptor pair transitions at T ≤ 30 K and the conduction-band-electron to neutral-acceptor transitions at T > 30 K. The two acceptor levels were determined to be at E\textsubscript{a} + 0.069 eV and E\textsubscript{a} + 0.174 eV. Intrinsic pair defects such as V\textsubscript{Ga}-Ga\textsubscript{As} are proposed for the new acceptor levels. However, the Hall-effect level\textsuperscript{3} at E\textsubscript{c} − 0.13 eV was not observed by photoluminescence, indicating a large Franck-Condon shift for the center.

ACKNOWLEDGMENT
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