Controlling light emission of nanoparticles

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Enhanced light extraction of Eu-related emission from a nano-patterned GaN layer grown by MOCVD.

Eu-doped GaN (GaN:Eu) is a promising material for the active layer in red light emitting diodes. Although the output power of LEDs based on GaN:Eu has been increasing by a combination of structural and growth optimizations, there is still a significant limitation resulting from poor light extraction efficiency, typical for high refractive index materials. Here we studied nano-structuring the top of the optical active layer using nano-cuboids for enhancement of the light extraction efficiency, and its effect on the optical emission characteristics. By etching nano-cuboids into the active layer, we observed an increase in directional light output power of Eu$^{3+}$ ions of up to 60%, as well as a grating effect. Simultaneously, the absorption of excitation light into the optical active layer was improved, leading to a 12.8 times increase of directional output power per available Eu$^{3+}$ ion.
4.1 Introduction

GaN-based efficient red light emitters are a key development to complement the already available blue and green colors, and realize monolithically produced full-color displays. The recently introduced Rec. 2020 standard defines a wide color gamut for ultra-high definition televisions (UHDTV). The RGB primaries used by the Rec. 2020 standard should be monochromatic light sources. Although monochromatic laser sources can be used for the realization hereof, they are too expensive and have the speckle problem [84]. InGaN multi-quantum well structures are being used for the active component of commercially available LEDs. [85–87] However, it is difficult to achieve narrow emission linewidth from InGaN, because of the band-to-band nature of the optical transition responsible for light emission in these materials. Yet additional broadening results from the compositional fluctuation of group III elements in InGaN caused by segregation. [88, 89] Rare earth doped GaN offers an alternative solution, and in particular Eu-doped GaN (GaN:Eu) is a promising material to resolve the above mentioned limitations for red emitters. Eu$^{3+}$ ions have been widely used as phosphors, for their strong red luminescence. This arises due to relatively efficient, well defined, and temperature stable transitions of the intra-4f shell, in the wavelength range around 620 nm.

The red emission from organometallic vapor phase epitaxy (OMVPE) grown GaN:Eu LEDs was first demonstrated. [90] and with further optimization of growth conditions, layer configuration and device structure have resulted in a steady increase of the light output of red emitting GaN:Eu devices over the last few years [91, 92]. One important limitation of GaN-based LEDs is the light extraction efficiency (LEE), due to the large difference of the refractive index of the GaN structure with the surrounding medium. Different approaches have been attempted to counter this deficiency, like nano-structuring of the surface [93], using nanotubes [94], or localized surface plasmons [95].

In this work, we study the influence of surface patterning the optically active GaN:Eu layer on the emission characteristics. We prepared three different samples, where one has a plain surface, serving as a reference, and the other two have different patterning geometries. The pattern consists of cuboids organized in a square lattice and was formed by a nano-imprint lithography process. We have studied the directional emission of these structures and observed an increase of the light extraction efficiency of 60% for the structured samples as compared to the reference. From additional total luminescence experiments and time-resolved photoluminescence studies at different temperatures, we deduced that the internal quantum efficiency (IQE), defined by the ratio between the integrated area under an PL decay graph and that of a single-exponential decay with the time constant determined at low temperature (which we assume to be purely radiative), of the layers goes down at room temperature (RT), but
is restored at lower temperature. The non-radiative recombination channels are ther-
mally activated, with 22 meV. Finally, an expected nano-resonator effect that could
enhance the radiative transitions in the Eu$^{3+}$ ions, was not observed. This is most
likely a result of the non-optimized structure of the surface patterning.

4.2 Experimental details

4.2.1 Sample preparation

Samples are produced with the following procedure: Europium and oxygen co-
doped GaN (GaN:Eu,O) was grown on double-side polished (0001) sapphire sub-
strates by OMVPE at 100 kPa. The sample structure consisted of a 1.7 µm-thick
undoped GaN layer and a 200 nm-thick GaN:Eu,O layer. Trimethylgallium, and am-
monia were used as starting sources. Eu was doped using
bis(n-propyl-tetramethylcyclopentadienyl)-europium [(EuCppm2)]. Doping concen-
tration of Eu$^{3+}$ ions was 4 · 10$^{19}$cm$^{-3}$. Ar-diluted O$_2$ was also used for oxygen
coding, to enhance Eu emission intensity [96]. After the growth of the GaN:Eu,O
structure, resist patterns were fabricated on the samples by a standard nanoimprint
lithography process. Subsequently, the samples were etched with Cl$_2$ in an induced
coupled plasma (ICP) etcher using the nanoimprint lithography pattern as a mask.
Two samples were produced with different etching times, which are designated P100
and P200, featuring the depth of etching of 100 and 200 nm, respectively. In the final
step, the resist was removed by toluene. The unpatterned layer which has been used
as a reference is designated P0. A second unpatterned reference sample has also been
exposed to the etching treatment in order to explore the effects of etching itself on
emission characteristics, without the effect of the nano-structure. The pattern consists
of cuboids organized in a square lattice. The cuboid sides are 200 nm, with a height of
100 nm, and the edge-to-edge distance between neighboring cuboids is 200 nm. Fig-
ure 4.1 depicts schematics of the 3 different sample designs, and a scanning electron
micrograph (SEM) and atomic force microscope (AFM) image of sample P100.

4.2.2 Optical characterization

An angle-resolved PL setup was purposely built to investigate directionality of
emission. The system allowed both spectral, as well as time resolved measurements.
A xenon lamp (L2273 Hamamatsu) coupled to a Solar MSA130 double grating mono-
chromator, was used as excitation source for the spectral measurements. For time-
resolved measurements an optical parametric oscillator (OPO) pumped by the third
harmonic of a 100 Hz Nd:YAG laser, with a pulse duration of 5 ns was used. Emis-
sion was dispersed by an M266 (Solar LS) monochromator coupled to either a sil-
icon charge-coupled device (CCD, Horiba scientific) or a photo multiplier tube (PMT,
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Figure 4.1: Nano-patterned GaN:Eu Schematics and structural characterization of the three samples. a Schematic cross-sections of the sample structures. b SEM and c AFM images of sample P100 (Note that the wall-structures between the cuboids are a scanning artifact).

Horiba scientific) for photon detection. The sample was placed perpendicular to the rotation plane, such that the normal to the surface has the zero degree detection angle. The excitation was fixed to the sample at an angle of 20 degrees above the plane. To investigate emission independent of directionality an integrating sphere was used (Newport, 7.5cm diameter). Excitation proceeds using a xenon lamp (L2273 Hamamatsu) coupled to a double grating monochromator (Solar MSA130).

4.3 Results

The angular emission distribution of Eu-related luminescence for the samples was characterized in the angle-resolved PL setup under excitation of 355 nm. The angle is defined relative to the normal of the surface, results hereof are depicted in Fig [4.2]. The emission intensity distribution for P0 follows a flat profile, with an intensity dropping with increasing angle, thus featuring the typical escape cone for light from this sample. For the patterned samples P100 and P200, the angular distribution looks very different, with peaks and dips of intensity as a function of angle. The peaks are most likely a result of the grating-like structure of the nano-pattern, giving rise to diffracted wave guide modes, and leading to an interference effect that can be observed in the far-field [97]. In addition, it can be observed that the integrated light output for both
4.3. Results

Figure 4.2: Room temperature PL. Left, The RT PL spectrum showing the Eu emission lines: $^5D_0$ to $^7F_2$ ($\approx 621$ nm) and the $^5D_0$ to $^7F_3$ ($\approx 665$ nm). Right, Angular dependence of the PL intensity at a detection wavelength of 621 nm.

Figure 4.3: Angle-dependent PL. Normalized angle-dependent spectral intensities for the three samples.

Nano-patterned samples is larger than that of the unpatterned one. The enhancement in directional output power is 50% for P100 and 60% for P200 (see table 4.1). The angle-dependence of the complete emission spectrum for all three samples is shown in Fig. 4.3.

Next to the angle-dependent emission, also the total emission of the samples has been determined. The samples were placed in an integrating sphere, ensuring that also the light outside of the “light cone” direction is captured. While an integrating sphere normally also allows to determine absorption, which in turn allows estimation of PLQY, here we have a complication. While we can determine the absorption of the whole sample we cannot determine the absorption of the GaN:Eu layer itself. The thick GaN layer, ensures all light that is not reflected nor absorbed by the GaN:Eu layer will be absorbed by the GaN layer. Therefore, we can only determine an upper limit of absorption and ergo a lower limit of PLQY. This in turn means that comparison of PLQY values of the different samples is meaningless. The total emitted power for all three samples decreased for increased etching times, especially remarkable...
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<table>
<thead>
<tr>
<th>Sample</th>
<th>IQE at RT [%]</th>
<th>Rel. total output power</th>
<th>Rel. output power in light cone</th>
<th>Rel. volume of optically active layer</th>
<th>Rel. output normalized to # of Eu$^{3+}$ ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>P0</td>
<td>34</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>P100</td>
<td>36</td>
<td>0.66</td>
<td>1.5</td>
<td>0.612</td>
<td>2.45</td>
</tr>
<tr>
<td>P200</td>
<td>27</td>
<td>0.61</td>
<td>1.6</td>
<td>0.125</td>
<td>12.8</td>
</tr>
</tbody>
</table>

Table 4.1: PL properties. Room-temperature quantum efficiency, relative optical output in the emission cone normal to the surface, relative volume of the optical active layer, and the output increase normalized to optical active layer volume. For all relative parameters the un-etched sample was set to 1.

considering the increase in intensity perpendicular to the surface. The results hereof are shown in table 4.1.

For completeness, we also investigated the emission at shorter wavelengths, in the range of the commonly appearing defect-related “yellow band” of GaN, since we observed that the intensity of this band was increased in the patterned samples. The reference layer, which received the same ICP etching treatment as P100, had a similar intensity of the “yellow band” as the said sample. Lastly, in order to get more information about the optical activity of the Eu$^{3+}$ ions and its possible enhancement due to nano-photonic effects, we performed a series of time-resolved PL measurements at different temperatures. The results hereof are depicted in Fig. 4.4. At room temperature, the PL, for all the samples, decays with a stretched exponential character. This is a clear sign that non-radiative channels are active. Upon temperature decrease, the dynamics for all three samples transforms towards a single exponential decay, which is reached at 10 K. This demonstrates that there is no change of the radiative rate due to the nano-patterning, but also that the IQE is likely close to unity. Furthermore, it shows that the non-radiative channels are thermally activated. We have determined the activation energy of this non-radiative channel to be approximately 22 meV.
4.4 Discussion

An apparent discrepancy appears when comparing the results of the two PL setups; the angular dependent and independent PL spectra. In the angular dependent measurements the patterned samples show enhanced emission for the entire range of angles studied which are within a cone perpendicular to the surface, the angular integration of PL (at 621 nm) returns higher yields for the entire range (0 – 50°) studied. While in the integrating sphere the angular integration happens optically, and yields stronger PL values for the unpatterned sample. We can resolve this discrepancy, and conclude that a part of the emission that is not within the measured forward emission cone, is measured in the integrating sphere, and has a strong contribution in the unpatterned sample, and this is most likely emission that is coupled in-plane to the sample/substrate.

The total emitted power in the forward direction at RT increases for longer etching times, even though the number of Eu$^{3+}$ ions and the IQE varies considerably between patterned and unpatterned samples. The temperature dependence of the IQE for all samples is depicted in Fig. 4.4 and the values at RT are shown in Table 4.1. The lower IQE value for the patterned samples could result from the ICP treatment, which introduces defects that might act as non-radiative recombination. Since a considerable
amount of the optically active layer is removed by the etching process of the nano-pattern, we also have to take that into account to get an estimate of the amount of Eu$^{3+}$ ions contribution to the emission in the excited volume. From Ref. [98] it can be found that the penetration depth for GaN at a wavelength of 355 nm, is $\sim 100$ nm. The geometrical volume of the Eu-doped layer from Fig. 4.1 can be estimated from the layer thickness, and the knowledge that 75% percent of the surface area is etched down. The relative volumes of the optical active layer are depicted in Table 4.1. Purely from the geometrical point of view of where the light can be absorbed, there is a large discrepancy with the total output power, showing an increase per Eu$^{3+}$ ion of up to 12.8 times for P200 (Table 4.1).

There are three important effects here that have not been taken into account that enhance the directional optical output of the etched samples. Firstly, the nano-patterning is on the scale of the incoming excitation light wavelength and can induce efficient scattering of the normal incident light into the layer. In this way, the effective path length of the light into the optical layer is increased, leading to absorption enhancement. Secondly, the nano-pattern can also induce scattering of the emission light which is coupled in-plane, i.e. within the layer/substrate, as discussed above. A third contributing factor is the energy transfer from GaN to the Eu$^{3+}$ ions. The light is absorbed in GaN and, subsequently, generated carriers can excite the Eu$^{3+}$ ions. The effectiveness of this excitation mechanism is strongly dependent on the local crystal environment of the Eu$^{3+}$ ions, and is influenced by defects and strain [99, 100].

We found that both total output power as well as the IQE are lowered with increased etching. While the total output is most probably influenced by the decreased number of Eu$^{3+}$ ions in the layer, the IQE should not. Furthermore, while the decrease of the IQE could be linked to a decrease of the transfer efficiency from the GaN to the ions, it will not readily agree with an increase in transfer efficiency.

We therefore conclude in favor of the first two effects as the most likely explanations for the high directional PL output in the etched samples, having a much smaller effective concentration of Eu$^{3+}$ ions. It is thus the enhanced scattering of the excitation light, preferentially into the optically active layer, and successive enhanced scattering, out of plane, of the emitted light that are most probable. Even further enhancement of this effect could be achieved in the future by optimization of the nano-patterning structures, both in shape and in size.

### 4.4.1 Grating effect

Besides the overall enhancement in directional emission, clear peaks and dips as a function of detection angle are observed in the emission. Especially in Fig. 4.1, this behavior is evident and shows strong similarity to the behavior of an optical diffraction grating. Here we evaluate the validity of this assumption in relation to the observed results. The grating equation, $d \sin \theta = m \lambda$, is defined by geometrical interference
considerations, where $d$ is the pattern pitch distance (400 nm), $m$ the diffraction order (1, 2, 3...), and $\lambda$ the wavelength of light (620 nm). When filling in these values, and consider the refractive index of the material, $n = 2.4$, it is apparent that we are actually outside of the classic grating regime. The nano-structure pitch is too small for a pure grating effect. Alternatively, a diffraction could occur due to higher orders of the nano-pattern symmetry, and we can find feasible solutions for $4 \times$ the pitch at 1600 nm. Ref. [97] gives an alternative explanation, using an undoped GaN-based ultrathin microcavity array, similar to the one used here, which gives rise to diffracted wave guide modes and leads to an interference effect that can be observed in the far-field. But the crucial difference is that in our work, the emission comes from the Eu ions embedded within the GaN, which also emit at different wavelength. It is quite likely we are observing similar effects here as in Ref. [97], or higher order diffraction grating effects, or a combination. In either case, this would require calculation such as the rigorous coupled wave approach employed in chapter 3 but those were outside the scope of this work.

4.5 Conclusion

We have fabricated GaN:Eu layers, which were nano-patterned with a square lattice array of cuboids, and studied the properties of the Eu emission by PL spectroscopy. In the light emission cone perpendicular to the surface of the optical layers, we observed an increase in intensity of 50\% and 60\% for both patterned samples. Additionally, the periodic structure of the nano-patterning gave rise to peaks and dips in the angle-dependent PL intensity. Although the amount of Eu\textsuperscript{3+} ions in the optical excitation volume of the patterned samples was considerably lower, and there was no enhancement of the radiative rate of the Eu\textsuperscript{3+} ions, we observed only a minor decrease in the total output power of Eu-related emission. The increase in directional emission during PL measurements is attributed to two effects: firstly, increased scattering at the nano-patterned surface, of the incoming excitation light into the GaN:Eu layer, effectively increasing the path-length that excitation light travels within the GaN:Eu layer. Secondly, the same nano-patterned surface, now scatters emission light out of the GaN:Eu layer, a highly desired effect in a material with high refractive index such as GaN, in which light is often trapped. Especially the latter could be optimized further with an eye at direct applications in GaN:Eu light emitting devices.