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Thermal Quenching of Er-Related Luminescence in GaInP Doped with Er by Organometallic Vapor Phase Epitaxy

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Thermal quenching of Er-related photoluminescence (PL) due to intra-4f shell transitions of Er^{3+} ions has been investigated in $Ga_xIn_{1-x}P$ ($0 \leq x \leq 1$) doped with Er by organometallic vapor phase epitaxy (OMVPE). In GaInP grown on GaP and InP, the 4.2 K PL intensity gradually increases with increasing Ga composition, while the spectral shape remains unchanged. In GaInP grown on GaAs, the 4.2 K PL spectrum is dominated by three emission lines whose relative intensity depends on the Ga composition. Thermal quenching of the Er-related luminescence gradually decreases with increasing Ga composition, i.e., increasing band gap. PL lifetimes and their temperature variations are discussed in relation to deep-level properties of Er in the excitation mechanism of the 4f shell.

KEYWORDS: erbium, GaInP, organometallic vapor phase epitaxy, photoluminescence, thermal quenching, lifetime, energy-transfer model

1. Introduction

Er-doped III-V semiconductors have been attracting increasing attention because they have great potential for use in optical communication systems operating near the 1.5 μm wavelength region that is the region of minimum transmission loss in silica-based fibers.[1)] The intra-4f shell transitions from the first excited state ($^4I_{13/2}$) to the ground state ($^4I_{15/2}$) of the Er^{3+} ions result in emission near 1.5 μm.

We have intensively investigated Er-doped P-based III-V semiconductors such as InP and GaP grown by organometallic vapor phase epitaxy (OMVPE). In Er-doped InP (InP:Er), Er-related photoluminescence (PL) spectra exhibit strong dependence on growth temperature, and the intensity of the main emission line at 0.8045 eV ($\lambda = 1.5411\,\mu$m) increases greatly from 580 to 550°C, and saturates with decreasing growth temperature, which is well interpreted in terms of a drastic change in atom configurations around Er doped in InP.[2–6)] In Er-doped GaP (GaP:Er), Er-related PL spectra are dominated by numerous extremely sharp emission lines. The intensity of the emission lines strongly depends on the growth temperature, Er concentration and reactor pressure, indicating the coexistence of various Er-related luminescence centers in the samples.[7,8)] There have been limited studies on Er-doped GaInP (GaInP:Er), although knowledge about the behavior of the Er-related luminescence in GaInP provides a clue for understanding the mechanisms of 4f-shell excitation and relaxation in Er doped in P-based III-V semiconductors.

In this paper, we report the observation of luminescence due to the intra-4f shell transitions of Er^{3+} in GaInP:Er with Ga compositions varied by steps between 0 and 1 with cw and pulse excitations. Thermal-quenching properties of the Er-related luminescence are discussed in the framework of an energy transfer model.

2. Experimental

The low-pressure growth system with a vertical quartz reactor was utilized in this work. Details of the growth system have been described previously.[9)] TEGa, TMIn and TBP were used as source materials for GaInP growth on InP and GaAs, and TMGa, TMIn and TBP were used for GaInP growth on GaP. $Er(MeCp)_3$ (tris(methylcyclopentadienyl)erbium), as the Er source, was maintained at 100°C and introduced into the reactor by H_2 flow through the Er source cylinder. The rate of the H_2 flow, called the Er flow rate hereafter, was kept mainly at 50 sccm, corresponding approximately to an Er concentration of 1–2 $\times$ 10^{18} cm^{-3} in GaInP:Er. The Ga composition of GaInP:Er was determined by double-crystal X-ray diffraction.

In PL measurements at 4.2 K, the samples were directly immersed into liquid He. Temperature-dependent PL measurements were carried out with the samples set on a cold finger of a temperature-variable closed-type He cryostat. In conventional PL measurements, the photoexcitation source was a cw He–Cd laser, operating at 365 nm, with an incident power of 30 mW. The luminescence of the sample was dispersed with a 1.25 m monochromator and detected by a Ge pin photodiode cooled by liquid N_2. In time-resolved PL measurements, a pulsed dye laser, operating at 385 nm, pumped by an excimer laser was used as a photoexcitation source. The luminescence was detected through a 0.32 m monochromator using a GaInAs photomultiplier tube. The PL decay behaviors were obtained using a digital oscilloscope.

3. Results and Discussion

3.1 Er-related luminescence in GaInP:Er grown on GaP and InP

GaInP:Er was grown pseudomorphically on GaP and InP to investigate the effects of In addition to GaP:Er and Ga addition to InP:Er on the Er-related luminescence. The 4.2 K PL spectra of the GaInP:Er samples grown on GaP with the Ga compositions of 0.996 and 0.99 are exactly the same as that of GaP:Er, exhibiting extremely sharp emission lines.[7,8)] The PL intensity gradually increases with increasing Ga composition, i.e., increasing band gap, and similar behaviors are observed in GaInP:Er grown on InP.

The PL intensity increase with increasing Ga composition is explained by an enhanced probability of the intra-4f shell

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transitions of Er^{3+}. A recent study of time-resolved PL shows that the lifetime of the Er-related luminescence decreases with increasing Ga composition at 4.2 K, supporting the enhancement of the transition probability. The enhancement might be due to an increased mixture of wave functions of Er and its first- or second-nearest neighbor atoms because the lattice constant of host materials decreases with increasing Ga composition.

3.2 Er-related luminescence in GaInP:Er grown on GaAs

The Er-related luminescence has been investigated in GaInP grown on GaAs. Figure 1 shows the Er flow rate dependence of 4.2 K Er-related PL spectra in GaInP:Er, which is approximately lattice-matched to GaAs, together with the spectrum of the lattice-mismatched GaInP:Er prepared with the Er flow rate of 50 sccm at 610°C. We observe three emission lines at 0.8020, 0.8045 and 0.8087 eV. In the lattice-matched GaInP:Er, the intensity of the main emission line at 0.8045 eV increases roughly with the Er flow rate, i.e., the Er concentration, but the flow rate dependence is sublinear, as described previously for GaP:Er and InP:Er.[2,7)]

We notice the difference in relative intensity between the lattice-matched and -mismatched GaInP:Er. In the lattice-mismatched GaInP:Er, the intensity of the emission line at 0.8087 eV is relatively strong among the three lines compared with the spectra of the lattice-matched samples. These results indicate that there are two types of Er-related luminescence centers in GaInP:Er, and that the center responsible for the 0.8087 eV line differs from the center for the 0.8020 eV and 0.8045 eV lines.

3.3 Thermal quenching of Er-related luminescence in GaInP:Er

Thermal-quenching properties of the Er-related luminescence have been investigated in GaInP:Er with various Ga compositions. Figure 2 shows temperature dependences of the PL intensity of the Er-related emission line at 0.804 eV in GaInP:Er with different Ga compositions, together with those of InP:Er and GaP:Er. Thermal quenching of the Er-related luminescence gradually decreases with increasing Ga composition; compared with the PL intensity at 18 K, the intensity at 290 K is smaller by a factor of 65 for InP:Er, and by 4 for GaP:Er. Neuhalfen and Wessels also investigated the temperature dependence of the luminescence intensity for several GaInP:Er samples grown on InP with Ga compositions of less than 0.31 and showed that the temperature at which thermal quenching occurs increases with the Ga composition.[10)] Our observation is consistent with their results.

The temperature dependence of the PL intensity, $I(T)$, was analyzed using the following equation[11)]

$$I(T) = I(0)/(1 + A_1 \exp(-E_1/k_B T) + A_2 \exp(-E_2/k_B T)), \quad (1)$$

where $I(0)$ denotes the PL intensity at 0 K. A_1 and A_2 are pre-exponential factors, and E_1 and E_2 are activation energies. In Fig. 3, the activation energies determined by fitting eq. (1) to the experimental results are shown as a function of Ga composition. With increasing Ga composition, E_1 increases slightly (6.1 meV to 9.0 meV) and E_2 decreases drastically from 125 meV to 36 meV. Using the same procedure, Fang *et al.* obtained the activation energies of 11 meV (E_1) and 74 meV (E_2) in Er-doped GaAs.[12)]

In order to obtain further information about the thermal-quenching properties of the Er-related luminescence in GaInP:Er, we performed time-resolved PL measurements on GaP:Er and InP:Er. Figure 4 shows the temperature dependence of the lifetimes (closed circles) of an Er-related PL line measured at 0.804 eV in GaP:Er. For comparison, the PL intensity is replotted as a function of temperature by open circles. The lifetime remains almost constant with increasing temperature up to 260 K, though the intensity exhibits thermal quenching. The results for InP:Er are shown in Fig. 5. The lifetime also remains unchanged at temperatures below 100 K, while it decreases gradually with increasing temperature above 140 K. It should be noted that the temperature at

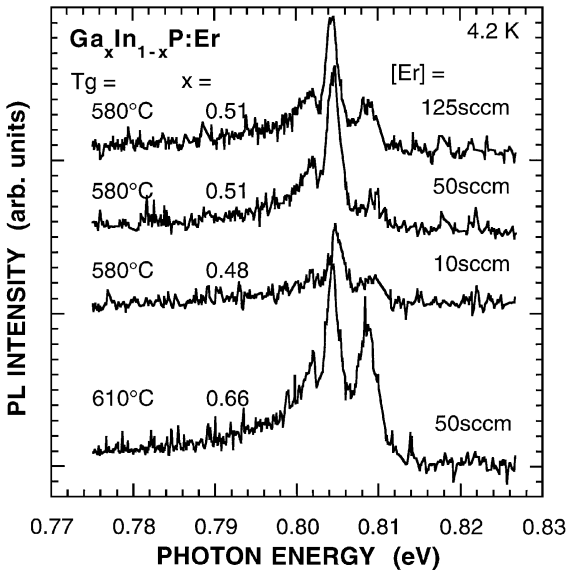

Fig. 1. 4.2 K Er-related PL spectra in GaInP:Er grown on GaAs.

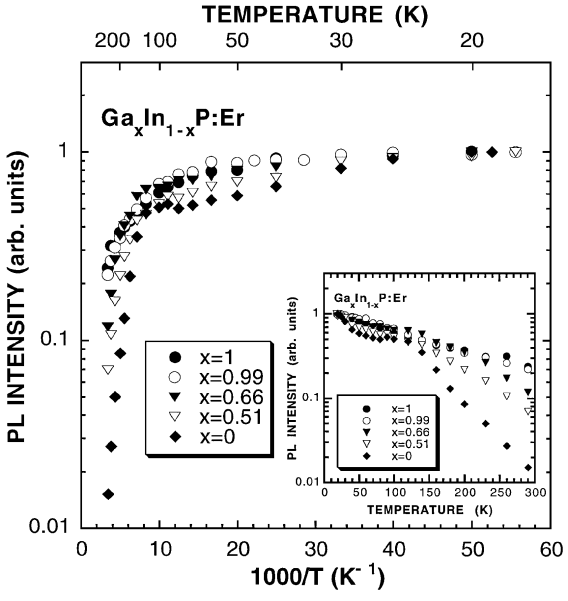

Fig. 2. Temperature dependences of the PL intensity of the Er-related emission line at 0.804 eV in GaInP:Er with different Ga compositions.

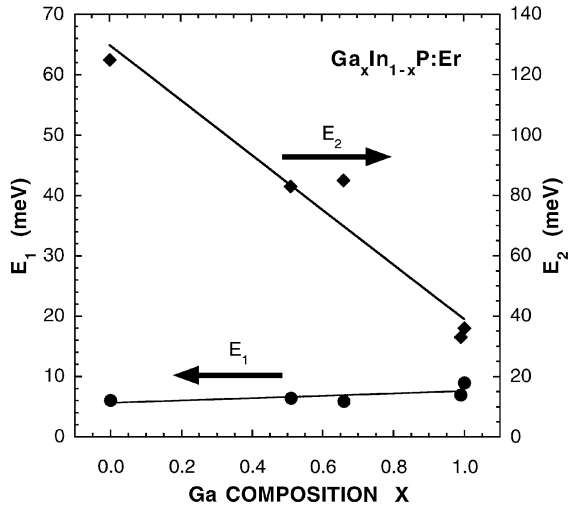

Fig. 3. Ga composition dependence of the activation energies in GaInP:Er.

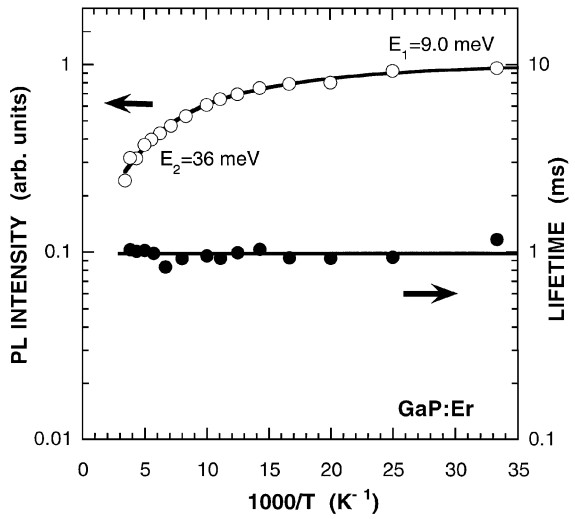

Fig. 4. Temperature dependence of lifetimes of the Er-related emission line at 0.804 eV in GaP:Er (closed circles). The normalized PL intensity as a function of temperature is also shown by open circles.

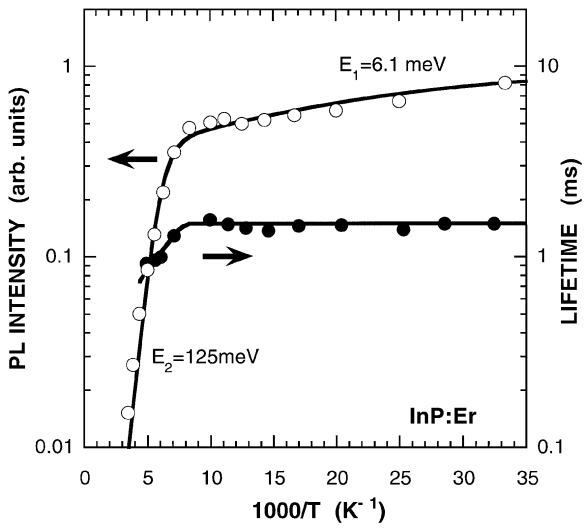

Fig. 5. Temperature dependence of lifetimes of the Er-related emission line at 0.804 eV in InP:Er (closed circles). The normalized PL intensity as a function of temperature is also shown by open circles.

which a kink appears coincides with the temperature at which the PL intensity starts to decrease steeply.

Now let us discuss the thermal-quenching properties of the Er-related luminescence in GaInP:Er. Mechanisms for 4f-shell excitation and relaxation in rare-earth (RE) ions in semiconductors are generally explained by an energy transfer model.[13] In the model, the RE 4f shell is excited by the recombination of an electron-hole pair at a carrier trap. In the case where Er forms an electron trap, a free electron which is generated by the above-bandgap excitation is captured by the trap, and subsequently, the negatively charged trap captures a hole. The trapped electron and hole form a weakly correlated electron-hole pair or an exciton. Such an electron-hole pair recombines radiatively and a part of the recombination energy is transferred to the Er 4f shell, leading to a 4f-shell excitation.

As shown in Fig. 4, the time-resolved PL measurements on GaP:Er revealed that the lifetime of the Er-related luminescence remains almost constant with increasing temperature up to 260 K, which suggests that the decrease of the PL intensity at elevated temperatures is associated with nonradiative processes taking place prior to the 4f shell excitation. Therefore, the observed activation energy E_1 of 9.0 meV can be assigned to the binding energy of the electron-hole pair because the energy is comparable to the binding energy of excitons in P-based III-V semiconductors. On the other hand, E_2 might be ascribed to the energy of electron emission from the electron trap to the conduction band.

In InP:Er, the lifetime gradually decreases in the temperature region where E_2 is dominant. The decrease of the lifetime indicates that nonradiative processes are involved in the relaxation process of excited 4f electrons. Taguchi and Takahei have reported that for Yb-doped InP, Er and O-codoped GaAs, Nd-doped GaP and Nd-doped GaAs a multiphonon-assisted energy transfer from RE 4f shell to host materials plays an important role in the nonradiative processes.[14] A detailed study should be performed for comprehensive understanding of E_2 in InP:Er.

4. Conclusion

We have investigated the Er-related luminescence due to the intra-4f shell transitions of Er^{3+} in GaInP:Er grown by OMVPE. In GaInP:Er grown on GaP and InP, the 4.2 K PL intensity gradually increased with increasing Ga composition, while the PL spectrum remained unchanged. The enhancement of the PL intensity with increasing Ga composition is interpreted in terms of the enhanced probability of the intra-4f shell transitions of Er^{3+}. In GaInP:Er grown on GaAs, the 4.2 K PL spectrum was dominated by three emission lines whose relative intensity was dependent on the Ga composition, indicating that there coexist a few Er-related luminescence centers in GaInP:Er. Thermal quenching of the Er-related luminescence gradually decreases with increasing Ga composition, and the analysis of the behaviors gave two types of activation energies, E_1 and E_2. E_1 and E_2 can be assigned to the binding energy of an electron-hole pair at the Er trap and the electron emission energy from the trap to the conduction band, respectively. In GaP:Er, the lifetime of the Er-related luminescence remained constant up to 260 K, which suggests the existence of the nonradiative processes prior to the 4f-shell excitation. In InP:Er, on the other hand, the

lifetime gradually decreased in the temperature region above 140 K, indicating that the nonradiative processes in the relaxation of excited 4f electrons contribute to thermal quenching in the high-temperature region.

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