Photoluminescence properties of in situ Tm-doped Al$_x$Ga$_{1-x}$N

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We report on the photoluminescence (PL) properties of in situ Tm-doped Al$_x$Ga$_{1-x}$N films ($0 \leq x \leq 1$) grown by solid-source molecular-beam epitaxy. It was found that the blue PL properties of Al$_x$Ga$_{1-x}$N:Tm greatly change as a function of Al content. Under above-gap pumping, GaN:Tm exhibited a weak blue emission at $\sim 478$ nm from the $^1G_4 \rightarrow ^3H_6$ transition of Tm$^{3+}$. Upon increasing Al content, an enhancement of the blue PL at 478 nm was observed. In addition, an intense blue PL line appeared at $\sim 465$ nm, which is assigned to the $^1D_2 \rightarrow ^3F_4$ transition of Tm$^{3+}$. The overall blue PL intensity reached a maximum for $x=0.62$, with the 465 nm line dominating the visible PL spectrum. Under below-gap pumping, AlN:Tm also exhibited intense blue PL at 465 and 478 nm, as well as several other PL lines ranging from the ultraviolet to near-infrared. The Tm$^{3+}$ PL from AlN:Tm was most likely excited through defect-related complexes in the AlN host.

Figure 1 shows an overview of the normalized PL spectra of Tm-doped Al$_x$Ga$_{1-x}$N with $x=0$, 0.16, 0.21, 0.39, 0.62, and 0.81. The calculated bandgap energies using Végard’s law and a bowing parameter of $b=1$ are 3.39 eV (GaN), 3.71, 3.82, 4.26, 4.91, and 5.56 eV, respectively.

The PL was excited using the 250 nm ($\sim 4.96$ eV) output of an OPO system, which corresponds to above-gap pumping for Al$_x$Ga$_{1-x}$N samples with $x\leq0.62$. Similar to previous reports, the visible PL from GaN:Tm is characterized by a broad band extending from $\sim 400$ to 600 nm and near-band-edge emission at $\sim 367$ nm. A weak blue PL line located at $\sim 478$ nm from the $^1G_4 \rightarrow ^3H_6$ transition of Tm$^{3+}$ is hardly observable. The infrared PL at $\sim 803$ nm is tentatively assigned to the intra-4f transition $^3H_4 \rightarrow ^3H_6$ of Tm$^{3+}$ ions.

Changing from GaN:Tm to Al$_x$Ga$_{1-x}$N:Tm led to pronounced changes in the PL properties. Upon increasing Al content, the 478 nm PL line gained in intensity and was clearly observed. The broadband emission was also sharply reduced. The strongest emission from the $^1G_4 \rightarrow ^3H_6$ transition at 478 nm was obtained for $x=0.39$. Interestingly, two other PL lines were observed: a weaker line at $\sim 370$ nm and a dominant blue line at $\sim 465$ nm. The PL intensity of the 465 nm line was several times larger compared to the 478 nm PL. The overall strongest blue PL intensity was measured.

Light emission from rare-earth (RE)-doped III-N semiconductors is of significant current interest for applications in electroluminescence (EL) devices. Previous work on visible emission from RE-doped III-Ns was mainly focused on RE-doped GaN. Photoluminescence (PL) and cathodoluminescence (CL) data have been reported from nearly all lanthanide ions doped into GaN. Visible EL devices based on RE-doped GaN, however, have only been demonstrated from GaN:Eu (red), GaN:Er (green), and GaN:Tm (blue). One of the main challenges in using RE-doped GaN for full-color display applications is obtaining efficient blue emission. While dominant blue emission has been reported from GaN:Tm EL devices, the visible PL from GaN:Tm is characterized by a broadband emission. The signal was processed using a boxcar averager, and PL lifetime transients were recorded using a digitizing oscilloscope.
from Al$_{0.62}$Ga$_{0.38}$N:Tm with the 465 nm line being roughly ten times more intense than the 478 nm line.

The observation of new PL lines in Al$_x$Ga$_{1-x}$N:Tm can be explained by the change in bandgap energy of the host. Tm$^{3+}$ has higher excited states above the 1$^I_4$ level, which are located at 3.4 eV ($1D_2$) and 4.2 eV ($1I_6/3P_0$). The energy of the $1D_2$ level is very similar to the bandgap energy of GaN (see Fig. 3). Therefore, no emission from the $1D_2$ level is observed from GaN:Tm. Upon increasing the bandgap energy of Al$_x$Ga$_{1-x}$N, the $D_2$ level moves within the bandgap of the host, which results in the observation of PL lines at 370 and 465 nm. Based on the comparison to existing literature, the 370 and 465 nm lines are assigned to the $1D_2$!$3F_4$ transitions of Tm$^{3+}$.

Figure 1 also indicates that the excitation efficiency of the 1$^I_4$ level of Tm$^{3+}$ is enhanced in Al$_x$Ga$_{1-x}$N:Tm samples compared to GaN:Tm. As mentioned earlier, hardly any blue Tm$^{3+}$ PL was observed in GaN:Tm. A similar poor above-gap pumping efficiency was reported for Tb$^{3+}$ ions in GaN:Tb. The weak PL excitation efficiency was explained using a defect-related energy transfer model as proposed by Takahei et al. for RE-doped semiconductors. In this model, RE doping of a semiconductor leads to the formation of RE-related levels in the bandgap of the host. These levels can trap free carriers, which subsequently recombine and transfer their energy to intra-4$f$ RE transitions. Recent studies have identified RE-related traps for GaN:Eu, GaN:Tb, and GaN:Er at ~0.3–0.4 eV below the conduction band of GaN. The recombination energy of carriers trapped at the RE-related defects in GaN is then estimated to be ~3.0–3.1 eV, which energetically matches intra-4$f$ transitions of Eu$^{3+}$ and Er$^{3+}$, respectively. On the other hand, Tb$^{3+}$ ions do not exhibit intra-4$f$ transitions in that energy range, preventing an efficient carrier-mediated excitation process in GaN:Tb. Assuming that Tm$^{3+}$ also induces a defect-level in GaN, similar arguments for the weak above-gap excitation efficiency can be applied to GaN:Tm. Within the defect-related energy transfer model, however, the excitation efficiency of the Tm$^{3+}$ can be optimized by a modification of the bandgap energy. Upon increasing Al content, higher excited states of Tm$^{3+}$ ($1D_2/1I_6/3P_0$) move within the bandgap of Al$_x$Ga$_{1-x}$N, which provide additional channels for the energy transfer between defect levels and Tm$^{3+}$ ions. Future investigations are necessary to identify Tm-related defects in Al$_x$Ga$_{1-x}$N:Tm to support the defect-related energy transfer model. In addition, it cannot be excluded that chemical effects related to the presence of Al change the Tm$^{3+}$ incorporation and excitation mechanisms, similar to observations made for Er-doped AlGAs.

The high-resolution PL spectrum, with excitation at 250 nm, of AlN:Tm at room temperature is shown in Fig. 2. The PL was dominated by intense blue PL lines centered at ~465 and ~478 nm. The average lifetimes of the 465 and 478 nm lines were determined to be ~2 and ~3.3 µs, respectively. The lifetimes were nearly temperature independent, suggesting that nonradiative decay processes are small.

FIG. 1. Room-temperature PL spectra of Al$_x$Ga$_{1-x}$N:Tm excited at 250 nm. The dotted lines indicate the position of the blue PL arising from the transitions $1^I_4$!$3H_6$ (~478 nm) and $1^I_2$!$3F_4$ (~465 nm). The calculated bandgap energies ($E_g$) are also indicated in the figure.

FIG. 2. High-resolution PL spectrum of AlN:Tm at room temperature. The PL was excited at 250 nm, which correspond to below-gap pumping. The assignment of the intra-4$f$ transitions of Tm$^{3+}$ is indicated in the figure. The inset shows the infrared PL spectrum around 1450 nm.

FIG. 3. Free-ion energy level diagram of Tm$^{3+}$ ions and observed transitions in AlN:Tm. The bandgap of GaN is also indicated in the figure, along with PL lifetimes for several excited states of Tm$^{3+}$. This figure illustrates the relationship between the energy levels of Tm$^{3+}$ and the bandgap of GaN, comparing the excitation and emission transitions observed in AlN:Tm with the calculated bandgap energies for GaN.
respectively and transition absorption line close to 250 nm, the excitation of \[^1\text{H}_4\] has to be due to the \[^3\text{H}_4\] states of Tm\(^{3+}\), which are sufficiently excited below the bandgap of AlN using the 250 nm excitation. However, requires further investigations. tentatively located the \[^1\text{I}_6\] level below the \[^3\text{P}_0\] state. A final identification of the energy position of \[^1\text{I}_6\] and \[^3\text{P}_0\] levels, efficiency of the RE excitation and emission properties was found that the Tm\(^{3+}\) excitation. The large sensitivity of the blue emission from Tm\(^{3+}\) on the Al content of Al\(_x\)Ga\(_{1-x}\)N indicates the possibility to optimize the RE excitation and emission properties through careful bandgap engineering of the host. The authors from H. U. acknowledge financial support by ARO through grant DAAD19-02-1-0316. The work at U. C. was supported by ARO grant DAAD 19-99-1-0348.

It is also interesting to note that the Tm\(^{3+}\) PL was efficiently excited below the bandgap of AlN using the 250 nm output from an OPO system. Since Tm\(^{3+}\) has no intra-4f transition absorption line close to 250 nm, the excitation of Tm\(^{3+}\) ions in AlN must occur through defects in the AlN host. A similar below-gap excitation mechanism was observed for AlN:Er. Excitation-wavelength-dependent studies showed that the Tm\(^{3+}\) PL can be excited over a wide wavelength range starting from \(~320\) down to 220 nm, as shown in Fig. 4. It can be seen that the ratio of emission from the \[^1\text{D}_2\] (\(\sim 465\) nm) and \[^1\text{G}_4\] (\(\sim 478\) nm) levels varies as a function of excitation wavelength. This result suggests the existence of different Tm\(^{3+}\) centers, which are selectively excited through different defects.

In summary, the PL properties of Al\(_x\)Ga\(_{1-x}\)N:Tm were investigated. Under above-gap pumping, GaN:Tm exhibited only a weak blue emission from the \[^1\text{G}_4\]→\[^3\text{H}_6\] transition of Tm\(^{3+}\). A significant enhancement of the blue Tm\(^{3+}\) emission was observed from Tm-doped Al\(_{x}\)Ga\(_{1-x}\)N samples. Besides emission from the \[^1\text{G}_4\]→\[^3\text{H}_6\] transition, a second blue emission line appeared around 465 nm, which was assigned to the \[^1\text{D}_2\]→\[^3\text{F}_4\] transition of Tm\(^{3+}\). The overall strongest blue PL emission was measured from Al\(_x\)Ga\(_{1-x}\)N:Tm with \(x=0.62\). Strong blue emission from the \[^1\text{D}_2\] and \[^1\text{G}_4\] levels of Tm\(^{3+}\) was also observed from AlN:Tm under below-gap excitation. The large sensitivity of the blue emission from Tm\(^{3+}\) on the Al content of Al\(_x\)Ga\(_{1-x}\)N indicates the possibility to optimize the RE excitation and emission properties through careful bandgap engineering of the host.

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