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MOCVD Growth and PL-Characteristics of Nd Doped GaAs

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Nd-doped GaAs epitaxial layers were grown by low-pressure metalorganic chemical vapour deposition. Using an organic rare-earth source, $(CH_3C_5H_4)_3Nd$, Nd concentrations in GaAs were controlled by source temperature in the range from 10^{17} to 10^{19} cm^{-3}. Photoluminescence due to intra-4f-shell transitions in Nd^{3+} ions was observed around 0.9 eV, 1.1 eV, and 1.4 eV. The spectra are nearly independent of Nd concentration and show maximum intensity at $3x10^{18}$ cm^{-3}. However, the spectra depend slightly on the growth temperature, reflecting the change in relative density of Nd^{3+} emitting centers with different surrounding atomic configurations.

1. INTRODUCTION

Rare-earth-doped Ⅲ - Ⅴ semiconductors are attracting increasing interest for possible application to temperature-stable light sources.[1] Such devices combine the advantages of sharp and stable temperature-independent rare-earth luminescence[2] with the ability of semiconductors to activate the emitting rare-earth center by carrier injection. Among various rare-earth elements, neodymium (Nd) is of particular interest because of its four-level lasing scheme allowing low threshold lasing. Nd doping in Ⅲ - Ⅴ semiconductors (GaP and GaAs) has been achieved by ion implantation, and photoluminescence (PL) due to intra-4f-shell transition in Nd^{3+} ions was observed.[3,4]

This paper reports growth of Nd-doped GaAs epitaxial layers by metalorganic chemical vapour deposition. Uniform high Nd doping is achieved using $(CH_3C_5H_4)_3Nd$ as a rare-earth source, and PL due to Nd^{3+} intra-4f-shell transition was observed. Nd concentration and growth temperature dependences of the PL spectra is described.

2. Nd SOURCES

Tris-cyclopentadienyl neodymium $[(C_5H_5)_3Nd]$ is probably the most well studied organic compound of Nd. The vapour pressure of this compound as a function of temperature as reported previously is shown in Fig. 1.[5,6] The vapour pressure of this material is much lower than for materials typically used in MOCVD, such as triethylgallium (TEG) also shown in the figure.

We have reported that in the case of erbium(Er), $(CH_3C_5H_4)_3Er$ has a higher vapour pressure than $(C_5H_5)_3Er$.[7] We therefore synthesized $(CH_3C_5H_4)_3Nd$ as well as $(C_5H_5)_3Nd$, and measured vapour pressure by a mass transport method which simulates actual source transport by carrier gas in MOCVD growth. An appropriate amount of source material was charged in a bubbler and carrier gas was allowed to flow through the bubbler. The transport rate was confirmed to be proportional to the carrier gas flow rate. From the weight loss of the source material in the bubbler, the vapour pressure at the temperature of the bubbler was calculated as shown in the figure. Here, the source material was assumed to vaporize as mono-molecules.

The vapour pressure of $(C_5H_5)_3Nd$ measured in this study lies between the two set of data reported previously, but their gradients against temperature are nearly the same. Comparison of the vapour pressure of $(CH_3C_5H_4)_3Nd$ and $(C_5H_5)_3Nd$ shows that the former can provide the same vapour pressure at much lower temperature. This reduction in temperature simplifies the system design of the MOCVD apparatus and probably reduces contamination from source feedlines.

3. EPITAXIAL GROWTH

Epitaxial layers were grown on Cr-doped GaAs at 76 Torr in a horizontal quartz reactor using trimethylgallium, arsine and $(CH_3C_5H_4)_3Nd$. Growth temperatures were either 550 ℃ or 600 ℃ with growth rates of 1 to 2 µm/h.

Depth profiles of Nd measured by secondary ion mass spectroscopy (SIMS) revealed a uniform and reproducible Nd-doping up to a concentration as high as 10^{19} cm^{-3}. Nd concentration dependence on source temperature was investigated with carrier gas flow rate fixed at 200 sccm (Fig. 1). Although the temperature region of the vapour pressure measurements and the Nd source temperature for the epitaxial growth are different, nearly equal gradients against temperature suggest that the Nd source is reasonably well transported to the reactor.

Nd concentration slightly saturates at a bubbler temperatures above 100 ℃, probably due to condensation of the Nd in some part of the feedline to the reactor. It should be noted that, even at 80 ℃, doping as high as 10^{18} cm^{-3} is possible using $(CH_3C_5H_4)_3Nd$, whereas a temperature over 150 ℃ should be required to attain the same doping level using $(C_5H_5)_3Nd$. Doping levels higher than 3×10^{18} cm^{-3} led to a change in surface morphology from mirror-like to cloudy. This results in the reduction of PL intensities, as shown in the next section.

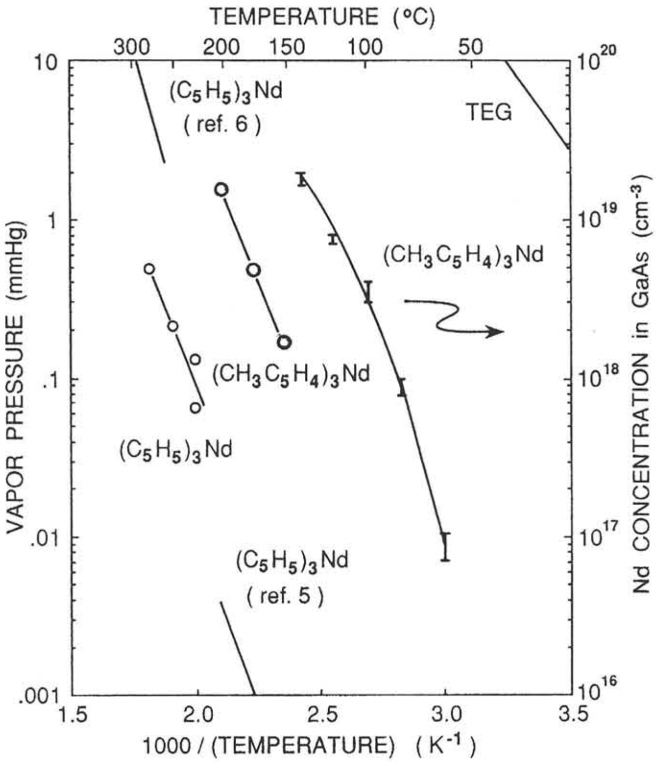

Fig. 1. Vapour pressure of organic Nd compounds and Nd concentration in GaAs as functions of source temperature. Vapour pressure of $(C_5H_5)_3Nd$ and TEG reported previously are also shown.

4. PHOTOLUMINESCENCE

PL spectra were measured using an Ar laser (514.5 nm) and a monochrometor coupled to a cooled Ge p-i-n detector. No corrections were made for the spectral response of the detector and the spectrometer.

Three sets of sharp emission lines are observed in the PL spectrum of a Nd-doped GaAs layer grown at 600 ℃ with a source temperature of 80 ℃ (Fig. 2). These lines correspond to the Nd^{3+} intra-4f-shell transitions $^4F_{3/2} \rightarrow {}^4I_{13/2}$ at 0.9 eV, $^4F_{3/2} \rightarrow {}^4I_{11/2}$ at 1.1 eV and $^4F_{3/2} \rightarrow {}^4I_{9/2}$ at 1.4 eV.

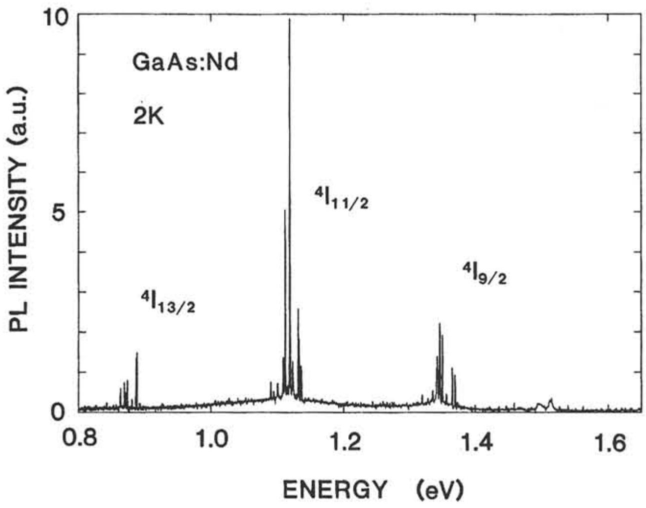

Fig. 2. PL spectra of Nd-doped GaAs grown at 600 ℃. The broad peak at 1.5 eV is related to the energy bands of host GaAs.

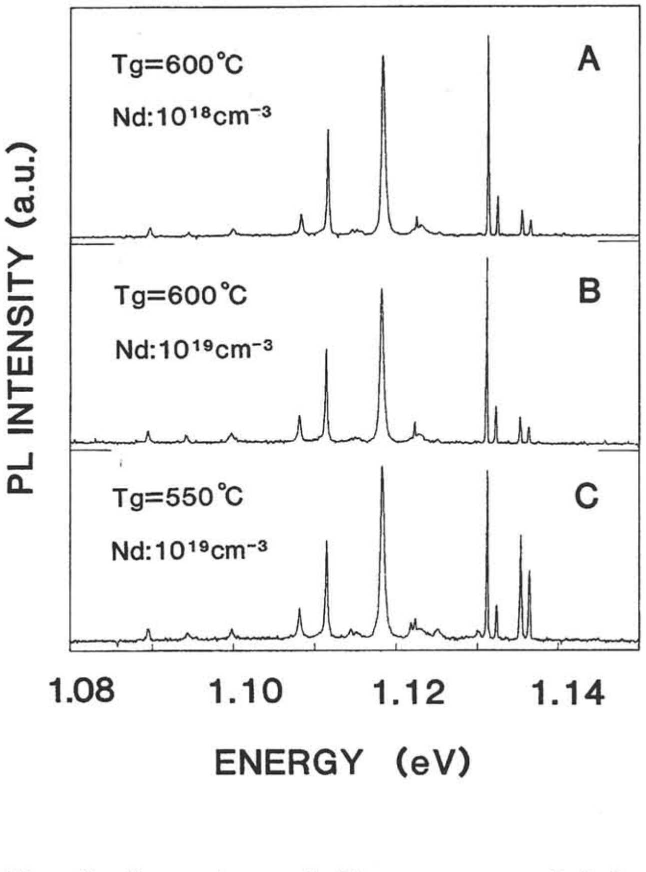

Fig. 3. Comparison of PL spectra at 2 K for Nd-doped GaAs with different Nd concentration [A and B] and those grown at different growth temperature [B and C].

The weak structure around 1.5 eV arises from band-related emission; its intensity decreases as Nd concentration increases. There is also a weak but broad background luminescence superimposed on the sharp intra-4f-shell luminescence. The general features of MOCVD-grown Nd-doped GaAs are similar to those of Nd-implanted GaAs.3)

Figure 3 compares spectra of the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition for epitaxial layers grown under different conditions. A spectral resolution for Fig. 3 (0.08 meV) is higher than that for Fig. 2 (0.4 meV). Fig. 2 and Fig. 3 (A) are the spectra of the same epitaxial layer but relative intensities of corresponding lines appear different. This is due to the fact that actual widths of some lines are smaller than the spectral resolutions.

The spectra of samples A and B are nearly identical in spite of the change in Nd concentration from 10^{18} to 10^{19} cm^{-3}. The spectrum of a sample with Nd concentration of 10^{17} cm^{-3} is also identical, although a high resolution spectrum could not be measured due to weaker PL intensity. On the other hand, reduction of the growth temperature from 600 ℃ to 550 ℃ (Fig. 3 (B) and (C)) results in a change in the relative intensities of the emission lines. This suggests that there are several kinds of Nd emitting centers with different nearest-neighbour atomic configurations, and that their relative densities depend on growth temperature.

Nd-related emission peak intensity at 1.131 eV versus Nd concentration is plotted in Fig. 4. The intensity increases in proportion to Nd concentration up to 10^{18} cm^{-3}; above 10^{18} cm^{-3}, the intensity saturates and begins to decrease at a concentration of 3×10^{18} cm^{-3}. Visually observable degradation of surface morphology takes place at concentrations above 3×10^{18} cm^{-3}, as mentioned in the previous section. Therefore, the decrease in the Nd-related emission intensity is probably caused by the decrease in minority carrier life time due to an increase in the density of defect-related recombination centers.

The linewidth of the Nd-related luminescence line at 1.131 eV is less than 0.05 meV at 2 K and 0.16 meV at 77 K. These values are comparable to those of Nd-doped in insulators such as YAG:Nd,[8] indicating that there is no linewidth broadening mechanism specific to a semiconductor host. However, PL intensity shows a remarkable decrease above 77K.

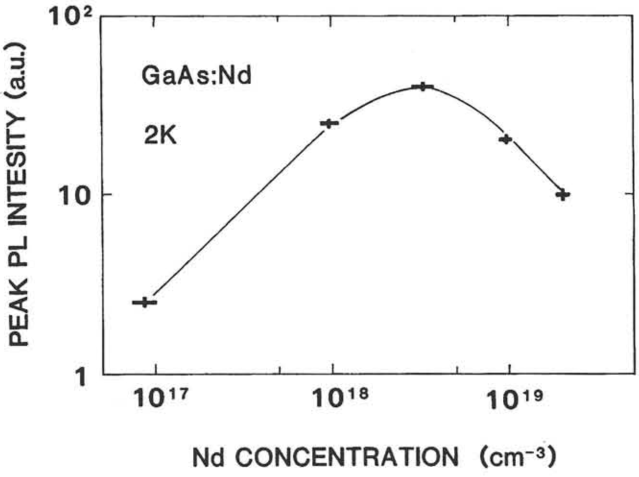

Fig. 4. Peak PL intensity of 1.131 eV emission line at 2 K versus Nd concentration measured by SIMS.

5. CONCLUSIONS

Nd-doped GaAs layers were grown by low-pressure MOCVD using $(CH_3C_5H_4)_3Nd$. Uniform and reproducible doping of Nd as high as 10^{19} cm^{-3} was achieved by variation of Nd source temperature. PL spectra due to Nd^{3+} intra-4f-shell transition were independent of Nd concentration, but slightly dependent on growth temperature. The linewidths of the Nd-related emissions for Nd^{3+} ions doped in GaAs and in YAG are on the same order.

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