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メタデータ	言語: English
	出版者:
	公開日: 2011-03-17
	キーワード (Ja):
	キーワード (En):
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URL	http://hdl.handle.net/10098/3079

Photoluminescence and Photoluminescence Excitation Spectra from AlN doped with Gd^{3+}

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The photoluminescence (PL) spectra from $Al_{0.98}Gd_{0.02}N$ and $Al_{0.87}Gd_{0.13}N$ consisting of Gd^{3+} related 3.95 eV sharp emission lines and other bands, and the PL excitation (PLE) spectra from 3 to 7 eV have been investigated by using a highly linear polarized synchrotron radiation light source. The Gd related 3.95 eV sharp lines in the PL spectra are similar to those in other cathodoluminescence (CL) and PL research. However, the broad emission bands around 3.95 eV lines which are normally found in other CL works are not ob-

served. Other broad emission bands are clearly observed in the energy region of 1.5 ~ 3.5 eV. PLE spectra monitored at both the 3.95 eV sharp line and the broad emission band of $Al_{0.98}Gd_{0.02}N$ clearly indicate that these emission processes are host excitations which are reflected by an AlN-like band structure and crystalline anisotropy. On the other hand, the PLE and optical reflectance spectra of $Al_{0.87}Gd_{0.13}N$ reveal an unclear band structure with a long band tail in the lower energy side.

1 Introduction III-V nitride compound semiconductors doped with rare earth elements are attractive systems because of the possibility of magnetic ordering coupled with a semiconducting nature and luminescence properties. In the ultraviolet region, a wide bandgap matrix semiconductor in combination with a Gd element is one of the target systems. $Ga_{1-x}Gd_xN$ exhibits a ferromagnetic property even at room temperature [1]. GaN does not have enough bandgap as a host material for Gd. On the other hand, in the case of $Al_{1-x}Gd_xN$ there are several cathodoluminescence (CL) [2-5], electroluminescence [6], and photoluminescence (PL) [7] properties, and in this case every result shows a sharp line at 3.90 ~ 3.94 eV which is clearly observed and well assigned to the $^6P_{7/2} \rightarrow {}^8S_{7/2}$ 4f intra transition of Gd^{3+}. However, the electronic structure of $Al_{1-x}Gd_xN$ is still not clear. In consequence, we have performed not only PL measurements but also PL excitation

(PLE) measurements of $Al_{0.98}Gd_{0.02}N$ and $Al_{0.87}Gd_{0.13}N$. To the best of our knowledge, this is the first report concerning the PLE spectra from $Al_{1-x}Gd_xN$.

2 Experimental $Al_{1-x}Gd_xN$ thin films were grown in a MBE system with a RF-plasma assisted radical cell on the Si-face of (0001)-oriented 6H-SiC substrates. The thicknesses of the $Al_{1-x}Gd_xN$ layers are about 120 nm. The details of the crystal growth have been reported elsewhere [8,9]. Both the PL and the PLE spectra measurements are performed at the 3 m normal incidence monochromator beamline (BL7B) at UVSOR [10]. The intensity of the excitation light is in the order of 10^9 ~ 10^{10} photons/s. Strongly polarized linear monochromatized lights in the region of 3 to 7 eV were used to excite the samples with θ = 8° and 60° in respect to the sample surface in the p configuration, where θ is an incident angle. Since the c-axis of the sample is perpendicular to the sample surface, the elec-

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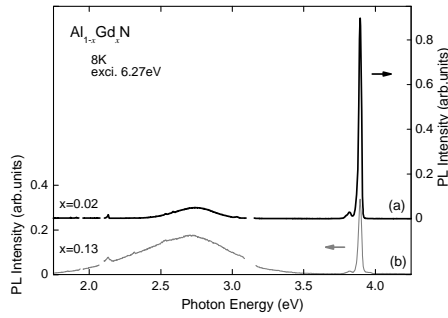
Figure 1 Photoluminescence spectra from (a) Al$_{0.98}$Gd$_{0.02}$N and (b) Al$_{0.87}$Gd$_{0.13}$N at 8 K. Excitation photon energy is 6.27 eV. Both the 2nd and the 3rd higher orders of the scattered excitation light and the 2nd order of the 3.95 eV sharp emission lines are erased for convenience.

tric field E of the incident light at $\theta = 8°$ mostly consists of the $E \perp c$ component. On the other hand, if $\theta = 60°$ consists of both the $E \perp c$ and the $E /\!/ c$ components, then the comparison between the spectra at $\theta = 8°$ and $60°$ shows the contribution of the $E /\!/ c$ component. This simple method is useful in investigating the optical properties of the wurtzite III-V nitrides, because they have uniaxial anisotropy along the c-axis. All of the PL spectra are measured by using a 30 cm conventional monochromator.

3 Results and Discussions Figure 1 shows the PL spectra of (a) Al$_{0.98}$Gd$_{0.02}$N and (b) Al$_{0.87}$Gd$_{0.13}$N at 8 K. The excitation photon energy is 6.27 eV. Both the 2nd and the 3rd higher orders of the scattered excitation light and the 2nd order of the 3.95 eV sharp emission lines are erased for convenience. No incidence angle dependence is found. The PL spectra mainly consist of three parts. The first part is the sharp lines seen at around 3.95 eV. These sharp lines are in agreement with previous research [2] and other results [3-7], and are assigned to be the emission lines due to the intra-transition from $^6P_{7/2}$ to $^8S_{7/2}$ of the Gd^{3+} $4f$ electrons. The emission intensity decreases while increasing the Gd fraction ratio. This phenomenon is explained by so-called concentration quenching [2]. However, no broad emission bands around the 3.95 eV sharp lines are found, despite the fact that they are clearly observed in CL spectra. The second part is the broad emission bands observed in the lower energy side which may have been weakly observed in previous CL work [2]. Since the band width of the broad emission band in (b) is much wider than in (a), it is supposed that this band is correlated to the Gd concentration. The final part is the weak sharp lines below 3.95 eV, especially the 2.13 eV emission lines. Their occurrence is probably due to the transitions between isolated intra-atomic levels. However, it is very difficult to attribute these transitions to Gd^{2+} ions, because to our knowledge there is no emission line due to Gd^{2+} ions mentioned in other scientific journals. They may be due to other impurities.

Figures 2(a) to 2(d) show the optical reflectance (OR) spectra at 22K from Al$_{0.98}$Gd$_{0.02}$N at $\theta = 8°$, at $\theta = 60°$,
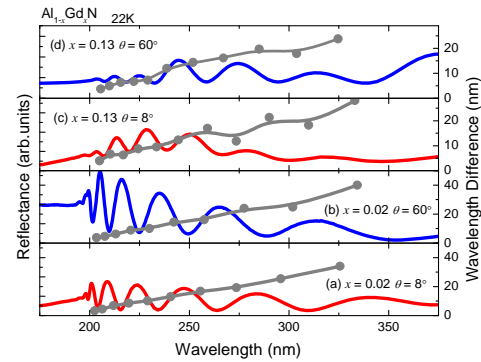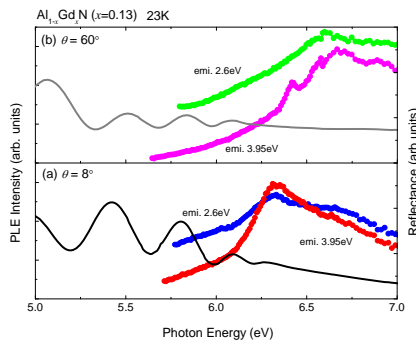

Figure 2 Optical reflectance spectra at 22K from (a) Al$_{0.98}$Gd$_{0.02}$N at $\theta = 8°$, (b) $\theta = 60°$, (c) Al$_{0.87}$Gd$_{0.13}$N at $\theta = 8°$, (b) $\theta = 60°$, respectively, where θ is the angle of incident. The curve with dots in each figure represents the wavelength differences between adjacent peaks and the bottoms of the interference fringes as a function of the average wavelength between adjacent peaks and bottoms.

from Al$_{0.87}$Gd$_{0.13}$N at $\theta = 8°$, at $\theta = 60°$, respectively. These wave-like spectral features suggest that multiple interferences occur between the Al$_{1-x}$Gd$_x$N thin film surfaces and the rear faces. Though the reflectance in each figure is plotted as a function of the wavelength, the interference fringes are not even intervals. Thus, the refractive indexes in the transparency energy region have wavelength dependence. The curve with dots in each figure represents the wavelength differences between the adjacent peaks and bottoms of the interference fringes as a function of the average wavelength between the adjacent peak and bottom. The monotonic increase in accordance with the increasing wavelength in Figs. 2(a) and 2(b) indicates a gradual decrease in the refractive index with increasing wavelength below the band edge in Al$_{0.98}$Gd$_{0.02}$N. In contrast, there are sudden increases at ~207 nm (6 eV) and ~ 234 nm (5.3 eV) in Figs. 2(c) and 2(d), respectively, which suggest the existence of refractive index jumps. It is noted that these jumps correspond to the abrupt peak to peak amplitude changes of the interference fringes.

The PLE spectra and the OR spectra from Al$_{0.98}$Gd$_{0.02}$N at 23 K are shown in Figs. 3(a) ($\theta = 8°$) and 3(b) ($\theta = 60°$).
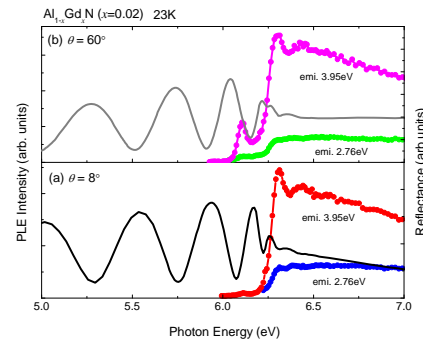
Figure 3 Photoluminescence excitation spectra and optical reflectance spectra from Al$_{0.98}$Gd$_{0.02}$N at 23 K. The emission photon energies are 3.95 eV and 2.76 eV, and the angles of incidence θ are (a) $8°$ and (b) $60°$.

Figures 4 Photoluminescence excitation spectra and optical reflectance spectra from $Al_{0.87}Gd_{0.13}N$ at 23 K. The Emission photon energies are 3.95 eV and 2.76 eV, and the angles of incidence θ are (a) 8° and (b) 60°.

The emission photon energies are 3.95 eV and 2.76 eV which correspond to the peak energy positions of the sharp line and the broad band, respectively. Notable features in Fig. 3 are as follows: (i) PLE spectra monitored at 2.76 eV clearly show the band edge. (ii) PLE spectra monitored at 3.95 eV also show the band edge with a peak structure at 6.3 eV. (iii) Additional peaks and shoulders at 6.11 eV are obviously found in the PLE spectra at $\theta = 60°$. (iv) The rising edges, shoulders and peaks in all of the PLE spectra have higher photon energy values than those of pure AlN. These (i) ~ (iii) features suggest that the crystal structure of $Al_{0.98}Gd_{0.02}N$ is basically similar to that of AlN, and the uniaxial anisotropy character of AlN is still present. Furthermore, the emission processes of both the 3.95 eV sharp line and the broad band at around 2.76 eV are host excitations. Therefore, the photon energy which stimulates valence electrons to the conduction band is transferred partially (or fully) to the Gd^{3+} ion, causing an intra-4f excitation from the $^8S_{7/2}$ ground state to an excited state, and is finally used as 3.95 eV emission line for some relaxation process. Other excited electrons migrate and are trapped in some defects induced by Gd doping. This may be the origin of the 2.76 eV broad emission band. This phenomenon (iv) requires further investigation, such as strain estimation. However, since the bandgap energy of $Al_{0.98}Gd_{0.02}N$ is so close to that of AlN, it is supposed that there is segregation or clustering of the Gd ions even in the $Al_{0.98}Gd_{0.02}N$ sample.

The PLE spectra and the OR spectra from $Al_{0.87}Gd_{0.13}N$ at 23 K are shown in Figs. 4(a) ($\theta = 8°$) and 4(b) ($\theta = 60°$). The emission photon energies are 3.95 eV and 2.6 eV which correspond to the peak energy positions of the sharp line and the broad band, respectively. No clear band edge structures are found in the PLE spectra and long tail structures in the lower energy side. Since the GdN is reported as a semiconductor whose bandgap is in the infrared region [11], a red shift of the band edge is reasonable. The correlation between the peak to peak amplitude of the interference fringes in the OR spectrum and the spectral shape of PLE spectra represent characteristic points in when $\theta = 8°$

and 60° is located at about 6.05 eV and somewhere below 5.5 eV. Therefore, the partially transparent energy region is observed over a wide energy range in the case of $Al_{0.87}Gd_{0.13}N$.

4 Summary The Optical reflectance (OR) and the photoluminescence (PL) and the PL excitation (PLE) spectra from $Al_{1-x}Gd_xN$ ($x = 0.02$ and 0.13) have been investigated by using a highly linear polarized synchrotron radiation light source. A Gd related 3.95 eV sharp emission line is observed, in good agreement with the $^6P_{7/2} \rightarrow ^8S_{7/2}$ 4f intra transition of the Gd^{3+} and a broad emission band in the lower energy side whose intensity and band width depend on the Gd concentration are observed in the PL spectra. The PLE spectra monitored in the emission lines and the band peaks reveal that these two emission processes are host excitations. In particular, the 3.95 eV sharp line emission process is not a direct excitation and recombination process due to the 4f intra transitions of Gd^{3+}. In the case of the $Al_{0.98}Gd_{0.02}N$, band structure and the crystalline anisotropy, they are quite similar to those of pure AlN. However, in case of $Al_{0.87}Gd_{0.13}N$, the band structure is heavily distorted with an additional long band tail.

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