Ultraviolet photoluminescence from Gd-implanted AlN epilayers

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Deep ultraviolet emission from gadolinium (Gd)-implanted AlN thin films has been observed using photoluminescence (PL) spectroscopy. The AlN epilayers were ion implanted with Gd to a total dose of $\sim 6\times 10^{14}$ cm^{-2}. Using the output at 197 nm from a quadrupled Ti:sapphire laser, narrow PL emission was observed at 318 nm, characteristic of the trivalent Gd ion. A broader emission band, also centered at 318 nm, was measured with excitation at 263 nm. The PL emission intensity decreased by less than a factor of 3 over the sample temperature range of 10–300 K and decay transients were of the order of nanoseconds. © *2006 American Institute of Physics.*
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Rare earth doped III-V nitride semiconductor materials have received considerable attention primarily for potential use in optoelectronic devices.[1–14] In particular, the large band gaps of GaN, AlN, and their alloys allow emission of higher energy rare earth transitions that are otherwise absorbed in smaller band gap host materials. Therefore, these materials may have application in visible displays or in white light systems that employ color-combining techniques. Recently, rare earth doped GaN and AlN thin films have also shown potential impact for application in spintronics.[15–19] Whereas doping of GaN crystals with Eu atoms to a few atomic percent has led to observations of weak ferromagnetic behavior,[15] doping with Gd atoms to less than 1 at. % has produced extremely large magnetic moments per ion at room temperature.[17] These reports of colossal magnetic moments with Curie temperatures above 400 K in Gd-doped GaN (GaN:Gd) thin films have sparked interest in exploring other rare-earth–nitride systems as candidate materials for spintronic devices. The doping of nitrides with rare earth ions may serve as an alternative to transition metal doping with the possibility of room temperature ferromagnetism mediated either by carriers or by conduction through bands induced by the rare earth ions. In addition, since the rare earth dopants may be optically active in these materials, magnetic and optical functionalities on a single chip may be possible. Already cathodoluminescence (CL) measurements of Gd-implanted AlN thin films have yielded intense UV emission at 318 nm as well as weaker emissions at other wavelengths.[20–22] Consequently, a greater understanding of the behavior of Gd-doped wide band gap nitride semiconductors is of high interest.

In this work, we have used ion implantation to incorporate Gd ions into AlN films grown by molecular beam epitaxy (MBE). The undoped AlN epilayers were grown by rf-plasma-assisted MBE at 900 °C on *c*-plane sapphire substrates and were insulating ($>10^6\ \Omega$ cm) as determined by Hall measurements. The samples were implanted with Gd ions at two energies (160 and 320 keV) with doses of either 10^{14} (160 keV) plus 2×10^{14} (320 keV) cm^{-2} or 2×10^{14} (160 keV) plus $4-10^{14}$ (320 keV) cm$^{\times 2}$. The samples were held near room temperature during the implantation, and from visual inspection, the implanted regions were not amorphous. Annealing was performed for 5 min under a flowing N_2 gas at a temperature of 1178 K. No indication of the formation of second phases was found based on powder x-ray diffraction (XRD) measurements. Portions of the samples were examined using a superconducting quantum interference device magnetometer (Quantum Design magnetic properties measurement system) and clear hysteretic behavior at 300 K was observed.[23] After annealing the Gd-implanted AlN epilayers were characterized by photoluminescence (PL) and time resolved photoluminescence (TRPL) ultraviolet (UV) spectroscopy. A prominent emission line at 318 nm was observed under excitation at 197 nm as well as

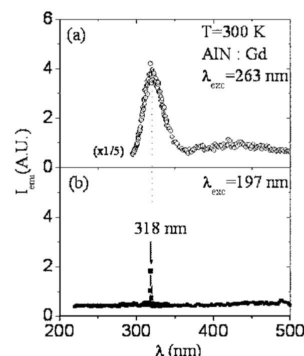

FIG. 1. PL spectra measured at 300 K from the Gd-implanted AlN sample annealed at 1178 K with (a) below-band-gap excitation at 263 nm (b) above-band-gap excitation at 197 nm. The main emission at 318 nm occurs from the ^6P_j-$^8S_{7/2}$ transitions of the Gd^{3+} ion.

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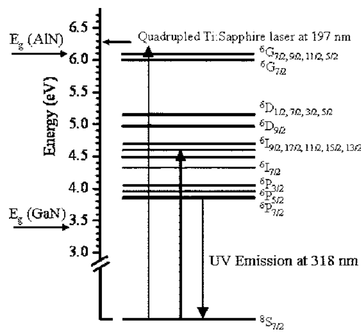

FIG. 2. Two excitation paths for Gd in AlN and the resulting emission.

with pumping at 263 nm. The peak intensity of the Gd-related emission has a high thermal stability from 10 to 300 K and the transient behavior is on the order of nanoseconds.

The trivalent Gd ion (Gd^{3+}) has seven unpaired electrons in the unfilled 4f shell, which is shielded by the completely filled 5s and 5p shells. The first excited manifold ^6P_j of the Gd^{3+} lies ~4.5 eV (318 nm) above the ground state $^8S_{7/2}$.[24] Since wurtzite AlN semiconductor material has a very large band gap, ~6.1 eV (203 nm), PL spectroscopy of this system requires deep UV sources. In the present experiments the quadrupled output from a Ti:sapphire laser led to above-band-gap excitation of the AlN host. The PL excitation consisted of a series of 197 nm laser pulses having 100 fs width and 76 MHz repetition rate. Below-band-gap excitation at 263 nm was done by tripling the laser source to yield a similar series of pulses. The PL emission was collected and analyzed with a 1.3 m grating monochromator equipped with a microchannel plate photomultiplier tube used in a single photon counting mode. TRPL spectroscopy was done using the 197 nm excitation pulses.

Figure 1 shows room temperature PL spectra over the range of 250–500 nm for a Gd-implanted AlN sample after annealing. The main emission line at 318 nm, which arises from the ^6P_j-$^8S_{7/2}$ transitions of the Gd^{3+} ion, was observed with both above-band-gap (197 nm) and below-band-gap (266 nm) excitations. With above-band-gap excitation [see Fig. 1(b)] the emission line at 318 nm is very narrow with a full width at half maximum (FWHM) of ~0.6 nm. The 197 nm laser pulses are of sufficient energy to create electron-hole pairs in the AlN host and to subsequently transfer energy to the Gd^{3+} ion. Since the emission at 318 nm occurs from the first excited manifold of the rare earth ion, the precise relaxation process cannot be determined at this time. With below-band-gap excitation [see Fig. 1(a)] the emission at 318 nm is quite broad with a FWHM of ~22 nm. Higher emission intensity under below-band-gap excitation is due to much higher excitation power. In this case it appears that the Gd^{3+} ions are excited either resonantly through the ^6I_j multiplet of levels or through material defects in the AlN host. The XRD rocking curve measurement of the Gd-implanted AlN layer yielded a value of 2196 arc sec, which is more than four times the value of a high quality undoped AlN grown layer. Therefore, a combination of excitation paths via defects in the host and direct intra-4f transitions seems very likely for the below-band-gap PL data. The difference in linewidth suggests that different subsets of Gd^{3+} ions are excited using above- and below-band-gap pumping.[4] In Fig. 2, a schematic diagram illustrates the two methods used for excitation of the Gd^{3+} ions and the resulting emission. Also shown in the diagram are the band gap energies of AlN and GaN host materials. Since the initial ferromagnetic measurements were done on GaN samples, no UV emission would have been observable. Only with wider band gap AlGaN alloys can some of the transitions of the Gd^{3+} ions be observed.

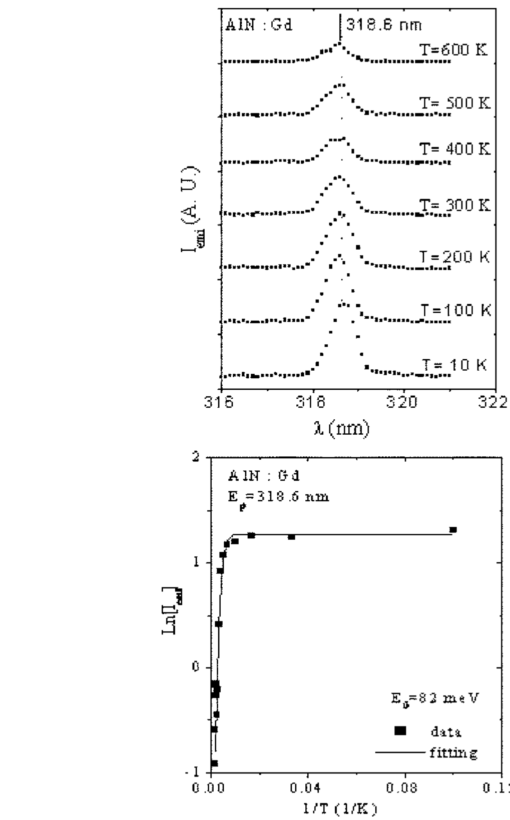

FIG. 3. Dependence of the PL intensity at 318 nm on the sample temperature: (top) PL spectra measured at temperatures from 10 to 600 K and (bottom) peak PL intensity plotted as a function of inverse sample temperature. The best fit using Eq. (1) is shown by the solid line.

The dependence of the intensity of the Gd^{3+} PL emission on the sample temperature is shown in Fig. 3. Spectral measurements that were done over a range from 10 to 600 K, see Fig. 3 (top), indicate a seven fold reduction in peak intensity I_{emi} with increasing temperature T. The data are plotted in Fig. 3 (bottom) and fitted with an inverse exponential,

$$I_{emi}(T) = I_0/\{1 + c \exp(-E_A/kT)\}, \tag{1}$$

yielding a value of 82 meV for the activation energy E_A of this thermal quenching. This value compares favorably with that found in other rare-earth-semiconductor material systems such as GaN:Eu.[25] Although the PL intensity is quenched at higher temperatures, the transition linewidth does not change with increasing temperature from 10 to 600 K, as seen in Fig. 3 (top). It should be noted that there is some contribution to the observed linewidth from the monochromator slit width. During PL measurements, the slit width was 250 μm, which corresponds to a spectral dispersion of 0.25 at 318 nm.

Time resolved photoluminescence measurements of the emission at 318 nm were performed at 10 K using 197 nm excitation. The data are plotted in Fig. 4 and show two distinct decay transients of the UV emission. A good fit to the

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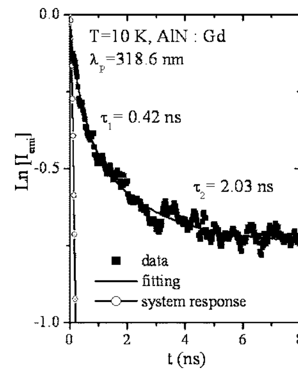

FIG. 4. Time resolved photoluminescence measurements measured at 10 K of the main emission line at 318 nm. The data indicate two distinct decay transients of the UV emission.

experimental data was obtained using a double-exponential time dependence,

$$I_{\rm emi}(t) = I_1 \exp(-\tau_1/t) + I_2 \exp(-\tau_2/t). \tag{2}$$

The fast component had a lifetime of $\tau_1=0.5$ ns and the slow component a lifetime of $\tau_2=2.0$ ns. The double-exponential nature of the decay transient is similar to reports by Vetter *et al.*[20] The observed decay times in this study, however, are several orders of magnitude smaller. A possible explanation for the nanosecond lifetimes could be efficient cross-relaxation processes due to a high peak Gd concentration ($>10^{19}$ cm^{-3}). The ion implantation dose in these experiments was nearly an order of magnitude higher than that used in the CL study. It also seems possible that the excitation of Gd^{3+} ions may be occurring indirectly from the e-h recombination through induced defect levels. These defect levels may at the same time provide efficient relaxation channels for energy back transfer to the AlN host.[26]

The PL data presented here are quite different than results of CL measurements done on similar Gd-implanted AlN thin films.[20–22] While both PL and CL measurements yield an intense UV emission at 318 nm, only the CL measurements have shown evidence of Gd^{3+} transitions at other wavelengths, near 259 and 285 nm, arising from higher energy manifolds. In CL measurements the intensity of emission at these wavelengths is about 50 times weaker than the main transition. With the present PL excitation, transitions at these wavelengths would need to occur indirectly through internal relaxation of the higher energy $4f$ states of the excited Gd^{3+} ion and may be even weaker in intensity.

Results of the dependence of the UV emission on sample temperature are in greater disagreement. In CL measurements reported previously[20–22] the integrated emission intensity actually decreases at lower temperatures. The behavior found here, where the PL intensity increases by more than a factor of 3 from 300 to 10 K, is consistent with predominant data taken over a range of different rare-earth-semiconductor host systems.[27,28] In addition, decay transients of the UV emission are much faster in the PL measurements (on the order of nanoseconds) than in the CL measurements (on the order of milliseconds). Further experiments are needed to clarify these differences but they may simply be due to differences in the defects present in the starting materials.

In summary, Gd ions have been incorporated into AlN epilayers by ion implantation and $4f$-related UV emission was observed with optical excitation. An emission line at 318 nm, associated with the ^6P_j-$^8S_{7/2}$ transitions of the Gd^{3+} ion, was observed with both above-band-gap and below-band-gap excitations. The 318 nm emission was studied as a function of sample temperature and the peak PL intensity was found to be very stable with temperature from 10 to 300 K. This work demonstrates that spectrally narrow, deep UV emission lines can be obtained from Gd-implanted AlN under optical excitation. Furthermore, with proper *in situ* doping during epitaxial growth and device design, it may be possible to form electroluminescence III-V emitters for specific UV optoelectronic applications such as white lighting.[29] In addition, these experiments provide evidence that integration of ferromagnetic behavior and UV emission can achieved in the same Gd-doped AlN thin film.

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