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Substantial enhancement of red emission intensity by embedding Eu-doped GaN into a microcavity

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We investigate resonantly excited photoluminescence from a Eu,O-codoped GaN layer embedded into a microcavity, consisting of an AlGaN/GaN distributed Bragg reflector and a Ag reflecting mirror. The microcavity is responsible for a 18.6-fold increase of the Eu emission intensity at ∼10K, and a 21-fold increase at room temperature. We systematically investigate the origin of this enhancement, and we conclude that it is due to the combination of several effects including, the lifetime shortening of the Eu emission, the strain-induced piezoelectric effect, and the increased extraction and excitation field efficiencies. This study paves the way for an alternative method to enhance the photoluminescence intensity in rare-earth doped semiconductor structures.

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Red luminescence from GaN-based semiconductors is a key technology for realizing novel luminescent devices such as integrated full-color displays. To date, InGaN-based laser diodes (LDs) and light-emitting diodes (LEDs) have achieved high device performance in the near-ultraviolet to green spectral regions.1–3 However, obtaining red emission from InGaN/GaN quantum wells remains a challenge owing to problems such as phase separation4 and polarization induced internal electric fields.5 Rare-earth (RE)-doped nitride semiconductors that exhibit red emission, such as Eu-doped GaN (GaN:Eu),6 are promising alternatives, with GaN:Eu-based red LED grown by organo-metallic vapor phase epitaxy (OMVPE) having already been demonstrated.7 By optimizing growth conditions and device structures, the light output power has increased steadily to 93 µW in recent years.8 By considering that a commercially available AlGaInP/GaAs based red LED can emit a few mW, further improvement in light output power of the GaN:Eu LED is necessary for practical use.

Previous reports on GaN:Eu indicate that the number of optically active Eu centers and the energy transfer efficiency from GaN to the Eu ions are the major factors limiting light output.9,10 One method for increasing the energy transfer efficiency is to co-dope with impurity atoms such as Mg11,12 or Mg and Si.13 These impurities have been shown to couple with the Eu ions, enhancing their emissivity. However, another limiting factor is the relatively long radiative lifetimes of the Eu ions in GaN:Eu (∼300 µs). The present study is motivated by the possibility of increasing the emission intensity by modifying the spontaneous emission rate of Eu. According to Fermi’s golden rule, this can be achieved by increasing the photonic density of states (PDOS) at the frequency of spontaneous emission, as already demonstrated with a planar Fabry-Perot cavity.14 Alternatively, the PDOS can be increased by coupling the emission centers with surface plasmon polaritons.

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(SPPs) propagating at a metal/dielectric interface. While coupling to SPPs was previously believed to be detrimental to the light output, it has been shown that light can be efficiently extracted by means of SPP scattering from a surface with adequate roughness.

In this paper, we investigated the spontaneous emission from an Eu$_2$O-codoped GaN (GaN:Eu,O) layer embedded into a resonant microcavity made by a distributed Bragg reflector (DBR), and a Ag mirror. We observe a 18.6-fold enhancement of the emission intensity at ∼10K, and a 21-fold enhancement at room temperature, with respect to a reference sample without the microcavity. From our experiments and detailed modeling, we assign this enhancement to a combination of several concurrent effects, namely: the lifetime shortening of the Eu emission, the strain-induced piezoelectric effect, and the increased extraction and excitation field efficiencies.

Our investigation focuses on a 250nm-thick GaN:Eu,O photoluminescent layer emitting at ∼622 nm, and embedded in four different structures, as depicted in Fig. 1. The ‘reference’ structure (Fig. 1(a)) consists of the active layer with GaN spacing layers on its top surface. In the ‘Ag-mirror’ structure (Fig. 1(b)), an Ag mirror and GaN spacing layers are grown on top of the active layer. In these structures, the GaN cap layer has been grown with increasing thickness (7.5, 15, 50, 85 and 120 nm) in order to reveal the effect of SPPs on the radiative lifetimes. In the ‘DBR’ sample (Fig. 1(c)), the structure consisted of an undoped GaN layer, followed by a 10 pairs of AlN/Al$_{0.25}$Ga$_{0.75}$N (8 / 22 nm) superlattices (SLs), a 10.5 pairs of GaN /Al$_{0.4}$Ga$_{0.6}$N (75 / 60 nm) DBR, the active layer, and a 15 nm GaN cap layer. The SLs were inserted to suppress the crack on the DBR, which has the maximum reflectance of approximately 50% at the Eu emission range. The ‘microcavity’ sample (Fig. 1(d)) has the same structure as the ‘DBR’, but with an additional Ag layer on its top surface.

All samples were grown on double-side polished (0001) sapphire substrates by OMVPE. Trimethylgallium, trimethylaluminum, and ammonia were used as sources. The Eu precursor was bis(n-propyl-tetramethylcyclopentadienyl)europium [(EuCp$^{n}$)$_2$], and Ar-diluted O$_2$ was used for oxygen co-doping, which is known to improve the Eu incorporation and luminescence properties, when this Eu source is used.

The samples were characterized by photoluminescence (PL) and time-resolved PL (TR-PL). In OMVPE grown GaN:Eu, Eu is known to incorporate into multiple environments, and at least eight distinct optically-active centers have been identified. Each of these centers has a different emission and resonant excitation wavelength, and a distinct lifetime. To avoid simultaneous contributions from various Eu centers, the PL and TR-PL measurements were carried out by resonantly

FIG. 1. Schematic of samples ‘reference’ (a), ‘Ag-mirror’ (b), ‘DBR’ (c), and ‘microcavity’ (d). The GaN spacer thickness dependence was investigated in the ‘reference’ and ‘Ag-mirror’ structures. In the ‘DBR’ and ‘microcavity’ samples, the GaN spacer thickness was fixed at 15 nm.
exciting the majority center OMVPE 4 with a dye laser with wavelength 571 nm. At this wavelength, light is not absorbed by the GaN substrate, and this enables excitation and detection through the backside of the sample. The emission spectra were recorded using a micro-PL system (Horiba: LabRAM HR-800). The PL decay signals were detected using a photon-counting system with a thermoelectrically cooled photomultiplier tube. For measurements at low temperature, the samples were mounted in a closed-cycle cryostat and cooled to \( \sim 10\text{K} \).

At first, we investigated the SPPs effects on the Eu transition rate, as summarized in Fig. 2, by focusing on the ‘reference’ (square) and ‘Ag-mirror’ (circle) structures. Specifically, we investigated the dependence of the radiative lifetime on the thickness \( t_{\text{cap}} \) of the GaN spacer by both experiments TR-PL (black) and calculations (red). We calculated the spontaneous decay rate enhancement by using the same approach of Ref. 21 as \( \Gamma(z)/\Gamma_0 = P_0/P(z) \), where \( P_0 \) and \( \Gamma_0 \) are the spontaneous emission power and the decay rate of the OMVPE 4 luminescent site in bulk GaN. On the other hand, \( P(z) \) and \( \Gamma(z) \) are the spontaneous emission power and the decay rate of a luminescent site placed at a distance \( z + t_{\text{cap}} \) from the Ag layer, respectively. In the experiments, the peak of the Eu emission was selected by using a monochromator, as indicated by the triangle in the inset of Fig. 2.

The PL decay comprises contributions from all the OMVPE 4 luminescent sites located within the active layer with a thickness of 250 nm. Therefore, we fitted the TR-PL profiles by a stretched exponential function, for both calculated and measured data, and we found a very good agreement between the two. Specifically, the radiative lifetimes for the ‘reference’ structures were all approximately 285 \( \mu\text{s} \), as indicated by the dashed line in Fig. 2. On the other hand, the lifetimes for the ‘Ag-mirror’ samples become shorter as the spacer thickness decreases, and they reach a minimum value of 234 \( \mu\text{s} \) for a spacer layer thickness of 7.5 nm. The reduction of radiative lifetime for spacer thicknesses less than 40 nm is a clear indication of the coupling between the Eu emission centers and the SPP modes, which decreases exponentially with distance from the Ag surface. In Ref. 24, it was observed that the PDOS for a monolayer of Eu ions undergoes spatial oscillations due to interference with reflections from an Ag mirror. However, in our experiments these variations average out, since the entire 250nm active layer thickness is excited and contributes to the total radiative lifetime.

We obtained the shortest lifetime for the sample with the lowest spacer thickness (7.5 nm). However, an LED device requires a thicker layer of \( p \)-type GaN. For this reason, we fix the spacer thickness at 15 nm for the following experiments. In Fig. 3, we compare the PL emission spectra
FIG. 3. PL spectra due to $^5D_0-^7F_2$ transitions acquired at $\sim 10$ K from a GaN:Eu active layer embedded in different structures: ‘reference’ (black), ‘Ag-mirror’ (blue), ‘DBR’ (green) and ‘microcavity’ (red). The inset shows TR-PL profiles of samples ‘DBR’ and ‘microcavity’.

of all the investigated structures: ‘reference’ (black), ‘Ag-mirror’ (blue), ‘DBR’ (green) and ‘microcavity’ (red). In Table I, we provide a list of PL intensities normalized to that of the ‘reference’ sample. The ‘Ag-mirror’ structure shows a PL increase factor of 4.9. Both the ‘DBR’ and the ‘microcavity’ samples show a red-shift of PL peaks and a strong enhancement of PL intensity, which we attribute to the compressive strain induced on the GaN:Eu,O active layer by the DBR. For Eu$^{3+}$ ions, the excitation from $^7F_0$ to $^5D_0$ is spin-forbidden, and is therefore quite sensitive to crystal field perturbations, since these can induce electron-phonon coupling and relax this selection rule. Therefore, the crystal lattice strain and resulting electric fields due to the piezoelectric effect can perturb the 4f energy level splitting of the Eu ions. This can influence the transition probabilities, which can enhance the excitation as well as radiative recombination. The ‘DBR’ and the ‘microcavity’ structures only differ by the presence of the Ag reflector. The addition of the metal layer further increases the PL enhancement at $\sim 10$K from 7.6 to 18.6 times, as compared to the ‘reference’ sample. At room temperature, the enhancement of the ‘microcavity’ reaches a value of 21 times.

In order to shed some light on the spontaneous emission rate and on the PL enhancement in the investigated samples, in the following we focus on TR-PL decays, as shown in Fig. 3. We fit the time profiles by stretched exponential functions with $\beta = 0.99$ and 0.92 for the ‘DBR’ and the ‘microcavity’ samples, respectively. These results indicate that PDOS is uniform across the active layer in the ‘DBR’ structure. On the other hand, we already concluded that the PDOS is enhanced in proximity of the Ag layer due to coupling with SPP modes, and this determines a distribution of spontaneous emission rates across the active layer in the ‘microcavity’ sample. The radiative lifetime of the ‘DBR’ sample was increased up to 305 $\mu$s due to the compressive strains mentioned.

<table>
<thead>
<tr>
<th></th>
<th>‘reference’</th>
<th>‘Ag-mirror’</th>
<th>‘DBR’</th>
<th>‘microcavity’</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL intensity enhancement</td>
<td>1</td>
<td>4.9</td>
<td>7.6</td>
<td>18.6</td>
</tr>
<tr>
<td>Normalized field excitation efficiency</td>
<td>1</td>
<td>1.7</td>
<td>1</td>
<td>2.6</td>
</tr>
<tr>
<td>Extraction efficiency $\eta$</td>
<td>0.44</td>
<td>-</td>
<td>-</td>
<td>0.92</td>
</tr>
</tbody>
</table>
above, being considerably longer than the 290 µs measured in the ‘reference’ structure. However, once the Ag mirror is added, the radiative lifetime of the ‘microcavity’ shortens to 228 µs. Looking back at Fig. 2, it is clear that this is even shorter than the lifetime of the ‘Ag-mirror’ structure (~240 µs). Thus, by combining the effects of SPPs with the increase in optical mode density due to the cavity modes, a 1.3-fold improvement in transition rate, as compared to the ‘reference’ sample, was attained.

We conclude that the observed high gain in luminescence intensity is a consequence of both the introduction of compressive strain due to the DBR, and of the faster spontaneous emission due to coupling with SPP modes. It is worth to remark that the SPPs are non-radiative modes, which dissipate heat while propagating along a flat metal/dielectric interface, and that an appropriate roughness is necessary for the SPPs to scatter light into radiative modes.

In our samples, while the surface of the DBR/SL layers is relatively flat, the incorporation of Eu into GaN results in the formation of pits, leading to roughness on the sample surface. When Ag is evaporated onto this rough surface, it forms nanostructures that enable scattering from the SPP modes.

One aspect of resonant excitation that needs to be considered is that the excitation field intensity in the active layer changes significantly between samples. Table I shows the normalized excitation field efficiency of the dye laser in the active layer of each sample, calculated by using the analytical solution of waves propagating in planarly layered media. The excitation efficiency of the ‘microcavity’ enhanced 2.6 times with respect to the ‘reference’. Unfortunately, this factor cannot be translated into an LED device. The enhancement of PL intensity is also affected by the extraction efficiency, because of the presence of the Ag mirror and DBR/SLs. We calculated the extraction efficiency by estimating the power ratio passing through the surface of $R_f$ ($\eta$) expressed as:

$$\eta = \frac{(1 - R_f)(1 + R_b)}{2(1 - R_f R_b)}$$

where, $R_f$ and $R_b$ are reflectivity of front and back mirror, respectively. The resulting values are reported in Table I and indicate that the extraction efficiency improves 2.1 times after the deposition of the Ag mirror. Both of the excitation and extraction efficiencies contribute to the emission intensity enhancement factor measured experimentally.

In conclusion, we investigated the spontaneous emission in a photoluminescent GaN:EuO layer embedded into a microcavity. We observed that the emission rate was enhanced by a factor of 1.3, due to increased PDOS resulting from a combination of SPPs and microcavity effects. The overall enhancement of Eu-related emission due to the microcavity structure was found to be 21 times at room temperature, with contributions from stress effects, increased excitation field amplitude and extraction efficiency, in addition to the faster spontaneous emission rates. While the samples in this study were optically pumped at resonance, our results strongly suggest that the use of a microcavity structure is also a promising method for improving the light output from electrically pumped GaN:Eu-based red LEDs. The enhancement of light output under indirect excitation and current injection configurations is a subject of ongoing work.

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