Characteristics of the electroluminescence and photoluminescence emission of erbium ions doped in InP and the energy transfer mechanism

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The characteristics of impact excitation of the 1.54-μm emission due to intrashell transitions of $4f$ electrons of erbium atoms ($^4I_{13/2} \rightarrow {}^4I_{15/2}$) doped into InP were investigated in comparison with the photoluminescence (PL) emission of the same peak from the same sample. The thermal quenching of this Er-related electroluminescence (EL) emission was found to be very small in contrast to the large thermal quenching of the PL emission. The EL emission intensity at room temperature was half that at 77 K, and the temperature dependence of the emission energy and the spectral width was very small. Due to almost temperature-independent nature of the impact excitation process, the quenching of the EL emission intensity reflected directly that of the fluorescence efficiency of this intrashell transitions of Er $4f$ electrons. Using this result, the temperature dependence of the PL energy transfer efficiency was also obtained. It was also found that the fine structure of the 1.54-μm emission was different between EL and PL. It was speculated that Er atoms on different lattice sites, which were in different crystal fields, were excited depending on excitation processes.

I. INTRODUCTION

Sharp luminescence peaks from rare-earth (RE) atoms doped in semiconductors have attracted increasing attention from the point of view of both physical interests and device applications.[1-14] Especially, the 1.54-μm emission peak from Er atoms is expected to be a potentially stable light source for the fiber communication. The room-temperature emission of the 1.54-μm peak was recently demonstrated in Er-doped GaAs and AlGaAs light emitting diodes (LEDs) fabricated by molecular-beam epitaxy (MBE)[4,5] and metalorganic chemical vapor deposition (MOCVD).[6] In LED structures, the energy released through recombination of injected electrons and holes was considered to be transferred to the $4f$ electrons of erbium as in the photoluminescence (PL) emission. In both LED and PL emissions, the quantum efficiency of the 1.54-μm emission at room temperature was very low (of the order of 10^{-6})[5] because of the strong thermal quenching of the emission intensity. This quenching would be related to the energy transfer mechanism. Various models have been proposed for the energy transfer mechanism of the electron-hole recombination energy to rare-earth atoms,[7,9] but there still exist lots of discussions about the energy transfer mechanism.

Recently, we have demonstrated that the Er-related electroluminescence (EL) peak at 1.54 μm was obtained from Er-doped InP by direct impact excitation of erbium atoms with energetic electrons accelerated by dc electric field.[13,14] As Er $4f$ electrons are excited directly by hot electrons and the recombination of electron-hole pairs is not involved in the EL excitation process, we are free from the complexities of the energy transfer mechanism confronted in the PL emission.

This paper deals with detailed characteristics of the erbium-related EL emission peak at 1.54 μm in comparison with those of PL emission, and discusses the energy transfer mechanism, emission efficiency, and fine structure of the emission spectra.

II. EXPERIMENT

Erbium ions were implanted into undoped liquid-encapsulated Czochralski (LEC) n-type ($n = 5 \times 10^{15}$/cm^3) InP at 150 keV to a dose of 7×10^{14}/cm^2 at room temperature. Thereafter, the samples were annealed at 600 °C for 20 h in an evacuated quartz ampoule together with phosphorus powder to suppress the phosphorus outdiffusion. Au/Sn ohmic contacts were deposited on both the surface and the backside of the substrate at 250 °C. The electroluminescence (EL) was observed by applying dc or pulse dc voltages between the electrodes. For comparison, the photoluminescence (PL) spectra were also measured for the same samples with the Ar 514.5-nm laser as an excitation source. The emission spectra were monitored using a Jobin-Yvon monochrometer (HR-320) with a cooled germanium p-i-n photodiode as a detector.

III. RESULTS

Figure 1 shows the secondary-ion mass spectroscopy (SIMS) profile of erbium atoms implanted into InP at a dose of 7×10^{14}/cm^2 for as-implanted and annealed samples. The peak Er volume density is 3×10^{20}/cm^3 at a depth of 40 nm with a width of about 70 nm at 1×10^{20}/cm^3. Little diffusion of Er atoms was observed after the 20-h long annealing at 600 °C. The current versus voltage was nearly linear and symmetrical in both directions. The sam-
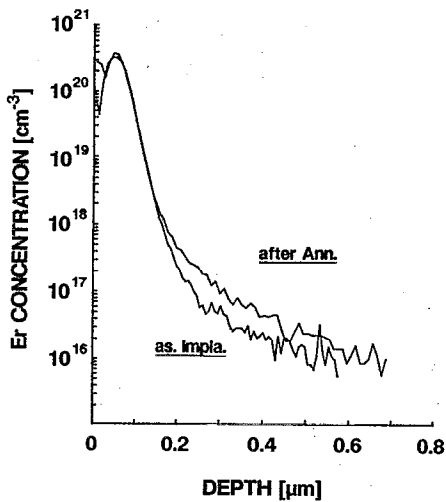
FIG. 1. Depth profile of Er atoms doped in InP by secondary-ion mass spectroscopy.

FIG. 3. PL spectrum of Er-doped InP at 77 K.

ple resistance of around 100 Ω was much higher than the substrate resistance and was attributed to the resistance of the Er-implanted layer.

In Fig. 2 are shown the EL spectra at (a) 77 K and at (b) 300 K as functions of applied voltage. At 77 K, with increasing applied voltage, the Er-related emission peak at 1.54 μm was first observed to appear at about 7 V with no other emission bands in the wavelength range between 800 and 1600 nm. This is quite different from the PL spectrum at 77 K, which is shown in Fig. 3. In the PL spectrum, the
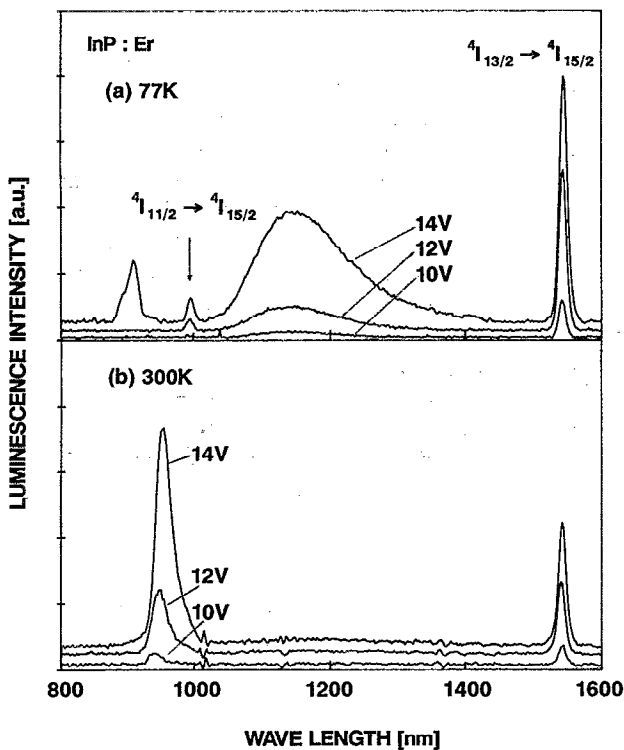
1.54-μm peak was always accompanied by the extremely large band-edge and/or defect-related emissions from the InP host material. In the EL spectrum, however, the emission bands observed in the PL spectra which were located at higher photon energies than the 1.54 μm emission were observed to arise one after another with further increasing applied voltages above 7 V. These host-material-related emission bands in the EL spectrum are considered to be caused by the recombination of electrons and holes which are impact ionized by hot electrons.

The intensity of the 1.54-μm EL peak was strong even at 300 K, about half that at 77 K [Fig. 2(b)]. The 1.54-μm PL emission peak was, however, quenched strongly with increasing temperature and was not detected above 230 K. The EL emission spectrum at 300 K showed nearly the same behavior as for the voltage dependence, except that the defect-related emission bands were not observed. It should be noted that the sharp emission at 0.99 μm was found to appear in the 77-K EL spectrum at about 10 V. This peak is speculated to be related to the intrashell transitions from the second excited state to the ground state of the 4f electrons of erbium ($^4I_{11/2} \rightarrow {}^4 I_{15/2}$). This peak was not, however, observed at 300 K.

Figure 4 shows the bias voltage dependence of the EL emission intensity of the 1.54- and 0.99-μm peaks at 85 K. The 1.54-μm emission peak began to increase very rapidly at 7 V (apparent threshold voltage V_{th}), and above this threshold voltage the intensity increased almost linearly with increasing voltage. The threshold voltage did not change over the temperature range from 77 to 330 K.

The 0.99-μm peak appeared at 10 V, which was about 1.5 times as large as that of the 1.54-μm peak. The ratio of these two thresholds was just that of the emission energy of the two peaks, supporting the impact excitation mechanism. The emission energies of the 1.54- and the 0.99-μm peaks did not change with applied voltage.

Figure 5 shows the EL high-resolution spectra of the Er-related 1.54-μm peaks, and in Fig. 6 is shown the PL fine spectrum for comparison. The PL high-resolution

FIG. 2. EL spectra of Er-doped InP as functions of applied voltages at (a) 77 K and at (b) 300 K.

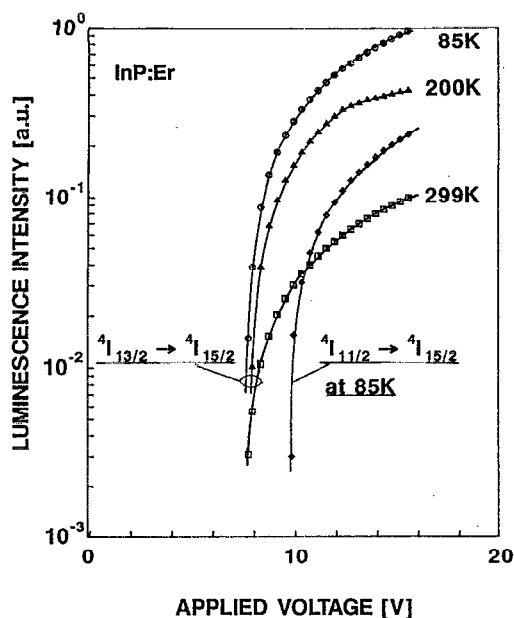FIG. 4. Temperature dependencies of the 1.54-μm EL emission intensity(L) vs applied voltages(V) and the 0.99-μm L-V characteristic at 85 K.

spectrum at 77 K seemed to be composed of several sharp peaks of narrow linewidth (less than 0.7 meV) ranging from 1.538 to 1.550 μm, with the dominant peak at 1.541 μm. This fine structure was almost identical to that of the PL fine structure obtained from Er-doped InP fabricated by MOCVD.[15] It is speculated that each sharp peak might
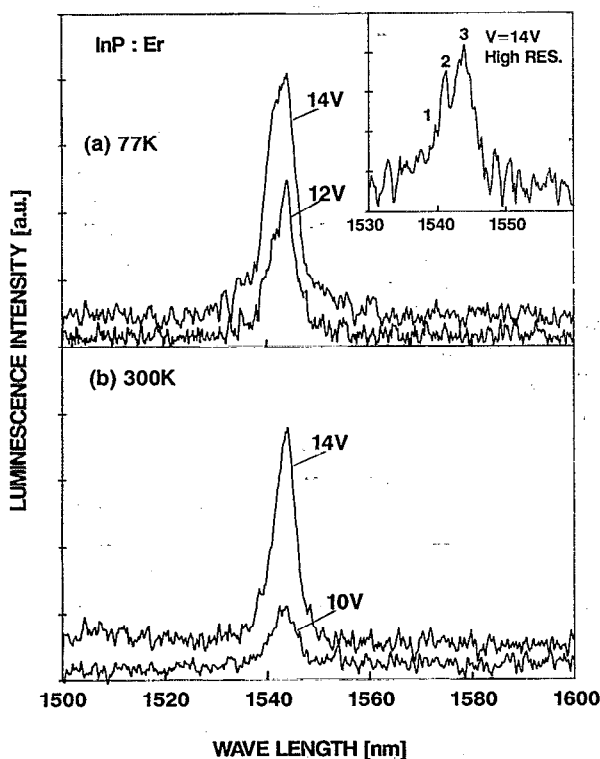

FIG. 5. Er-related EL spectra as functions of applied voltages at (a) 77 K and (b) 300 K.
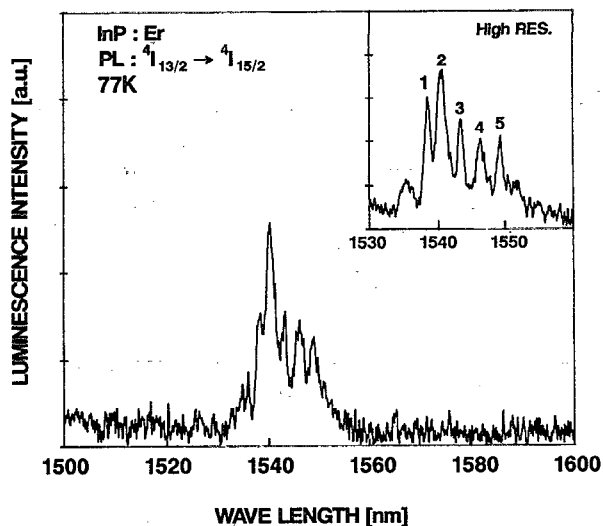

FIG. 6. Er-related PL spectrum at 77 K.

come from different complex centers which are related with Er atoms on different lattice sites in the host material. The corresponding EL high-resolution spectrum at 77 K [Fig. 5(a)] showed a broad band with a total linewidth of about 2.6 meV. It could be resolved into three peaks corresponding to peaks 1, 2, and 3 of the PL peaks, with peak 3 at 1.543 μm as the dominant one. It was found that the linewidth of the EL peak was broadened with increasing applied voltage. This was due to the increased emission intensity of peak 2 at 1.541 μm, which was the PL-dominant peak. The EL fine structure at 300 K was almost the same as that at 77 K for low applied voltages [Fig. 5(b)] and no linewidth broadening, that is, no development of peak 2 was observed with increasing applied voltage. The development of peak 2 in the EL spectrum seems to be related to the appearance of the band-edge emission, which will be discussed in the next section.

IV. DISCUSSION

The emission spectrum as a function of applied voltage in Fig. 2 shows that, with increasing applied voltage, the emission peak at 1.54 μm appears first followed by peaks located at higher energies. The apparent threshold voltages V_{th} for the appearance of both 1.54-μm ($V_{th} = 7$ V) and 0.99-μm ($V_{th} = 10$ V) peaks are temperature independent and their ratio agrees nearly with that of the emission energies. This relation, together with their temperature independence, is evidence for the direct impact excitation of 4f electrons by hot electrons accelerated by the electric field.

The slow decrease in the 1.54-μm EL emission intensity with increasing temperature is also characteristic of the impact excitation compared with the PL emission.[14] The PL emission intensity of the same peak from the same sample decreased very rapidly with increasing temperature and was not detected above 230 K with our PL measuring system (Fig. 3).

The impact excitation rate R from the ground state to the excited state is given by[16]

$$R = n \int_0^\infty \sigma(E)v(E)f(E)dE = n\sigma_0 g(F); \qquad (1)$$

where n is the free-electron density, E is the kinetic energy of electrons, $\sigma(E)$ is the impact cross section of erbium luminescent centers, $v(E)$ is the electron velocity, $f(E)$ is the energy distribution function of electrons, and

$$g(F) = \int_0^\infty v(E)f(E)dE, \qquad (2)$$

where F is the electric field. Here, we assume that $\sigma(E)$ is independent of electron energy and temperature and can be approximated with an average cross section σ_0.

The emission intensity L at low excitation is given by

$$L = N\eta_f R, \qquad (3)$$

where η_f is the fluorescence efficiency and N is the erbium density. $f(E)$ can well be approximated by Baraff's distribution function, which is given by[17]

$$f(E) = CE^{-a-0.5}\exp(-bE), \qquad (4)$$

where

$$a = \frac{E_p - eF\lambda}{2E_p + eF\lambda},$$

$$b^{-1} = \frac{2eF\lambda}{3} + \frac{(eF\lambda)^2}{3E_p},$$

E_p is the energy loss due to scattering, and λ is the mean free path associated with this energy loss. In Baraff's equation, only the mean free path and the energy loss are factors which may be dependent on temperature. The energy loss of electrons may be due to collision either with phonons or erbium atoms (or erbium-related defects). As we do not observe any change in the apparent threshold energy with a change in temperature, it is considered that electrons lose energy due to collision with erbium atoms (or defects). This is very likely as the erbium density in the active layer is very high in our samples. As a result, the temperature dependency of the EL emission intensity comes from the change in electron density n and fluorescence efficiency η_f as shown in the following equation:

$$L_{EL}(T, F) = N\eta_f(T)R(T, F) = N\sigma_0\eta_f(T)n(T)g(F). \qquad (5)$$

The temperature dependence of $n(T)$ can be canceled out when L_{EL} is differentiated with respect to current I. With this procedure, we obtain direct information on the temperature dependence of the fluorescence efficiency $\eta_f(T)$ from the temperature dependence of dL/dI. We define the differential EL emission efficiency η_{der}^{EL}, which is given by

$$\eta_{der}^{EL} = d(SwL_{EL})/d(I/e) = wN\eta_f\sigma_0 = \eta_f\eta_{ET}^{EL}, \qquad (6)$$

where

$$\eta_{ET}^{EL} = wN\sigma_0, \qquad (7)$$

S is the current flowing area, and w is the active layer thickness. Here, we call η_{ET}^{EL} the EL energy transfer effi-
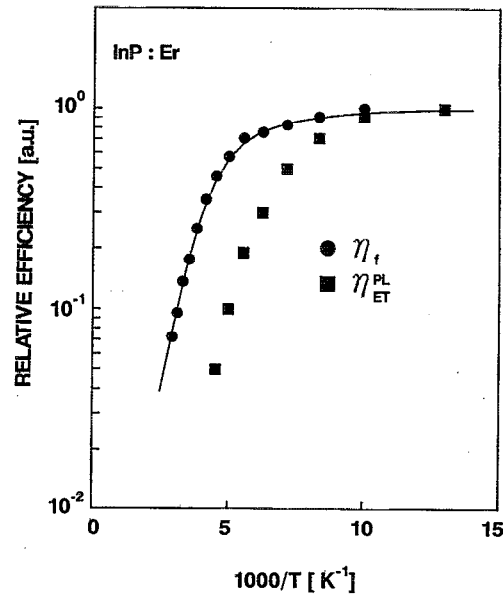

FIG. 7. Temperature dependence of the fluorescence efficiency (closed circle) which is normalized with respect to the value at 77 K and the fitting curve (solid line) using the analytical expression considering two nonradiative transition processes, $\eta_f(T) \sim [1 + A_1\exp(-E_1/kT) + A_2\exp(-E_2/kT)]^{-1}$, with the activation energies of $E_1 = 40$ meV and $E_2 = 150$ meV and the preexponential coefficients of $A_1 = 5.1$ and $A_2 = 1.8 \times 10^3$, respectively. The temperature dependence of the PL energy transfer efficiency (closed square) is also shown.

ciency (per unit electron flow). As η_{ET}^{EL} is independent of temperature, $\eta_f(T)$ is the only factor which induces the temperature dependence in η_{der}^{EL}.

The PL emission intensity L_{PL} (the number of photons emitted per unit time and volume) is given by

$$L_{PL}(T) = C\eta_f(T)\eta_{ET}^{PL}(T)G_{ex}, \qquad (8)$$

where $\eta_{ET}^{PL}(T)$ is the PL energy transfer efficiency, G_{ex} is the excitation rate of electron-hole pairs, and C is a constant. Here, we assume that the fluorescence process of the 1.54-μm emission is independent of the energy transfer process, and that the same fluorescence efficiency η_f can be used for both EL and PL.

Using the above relations, we can deduce the relative temperature dependence of $\eta_f(T)$ from experimental $dL_{EL}(T)/dI$, and then $\eta_{ET}^{PL}(T)$ from the above obtained $\eta_f(T)$ and experimental $L_{PL}(T)$.

In Fig. 7 are shown the relative changes in $\eta_f(T)$ and $\eta_{ET}^{PL}(T)$ as functions of temperature with respect to values at 77 K. It is found that the fluorescence efficiency $\eta_f(T)$ is a slowly decreasing function of temperature. As for the energy transfer efficiency, η_{ET}^{EL} is independent of temperature, whereas η_{ET}^{PL} decreases very rapidly with increasing temperature, to which the large thermal quenching of the 1.54-μm PL emission peak may be attributable.

The fluorescence process of rare-earth ions has been investigated by measuring the time decay of the PL emission.[7-12] In the case of 1.54-μm emission from Er^{3+} ions in semiconductors, Klein and Pomrenke[10] reported that the PL decay time of about 1 ms at 10 K, which was

comparable to the 4–5-ms decay time measured for Er^{3+} ions in insulating crystals and glasses, indicating that the decay process was mostly radiative at low temperatures. They observed only a small contribution of competing nonradiative processes and attributed them to defects in close proximity to the rare-earth sites, or to free-carrier Auger processes.

The 1.54-μm fluorescence efficiency $\eta_f(T)$ obtained in the present experiment is nearly constant from 77 to 200 K, and then shows a decrease above 200 K. This thermal quenching is due to the increase in nonradiative transitions with increasing temperatures. Theoretically, the fluorescence efficiency should be proportional to the fluorescence decay time which is the combination of the temperature-independent radiative lifetime and temperature-dependent nonradiative lifetimes. The above obtained curve $\eta_f(T)$ can well be fitted to a theoretical curve (solid line in Fig. 7) with two nonradiative processes[8] with the activation energies of 40 and 150 meV, respectively. The activation energy of 40 meV which is related to the initial decay in the temperature range of 150–220 K agrees very well with that of the PL time decay for Er^{3+} ions doped in GaAs (up to 240 K)[11] and in AlGaAs (up to 220 K).[12]

Multiphonon relaxation may be a possible process for the nonradiative transition, but it needs a large number of phonons (about 20 pcs) to account for the activation energy of 150 meV. We speculate that the Auger effect related to free carriers and/or to Er-related defects may be responsible for the nonradiative processes.[18,19]

The thermal quenching curve of the PL energy transfer efficiency is not so simple either that it can be fitted to a theoretical curve with a single activation energy. We consider that two or more nonradiative processes of electron-hole pairs in InP (e.g., Auger recombination, recombination through defects, and so on) are involved in the large thermal quenching of the PL emission of Er ions. Recently, it has been reported that the thermal quenching of the PL emission intensity of Er^{3+} ions is strongly mitigated with increasing the band-gap energy of the host semiconductor materials.[20] This result might suggest the involvement of the Auger process for the thermal quenching.

It was shown that the fine structure of the 1.54-μm peak was different between PL and EL emissions from the same sample (Fig. 5). Each fine peak 1–5 is located both in PL and EL at the same energy, but the relative intensity of each peak is different between EL and PL. Peak 2 at 1.541 μm is dominant in PL, whereas peak 3 at 1.543 μm is dominant in EL.

The relative intensity of each fine peak was also process dependent.[21,22] We speculate that Er atoms are incorporated on various lattice sites depending on doping methods, erbium concentrations, or impurities/defects. Er atoms on different lattice sites may be subjected to different crystal fields, resulting in multiplex peaks at different emission energies.

The reason for different fine spectra between EL and PL may be that Er atoms on different sites are excited depending on the excitation methods. Peak 2, which was dominant in PL but small in EL, was found to increase in
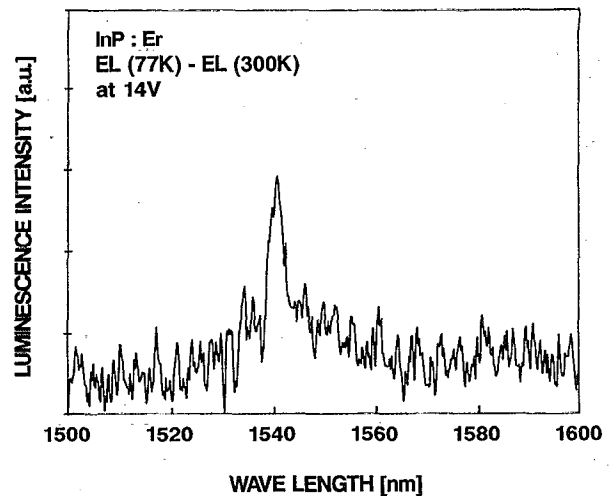

FIG. 8. Difference in spectra of the Er-related EL emission between 77 and 300 K under the same applied voltage of 14 V.

the 77-K EL with increasing applied voltage when the band-edge-related emission bands of the InP host material appeared. The difference in the 77-K EL fine spectra between 14 and 12 V shown in Fig. 5 was found to give a fine peak corresponding to peak 2. This peak was also obtained when the difference in the fine spectra was taken between 77 K and room temperature at 14-V bias. The result is shown in Fig. 8. The appearance of peak 2 by the above-mentioned subtraction procedure indicates that peak 2 was related to the recombination of electron-hole pairs caused by the impact ionization. The absence of peak 2 at room temperature in spite of the emission of the band-edge-related emission bands is consistent with the strong thermal quenching of the Er-related PL emission peak, although the band-edge-related emission was observed at room temperature. Peak 3 is, on the other hand, related to the impact excitation mechanism.

Although the reason for the selective excitation of Er atoms on special lattice sites depending on the excitation methods is not clear, a recent report by Taniguchi et al.[23] in the emission of Nd in GaP supports our speculation. They observed that the intensity of Nd-related emission obtained by illuminating above-band-gap energy light (photoluminescence) was very much weaker than those obtained by exciting Nd $4f$ electrons directly with light from the ground state to the excited states using the photon energy corresponding to the transition energy of $4f$ electrons. They speculated that the recombination energy of electron-hole pairs excited Nd atoms only on special lattice sites and therefore this energy transfer process was very ineffective. Both Taniguchi et al.'s and our results may give us a clue for investigating the energy transfer mechanism and improving the emission efficiency of the rare-earth atoms in semiconductors.

V. CONCLUSION

The Er-related 1.54- and 0.9-μm emission peaks were observed by applying dc voltage to the Er-implanted layer

in InP. It was shown that the excitation was due to the direct impact excitation of Er $4f$ electrons by hot electrons accelerated by the high electric field.

Analysis of the temperature dependence of the 1.54-μm emission peaks of both EL and PL from the same sample led to the following conclusive remarks.

(1) The EL energy transfer rate is almost independent of temperature.

(2) The PL energy transfer efficiency decreases, on the contrary, rapidly with increasing temperature, and this is the main cause for the strong thermal quenching of the PL emission of the Er-related 1.54-μm peak.

(3) The fluorescence efficiency which is common to PL and EL decreased slowly with increasing temperature, the value at 300 K being still half that at 77 K.

The fine structure of the 1.54-μm emission was found to be different between EL and PL. It was speculated that Er atoms on different lattice sites were excited depending on the excitation method.

ACKNOWLEDGMENTS

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