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Incorporation site of Tb in GaN studied by Rutherford-backscattering ion channelling measurements and x-ray absorption fine-structure analysis

Hyungjin Bang¹, Shinichi Morishima¹, Ziqiang Li¹, Katsuhiko Akimoto¹, Masaharu Nomura² and Eiichi Yagi³

¹ Institute of Applied Physics, University of Tsukuba, 1-1-1 Tennodai, Tsukuba 305-8573, Japan

² Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization, Oho, Tsukuba 305-0801, Japan

³ The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351-01, Japan

E-mail: bk993503@s.bk.tsukuba.ac.jp (Hyungjin Bang)

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Abstract

We report single-crystalline growth of Tb-doped GaN grown by gas source molecular beam epitaxy using NH₃ as a nitrogen source, and the incorporation site of Tb in GaN. It was found that most of the Tb atoms are substitutionally incorporated into the Ga lattice site by Rutherford-backscattering ion channelling and extended x-ray absorption fine-structure analysis. Photoluminescence spectra, which show sharp peaks originating from 4f intra-atomic transitions of Tb³⁺ ions, with near-band-edge emission of GaN, were observed from the film whose Tb content was roughly estimated to be 2%, and their properties are discussed.

1. Introduction

Rare earth ions in inorganic solids generally show sharp and intense luminescence originating from intra-atomic f–f transitions, and the peak position and intensity of the luminescence are hardly affected by chemical environment [1, 2]. There are several reports regarding infrared emission or visible light emission from various rare earth ions (for example, Er³⁺, infrared and green; Tb³⁺, Ho³⁺, green; Tm³⁺, blue; Sm³⁺, Pr³⁺, Eu³⁺, red) in GaN [3–9] and electroluminescence of red, green and blue colour from MIS structures has already been demonstrated [8, 10, 11]. Particularly, green to red emission seems to be interesting because of the difficulty of InGa_xN growth with high content of In.

We have reported that the luminescence from Eu-doped GaN shows a sharp peak at 623 nm due to the ⁵D₀–⁷F₂ transition of the Eu³⁺ ion, which is generated through an energy transfer

from GaN. We also showed that the peak position, intensity and full width at half maximum (FWHM) of the luminescence are extremely stable with temperature [7–9]. These results show that rare-earth-ion-doped GaN can be regarded as a promising material in application for novel optical devices.

There are few reports on the structural properties of rare-earth-doped GaN. Er and Eu have been reported to be incorporated into the substitutional Ga lattice site with the bond length of about 2.3 Å for both cases [12, 13]. Since the structural properties, especially coordination symmetry, are related to the optical properties of rare earth ions, it is important to clarify the coordination structure.

In this study, we report single-crystalline growth of Tb-doped GaN, and the substitutional incorporation site of Tb in GaN determined by extended x-ray absorption fine-structure (EXAFS) analysis and Rutherford-backscattering ion channelling (RBS/C). Photoluminescence (PL) from the Tb³⁺ ion was observed; however, the intensity is two orders of magnitude weaker than that of Eu³⁺ in GaN. The cause of the remarkable difference in the PL properties between Tb and Eu in GaN is discussed.

2. Experimental details

Tb-doped GaN films were grown on sapphire(0001) substrates by gas source molecular beam epitaxy (GSMBE) using uncracked ammonia for the nitrogen source. Metallic Ga with 6 N purity and Tb 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 the nozzle of a stainless steel tube. Before the growth, nitridation of the substrate surface was carried out under an ammonia pressure of 5.3×10^{-2} Pa for 20 min at 600 °C. The growth temperature of Tb-doped GaN was 700 °C and the cell temperature of Tb was 1300 °C. The Ga cell temperature and ammonia pressure were kept constant at 950 °C and 2.6×10^{-3} Pa, respectively. To investigate the structural property of the film, *in situ* reflection high-energy electron diffraction (RHEED) patterns were observed during growth.

The content of Tb in GaN was roughly estimated by Rutherford-backscattering spectroscopy (RBS) using a 2 MeV He ion beam.

PL measurements were performed at 77 K and room temperature using the 325 nm line of a He–Cd laser as the excitation source.

X-ray diffraction (XRD) was measured with θ – 2θ mode using both Cu $K\alpha_1$ and $K\alpha_2$ radiation.

RBS/C measurements were performed at room temperature with a 2 MeV He ion beam at The Institute of Physical and Chemical Research (RIKEN) on the sample grown at the Tb cell temperature of 1300 °C. The He ion beam was collimated to give divergence less than 0.076°. The beam current and size were about 1.5 nA and 1 mm in diameter, respectively. The backscattered He ions were measured with a surface-barrier Si detector placed at an angle of 160° with respect to the incident beam. The sample was mounted on a three-axis goniometer and channelling angular profiles were obtained for the (0001) channel.

The Tb L₃-edge EXAFS measurements were carried out in fluorescence mode at beam line 12C at the High Energy Accelerator Research Organization (KEK) to study the atomic structure around the Tb atom. The fluorescence was detected using a 19-element Ge detector. The analysis of the EXAFS data was performed in the general procedure [14, 15]; the EXAFS oscillation functions $k^3\chi(k)$, where k is the photoelectron wavevector, obtained by subtraction of background and normalized, were Fourier transformed into radial structure functions. A Fourier filtering technique was applied to the first-nearest-neighbour peak in the Fourier transform and the extracted $k^3\chi(k)$ on the shell is curve fitted using the parameters calculated

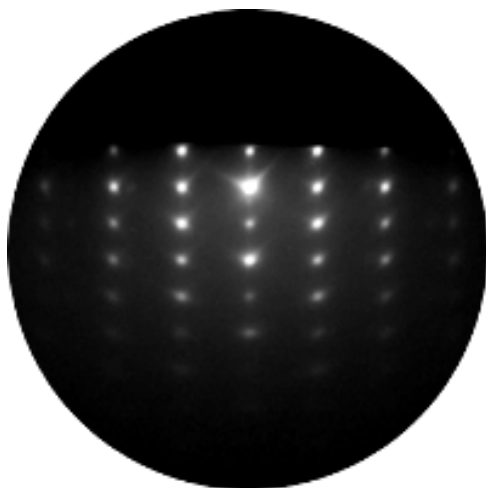


Figure 1. RHEED pattern of Tb-doped GaN after the growth of about 0.8 μm .

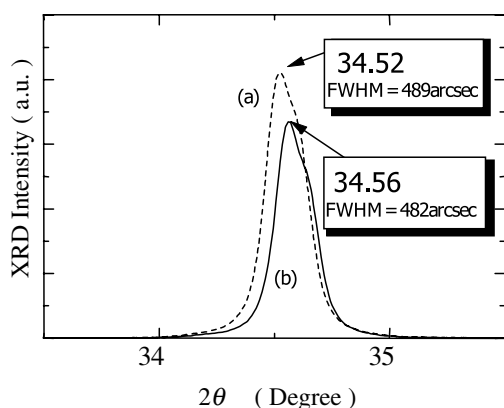


Figure 2. XRD from Tb-doped GaN (a), and undoped GaN (b).

with the FEFF8 [16] program. The bond length, coordination number and Debye–Waller factor were used as fitting parameters to yield optimum values.

3. Results and discussion

Figure 1 shows the RHEED pattern of Tb-doped GaN after the growth of about 0.8 μm on a sapphire substrate with the Tb cell temperature of 1300 $^{\circ}\text{C}$. A spotty pattern with no extra spot throughout the growth suggests single-crystalline growth. The RHEED pattern always changed from a streak pattern to a spotty pattern when the Tb was doped even when the Tb content was less than 0.1%. This result may suggest that the Tb atoms induce island growth.

Figure 2 shows the XRD profiles of Tb-doped GaN and undoped GaN. The peak position of Tb-doped GaN shifted a little to a lower angle possibly due to the large atomic radius of Tb. The values of the FWHM of both diffraction peaks are almost the same; therefore, it can be said that the doping of Tb does not affect the crystal quality much.

The RBS spectrum of Tb-doped GaN grown at the Tb cell temperature of 1300 $^{\circ}\text{C}$ is shown in figure 3(a). Correcting the cross section of the backscattering yield, the content of Tb was roughly estimated to be 2%. It can be seen from the figure that the Tb atoms are incorporated uniformly throughout the depth direction and there is no accumulation of Tb at

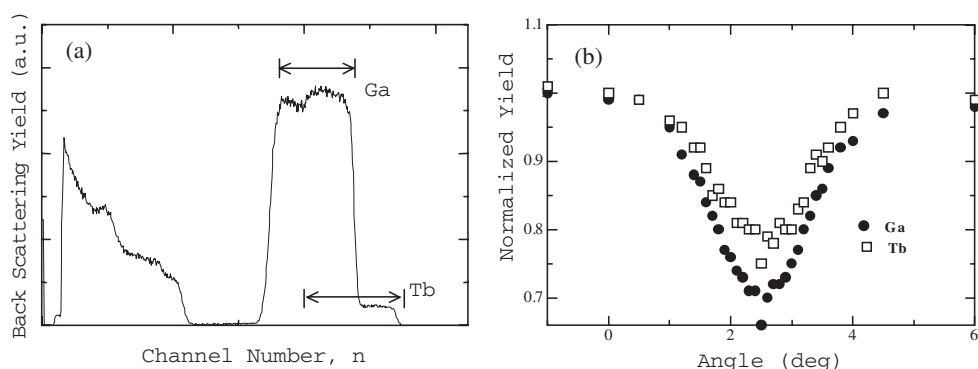


Figure 3. RBS spectrum of Tb-doped GaN (a) and channelling angular distributions of Tb-doped GaN (b).

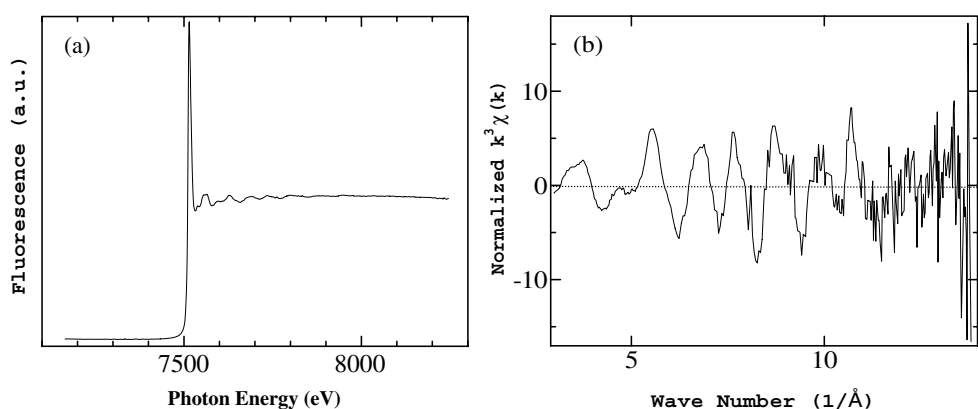


Figure 4. X-ray fluorescence of the Tb L_3 -edge with respect to incident photon energy E (a) and the k^3 -weighted Tb L_3 -edge EXAFS function plotted for wavenumber from 3 to 13.8 (b).

the surface or the interface between the sapphire substrate and GaN. Figure 3(b) shows the channelling angular distributions of Tb-doped GaN, which are normalized to the random yield. The angular distribution of the Tb signal clearly shows a dip at the same degree with roughly the same value of the full angle at half maximum as that of Ga, indicating that most of the Tb atoms are in substitutional sites in GaN. Comparing the depth of the dips between Ga and Tb, it can be estimated that about 80% of Tb atoms are incorporated into a substitutional lattice site and the rest of the Tb atoms may be incorporated into a random site or interstitial site.

To investigate the incorporation site of Tb in GaN, we carried out Tb L_3 -edge EXAFS measurements with fluorescence mode. X-ray fluorescence of the Tb L_3 -edge plotted against incident photon energy E is shown in figure 4(a). The EXAFS function with the k weighting value of three was extracted from figure 4(a) and the result is shown in figure 4(b).

Figure 5 shows the Fourier transform of $k^3\chi(k)$ in momentum k space into the radial distribution function in distance space with the k range from 3.0 to 13.8 \AA^{-1} . The relatively large peaks at about 1.8 and 3.0 \AA in figure 5 are attributed to the first- and second-nearest-neighbour atoms, respectively. The phase shift effect was corrected by using the Fourier filtering technique for the spectrum in figure 5. Back Fourier transform was applied to the range between 1.5 and 2.3 \AA in the radial distribution function, and the results are shown in

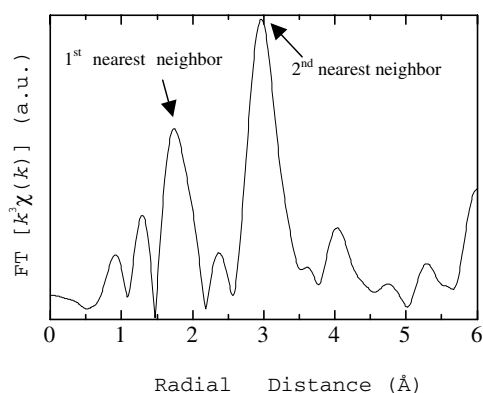


Figure 5. Radial distribution function of Tb-doped GaN.

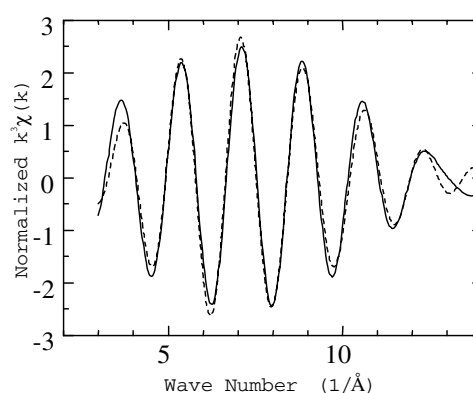


Figure 6. Fourier filtering spectrum ranging from 1.5 to 2.3 Å (solid curve), and fitting curve assuming the nearest-neighbour atom as nitrogen (dotted curve).

Table 1. Analytical results of Tb-EXAFS measurements.

| | |
|------------------------|---------------------|
| Nearest-neighbour atom | Nitrogen |
| Coordination number | 3.8 |
| Bond length | 2.2 Å |
| Debye-Waller factor | 0.17 Å ² |

figure 6. The solid curve in figure 6 is the Fourier-filtered EXAFS spectrum $k^3\chi(k)$ for the first-nearest neighbour. The dotted curve was obtained by calculation assuming the nearest-neighbour atom as nitrogen. The analytical results are listed in table 1. A good curve fitting was obtained only assuming the nearest-neighbour atom as nitrogen, and it was not possible to get a fitting in the case of Ga or Tb for nearest-neighbour atoms. Therefore, we can say that the nearest-neighbour atom is nitrogen. The coordination number obtained was about four, so it can be concluded that the Tb atom is incorporated into a substitutional Ga lattice site with tetrahedral symmetry. The bond length between Tb and N was analysed to be 2.2 Å, which is larger than that between Ga and N in GaN. It is well known that the bond length in a ternary alloy shows a very similar bond length to binary ones [17]. Although a four-coordinated TbN compound does not exist, the bond length of four-coordinated TbN can be supposed to be about 2.2 Å. The obtained results regarding structural properties are almost the same as those of Eu in GaN [13].

Figure 7 shows PL spectra, measured at 77 K and room temperature, of Tb-doped GaN with the Tb content of 2%. The spectra are very similar to that of Tb-ion-implanted GaN [18]. Though the spectrum measured at 77 K shows near-band-edge emission of GaN at around 360 nm and deep-level emission around 500–700 nm, three sharp peaks were observed at 491 nm (peak a), 545 nm (peak b) and 580 nm (peak c), which can be tentatively assigned as $^5D_4-^7F_6$, $^5D_4-^7F_5$, $^5D_4-^7F_4$ transitions of the Tb^{3+} ion, respectively [1, 2, 14].

In the case of the luminescence spectra of Eu-doped GaN, no luminescence related to GaN was observed, and the intensity of Eu-related luminescence was two orders of magnitude larger than that of Tb although the content of Tb is almost the same as that of Eu. As reported earlier [7, 8], the Eu-related luminescence is generated through an excitation of GaN as confirmed by PL excitation spectroscopy. The Tb-related luminescence can be considered to be generated also through an excitation of GaN since there is no excited level in the Tb^{3+} ion

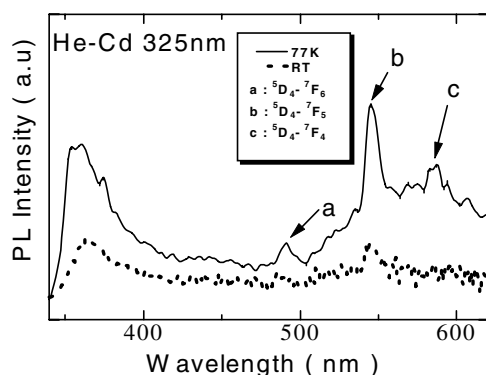


Figure 7. PL spectra of Tb-doped GaN at 77 K (solid curve) and room temperature (dotted curve). The peaks a, b and c can be tentatively assigned as ${}^5D_4-{}^7F_6$, ${}^5D_4-{}^7F_5$, ${}^5D_4-{}^7F_4$ transitions of the Tb^{3+} ion, respectively.

which coincides with the energy value of the He–Cd laser (3.81 eV); that is, direct transition from the ground state to an excited state of Tb^{3+} ion hardly occurs with the He–Cd laser [1]. Therefore, the large difference in luminescence intensity between Eu-doped GaN and Tb-doped GaN may be caused by the difference of energy transfer probability from GaN to the rare earth ions.

The reason for the poor energy transfer probability in Tb-doped GaN may not be a degradation of crystal quality or random incorporation sites of Tb, since most Tb atoms were found to be incorporated into Ga lattice sites just the same as in the case of Eu in GaN [13], and the FWHM of XRD and the full angle at half maximum of RBS/C from Tb-doped GaN are almost the same as those of undoped GaN. The poor luminescence of Tb in GaN may be correlated with the energy position of the intermediate state which is involved in the energy transfer [19]; however, more detailed study is necessary to clarify the reason for the poor luminescence of Tb in GaN.

4. Summary

Single-crystalline Tb-doped GaN was grown on sapphire(0001) substrates by GSMBE using ammonia. The first-nearest-neighbour atom of Tb was found to be nitrogen and the bond length between Tb and nitrogen was determined to be 2.2 Å by EXAFS analysis. From the RBS/C and EXAFS results, it can be concluded that the Tb atom is incorporated into a substitutional Ga lattice site. PL spectra of Tb-doped GaN show sharp luminescence peaks originating from 4f intra-atomic transitions of the Tb^{3+} ion.

Acknowledgments

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