

Recent progress in rare-earth-doped semiconductors

Yasufumi Fujiwara, Atsushi Nishikawa, and Yoshikazu Terai

Division of Materials and Manufacturing Science, Graduate School of Engineering,
Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan
fujiwara@mat.eng.osaka-u.ac.jp
(+81)-6-6879-7498

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Abstract

RE-doped semiconductors have attracted much attention as a new class of materials with unique luminescent and magnetic properties. We have grown Er,O-codoped GaAs and Eu-doped GaN by OMVPE, and demonstrated LEDs with the materials as an active layer, operating at room temperature under current injection. The LEDs exhibit characteristic emission due to intra-4f shell transitions of the trivalent RE ions which are effectively excited by the energy transfer from the hosts.

INTRODUCTION

The luminescent and magnetic properties of RE elements doped in insulators and metals have been thoroughly investigated, and they have been successfully applied to practically-used fluorescent substances and magnets. In these applications, however, either the luminescent or the magnetic property of the RE elements has been independently used. Furthermore, research on RE-doped materials has been based on experience obtained through trial and error, not on material design by the precise control of RE doping and understanding of the energy-transfer mechanism. In RE-doped semiconductors with atomic-level control, we have studied not only the exploitation of luminescent and magnetic properties but also the exploitation of new functionalities provided by their fusion.

Much attention has been paid in particular to the luminescent properties of RE ions doped in semiconductors because RE-doped semiconductors can emit light from the RE 4f shell by means of electrical injection. The intra-4f shell transitions of the RE ions give rise to sharp emission lines whose wavelengths are largely independent of both the host materials and temperature. This stability occurs because the filled outer 5s and 5p electron shells screen the transitions within the inner 4f electron shell from the interaction with the host.

We have intensively investigated RE-doped III-V semiconductors grown by OMVPE and fabricated LEDs with the materials. In this article, our recent progress in the OMVPE growth and the LED application of Er,O-codoped GaAs (GaAs:Er,O) and Eu-doped GaN (GaN:Eu) is reviewed.

ER,O-CODOPED GAAS

Particular attention has been paid to Er-doped III-V semiconductors because the intra-4f shell transitions from the first excited state (${}^4I_{13/2}$) to the ground state (${}^4I_{15/2}$) of Er^{3+} ions result in sharp luminescence lines near 1.5 μm . The wavelength is quite important for present silica-based optical communication.

Figure 1 shows an Er-related PL spectrum in GaAs:Er,O, which is compared with that in Er-doped GaAs. An Ar^+ laser operating at 515 nm was used as an excitation source. In Er-doped GaAs, there are many emission lines, reflecting coexistence of various Er centers not identified. In GaAs:Er,O, one kind of Er center is formed selectively as an Er atom located at the Ga sublattice with two adjacent O atoms (hereafter referred as Er-2O) together with two As atoms, resulting in drastic enhancement of the intensity of Er-2O luminescence due to intra-4f shell transitions of Er^{3+} ions [1].

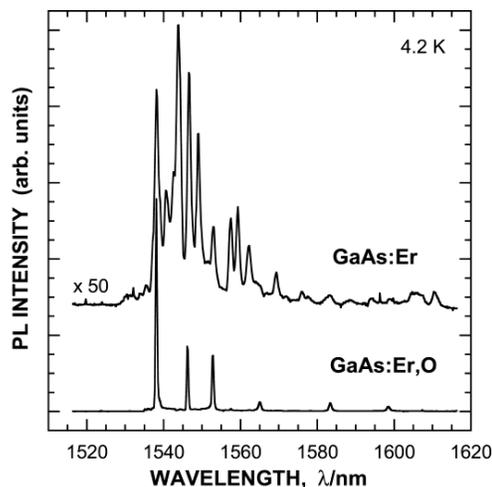


FIGURE 1 PL spectrum in GaAs:Er,O at 4.2 K, which is compared with that in Er-doped GaAs. In GaAs:Er,O, the Er-2O center is selectively formed, resulting in drastic enhancement of the Er intensity.

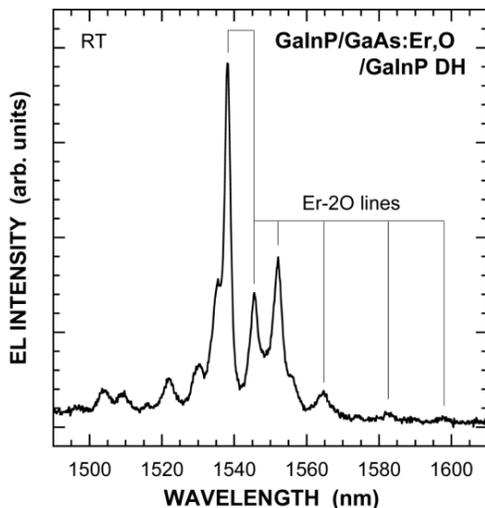


FIGURE 2 Room-temperature EL spectrum in the DH LED under forward bias. The spectrum is dominated by emission lines due to the Er-2O center.

We fabricated a GaAs:Er,O homostructure LED and a GaInP/GaAs:Er,O/GaInP DH LEDs [2,3]. Figure 2 shows room-temperature Er-related EL spectrum for a DH LED under forward bias. The EL spectrum exhibits only the emission lines originating from the Er-2O center. Moreover, GaAs band-edge emission was not observed under the measurement conditions. These results indicate that injected carriers contribute effectively to excitation of the Er^{3+} ions rather than the band-edge emission. This observation is due to ultrafast energy transfer from the GaAs host to the Er ions, which is confirmed directly by pump and probe reflection measurements on photoexcited carriers in GaAs:Er,O [4], and indirectly by behavior of the Er-2O intensity under the GaAs band-edge lasing in a LD with an GaAs:Er,O active layer [5].

The injected current dependence of the EL intensity and lifetime revealed an extremely large Er excitation cross section of 10^{-15} cm^2 , which is five orders in magnitude larger than optical excitation cross section in a conventional Er-doped fiber amplifier ($10^{-20} \sim 10^{-21} \text{ cm}^2$) [2,6].

Furthermore, we have fabricated a newly proposed LD with InGaAs QWs embedded in a GaAs:Er,O waveguide layer, exhibiting QW lasing at around 980 nm, and observed a gradual increase in Er-2O luminescence intensity under the QW lasing [7].

EU-DOPED GAN

Eu^{3+} ions have been widely used as red-emitting phosphors for cathode ray-tube and plasma display panels. In these applications, the ions are doped into an insulator and red emission is obtained mainly by optical excitation. GaN is an attractive host material for Eu doping because its wide

bandgap allows visible wavelength emission from Eu ions and reduces the thermal quenching effect for the emission intensity.

We have doped Eu to GaN by OMVPE and fabricated a LED with GaN:Eu as an active layer [8]. Figure 3 shows a SIMS profile of Eu in a typical GaN:Eu layer. Eu distributes uniformly along the growth direction in the layer. The Eu concentration is estimated to be $7 \times 10^{19} \text{ cm}^{-3}$.

Figure 4 shows room-temperature PL spectrum in the GaN:Eu layer. An excitation source was a He-Cd laser. Emission peaks observed at 543, 600, 621, 633, and 663 nm are associated with intra-4f shell transitions of ${}^3\text{D}_1-{}^7\text{F}_1$, ${}^5\text{D}_0-{}^7\text{F}_1$, ${}^5\text{D}_0-{}^7\text{F}_2$, ${}^5\text{D}_1-{}^7\text{F}_4$, and ${}^5\text{D}_0-{}^7\text{F}_3$, respectively, in Eu^{3+} ions.

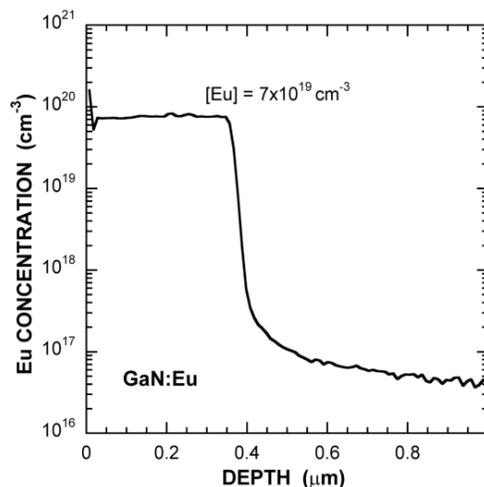


FIGURE 3 SIMS profile of Eu in a typical GaN:Eu layer. Eu distributes uniformly along the growth direction in the layer.

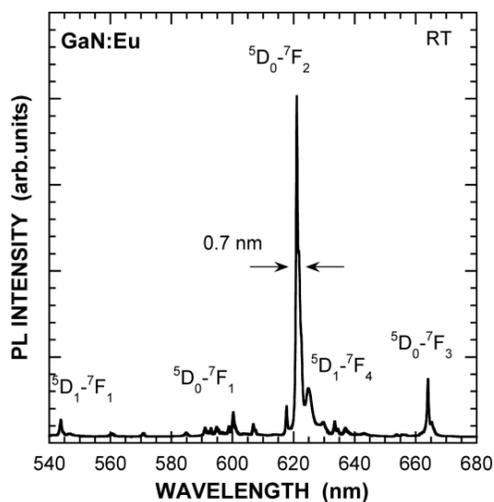


FIGURE 4 Room-temperature PL spectrum in the GaN:Eu layer. Emission peaks are associated with intra-4f shell transitions in Eu^{3+} ions.

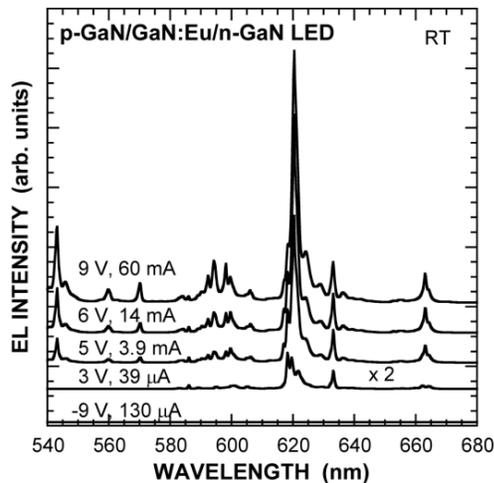


FIGURE 5 Room-temperature EL spectra in the LED with different applied voltages. No luminescence is observed in the reverse bias condition.

It should be noted that neither GaN band-edge emission (which is typically observed at 361 nm for undoped GaN) nor defect-related blue/yellow band luminescence was observed in this wavelength range. The excitation mechanism for the Eu^{3+} luminescence is thought to involve the excitation energy being transferred from the host material to the $^5\text{D}_3$ state of the Eu^{3+} ion and successive nonradiative (phonon) relaxation occurring from the higher $^5\text{D}_{3>0}$ states to the $^5\text{D}_0$ state. Therefore, almost no observation of GaN-related luminescence indicates that the excitation energy of the GaN host material is also effectively transferred to the Eu^{3+} ions for the Eu-related luminescence.

Figure 5 shows room-temperature EL spectra in a GaN:Eu LED with applied voltages of -9, 3, 5, 6, and 9V. As observed in the PL spectrum, the emission at 621 nm is dominant even in the case of the EL spectrum with forward applied biases. Notably, no luminescence is observed in the reverse bias condition. The fact that no EL was observed in the reverse bias condition indicates that the observed luminescence in the forward bias condition is not due to the impact excitation of the Eu^{3+} ions by hot carriers, but rather is caused by the energy transfer from the GaN host to the Eu^{3+} ions. At a dc current of 20 mA, the output power, integrated over the $^5\text{D}_0\text{-}^7\text{F}_2$ transition region (around 621 nm), was 1.3 μW ; the corresponding external quantum efficiency was $1.0 \times 10^{-3} \%$. Optimization for Eu-doping conditions, device structures and LED fabrication processes is now in progress.

CONCLUSIONS

Our recent progress in GaAs:Er,O and GaN:Eu was reviewed. In GaAs:Er,O, codoping of oxygen with Er produced selectively the Er-2O center, resulting in drastic enhancement of the Er^{3+} luminescence intensity. A LED

with GaAs:Er,O emitted the Er-2O luminescence at around 1.54 μm under current injection at room temperature. In GaN:Eu, on the other hand, uniform Eu distribution was obtained along the growth direction. Bright red emission due to the Eu^{3+} ions was successfully observed at room temperature under optical pumping and current injection.

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ACRONYMS

- RE: Rare-Earth
- OMVPE: OrganoMetallic Vapor Phase Epitaxy
- LED: Light-Emitting Diode
- PL: PhotoLuminescence
- DH: Double-Heterostructure
- EL: ElectroLuminescence
- LD: Laser Diode
- QW: Quantum Well
- SIMS: Secondary Ion Mass Spectroscopy