Organometallic Vapor Phase Epitaxy of Er,O-codoped GaAs using Tris(dipivaloylmethanato)erbium

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Abstract. Er,O-codoped GaAs (GaAs:Er,O) was grown by organometallic vapor phase epitaxy (OMVPE) using tris(dipivaloylmethanato)erbium [(C₁₁H₁₉O₂)₃Er : Er(DPM)₃] at different growth temperatures (Tg). In photoluminescence (PL) measurements, Er-related PL lines partly assigned as an Er-2O center were observed in the samples grown at Tg = 500-550 °C. The result revealed that the self formation of Er-2O center was accomplished by an incorporation of oxygen atoms in the Er(DPM)₃ source. In the dependence of a H₂ flow rate through the Er source on the PL properties, the intensity of the Er-related PL increased as that of the band-edge PL of GaAs host decreased. The correlation of PLs shows a highly efficient energy-transfer from GaAs host to the 4f-shell of Er ions in the GaAs:Er,O samples.

1. Introduction
Much attention has been paid to rare-earth (RE) doped semiconductors as a promising new class of materials that emit light from the RE 4f shell by means of electrical injection. The intra-4f shell transitions of RE ions give rise to sharp emission lines whose wavelengths are independent of both host materials and temperature. This stability occurs because the filled outer 5s and 5p electron shells screen transitions within the inner 4f electron shell from the interaction with the host. The intra-4f shell transitions from the first excited state (4I₁₃/₂) to the ground state (4I₁₅/₂) of Er³⁺ ions at 1.54 µm is of special interest because the wavelength matches the minimum loss region of silica fibers used in optical communications.

We have intensively investigated organometallic vapour phase epitaxy (OMVPE) and luminescence properties of Er-doped III-V semiconductors [1]. In Er,O-codoped GaAs (GaAs:Er,O), the codoping of oxygen gas with Er organic-source plays an important role in the production of an efficient Er-related luminescent center. The Er center has been identified as an Er atom located at the Ga sublattice with two adjacent O atoms (hereafter referred as Er-2O) together with two As atoms [2]. The formation of Er-2O center results in the intensive Er-related photoluminescence (PL) dominated by seven emission lines under host-excited conditions [3]. For applications of Er-related luminescence to optical devices, the high-efficiency formation of Er-2O center is essential. In the OMVPE growth of Er-doped III-V semiconductors, tris(cyclopentadienyl)erbium Er(EtCp)₃ [4], tris(methylcyclopentadienyl)erbium Er(MeCp)₃ [5,6] and isopropyl-tris(methyl-cyclopentadienyl)erbium Er(i-PrCp)₃ [3,7,8] have been mainly used as Er source, but these Er sources do not contain oxygen atom in

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itself. On the other hand, tris(dipivaloylmethanato)erbium [(C₁₁H₁₉O₂)₃Er : Er(DPM)₃] contains oxygen atoms around Er atom. Therefore, the self formation of Er-2O center without the codoping of oxygen gas is considered to be achieved by OMVPE growth using Er(DPM)₃.

In this paper, we have performed OMVPE growth of GaAs:Er,O using Er(DPM)₃ without the codoping of oxygen gas. The formation of Er-2O center in the GaAs:Er,O were investigated by PL measurements at 4.2 K and 77 K.

2. Experiments
The samples were grown on (001)-oriented semi-insulating GaAs substrates by a low-pressure OMVPE system with a horizontal quartz reactor. The reactor pressure was maintained at 76 Torr. Triethylgallium and tertiarybutylarsine were used for the GaAs growth. Er doping to the GaAs layer was carried out with Er(DPM)₃ source which was introduced into the reactor by a H₂ flow through the Er source cylinder (hereafter defined as Er flow rate). The Er cylinder was maintained at a constant temperature of 70 °C under low pressure (76 Torr). The 1-µm-thick GaAs:Er,O layer was grown at a growth rate of 1 µm/h. The growth temperature (Tg) of GaAs:Er,O was changed at 500-580 °C because the optimization of the temperature is necessary to obtain the highest PL intensity [9]. The Er concentration was controlled by changing the Er flow rate at 300-900 sccm. The Er concentration of all samples was below the detection limit of secondary ion mass spectroscopy (SIMS) measurements (10¹⁵ cm⁻³).

In PL measurements of GaAs:Er,O, the optical properties of the Er-related PL between the ⁴I₁₃/₂ and ⁴I₅/₂ levels was investigated at 4.2 K and 77 K. The photoexcitation source was a cw Ar⁺ laser, operating at 514.5 nm, with an incident power of 30 mW. The luminescence signal was detected by a single grating monochromator with a Ge detector cooled to 77 K.

3. Results and Discussion
Figure 1 shows the growth temperature dependence of the Er-related PL spectra at 4.2 K. The Er flow rate was fixed at 500 sccm. The Er-related PL spectra are observed in the samples grown at

![Figure 1](image1.png)

**Figure 1.** The growth temperature dependence of the Er-related PL spectra at 4.2 K. The Er flow rate is fixed at 500 sccm.

![Figure 2](image2.png)

**Figure 2.** The temperature dependence of PL spectra in GaAs:Er,O grown at 525 °C. The solid lines shows the emissions from Er-2O center.
temperatures lower than 550 °C. The dependence of PL spectra on the growth temperature reveals the existence of a threshold growth temperature at 550-580 °C. The PL intensity increases drastically at 525 °C, and the growth temperature for the Er-doping is optimized to 525 °C.

Figure 2 shows the temperature dependence of PL spectra in GaAs:Er,O grown at 525 °C. Emission lines assigned to Er-2O center (solid lines in the figure) are observed at 4.2 K and 77 K. The result indicates that the Er-2O center is formed by an incorporation of the oxygen atom in Er(DPM)₃. However, PL lines different from Er-2O center are also observed, indicating that Er atoms with different atomic configurations from Er-2O center coexist in the sample. The change of the relative intensity of the emission lines with temperature would be due to the mixing of the emission centers.

Figure 3 shows the band-edge spectra of GaAs (a) and the Er-related PL spectra (b) as a function of the Er flow rate. The growth temperature was fixed 525 °C. The samples show both the band-edge and the Er-related PL. The intensity of the band-edge PL in Fig. 3(a) is comparable to that of non-doped GaAs grown at high temperature of 650 °C. In OMVPE grown GaAs:Er,O samples, the optical property of the band-edge PL has not been investigated because the PL intensity of the band-edge PL was very weak. In this way, we succeeded for the first time in the investigation of the relationship between the band-edge and the Er-related PL intensity. The PL intensities depended on the Er flow rate. In the sample grown at 500 sccm, the PL intensity of the band-edge shows a minimum, while that of the Er-related shows a maximum. The results indicate that there is a correlation between the band-edge and the Er-related PL intensity. In Fig. 4, we summarize the dependence of the band-edge PL intensity on the Er-related PL intensity. As seen in the figure, the band-edge PL intensity becomes small with the increase of the Er-related PL intensity. The result is a clear evidence of a highly efficient energy-transfer from GaAs host to the 4f-shell of Er ions.

In the OMVPE growth of GaAs:Er,O, as mentioned before, the Er-2O center which induces the intensive 1.54 µm emission has been formed by the co-doping of oxygen gas with Er organic-source. However, it is well known that oxygen atoms in GaAs form the deep level in the band gap, resulting in the increase of the non-radiative recombination processes. Therefore, the formation of Er-2O center by the codoping of small quantity of oxygen gas is desirable to suppress the non-radiative recombination processes in the sample. In the growth of GaAs:Er,O using Er(DPM)₃ without the codoping of oxygen gas, the Er-2O center was partially formed by an incorporation of the oxygen

![Figure 3](image1.png)

**Figure 3.** The band-edge spectra of GaAs (a) and the Er-related PL spectra (b) as a function of the Er flow rate.

![Figure 4](image2.png)

**Figure 4.** The dependence of the band-edge PL intensity on the Er-related PL intensity.
atom in the source. The self formation of Er-2O center is expected to reduce the amount of oxygen gas in the codoping of Er and oxygen gas. In further experiments, GaAs:Er,O samples have been grown using Er(DPM)$_3$ with the codoping of oxygen gas. In the dependence of the oxygen content, the GaAs:Er,O sample grown at O$_2$ = 0.05 ppm showed only the emission form the Er-2O center, indicating that all the luminescent Er atoms have the Er-2O center. The O$_2$ content is smaller than that of 0.2 ppm reported [3].

4. Conclusions
GaAs:Er,O was grown by OMVPE using Er(DPM)$_3$ without the codoping of oxygen gas. The Er-related PL around 1.54 µm was observed in the samples grown at $T_g = 500$-$550$ °C, and the critical growth temperature for Er-doping was estimated to be from 550 °C to 580 °C. The PL intensity increased drastically at 525 °C, and the growth temperature for the Er-doping was optimized to 525 °C. In the temperature dependence of the Er-related PL spectra, it was revealed that the self formation of Er-2O center was accomplished by an incorporation of the oxygen atom in the Er(DPM)$_3$ source, although PL lines different from Er-2O center were also observed. The self formation of Er-2O center by the incorporation enabled the growth of the high-quality GaAs:Er,O which shows both the Er-2O emission and the band-edge PL of GaAs. The dependence of the band-edge PL intensity on the Er-related PL intensity showed an evidence of a highly efficient energy-transfer from GaAs host to the 4f-shell of Er ions in the GaAs:Er,O samples.

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