Extended Abstracts of the 19th Conference on Solid State Devices and Materials, Tokyo, 1987, pp. 87-90

1.54µm Emission from Er-Doped GaAs and InP Grown by Metalorganic Chemical Vapor Deposition

Kunihiko Uwai, Hiroshi Nakagome, and Kenichiro Takahei NTT Electrical Communications Laboratories 3-9-11 Midori-cho, Musashino-shi, Tokyo 180, Japan

Erbium-related photoluminescence spectra around $1.54\,\mu$ m are reproducibly observed from Er-doped GaAs and InP grown by metalorganic chemical vapor deposition using tris-cyclopentadienyl erbium [Er(C₅H₅)₃] as an Er source. Erbium doping as high as 1.5×10^{19} cm⁻³ was achieved. In the photoluminescence spectra at 2K, the highest peaks at 1542nm for InP:Er and at 1543nm for GaAs:Er are observed together with several other weaker lines at longer wavelengths. The Er-related peak is observed at 1539 ± 1 nm even at 300K for InP:Er, shifting toward the shorter wavelengths by as little as 3nm with increasing temperature from 2K to 300K.

1. Introduction

Rare-earth-doped semiconductors constitute a new class of materials for optoelectronic devices. Among the rare-earth elements, Er is of particular interest because of its sharp photoluminescence (PL) peaks around $1.54\,\mu$ m, which coincide with the minimum loss wavelength region of silica optical fibers. Thus, over the past few years, Er doping in silicon and III-V semiconductors has been attempted by ion implantation¹⁻³, molecular beam epitaxy,^{4,5} and liquid phase epitaxy (LPE).⁶⁻⁸

Recently, Tsang and Logan⁶ obtained single longitudinal mode operation of LPEgrown Er-doped GaInAsP/InP injection lasers. They attributed the single mode operation to the sharp gain profile of Er³⁺ intra-4f transitions. However, uniform Er doping by LPE is very difficult owing to 'the high chemical activity of Er.^{7,8} Inhomogeneities in the GaInAsP active layer due to Er doping are also believed to cause the single mode operation.⁷ Thus, high quality reproducible Er doping methods are desired to fabricate reliable Er-doped GaInAsP/InP injection lasers as well as to investigate the structure of the luminescent Er³⁺ center.

This paper describes the first successful growth of Er-doped III-Vsemiconductors by metalorganic chemical vapor deposition (MOCVD). We have grown Er-doped GaAs and InP epitaxial layers and observed several sharp crystal-field-split zero phonon lines (ZPL), which, to our best knowledge, show the simplest structures ever obtained. Moreover, a remarkable resemblance was revealed between the PL spectra of InP:Er and those of GaAs:Er.

2. Experiment

Growth procedures are similar to those employed for Yb-doped InP.^{9,10} $In(C_2H_5)_3$ or $In(CH_3)_3$ and PH₃ were used for growing InP and $Ga(C_2H_5)_3$ and AsH₃ for growing GaAs in a low-pressure (0.1atm) reactor with H₂ carrier gas. Erbium was doped using triscyclopentadienyl erbium $[Er(C_5H_5)_3]$. Substrates were Fe-doped InP and Cr-doped GaAs with a surface orientation of (100)1~3° off toward [110]. Typical growth temperatures were in the range from 550° C to 650° C for InP and from 600° C to 700° C for GaAs. Depth profiles of the concentrations of Er and other impurities were measured by secondary ion mass spectroscopy (SIMS) using 0_2^+ as a primary ion. Photoluminescence was observed using a He-Ne laser operating at 632.8nm and a 1.25-m monochromator coupled to a cooled Ge p-i-n detector. No corrections were made for monochromator and detector response.

3. Results and Discussions

SIMS measurements revealed that uniform Er doping up to a concentration as high as 1.5×10^{19} cm⁻³ can be obtained reproducibly. The main unintentionally doped impurities were found to be Fe and Mn, which are also incorporated in MOCVD-grown Yb-doped InP.⁹

Figures 1 and 2 show the surface morphology of Er-doped InP and GaAs, respectively, observed using a differential interference microscope. The surfaces of InP:Er with Er concentrations of $\sim 10^{19} \text{cm}^{-3}$ and $\sim 10^{18} \text{cm}^{-3}$ are shown in Fig.1(a) and (b), respectively. The surfaces of InP:Er with Er concentrations of less than 10^{19} cm⁻³ are shiny or slightly hazy to the naked eye. On the other hand. GaAs:Er with an Er concentration of $\sim 10^{18}$ cm⁻³ shows a rough surface, as exemplified in Fig.2(a). The detail of the surface texture of GaAs:Er is shown in Fig.2(b) under higher magnification. These photographs indicate that surface degradation by heavy $(>10^{18} \text{ cm}^{-3})$ Er doping is more severe in GaAs than in InP.

Photoluminescence from Er 4f electrons was distinctly observed in GaAs:Er and InP:Er around $1.54 \,\mu$ m with very weak near-band edge and deep level PL. Figure 3 compares the two spectra in the wavelength region from the band edge emission $(0.8 \,\mu$ m) to the Er emission $(1.5 \,\mu$ m) at 77K. Erbium concentrations



Fig.1 Surface morphology of Er-doped InP. (a): InP:Er with Er concentration of ~ 10¹⁹cm⁻³, (b): InP:Er with Er concentration of ~10¹⁸cm⁻³.



Fig.2 Surface morphology of Er-doped GaAs. (a): GaAs:Er with Er concentration of ~ 10¹⁸cm⁻³, (b): the same sample as (a) under higher magnification.

in the layers are about $1.5 \times 10^{19} \text{cm}^{-3}$ for the InP host and $\sim 10^{18} \text{cm}^{-3}$ for the GaAs host.

In contrast to the ion-implanted layers, which show complicated spectra varying from sample to sample with annealing conditions,^{2,3} the MOCVD-grown Er-doped layers show simple and reproducible spectra. The Er-related PL spectra at 2K and 120K are shown in Fig.4 for the InP:Er. The Errelated emission from GaAs:Er shows very



Fig.3 Photoluminescence spectra at 77K for (a) an Er-doped GaAs layer and (b) an Er-doped InP layer with Er concentrations of 10¹⁸~10¹⁹cm⁻³. Photoluminescence intensities are normalized at the highest peak in each spectrum.



Fig.4 Photoluminescence spectra from an Erdoped InP layer at (a) 120K and (b) 2K. Photoluminescence intensities are normalized at the highest peak in each spectrum. similar spectra around 1.54 µm. For example. at 2K. each spectrum has the dominant ZPL around 1540nm (1542nm in InP and 1543nm in. GaAs) with other ZPL's as well as phonon sidebands on the longer wavelength side of the main peak. Furthermore, as the measurement temperature is increased from 2K to 120K. the dominant ZPL shifts to the shorter wavelengths by 2~3nm and the halfwidth increases from 2 to 5~8nm in either host as shown in Fig.4 for InP:Er. This temperature dependence of PL spectra was found to be caused by the increase in the intensity of the crystal-field-split subpeaks rather than the change in the main peak itself. Hence. the PL line shapes and halfwidths above 10K



Fig.5 Temperature dependence of Er PL peak intensity. PL intensity I(T), is normalized by that at 2K I(2K).

are determined by the relative intensities of several crystal-field-split lines.

Temperature dependence of the Er-related peak intensity at $1.54\,\mu$ m for InP:Er is shown in Fig.5. The peak intensity at each temperature I (T), is normalized by that at 2K I (2K). The Er PL intensity decreases only slightly between 2K and 40K, although it is drastically quenched above 100K. Similar temperature dependence is observed for Ybrelated PL from InP:Yb.¹⁰

Erbium-related PL spectra from InP:Er were also observed at 300K, for the first time, although the intensity is reduced by more than three orders from that at 2K. The highest PL peak position was found to be 1539nm with the uncertainty of ± 1 nm caused by poor signal-to-noise ratio. The Errelated peak wavelength is shifted by less than 1nm from that at 120K. In contrast, the band-to-band luminescence peak position of InP is known to shift by as much as 30nm in the same temperature range. This small shift of the Er-related emission peak, together with the narrow halfwidths, clearly demonstrates the atomic character of this emission. Smith et al.⁵ observed the highest peak of Er-related PL from GaAs:Er at 1539nm at 300K, which coincides with the 300K peak wavelength of InP:Er mentioned here. These results suggest that GalnAsP:Er also shows similar Er spectra peaking at 1539nm.

4. Conclusion

We have achieved successful doping of Er in GaAs and InP by MOCVD, and observed characteristic PL spectra due to intra-shell transitions of Er 4f electrons at $1.54\,\mu$ m in both hosts. Uniform doping of Er as high as 10^{19} cm⁻³ was achieved. The PL spectra from Er in GaAs and in InP show a remarkable resemblance. These results suggest that Erdoped GaInAsP mixed crystals will yield similar sharp luminescence spectra peaking at 1539nm irrespective of the solid composition, and may be used for light emitting devices with a fixed wavelength.

Acknowledgments

The authors are grateful to Nakahachiro Homma for making the chemical analysis, Yoshikazu Homma for making the SIMS measurements, and Hiroshi Kanbe for his thoughtful discussions.

References

- V.V. Ushakov, A.A. Gippius, V.A. Dravin, and A.V. Spitsyn, Fiz. Tekh. Poluprovodn. <u>16</u>, 1127(1982) [Sov. Phys.-Semicond. <u>15</u>, 352(1981)].
- H. Ennen, J. Schneider, G. Pomrenke, and
 A. Axmann, Appl. Phys. Lett. <u>43</u>, 943(1983).
- Gernot S. Pomrenke, H. Ennen, and
 W. Haydl, J. Appl. Phys. <u>59</u>, 601(1986).
- 4) H. Ennen, G. Pomrenke, A. Axmann,
 K. Eisele, W. Haydl, and J. Schneider,
 Appl. Phys. Lett. <u>46</u>, 381(1985).
- R.S. Smith, H.D. Muller, H. Ennen,
 P. Wennekers, and M. Maier, Appl. Phys. Lett. <u>50</u>, 49(1987).
- W.T. Tsang and R.A. Logan, Appl. Phys. Lett. <u>49</u>, 1686(1986).
- 7) J.P. van der Ziel, M.G. Oberg, and R.A. Logan, Appl. Phys. Lett. <u>50</u>, 1313(1987).
- 8) H. Nakagome, K. Takahei, and Y. Homma, submitted to J. Cryst. Growth.
- Kunihiko Uwai, Hiroshi Nakagome, and Kenichiro Takahei, Appl. Phys. Lett. <u>50</u>, 977(1987).
- 10)Kunihiko Uwai, Hiroshi Nakagome, and Kenichro Takahei, Inst. Phys. Conf. Ser. No.83 p87.