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Full Length Article

# Influence of near-field coupling from Ag surface plasmons on InGaN/GaN quantum-well photoluminescence



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## ABSTRACT

We have investigated the borderline between photoluminescence quenching and enhancement of InGaN/GaN quantum-wells due to Ag nanoparticles and their surface plasmon modes. By embedding Ag nanoparticles inside nanohole structures on the *p*-type layer GaN, luminescence quenching is observed. Increasing the distance between the nanoparticles and quantum-wells has shown to enhance the emission. We have found that the nano-structure geometry of the metal-semiconductor interface in the near-field of the quantum-wells plays a crucial role in determining whether the emitter performance is enhanced or degraded.

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## 1. Introduction

The III-nitride semiconductor has proved to be an important material system for UV and visible solid-state lighting. Typical light-emitting diodes (LEDs) are nowadays composed of a *pn*-junction structure with multiple quantum-well (MQW) active region. This allows efficient carrier recombination, and are useful for high-brightness LEDs [1,2]. Currently, blue LEDs consisting of InGaN/GaN quantum-well (QW) structures have reached internal quantum efficiency (IQE) levels beyond 80% [2,3]. However, the IQE of the LEDs grown on *c*-plane sapphire substrates, decreases with increasing InN molar fraction in InGaN. Some of the factors limiting the efficiency include the large lattice mismatch and generation of misfit dislocations at the InGaN/GaN interface, as well as the large piezoelectric fields in the strained QW [4–6]. This issue has therefore sparked a lot of interest from researchers to improve the efficiency of III-nitride LEDs at green wavelengths and above.

One method of improving the low IQE of LEDs involves the application of surface plasmonics. With QW in the near-field of a metal-semiconductor interface, the electron-hole recombination process will have an additional decay channel where electron-hole pairs can recombine by exciting a surface plasmon (SP) mode

[7]. This process, due to the large density of states of the SP modes, happens at a much faster rate than the radiative and non-radiative processes [8–10]. The requirement for the SP-QW coupling is for the QWs to be within the SP mode fringing field which for Ag on GaN is around 40 nm [7,11]. The separation requirement poses a challenge for typical LED structures with *p*-GaN thickness above 100 nm. Bringing metal thin films (TFs) or nanoparticles (NPs) closer to the QWs of an LED to achieve SP-QW coupling have been investigated using various methods. One of them involves an interruption of the epitaxial growth process, where metal NP can be embedded inside the *n*- or *p*-GaN layer near the QWs [12–14]. Chamber contamination from the SP-metals is one of the disadvantages of this approach.

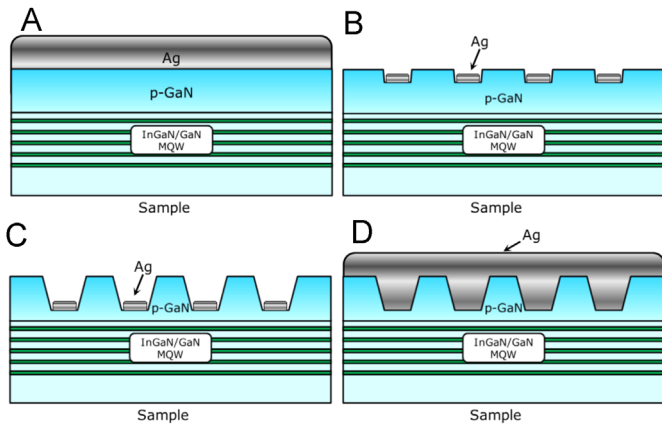
Another possibility is to partially etch the *p*-GaN, and deposit the metal in the etched regions. Nanohole (NH) structures in *p*-GaN has been investigated using Ag as SP-metal inside NHs, resulting in QW luminescence enhancement due to SP-QW coupling [15]. This concept was later applied to electrically driven LED devices demonstrating electroluminescence improvement [16,17]. The SP-QW coupling does not necessarily lead to emission enhancement, and several studies have in fact reported QW luminescence quenching due to Ag NPs in their near-field [18–20].

We have investigated the reasons behind luminescence quenching or enhancement from SP coupling with InGaN/GaN QWs. By etching NH structures through the *p*-GaN layer, SP-metal consisting of Ag TF and NPs brought within near-field of the QWs and its impact on the photoluminescence (PL) is studied.

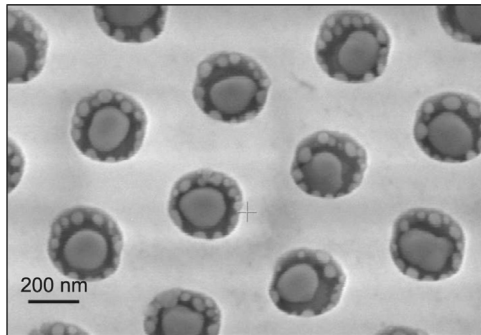
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**Fig. 1.** Schematic drawings of different patterns investigated, where sample A consists of the as-grown sample with 150 nm Ag TF, sample B has 50 nm etched *p*-GaN with Ag NPs, sample C has 100 nm etched *p*-GaN with Ag NPs, and sample D have 100 nm etched *p*-GaN with 150 nm Ag TF.



**Fig. 2.** SEM image showing the formation of Ag NPs on patterned *p*-GaN after lift-off and annealing of a 30-nm Ag TF at 350 °C in vacuum.

## 2. Sample preparation

The LED epitaxial structure was grown by metalorganic vapor-phase epitaxy (MOVPE) on the *c*-plane sapphire substrate. The structure on sapphire consisted of a 20-nm low temperature GaN buffer layer, a 2- $\mu$ m GaN layer, 2- $\mu$ m *n*-GaN:Si layer, 10 periods of InGaN:Si (3 nm)/GaN:Si (2 nm) superlattice layer, 5 periods of GaN:Si (12 nm)/InGaN (2 nm) QW active region covered with a 5-nm thick GaN capping layer, then a 125-nm *p*-GaN:Mg. The NH structures were defined on the *p*-GaN layer without breaching the QWs. Hexagonal hole-patterns were formed using nanoimprint lithography (NIL) process, where the hole diameter was 200 nm diameter, and the periodicity was 460 nm. The *p*-GaN was etched using inductively-coupled plasma (ICP) reactive-ion etching (RIE) with Cl<sub>2</sub>/Ar plasma chemistry. After the dry-etching, Ag was deposited using e-beam evaporation.

Four different samples were prepared to investigate the effectiveness of SP coupling with the QWs and how the distance between Ag NPs and QWs affects the coupling. All the samples were from the same epitaxial wafer, and have the following details (Fig. 1). Sample A consists of a 150-nm Ag TF coated on the as-grown epi-structure to estimate the maximum enhancement from a total reflection, when QW excitation and luminescence detection is done from the sapphire-side; sample B and C have NH structures with etch depths of 50 and 100 nm, respectively, and Ag NPs are formed inside the holes following a lift-off process from a 30-nm Ag TF; sample D also has NH structures with etch depth of 100 nm, and is coated with a 150-nm Ag TF to investigate whether the

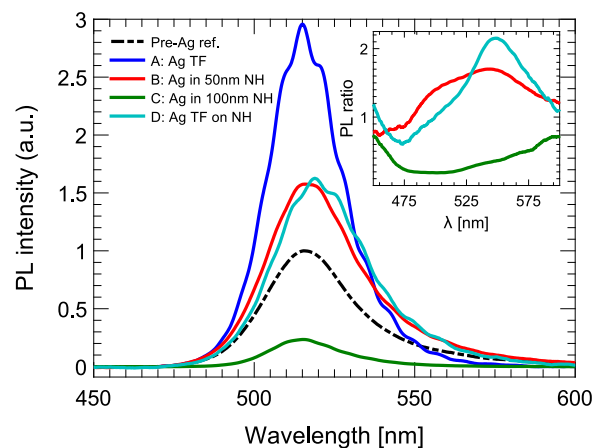
reflector properties can be combined with SP coupling. The distance between Ag and the top-most QW is therefore 130, 80 and 30 nm for samples A, B and C, respectively. The SP-QW coupling is expected to be too weak in case of sample A due to the large distance between the metal–semiconductor interface and the QWs [7,11,21], hence any resulting features would be due to the metal reflector properties.

After lift-off, the Ag NPs formed in the holes did not have a uniform shape. To mitigate this problem, a thermal annealing process at 350 °C was implemented to improve the NP shapes. This was applied for samples B and C after 30 nm Ag TF lift-off to shape the particles inside the holes. The formed Ag NPs inside the holes are shown in the scanning electron microscope (SEM) image of Fig. 2. It is also seen that besides the large NPs, smaller ones are formed inside the NH side-walls.

## 3. Characterizations

PL measurements are conducted using a 405-nm excitation laser, with excitation and detection from the polished sapphire-side of the samples, and the spectra are recorded using an Instrument System spectrometer. Normalization of the PL spectra is done for each sample relative to a given reference denoted “pre-Ag ref.”, which is a sample with similar nano-structure pattern but without Ag. That is, the pre-Ag reference for sample A is the as-grown structure, while the pre-Ag reference for C and D is the 100-nm etched structure and that of sample B is the 50-nm etched structure. The PL spectra of samples A–D are shown in Fig. 3. The peak intensity of sample A is increased by almost a factor of 3 compared to the as-grown sample, though the integrated PL enhancement factor is about 2.51. The results of 50 and 100 nm NHs with embedded Ag NPs appear opposite of each other, with one giving enhancement and the other suppression of PL, respectively. Sample D has a slightly higher enhancement than B (integrated enhancement of 1.85 and 1.57, respectively).

The results of samples B and C are contrary to expectations, since the NPs in C are closer to the QWs than in B and the SP-QW coupling should be stronger in the case of C. The observed PL suppression in sample C can hardly be attributed to anything besides the presence of Ag as the reference (and normalization) for this sample is the 100-nm NH structure without Ag NPs. Metals are in general known to quench emitter luminescence in their near-field due to increased non-radiative decay and also a decreased radiative decay rate [22]. In our case, however, the geometry of the metal have an influence on the emission. This is



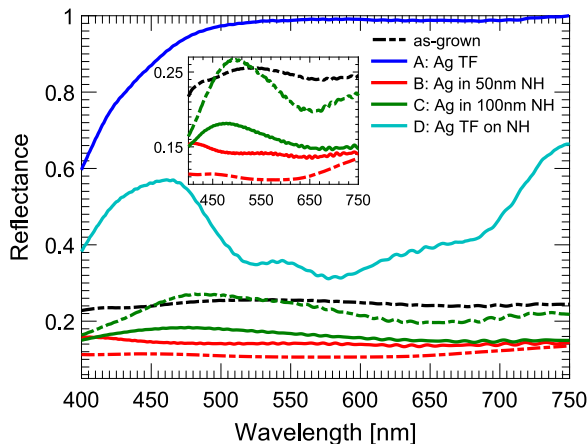
**Fig. 3.** PL spectra of samples A–D, where normalization is done relative to the peak intensity of the corresponding pre-Ag references. Inset shows the PL ratios relative to pre-Ag references.

seen from the fact that sample D has a similar etch structure as C except with a 150-nm Ag TF covering on the *p*-GaN, and the PL is enhanced instead of being suppressed.

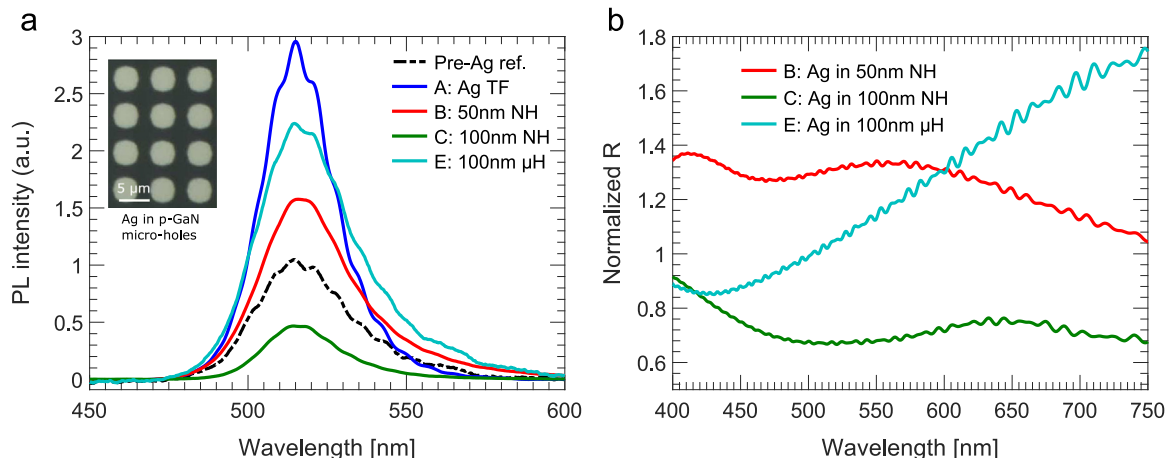
Additionally, comparing the PL intensity from sample D with that of sample A, the enhancement of D is seen to be significantly less than that of A, indicating that the coating does not function as a simple reflector.

To better understand the properties of included Ag TF and NPs on the samples, reflectance spectra are measured for all the samples using a white-light source with near normal incidence from the sapphire-side. The spectra are shown in Fig. 4, where sample A shows 98% reflectance at the emission wavelength (517 nm), which is an increase by a factor of 3.8 compared to the as-grown sample. The decrease in reflectance below 500 nm is due to absorption from the MQW structure. Considering sample B, the reflectance has increased from 11% to 14% due to Ag NP coating, while for sample C the reflectance is decreased from 26% to 18%. As a comparison the as-grown sample reflectance at the emission wavelength is 25%.

These values could explain why PL of sample B is enhanced while that of C is suppressed. A degraded reflectance indicates an increased absorption due to Ag NPs which in turn degrades the



**Fig. 4.** Reflectance spectra of samples A–D (solid curves) compared to their pre-Ag references (dashed curves of the corresponding colour). The inset is a zoomed view of sample B and C reflectance. Corresponding spectra without Ag are also shown (dashed lines). (For interpretation of the references to colour in this figure caption, the reader is referred to the web version of this paper.)



**Fig. 5.** (a) PL spectra showing the result of Ag coating on samples with various *p*-GaN pattern. (b) Normalized reflectance spectra relative to the structures without Ag but with patterned *p*-GaN.

emission from the QWs. The increased reflectance of sample B alludes to a better scattering from the NPs. The transmittance of sample B (not shown), is also larger than that of sample C, which at the emission wavelength is 58% for B and 47% for C, which further supports the notion that the increased reflectance of B is due to better scattering from the NPs in all directions.

Sample D reflectance shows a rather distinctive feature with three reflectance dips at 525, 577 and 683 nm, and a local maxima at 547 nm. The local reflectance maxima coincides with the PL ratio peak at the same position as shown in the inset of Fig. 3. The reflectance is, however, largely suppressed compared to the TF reflector case of sample A. It should also be noted that transmittance and reflectance spectra are measured on samples with an active region, so the observed features are not exclusively related to the Ag nano-structures, but rather the combined effect of active region and nano-structures.

One possibility for PL suppression can be related to the formation of small sized Ag NPs (around 10–50 nm in size) which is visible in Fig. 2 on the side-walls of the holes. We have previously demonstrated that small sized NPs can suppress the PL due to their large absorption compared to their scattering, and their SP mode spatial-extent is smaller than that of larger NPs [23,24]. The small-sized NPs are closer to the active region in 100 nm etched NHs compared to 50 nm, so this can explain why sample C is experiencing PL suppression while B is not.

To support the claim that small NPs are degrading the PL in the 100-nm etched sample, we investigated another sample with a 100-nm etched *p*-GaN, but in this case the holes were on the micro-scale (sample E). The fabrication process was done using photolithography with a square array to form holes with 6  $\mu$ m pitch and 3.8  $\mu$ m diameter. By a lift-off process, 30 nm Ag TF was deposited inside the holes. As opposed to the sample with 100 nm NHs, this sample shows an enhanced PL intensity as shown in Fig. 5(a), with an integrated PL enhancement factor of 2.6. This is similar to the case with Ag TF covering the 100-nm etched NHs which improved the PL instead of suppressing it. In both of these cases, small Ag NPs are not present in the near-field of the QWs. The normalized reflectance from the micro-pattern is shown in Fig. 5(b), where it is observed that the reflectance is not significantly modified near the emission wavelength. This emphasizes that the PL enhancement of sample E is not due to an enhanced reflectance from the metal coating.

#### 4. Conclusions

We have demonstrated PL intensity enhancement of green LED MQW structures using Ag as SP-metal both in the form of NP and TFs. It was found that bringing Ag NPs closer to the QWs did not necessarily result in an enhancement of the QW luminescence. This was despite the expectation of a stronger SP-QW coupling with smaller QW-metal separations. It was observed that PL quenching was not exclusively due to having Ag NPs in the vicinity of the QWs, but also depended on the Ag nano-structures. We attributed PL quenching to the presence of small-sized Ag NPs in the near-field of the QWs, since other geometries did not degrade the PL intensity.

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