Optical processes of red emission from Eu doped GaN

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Abstract

A single crystalline Eu-doped GaN was grown by gas-source molecular beam epitaxy and photoluminescence (PL) properties were studied. The PL spectra show red-emission at 622 nm originating from intra 4f–4f transition of Eu$^{3+}$ ion without band-edge emission of GaN. The peak shift of the red-emission with the temperature variation from 77 K to room temperature is less than 1.6 meV, and thermal quenching of the luminescence was found to be small compared with the band-to-band transition. Fourier transform infrared spectra showed an absorption peak at about 0.37 eV, which may be due to a deep defect level. The intensity of the red luminescence and the defect-related absorption peak increased with increasing Eu concentration, and a close correlation in the intensity was observed between them. These results suggest that the deep defect level plays an important role in the radiative transition of Eu$^{3+}$ ion in GaN and the optical process for the luminescence at 622 nm was discussed with the relation to the defect.

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1. Introduction

GaN-based semiconductors have been extensively investigated for application not only in optical devices but also in high-frequency and high-power devices [1]. Recently, doping of rare earth (RE) elements into GaN has attracted considerable attention in view of the unique optical, in particular, luminescence properties [2,3]. Luminescence due to an intra-4f transition of RE ion depends very little on the host material and the temperature because the 4f orbits of RE ions are surrounded by a closed electron shell [4,5]. These materials are regarded as important materials in the application for optical fiber communications, display devices, and high efficiency lighting. There are several reports regarding infrared or visible light emissions from various RE ($\text{Er}^{3+}$: infrared and green; $\text{ Tb}^{3+}$: green; $\text{Tm}^{3+}$: blue; $\text{Pr}^{3+}$, $\text{Eu}^{3+}$: red) ions in GaN [6–15], and electroluminescence of red, green and blue color from MIS structures have been demonstrated [12,14,15]. Among RE dopants, Europium (Eu) is an attractive element in GaN, since it shows a strong red-emission at 622 nm [12] which is hard to obtain by using InGaN as an active layer material due to serious phase separation [16]. In earlier articles, we have reported by studying optical spectra and structural properties that Eu was introduced up to 16 at.% into GaN but the external emission efficiency decreased when the Eu concentration was more than about 2 at.%. We have found that the reason for the quenching of the red-emission was the formation of EuN compound that is detected by extended X-ray absorption fine structure analysis [17]. In this paper, the optical process for the radiative recombination of the intra-4f transition of Eu$^{3+}$ in GaN is discussed.

2. Experimental

Eu-doped GaN films were grown on sapphire (0 0 0 1) substrates by gas-source molecular beam epitaxy (GSMBE) using uncracked ammonia as a nitrogen source. Metallic Ga with 6 N purity and Eu with 3 N purity were evaporated from conventional Knudsen effusion cells, and uncracked ammonia gas with 6 N purity was introduced to the growth surface through a nozzle of stainless steel tube. The growth temperatures of Eu-doped GaN were 700°C and the Eu cell temperature was varied from 390 to 500°C, which corresponds to 0.1–16 at.%. The Ga cell temperature and ammonia pressure were kept constant at 950°C and 2.6×10$^{-3}$ Pa, respectively. The thickness of the Eu-doped GaN was typically 0.8 μm. The detailed experimental procedure was described elsewhere [18].
The content of Eu in GaN was roughly estimated by Rutherford backscattering spectroscopy (RBS) using 2 MeV He ion beam. Photoluminescence (PL) measurements were performed at 77 K and room temperature using 325 nm line of a He–Cd laser as an excitation source. X-ray diffraction (XRD) measurements with \( \theta - 2\theta \) mode were carried out using both Cu K\(_{\alpha 1} \) and K\(_{\alpha 2} \) radiation. Fourier transform infrared (FTIR) spectra were measured at room temperature in the spectral region of 400–7000 cm\(^{-1} \) for all samples using Jasco FT/IR-300 system.

3. Results and discussion

Fig. 1(a) and (b) show reflection high-energy electron diffraction (RHEED) patterns of Eu-doped GaN grown with the Eu cell concentration of 2 at.% (sample A) and 16 at.% (sample B), respectively. The azimuth of the incident electron beam is parallel to GaN[\( 1 1 0 \)]. A spotty RHEED pattern was observed throughout the epitaxy in case of the lower doping concentration as shown in Fig. 1(a). Though the surface seems to be somewhat rough, Eu-doped GaN was found to be epitaxially grown on sapphire substrate. When the Eu was doped heavily, in addition to the normal hexagonal spots, extra spots were observed suggesting Eu compound formation and/or segregation as shown in Fig. 1(b).

Fig. 2 shows XRD profiles of sample A and undoped GaN. The peak position at \( 2\theta = 34.5 \) is almost in agreement with (0 0 0 2) reflection of hexagonal GaN. The full-width at half-maximum (FWHM) of the XRD peak was 1032 arc s and this value is more than twice larger than that of undoped GaN (426 arc s). From the results of RHEED and XRD, it is confirmed that single-crystalline Eu-doped GaN was grown on sapphire (0 0 0 1) substrate. It is amazing that the Eu can be incorporated into GaN more than 2 at.% with keeping single crystal. One of the reasons for the high solubility of Eu may be due to the same valence state as Ga. The deterioration of structural properties of GaN by Eu doping, as observed by RHEED and XRD, may be caused by a large difference of atomic radius between Ga and Eu.

Fig. 3 shows PL spectra measured at 77 K from samples A, and B, the same samples shown in Fig. 1, and undoped GaN. As shown in the figure, no band-edge emission was observed in the spectrum of Eu-doped GaN, and red-emission at 622 nm was observed which can be assigned as \( ^5D_0 \rightarrow ^7F_2 \) transition of Eu\(^{3+} \) ion. The intensity of the red-emission in sample B is 1/5 in comparison with that of sample A. The decrease of the red-emission by heavy doping may be caused by EuN and/or Eu segregation as suggested by RHEED and EXAFS [17]. Thus, to get a high efficient red-emission, precise control of Eu concentration is important.
Fig. 4 (a) and (b) show PL spectra of sample A, the same sample shown in Fig. 1, measured at 77 K and room temperature, respectively, and the intensity variation of the peak at 622 nm as a function of temperature is shown in the inset. The ratio of the luminescence intensity between 77 K and room temperature is about 4:1. On the other hand, the ratio of the intensity of band-edge emission in undoped III–V semiconductors such as GaAs and GaN between the same temperatures are almost 100:1. The peak position of the red-emission shifted to longer wavelength with temperature and the peak shift between 77 K and room temperature was observed to be less than 1.6 meV which corresponds to the coefficient of $K \approx 7.3 \times 10^{-6} \text{eV/K}$. The temperature coefficients for the peak shift in band-edge emission of GaAs and GaP are reported to be $K \approx 3.1 \times 10^{-4} \text{eV/K}$, respectively, in the temperature range from 77 K to room temperature. It was found that the intensity and the peak position of the red-emission originating from Eu intra 4f–4f transition is extremely stable with temperature compared with band-edge emission.

The Eu-doped GaN is a promising novel optical material with stable intensity and peak position against temperature variation.

Fig. 5 shows the photoluminescence excitation spectra (PLE) measured at 9 K and room temperature of the sample A. Both spectra have a peak around 350 nm corresponding to the bandgap energy of GaN. This result suggests that the red-emission of the 4f intra-transition in Eu$^{3+}$ is generated through an excitation of GaN. The large tailing in the longer wavelength region may be due to charge transfer from nitrogen to Eu$^{3+}$. The charge transfer excitation is frequently observed for Eu compounds in the spectral range between 420 and 360 nm in case that Eu is coordinated with O or N [19,20]. From the PLE results, it can be expected that high efficiency of red-emission is obtained by carrier injection using Eu-doped GaN as an active layer material.

FTIR spectra of Eu-doped GaN grown with various RE concentration are shown in Fig. 6. The spectra were normalized by that of undoped GaN. An absorption peak at around 2962 cm$^{-1}$ (0.37 eV) was clearly observed in all the five samples though undoped GaN shows a very weak peak at similar spectral position. With increasing Eu cell temperature, the absorption peak became stronger, but no peak shift was observed. The absorption peak at 2962 cm$^{-1}$ is not related with the intra-atomic transition of Eu$^{3+}$, since any other absorption peaks corresponding to $^7F_0$–$^7F_j$ ($j=1–6$) transitions were not observed and a similar absorption peak was observed in Tb-doped GaN. Therefore, it is reasonable to consider that the origin of the absorption peak at 2962 cm$^{-1}$ is a deep defect-related level in GaN induced by Eu doping. The FWHM of the absorption peak seems to be small. This may be due to the selection rule of the transition, that is, a certain restricted component, which is caused by a specific defect symmetry, only contributes to the transition. The relationship between the intensity of the red luminescence and the FTIR absorption
As discussed above, the red luminescence is generated through an excitation of GaN, that is, through an energy transfer from GaN to Eu. So it is important to clarify the energy transfer mechanism in understanding the luminescence properties. There are several proposed models regarding energy transfer from host material to RE ion such as defect related Auger transition model [21,22], resonant energy transfer model [23], bound exciton model [24,25], shallow center model [26] and so on. Among these models we took attention to the defect-related Auger transition model since a defect level was detected as shown above. Here, we tried to adopt the defect-related Auger transition model for the energy transfer from GaN to Eu\(^{3+}\) ion. A schematic diagram for the energy transfer model from GaN to Eu\(^{3+}\) ion is illustrated in Fig. 8. The defect level induced by Eu doping was assumed to be situated at 0.37 eV below the conduction band. This assumption may be reasonable as considered below. In case that the defect level is 0.37 eV from the valence band, energy transfer probability should be extremely low, since the interaction of mobile electron in conduction band with rare earth element is small. It should be noted that the energy value of the defect level from valence band is almost the same as that of \(^5\)D\(_0\) excited state of Eu\(^{3+}\) referring to Dieke’s energy diagram [27]. The optical process was simulated as follows. An electron excited from the valence band to the conduction band would be trapped at the defect level (step (a) in Fig. 8). A recombinination of the trapped electron with a hole in the valence band and an excitation of Eu\(^{3+}\) ion from ground state of \(^7\)F\(_0\) to the excited state of \(^5\)D\(_3\) would occur simultaneously similar to an Auger transition (steps (b) and (c)). This is an Auger energy transfer process. Then carriers on \(^5\)D\(_3\) will relax to \(^5\)D\(_0\) non-radiatively as step (d), and a radiative recombinination transition from \(^5\)D\(_0\) to \(^7\)F\(_2\) would occur resulting in red luminescence at 622 nm (step (e)). There have been several reports on electron traps in RE-doped semiconductors, however, the structures of the defects are not clear [28–30]. Further work is necessary to determine the defect structure.

4. Summary

Eu-doped GaN was grown by gas-source MBE and the structural and optical properties were investigated by RHEED, XRD, PL, PLE and FTIR. Single crystalline growth was confirmed with the Eu concentration up to 2 at.%. Photoluminescence spectra of Eu-doped GaN showed red luminescence at 622 nm due to intra-atomic f–f transition of Eu\(^{3+}\) ion. The intensity of the luminescence increased with increasing Eu concentration up to 2 at.%. The PLE spectra indicted that the red luminescence is generated through an excitation of GaN. FTIR transmission spectra of Eu-doped GaN showed a deep defect level with the energy of 0.37 eV. The intensity of the absorption peak proportionally increased to that of the red luminescence, which suggests that the defect level plays an important role in the emission of the red luminescence. The defect mediated energy transfer transition was proposed for the red luminescence of Eu-doped GaN.

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