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Emission spectra from AlN and GaN doped with rare earth elements

Sung Woo Choi [a], Shuichi Emura [a,*], Shigeya Kimura [a], Moo Seong Kim [a], Yi Kai Zhou [a], Nobuaki Teraguchi [b], Akira Suzuki [c], Akira Yanase [a], Hajime Asahi [a]

[a] The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan

[b] Device Technology Research Laboratories, Sharp Corp. Tenri, Nara 632-8567, Japan

[c] Research Organization of Science and Engineering, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan

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Abstract

Luminescent properties of GaN and AlN based semiconductors containing rare earth metals of Gd and Dy are studied. Cathodoluminescent spectra from AlGdN show a clear and sharp peak at 318 nm following LO phonon satellites. Photoluminescence spectra from GaDyN by the above-gap excitation also show several peaks in addition to the broad luminescence band emission. For GaGdN, the sharp PL peaks are also observed at 650 and 670 nm, and they are assigned to the intra-f orbital transitions by their time decay measurements. The broad band at around 365 nm for AlGdN, 505 nm for GaGdN and GaDyN are commonly observed. The origin of these broad bands is discussed.

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1. Introduction

Many lanthanide elements have played an important role in various optoelectronic and photonic applications [1], ranging from solid-state lasers (for example, Nd:YAG laser) and phosphors for color lamps and displays (for example, BaF_2:Eu, ZnS:Tb) to optical fiber telecommunications (using Er or Pr). These so-called “rare earth (RE)” elements have a partially filled inner ($4f^n$) shell shielded from its surroundings by completely filled outer ($5s^2$ and $5p^6$) orbitals. Due to the shielding, the intra $4f^n$ shell transitions result in very sharp optical emissions at wavelengths from ultraviolet to infrared. The wavelengths of these emission lines are determined by the energy of the transition between 4f states of atomic RE and are relatively independent of the host material. On the other hand, the host materials do have a very strong effect on the radiative transition probability.

In general, RE-doped semiconductors (Si, GaAs, etc.) have exhibited limited photoemission at room temperature due to low RE solubility and severe temperature quenching. It was shown by Favennec et al. [2], that the thermal quenching in Er-doped semiconductors decreases with increasing band gap. Therefore, wide-band gap semiconductors, AlN and GaN are attractive hosts for RE elements.

These rare earth elements will exhibit ferromagnetism in addition to the unique luminescent natures described above, and magnetic properties of $Ga_{0.94}Gd_{0.06}N$ have recently been reported [3]. We have reported the ab initio calculations on the magnetism of RE-doped GaN and AlN, and discussed the possibility of room temperature ferromagnetism in RE-doped nitrides [4]. Diluted magnetic semiconductors doped with adequate rare earth elements exhibiting both ferromagnetism and luminescence characters promise for materials of hopeful features devices.

Here, we will report on the luminescent properties of AlGdN, GaDyN and GaGdN. Luminescence spectra observed for these semiconductors are classified into two groups according to their spectrum form. One is broad luminescence band, and the other is very sharp peaks. The broad band peak intensities show significant temperature dependence. We will propose a model for the origin of the broad band.

* Corresponding author. Tel.: +81 6 6879 8407; fax: +81 6 6879 8409.
E-mail address: emura@sanken.osaka-u.ac.jp (S. Emura).

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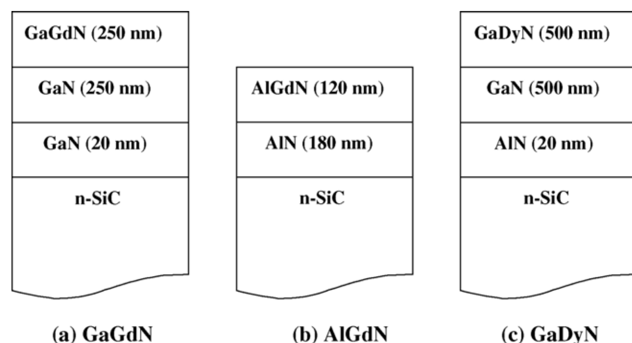

Fig. 1. Schematic drawings of the (a) GaGdN, (b) AlGdN and (c) GaDyN sample structures.

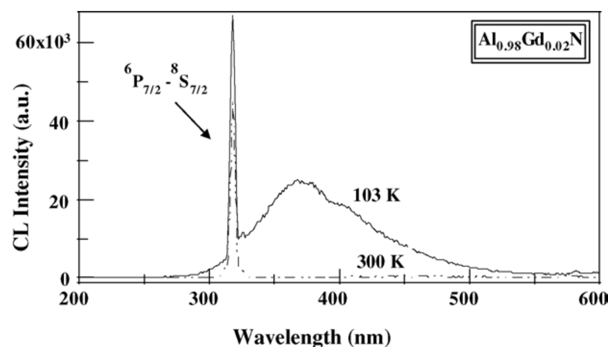

Fig. 2. CL spectra of the $Al_{0.98}Gd_{0.02}N$ sample, measured at 103 and 300 K.

2. Experimental

The films studied here were grown in the MBE system with a RF-plasma assisted radical cell on the Si-face of (0 0 0 1)-oriented 6H-SiC substrates. The backside of SiC substrates was coated with molybdenum to facilitate heating by radiation. The source materials were elemental Ga (7N purity), Al (6N purity), Gd (3N purity) and Dy (3N purity), and gaseous N_2. The growth temperature for the GaN and GaGdN was 720 °C and that for the AlN and AlGdN was 800 °C. The sample structures are as follows: GaGdN (250 nm)/GaN (250 nm)/AlN (20 nm)/SiC, AlGdN (120 nm)/AlN (180 nm)/SiC and GaDyN (500 nm)/GaN (500 nm)/AlN (20 nm)/SiC. The schematic drawings are shown in Fig. 1. The details of the crystal growth are described in Refs. [5,6].

On these samples, cathodoluminescent (CL), photoluminescence (PL) and time-resolved photoluminescence (TRPL) measurements were conducted. For AlN, CL method was used to observe emission spectra because of very wide band gap energy of 6.28 eV. PL spectra were obtained through excitation with a 325 nm line of a He-Cd laser, using a 1 m grating monochromater and a phase sensitive detection. PL measurements were conducted in a closed cycle He cryostat at temperatures from 10 to 300 K. An excitation power of the He-Cd laser is about 30 mW at the front surfaces of the specimen. For the TRPL measurements, the frequency-doubled mode-locked Al_2O_3:Ti laser emitting at 400 nm with the pulse width of 1.5 ps is used as an excitation source. A streak camera is used as a detector.

3. Results

Fig. 2 shows the CL spectra for the $Al_{0.98}Gd_{0.02}N$ at 103 and 300 K. A strong and sharp peak centered at around 318 nm is visible besides the oxygen-related defect luminescence band at 370 nm [7] of the AlN host. The intensity of the 318 nm sharp peak slightly decreases with increasing temperature, while the broad band peaking at around 365 nm completely vanishes at 300 K. The temperature dependence of the CL spectrum suggests that the satellite peak can be assigned to LO phonon side band of the main peak [8]. No more transitions are detected in the survey scan. By taking the spectrum shape and temperature dependences of the peak intensity, energy and line width into consideration, the sharp luminescence peak is concluded to be due to the radiative transition between the first exited state $^6P_{7/2}$ and the ground state $^8S_{7/2}$ of Gd^{3+} after Dieke energy diagram [9].

Fig. 3 shows CL spectra for the pure AlN (99 K), $Al_{0.98}Gd_{0.02}N$ (120 K), and $Al_{0.87}Gd_{0.13}N$ (134 K). The intensity of the sharp peak at 318 nm decreases with the increase of Gd concentration, suggesting a well-known concentration quenching. It means that the crystal field effect cannot be completely ignored even for the inner ($4f^n$) shells which are shielded by their outer ($5s^2$ and $5p^6$) filled orbitals. One of the evidences is the observation of the satellite weak peaks of the 318 nm main peak. The broad band is observed even in pure AlN, although the spectrum form is somewhat different from those for the AlGdN. Therefore, the broad band observed for the AlGdN specimens is not direct luminescence at the Gd ions such as a transition from the 5d orbital to the 4f orbital, but may be indirectly connected with Gd ions. The broad peak observed for the pure AlN is essentially related to imperfections in AlN, which are created during growth.

As a reference, the luminescence spectra of $Ga_{0.94}Gd_{0.06}N$ at several temperatures are shown in Fig. 4. The spectra were obtained through the above-gap excitation with a He-Cd laser

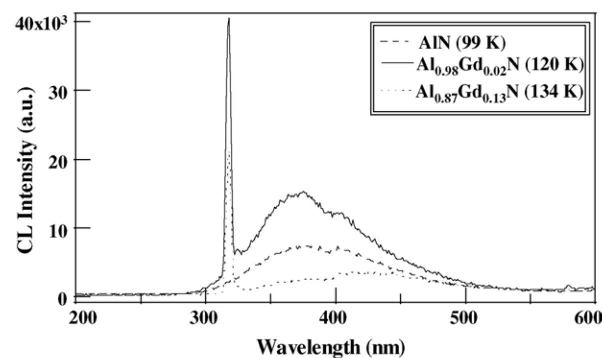

Fig. 3. CL spectra of pure AlN, $Al_{0.98}Gd_{0.02}N$, and $Al_{0.87}Gd_{0.13}N$ samples measured at 99, 120, and 134 K, respectively.

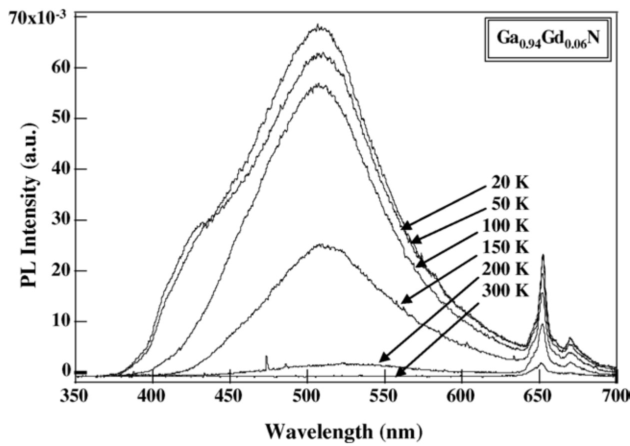

Fig. 4. PL spectra for the $Ga_{0.94}Gd_{0.06}N$ sample as a function of temperature.

line (325 nm). The CL spectrum of $Ga_{0.94}Gd_{0.06}N$ is fairly the same as the PL spectra [6].

The 318 nm peak was not observed in the CL spectra for the GaGdN. No observation of the 318 nm peak may be due to the re-absorption by the host GaN because 318 nm exceeds the band gap energy of GaN, or essentially no emission in GaN. The 318 nm peak, which was observed from the AlGdN as a radiative transition between the first exited state and the ground state of Gd^{3+} ions, was not detected because of the lower energy of the excitation source than that of 318 nm peak. However, a sharp peak is recognized at around 652 nm, which is originated in a transient Gd^{2+} state, which will be published elsewhere [10]. The summarized description is given in the last section.

A broad band peaking at 505 nm is also recorded in Fig. 4 at somewhat longer wavelength compared with that of AlGdN, but shorter wavelength than that of a well-known green band (550 nm) in GaN. The intensity of this band decreases rapidly with increasing temperature.

Fig. 5(a) shows PL spectra for the $Ga_{0.97}Dy_{0.03}N$ layer measured with the above-gap excitation (325 nm). These spectra are classified into the broad band and the sharp peaks similar to the case of AlGdN and GaGdN. Two sharp peak groups with fine structures are located at around 480 and 580 nm on the broad band. The sharp peaks can be assigned to the intra-4f transitions of Dy^{3+} ions judging from their characteristic features; these peaks are sharp, their peak-energies are independent of temperature, and the lifetimes of these emissions are several ten microseconds. We assign these sharp peaks at 480 and 580 nm to the following intra-4f orbital transitions [11,12], $^4F_{9/2}$–$^6H_{15/2}$ and $^4F_{9/2}$–$^6H_{13/2}$, respectively. Therefore, we think that these intra-4f orbital transitions are related to the broad luminescence band, and that they are caused after the carriers are transferred to the intra-4f orbital level through the defect level. Fig. 5(b) shows the time decay curves of the luminescence intensity at 580 nm at different temperatures, and their lifetimes are 87 μs at 13 K and 65 μs at 100 K. The long lifetime values support our assignment of the sharp line peaks.

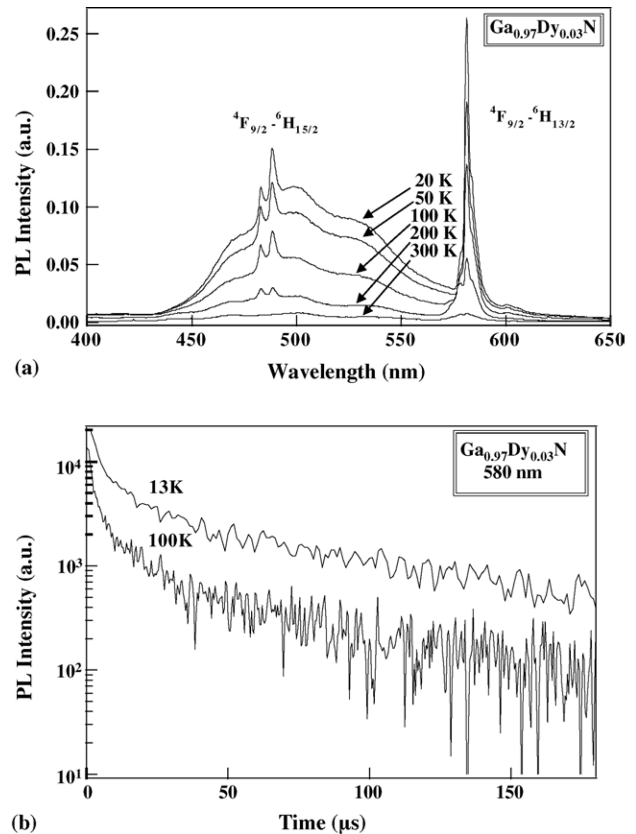

Fig. 5. (a) Temperature dependent PL of the $Ga_{0.97}Dy_{0.03}N$ sample. (b) Temporal responses of the 580 nm emission band measured at 13 and 100 K.

4. Discussion

We have discussed on the nature of the sharp 652 nm luminescence in Ref. 10. Here, we will briefly summarize the nature at first. As observed in AlGdN (318 nm), the luminescence from the lowest excited state lies in the ultraviolet region in the trivalent state of Gd ion, which is the most stable state in rare earth ions, and the trivalent state of Gd ions in $Ga_{0.94}Gd_{0.06}N$ is confirmed by XPS and XANES spectrum [13]. No any luminescence has been reported in the visible to infrared wavelength region. However, we found the sharp luminescence peaks in a serial form locating in the range of red to near infrared through the above-gap excitation with a He-Cd laser line of 325 nm. This chain of luminescence peaks is not understandable at all within a framework of the trivalent state of Gd ions. Thus, a fantastic idea was proposed on the analogy of the spectrum of trivalent Tb ion, which is one atomic number heavier element than Gd. The divalent Gd ion has the same electron configuration as the trivalent Tb ion, that is, $4f^8$. Therefore, it has been concluded that the luminescence series observed in $Ga_{0.94}Gd_{0.06}N$ comes from the transient divalent state of the Gd ions in $Ga_{0.94}Gd_{0.06}N$, while this model is hardly acceptable from many points of view. The details of the model will be presented in Ref. [10].

Now, we have still a matter, which should be discussed, on the primary luminescence band peaking at 505 nm in

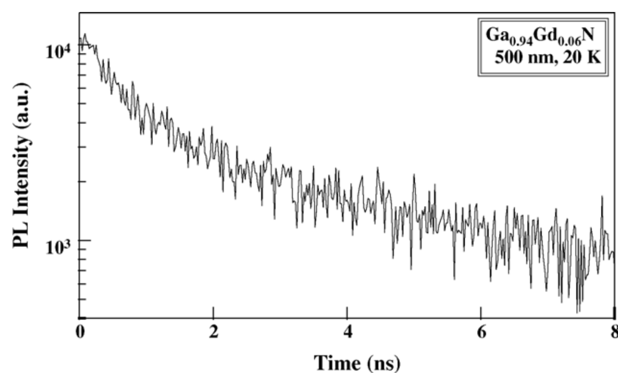

Fig. 6. Temporal response of the 500 nm emission band measured at 20 K in $Ga_{0.94}Gd_{0.06}N$.

$Ga_{0.94}Gd_{0.06}N$. Now, we discuss this problem by taking into account of the decay data observed newly. The decay curves were recorded at several wavelengths at 20 K. Fig. 6 shows one of those taken at 500 nm. The decay indicates very fast life in comparison with 41 μs of the 652 nm line. The decay curve is of two components with lifetimes of 1 and 15 ns, suggesting that the transition is dipole allowed. The frequently observed green band that usually locates at around 550 nm in pure GaN gives the different decay times in the range of 1 μs to 1 ms, depending on the growth condition. Our decay lies at out of the range. The faster decay and the energy position suggest that the primary broad band is different source from the so-called green band.

Possible models for the band peaking at 505 nm are considered in our hand. The first one is a transition from 5d orbital to 4f orbital of the Gd ion. The fast decay supports this model because this is entirely a dipole allowed transition. The second is a modified green band model, where the nitrogen vacancy adjoins the Gd ion. The XAFS analysis around the Gd ions suggests one vacancy for the coordination of the Gd ion. The lowering of symmetry of the circumstance around luminescent center makes the decay faster generally. The third is recombination of excitons bound at the Gd ion or the Gd ion complex. Rather wide spectral width of the band does not seem to support. At present stage, the first two models are more favorable, but further experimental and theoretical studies are necessary for more detailed description.

5. Summary

We examined luminescent nature of wide gap semiconductors AlN and GaN containing rare earth elements Gd and Dy. CL for AlGdN, and PL for GaGdN and GaDyN and its time resolved one are studied. The CL spectra from AlGdN show a clear and sharp peak at 318 nm with LO phonon satellites. The PL of $Ga_{0.97}Dy_{0.03}N$ through the above-gap excitation also shows several peaks in addition to the broad luminescence band. The decay curves of the peaks confirm that they can be assigned to those within a framework of intra-4f transition of rare earth ion. After Dieke energy diagram of trivalent rare earth ion, we concretely assign each peak as follows, $^6P_{7/2}$–$^8S_{7/2}$ for 318 nm peak in AlGdN, $^4F_{9/2}$–$^6H_{15/2}$ for 480 nm peak in $Ga_{0.97}Dy_{0.03}N$, and $^4F_{9/2}$–$^6H_{13/2}$ for 580 nm peak in $Ga_{0.97}Dy_{0.03}N$. The 652 nm peak in $Ga_{0.94}Gd_{0.06}N$ is already proposed in Ref. [10], that is, $^5D_4$–$^7F_6$ from an electron configuration of divalent Gd ion. The broad bands peaking at around 365 nm in AlGdN, 505 nm in GaGdN, and 505 nm in GaDyN are commonly observed. The origin of the broad band is discussed and focused on the two models, 5d to 4f allowed transition supported by the measured lifetime, and a modified green band (nitrogen vacancy adjoining the Gd ion) supported by XAFS analysis.

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