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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 $E_c - 0.13$ eV and two acceptor levels at $E_v + 0.069$ eV and $E_v + 0.174$ 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 defect¹ EL2 or Ga-antisite double acceptor² 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 Si_{Ga} , a shallow acceptor C_{As} , and a deep donor EL2. Recently, we showed³ that (i) the bulk crystals can be grown with $[C]$ and $[Si] < 5 \times 10^{14} \text{ cm}^{-3}$ by the low-pressure, liquid-encapsulated Czochralski technique (LPLEC), (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, 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 ($\sim 1 \Omega \text{ cm}$) 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 ($\sim 10^7 \Omega \text{ cm}$) 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 of n vs T . The centers at $E_c - 0.13$ eV and $E_c - 0.77$ eV (EL2) are mainly responsible for the electron conduction, respectively, in the annealed (conducting) and the quenched SI crystals. Also, we note that the concentration of the center at $E_c - 0.13$ eV in sample 950 °C-A increases greatly compared to that in the as-grown sample. The impurity concentration was checked by local vibrational mode absorption spectroscopy, secondary-ion mass spectroscopy (SIMS), and spark-source mass spectroscopy. The results are $[B] \approx 8 \times 10^{16} \text{ cm}^{-3}$, $[C] \approx 3 \times 10^{14} \text{ cm}^{-3}$, and $[Si] \leq 2 \times 10^{14} \text{ cm}^{-3}$ with all other impurity concentrations $\leq 1 \times 10^{15} \text{ cm}^{-3}$. No B_{As} was detected by the absorption spectroscopy. Another important result is that the donor and acceptor concentrations are higher than the electrically active impurity concentrations, at least for sample 950 °C-A.

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 I. Electrical properties after anneal and quench cycles.

Treatment	ρ ($\Omega \text{ cm}$)	n (cm^{-3})	Major level (eV)
As grown	2.5	4.7×10^{14}	$E_c - 0.003$
950 °C-Q	9.4×10^6	1.3×10^8	$E_c - 0.77$
950 °C-A	7.8	1.7×10^{14}	$E_c - 0.13$
950 °C-Q	9.6×10^6	1.3×10^8	$E_c - 0.77$
950 °C-A	3.3	2.7×10^{14}	$E_c - 0.13$
950 °C-Q	2.7×10^7	3.4×10^7	$E_c - 0.77$

was analyzed by a $f = \frac{3}{4}$ m Spex spectrometer. Lock-in amplifiers were used for the standard synchronous detection. Temperature was varied with a Janis optical Dewar from $T = 2$ to 300 K.

III. RESULTS AND DISCUSSION

Figure 1 shows the 2-K PL characteristics of (a) as-grown, (b) annealed, and (c) quenched crystals. The PL spectrum of the as-grown crystal consists of the near-intrinsic transitions, shallow-acceptor-related bands, and their longitudinal (LO) phonon ($\hbar\omega_{LO} = 36$ meV) sidebands, separated by energies of $\hbar\omega_{LO}$ and $2\hbar\omega_{LO}$. The detailed features due to the near-intrinsic and shallow-acceptor-related bands are shown in Fig. 2 for as-grown and heat-treated crystals (in this energy range no significant difference between PL spectra of quenched and annealed crystals was observed). The near-intrinsic emission primarily consists of the free exciton (X) at 1.515 eV, the neutral-donor-bound exciton (D^0X) at 1.514 eV, and the neutral-acceptor-bound exciton (A^0X) at 1.512 eV. The shallow-acceptor-related bands are due to the neutral donor-acceptor (D^0A^0) pair and the conduction-band-electron to neutral-acceptor (eA^0) transitions. The acceptors involved are C_{As} and Zn_{Ga} in the as-grown sample, whereas the appearance of Si_{As} is clear in addition to Zn_{Ga} and C_{As} for both the annealed and quenched crystals. The emission due to Si_{As} 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). The $X1$ and $X2$ transitions are at 1.510 and 1.508 eV, respectively. D^0A^0 and eA^0 mean the neutral donor-acceptor pair and the conduction-band-electron to neutral-acceptor transitions, respectively.

The PL spectrum of the as-grown crystal [Fig. 1(a)] consists of the C_{As} - and Zn_{Ga} -related D^0A^0 and eA^0 no-phonon transitions and their one-LO- and two-LO-phonon sidebands. However, the PL spectra of heat-treated crystals, both annealed and quenched, clearly show the appearance of two PL peaks near 1.34 and 1.45 eV and their one-LO- and two-LO-phonon sidebands. The two no-phonon peaks near 1.45 and 1.34 eV are designated as A1 and A2 in Figs. 1(b) and 1(c), respectively. The A1 band is present at a slightly lower energy than the one-LO-phonon sidebands of the C_{As} , Zn_{Ga} -, and Si_{As} -related D^0A^0 and eA^0 transitions, but is somewhat superimposed with those bands. The relative PL intensity of the A1 band is larger for the quenched SI crystals compared to the annealed conducting crystals.

At low temperatures, the emission of LO phonons of an optical transition can be clearly seen in GaAs. The intensities of no-phonon and LO-phonon transitions follows the Poisson distribution

$$I_n = I_0 \bar{N}^n / n!, \quad n = 0, 1, 2, \dots \quad (1)$$

as first suggested by Hopfield,⁴ where I_0 is the intensity of a zero-phonon transition, I_n is the intensity of an n -phonon transition, and $\bar{N}$ is the average number of emitted phonons determined by the carrier-phonon interaction. $\bar{N}$ increases as the depth of center responsible for the optical transition increases. For GaAs, the $\bar{N}$ versus acceptor binding energy relationship has been established. The value of $\bar{N}$ ranges⁵ from 0.02 to 0.5 as the acceptor binding energy ranges from 26 to 150 meV, respectively. The A1 emission can be easily separated from the shallow acceptor (Zn_{Ga} , C_{As} , and Si_{As}) related one-LO-phonon sidebands using the relation given by Eq. (1). The values of $\bar{N}$ for the A1 and A2 transitions are ~ 0.078 and 0.40 , respectively, which agrees well with a general trend that $\bar{N}$ increases with the depth of the center responsible for a transition.

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 given⁶ by

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

where the symbols have their usual meanings. The temperature dependence of the energy gap $E_g(T)$ is taken as⁷

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

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 $E_a = 69 \pm 3$ and 174 ± 5 meV for the A1 and A2 centers at temperatures higher than ~ 30 K. In this temperature range, the A1 and A2 bands are due to the $e-A^0$ transitions. At temperatures lower than ~ 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

FIG. 3. Temperature dependence of the quenched crystal. NI means near-intrinsic transitions and SA indicates the shallow-acceptor-related bands.

FIG. 4. Temperature dependence of the A1 and A2 transition energies. Solid lines are the calculated energies of the $e-A^0$ transitions with $E_a = 0.069$ and 0.174 eV, respectively, for the A1 and A2 bands.

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 ± 15 meV are obtained from the $\ln I$ -vs- $10^3/T$ relation by using the simple following relationship:

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

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 $E_v + 0.069$ eV and $E_v + 0.174$ 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-

FIG. 5. Photoluminescence intensity vs $10^3/T$ relationship for three transitions of SA, A1, and A2. SA means the shallow-acceptor-related bands.

tor complexes were also discussed. The two lines in the present experiment are at the same transition energies as the excitons bound to donor-acceptor-type complexes. In another experiment a sharp line at 1.507 eV was observed⁹ in Sn-doped GaAs. This line was explained with an exciton bound to neutral Sn acceptor, having a binding energy of 167 meV. Considering the above facts we can suggest that the 1.508- and 1.510-eV lines in heat-treated crystals are due to bound excitons associated with the two acceptor levels of $E_v + 0.069$ eV and $E_v + 0.174$ eV (the nature of the bound exciton is not yet determined).

An immediate candidate for the observed acceptor levels in view of high-impurity concentration is B on an As site, B_{As} . The SIMS data show that $[B]$ is $\sim 8 \times 10^{16} \text{ cm}^{-3}$ and concentrations of other impurities are $\leq 10^{15} \text{ cm}^{-3}$. The double acceptor B_{As} was observed from both as-grown¹⁰ and electron-irradiated¹¹ GaAs by local vibrational mode absorption of the single negative charge state B_{As}^- at 601 cm^{-1} . However, no B_{As}^- absorption was detected from the present crystals. This indicates that $[B_{As}]$ is $< 10^{15} \text{ cm}^{-3}$ if it exists. Other types of centers which can be considered are intrinsic native defects. Invoking intrinsic defects as responsible centers for the acceptor levels is rather more plausible than impurities when one considers that (i) there are not sufficient quantities of impurities to account for the total acceptors and donors and (ii) the relative PL intensities of the A1 and A2 bands vary depending on the heat treatment (larger for the quenched sample), as shown in Figs. 1(b) and 1(c) (this indicates more acceptor production in quenched crystals). In fact, thermodynamics^{12,13} of the 5-h, 950 °C heat

treatment shows the presence of vacancies of 10^{16} – 10^{18} cm^{-3} , mostly As vacancies V_{As} due to the quenching to room temperature after the heat treatment.

The actual concentration of vacancies is expected to be diminished due to room-temperature annealing for many hours. We find numerous examples of PL bands associated with As and Ga vacancies V_{As} and V_{Ga} , which are produced by growth conditions, heat-treatment conditions, or crystal stoichiometry. A 1.45-eV band ascribed¹⁴ to $Ge_{As}-V_{As}$ in Ge-doped crystals, a 1.37-eV band¹⁵ associated with $Zn_{Ga}-V_{As}$ in Zn-doped crystals, a band¹⁶ at 1.44–1.46 eV after a 3–5 h annealing at 830 °C in n^+ -type Si-doped samples, and a 1.44-eV band due to Ga_{As} in Ga-rich LEC GaAs (Ref. 2) are typical examples of PL bands associated with V_{As} . Photoluminescence bands associated with V_{Ga} can be found from a 1.2-eV band¹⁷ due to donor $Ga-V_{Ga}$ and an 0.68-eV band¹⁸ attributable to EL2 (As_{Ga} antisite or any association of As_{Ga}). In most of the examples cited above the association of the vacancy with an impurity is common. However, in our case, we must consider intrinsic defects except possibly any association with B_{Ga} . The simplest assignment for the acceptor level would be V_{Ga} . However, V_{Ga} is known¹⁹ to be unstable at relatively low temperatures. In particular, the simple vacancies would not survive during the annealing, but would either annihilate with interstitials or form complexes similar to impurity-vacancy complexes.

In light of the above discussions and recent works^{20,21} on the intrinsic defect complexes, it would be reasonable to consider the intrinsic pair defects $V_{Ga}-Ga_{As}$ as a candidate for the acceptors. The $V_{Ga}-Ga_{As}$ can be created²¹ from the crystal containing V_{As} by a single Ga atom hop, namely $V_{As} \rightarrow V_{Ga} + Ga_{As}$. The binding energy of $V_{Ga}-Ga_{As}$ is lower in p -type material than n -type material. In fact, our crystals are either semi-insulating or n -type conducting, which means the Fermi level is above midgap. The $V_{Ga}-Ga_{As}$ evidently has a $(-)/0$ transition at $E_v + 0.3$ eV. The observed experimental acceptor energies are within theoretical uncertainties. Formation of paired intrinsic defects can also explain the case for the heat treatment of pure LEC GaAs.

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 $T \leq 30$ K and the conduction-band-electron to neutral-acceptor transitions at $T > 30$ K. The two acceptor levels were determined to be at $E_v + 0.069$ eV and $E_v + 0.174$ eV. Intrinsic pair defects such as $V_{Ga}-Ga_{As}$ are proposed for the new acceptor levels. However, the Hall-effect level³ at $E_c - 0.13$ eV was not observed by photoluminescence, indicating a large Franck-Condon shift for the center.

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