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Photoluminescence excitation of the 0.77-eV emission in undoped semi-insulating GaAs

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Photoluminescence excitation spectra have been obtained at 4.2 K for the 0.77-eV broad emission band present in undoped semi-insulating GaAs. The oscillating structures at the above-band-gap energy can be attributed to the energy relaxation of the conduction-band electron by the successive emission of the zone-center longitudinal phonon. The electron capture into the deep donor responsible for the 0.77-eV emission is made through a shallow donor state. The possible radiative mechanism of the 0.77-eV emission is discussed.

Characterization of undoped semi-insulating (SI) GaAs is of great importance due to its scientific and technological needs. It is a commonly accepted view that the SI properties result from the compensation mechanism[1] between the deep intrinsic defect donor (EL2) (Ref. 2) at $E_c-0.75$ eV and shallow acceptor. The shallow acceptor is most likely due to residual carbon. The origin of EL2 is not definitely identified. However, recently EL2 has been attributed to the anion antisite donor $\mathrm{As_{Ga}}$ or its complex by the consideration of As/Ga-ratio stoichiometry-dependent behaviors[1,3] and photoelectron paramagnetic resonance characteristics[4] on the plastically deformed GaAs.

We have recently shown[5–7] that three broad featureless photoluminescence (PL) bands at 0.63, 0.68, and 0.77 eV are present at 4.2 K in undoped SI crystals. The 0.63-eV band is usually present[7] with a strong emission intensity in the samples doped with O, whereas the 0.68-eV band is present in undoped crystals with a weak emission intensity. The 0.68- and 0.77-eV bands are usually present[5,8] together with a different relative strength. The 0.68-eV band was attributed[6] to the radiative transition involving EL2 by studying temperature-dependent behaviors. The 0.63-eV band was assigned[7] to a center related directly or indirectly with O; but, the 0.63-eV emission was also assigned as a radiative recombination related to EL2 by other workers.[9,10] The 0.77-eV band was designated as 0.80-eV emission by Windsheif *et al.*[11] The origin was suggested[11] to arise from the doubly ionized antisite donor $\mathrm{As_{Ga}^{2+}}$ by comparing the annealing behavior of the 0.80-eV emission with the $\mathrm{As_{Ga}}$ electron paramagnetic resonance signal. In this work, we report the results of a study made on the 0.77-eV band by means of photoluminescence excitation (PLE) and temperature change. This is the first report of PLE spectrum of the 0.77-eV band. The possible radiative mechanism is discussed.

The photoluminescence signal was obtained with a $\frac{3}{4}$-m grating spectrometer and a liquid-nitrogen-cooled PbS detector. Excitation was made with a Kr-laser 647.1-nm line with an excitation intensity of ~ 2 W/cm^2. PLE spectra were obtained at 4.2 K by immersing samples in liquid helium. The excitation light source was a tungsten-iodine lamp dispersed with a $\frac{1}{4}$-m grating monochromator. The PLE spectrum was obtained with a cooled intrinsic Ge detector attached to another $\frac{1}{4}$-m grating spectrometer. The detector was usually set at 1.55 μm. *n*-type SI samples grown by the liquid-encapsulated Czochralski method were used. Typical room-temperature electron concentration is 4×10^7 to 8×10^8 cm^{-3}. Impurity analysis on similar samples was given in an earlier work.[7]

The 0.77-eV band present together with the 0.68-eV band is shown as an illustration in Fig. 1(b). The samples having a negligible component of the 0.68-eV band were mainly used for the experiment. The 4.2-K PL spectrum of such samples is shown in Fig. 1(a). The peak is at 0.775 eV with a half-width of 0.25 eV. The band has a nearly Gaussian shape without any structure. The temperature dependence of the 0.77-eV band is illustrated in Fig. 2. The emission intensity remains almost the same at $T=\sim 4-45$ K and decreases with the appearance of the 0.68-eV emission[6] at $T>\sim 60$ K. Figures 2(c) and 2(d) clearly show the appearance of the 0.68-eV emission and the quenching of the 0.77-eV emission. An activation energy of ~ 28 meV was obtained from the emission intensity-vs-$(1/T)$ relation for the 0.77-eV band at $T>70$ K.

The broad structureless characteristics of the 0.77-eV band indicate a large electron-phonon interaction. Usually, broad PL behaviors are well explained by the configuration coordinate model. In a simple case where the electron state of a deep center couples linearly with a single-phonon mode, the thermal energy of the center can easily be estimated assuming a transition between the band edge and deep center. For the 0.77-eV band, with the peak energy at 0.775 eV, the half-width of 0.25 eV, and the band shape, we estimate that the deep center responsible for the 0.77-eV band lies at ~ 0.45 eV from the conduction- or valence-band edge. Thus two centers at ~ 0.45 and 1.07 eV from the conduction-band edge can possibly be considered as responsible centers for the 0.77-eV emission. PLE results which will be discussed later show that a deep donor involved in the 0.77-eV emission captures the conduction-band electron through a shallow donor state. We can find many levels approximately corresponding to the above centers from previous work[12] performed with various experimental methods. However, it is proper to discuss the center in the light of a defect or defect complex in view of the dependence of the 0.77-eV emission characteristics on the crystal growth parameter[5] and inhomogeneity pattern.[8] Thus we suggest the following possible candidates for the above centers: the doubly ionized antisite donor $\mathrm{As_{Ga}^{2+}}$ at $E_c-1.0$ eV (Ref. 4), and a donor[13] at $E_c-0.42$ eV. The latter center was observed to be of the defect type from Hall measurements.

Photoluminescence excitation spectra were obtained from

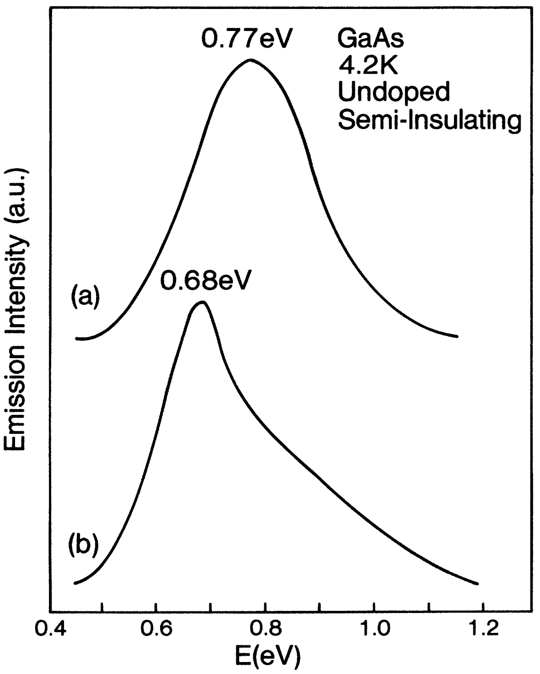

FIG. 1. (a),(b) 4.2-K PL spectra of two undoped SI samples.

two kinds of samples showing the PL characteristics of Figs. 1(a) and 1(b). The PLE characteristics of the 0.77-eV band are the same regardless of the presence of the 0.68-eV band. Figure 3 shows the PLE spectra obtained from two samples. The PLE spectrum consists of pronounced oscillation at the energies larger than the band gap, a small peak at ~1.50 eV, and two PLE thresholds at ~1.44 and 1.49 eV. The pronounced main oscillation structures extend from the band-edge region to ~2.1 eV. Similar oscillation has been obtained in photoconductivity,[14] PLE spectra on C_{As}-related emissions,[15,16] 1.441-eV emission,[17] and deep 0.63-eV emission.[10] In our PLE spectra of the 0.77-eV emission, the period of oscillation is 41.4 ±0.5 meV and can be described by

$$\Delta E = \hbar\omega_{LO}(1 + m_e/m_{hh}) \; , \tag{1}$$

where $\hbar\omega_{LO}$ is the longitudinal-optical (LO) -phonon energy at Γ point 36.74 meV, m_e is the effective-mass electron, and m_{hh} is the heavy-hole effective mass. The obtained m_e/m_{hh} is 0.126, which agrees well with other experiments.[14,17]

The PLE oscillation of the C_{As}-related emissions[16] and the 1.441-eV emission[17] was explained by the energy-dependent capture of the conduction-band electron into a shallow ionized donor via the LO-phonon emissions. However, a deep center is not expected to directly show any oscillatory change in the electron-capture process as a result of the different energy of the conduction-band electron. Thus the presence of an ionized shallow donor, which exhibits the energy-dependent capture of the conduction-band electron, is essential for the observation of oscillatory structures from the deep center. Oscillatory structures from the deep center can occur (i) when the number of conduction-band electrons directly captured into the deep center is modified by other competitive processes involving electron capture into a shallow donor which reduces the population of the conduction-band electron, or (ii) when the conduction-band electrons are indirectly captured into the deep center through a shallow donor. The above two modes (i) and (ii) of the conduction-band electron capture into the deep center are quite analogous to the case for the conduction-band electron-to-neutral acceptor and the shallow neutral donor-to-acceptor pair transition, respectively. The two mechanisms for electron capture nearly interchange the maxima and minima of the corresponding oscillation versus energy. The observed maxima and minima of the oscillation of the 0.77-eV emission PLE spectrum show the same maxima and

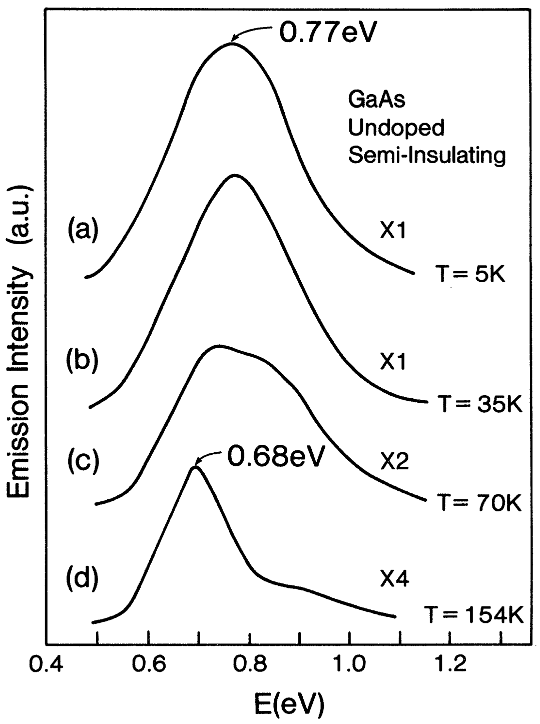

FIG. 2. (a)-(d) Temperature dependence of the 0.77-eV emission which has a negligible component of the 0.68-eV emission.

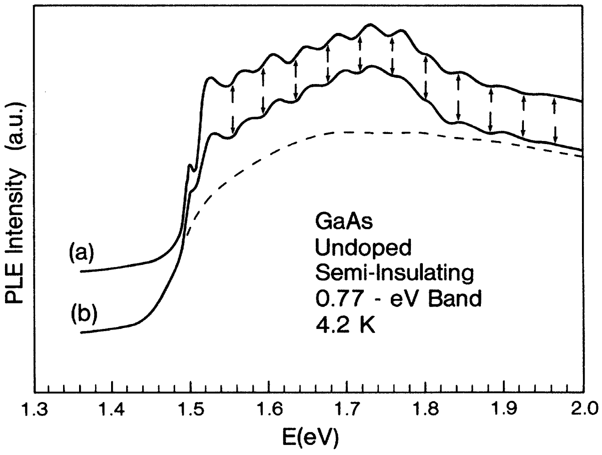

FIG. 3. (a),(b) PLE spectra of the 0.77-eV emission obtained from two samples. The arrows indicate the energy positions of E_n as given by Eq. (2). The broken lines show the relative excitation intensity used for obtaining the PLE. The excitation intensity is $\sim 2\times 10^{-6}$ W/cm^2 at ~1.73 eV.

minima obtained from the PLE oscillatory spectra of the shallow neutral donor-to-acceptor pair transition.[16,17] Thus the PLE oscillation of the 0.77-eV emission reported here is due to the electron-capture process (ii), as is the PLE oscillation of the 0.63-eV emission.[10] Thus the oscillatory structure of the 0.77-eV emission PLE spectrum is due to the energy relaxation of the conduction-band electron through the successive LO-phonon emission with the energy-dependent capture of the conduction-band electron by a deep donor being made via a shallow donor state. The energy relation for the PLE spectrum of the 0.77-eV emission is, therefore, given as follows:

$$E_n = E_g + (n\hbar\omega_{\mathrm{LO}} - E_D)(1 + m_e/m_{\mathrm{hh}}) \;, \qquad (2)$$

where the symbols have the usual meanings. The arrows in Fig. 3 indicate the energy positions of E_n as given by Eq. (2). The used parameters are $E_g = 1.5196$ eV, $E_D = 5.8$ meV, $\hbar\omega_{\mathrm{LO}} = 36.74$ meV, and $m_e/m_{\mathrm{hh}} = 0.126$.

The photoluminescence excitation spectrum in the extrinsic energy range consists of the two PLE thresholds at ~1.44 and 1.49 eV, the subsequent PLE, and a small peak at ~1.50 eV. The 1.49-eV threshold corresponds to the conduction-band - to- $\mathrm{C_{As}}$-energy level. $\mathrm{C_{As}}$ is present as a main acceptor in the Czochralski-grown undoped SI materials. The possible center for the 1.44-eV threshold is the center at $E_v + 0.077$ eV which was attributed[18] to the cation antisite acceptor $\mathrm{Ga_{As}}$. The level at $E_v + 0.077$ eV is characterized by the 4.2-K PL emission at 1.441 eV. The presence of the 1.441-eV emission in the Czochralski-grown undoped SI materials was shown in the earlier work.[5] Thus the threshold and subsequent PLE can be attributed to the increase of the conductance-band electron due to the electron excitation from the ionized acceptor.

In conclusion, we have observed oscillatory structures in the PLE spectrum of the 0.77-eV band presented in undoped SI materials. A shallow donor state plays an important role for the formation of the oscillation.

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