Enhanced Red Emission of Eu,O-Codoped GaN Embedded in a Photonic Crystal Nanocavity with Hexagonal Air Holes

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In this work, we fabricate a nitride-based photonic crystal (PhC) nanocavity with an embedded active layer for unexplored red regions using simplified selective wet etching of an Al0.82In0.18N sacrificial layer. Eu,O-codoped GaN (GaN:Eu,O) is embedded in L7-type two-dimensional-PhC (2D-PhC) nanocavities with hexagonal holes. Room-temperature photoluminescence (PL) shows Eu emission coupled to the cavity modes at wavelengths around 620 nm. The quality factor of the fundamental mode in an L7 nanocavity is 5400, which is comparable to those of state-of-the-art 2D-PhC nanocavities with embedded nitride-based active layers for the blue and ultraviolet regions. We show that the Purcell effect due to the small mode volumes of the 2D-PhC nanocavities and enhanced light extraction lead to a 54-fold increase in the integrated PL intensity per unit area with respect to the typical GaN:Eu,O emission.

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I. INTRODUCTION

Over the past few decades, III-nitride semiconductors have attracted much attention for optical devices. The development of nitride-based light-emitting diodes (LEDs) and laser diodes revolutionized the field of solid-state lighting [1–3]. To address next-generation applications such as single-photon emitters [4,5] and fluorescence-based nano- and micro-optoelectromechanical systems [6,7], nitride-based nanostructures such as photonic crystals (PhCs) have been intensively studied [8–10]. PhCs can spatially manipulate photons within nanometer-scale waveguides [11,12] and vary the optical properties of embedded active media by modulating the optical density of states of the radiation field [13]. In particular, two-dimensional-PhC (2D-PhC) nanocavities, which have small mode volumes and strong light confinement, are one of the most promising structures for demonstrating enhanced light emission due to the modulated optical properties [14,15].

Although most 2D PhCs have been investigated in the infrared range due to the well-established processing techniques for mature semiconductors such as group-III arsenides [14–17], PhCs utilizing nitride-based quantum wells and quantum dots (QDs) emitting at wavelengths from the ultraviolet to the blue region have recently been reported in work aimed towards next-generation light sources [18–23]. The quality factors (Q-factors) of state-of-the-art nitride-based 2D-PhC nanocavities with embedded active layers are developing towards approximately 5000 [21–23], whereas similar nanocavities operating in the red region have yet to be fabricated. This is mainly because InxGa1−xN with a high InN molar fraction, which is required for red emission, has a significantly degraded crystal quality due to phase separation [24] and the large lattice mismatch between GaN and InxGa1−xN [25].

To date, we have fabricated a nitride-based red LED using Eu,O-codoped GaN (GaN:Eu,O) as an active layer [26]. A maximum external quantum efficiency of 9.2% and an output power of 1.25 mW at 20 mA have been achieved [27]. A 2D-PhC slab is a promising candidate for improving the optical properties of spontaneous emission further or realizing laser oscillations in GaN:Eu,O [28]. PhCs are widely used to increase the light-extraction efficiency (LEE) [29,30] by controlling the path of light propagating in a medium and to enhance the internal quantum efficiency (IQE) by means of the Purcell effect [13]. In this paper, we demonstrate a 2D-PhC nanocavity with GaN:Eu,O embedded in it for enhanced red emission, and characterize the optical properties.

II. SAMPLE FABRICATION

A. Selection of the sacrificial layer

To fabricate 2D-PhC slabs, a process for removal of a sacrificial layer to produce an air-bridge structure is
indispensable. Standard wet etching is generally considered difficult due to the chemical stability of III-nitride semiconductors. Thus, photoelectrochemical (PEC) etching, either to remove an In$_x$Ga$_{1-x}$N layer [18] or to release an AlN layer from a 6H-SiC (or Si) substrate [19,20], and selective thermal decomposition of GaN with respect to an Al$_x$Ga$_{1-x}$N layer have been employed [22]. However, crystal growth of a thick In$_x$Ga$_{1-x}$N sacrificial layer to fabricate a wide air gap underneath a 2D-PhC slab, which is required for confinement of red light, is too difficult due to the large lattice mismatch between In$_x$Ga$_{1-x}$N and GaN. Furthermore, a GaN slab is preferred to an Al$_x$Ga$_{1-x}$N slab in terms of the refractive-index difference between air and the active layer as well as from the point of view of crystal quality. Therefore, the aforementioned PEC etching and thermal decomposition are not well suited to fabricating 2D-PhC nanocavities for GaN:Eu,O luminescence.

In this study, we use selective wet etching with hot nitric acid for the Al$_x$In$_{1-x}$N sacrificial layer [31], where the In composition is adjusted to 0.18. The $a$-axis lattice constant of Al$_{0.82}$In$_{0.18}$N completely matches that of GaN, and a high crystalline quality is maintained even for growth of a thick sacrificial layer. Moreover, the selective wet etching of the Al$_{0.82}$In$_{0.18}$N layer is a remarkably simple and more controllable process compared with PEC etching and thermal decomposition.

**B. Finite-difference time-domain simulation and structural design**

Figure 1(a) shows a 2D-PhC nanocavity, which is an L7-type cavity comprising a triangular lattice pattern of air holes. Similarly to the case for PEC etching and thermal decomposition, the air holes become hexagonal [20–22] during the aforementioned wet etching to remove the sacrificial layer, reflecting the wurtzite structure of GaN, even though circular holes are patterned. We calculate the photonic band of a 2D PhC with hexagonal air holes using the finite-difference time-domain (FDTD) method. Then, we design the periodicity ($a$) and radius ($r$) of the air holes appropriately, where $r$ is the side length of the hexagons. The FDTD calculations are performed assuming that the refractive index of the GaN:Eu,O slab ($n_{\text{GaN:Eu,O}}$) is 2.35, which is a typical value for GaN at wavelengths around 622 nm [32]. This wavelength corresponds to the dominant $^2D_0-^2F_2$ transitions of the Eu$^{3+}$ ions in GaN:Eu,O [26]. Since the refractive index of GaN is almost constant throughout the entire emission-wavelength range (615–630 nm) of the $^2D_0-^2F_2$ transitions, the calculations neglect the wavelength dependence. We choose the model size for the calculations as 12, 10, and 2.5 $\mu$m along the $(11\bar{2}0)$, $(1\bar{1}00)$, and (0001) directions, respectively. The calculation area is sufficiently large, considering the cavity size and light propagation.

![Image](image_url)

**FIG. 1.** (a) Schematic image of the structural design of a GaN:Eu,O-based 2D PhC with an L7-type nanocavity comprising a triangular lattice pattern of air holes; ud-GaN, undoped GaN. (b) Photonic band structure of a GaN 2D-PhC slab with a triangular lattice pattern of hexagonal air holes with $r/a = 0.29$ for TE polarization.

Figure 1(b) illustrates the calculated photonic band structure of a GaN 2D PhC with hexagonal air holes assuming a radius-to-period ratio ($r/a$) of 0.29 for transverse-electric (TE) polarized light. We find that a photonic band gap is formed for GaN 2D PhCs with $r/a$ ranging from 0.19 to 0.55. Consequently, we design 2D PhCs with various values of $r/a$ from 0.15 to 0.38 with a fixed $a$ of 212.5 nm to determine whether or not a photonic band gap is formed in the respective samples.

Figures 2(a)–2(c) show results of FDTD simulations of the designed L7-type 2D-PhC nanocavity with $r/a = 0.32$ assuming TE-mode luminescence. The first two cavity modes are observed as depicted in Fig. 2(a), where the fundamental mode ($M_1$) has a higher $Q$-factor of approximately 28 000, and that of the second mode ($M_2$) is approximately 1800. The assignment of the cavity modes is confirmed by the distributions of the electric field intensity for the respective modes as shown in Figs. 2(b) and 2(c).

**C. Crystal growth**

All samples are grown on (0001) sapphire substrates using the organometallic-vapor-phase-epitaxy (OMVPE) method. Trimethylgallium, trimethylaluminum, trimethy-
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FIG. 2. Results of FDTD simulations of the designed L7-type 2D-PhC nanocavity with $r/a = 0.32$ assuming TE-mode luminescence. (a) First two cavity modes in the L7 cavity, where the fundamental mode ($M_1$) and second mode ($M_2$) have $Q$-factors of approximately 28 000 and approximately 1800, respectively. (b,c) Calculated distributions of the electric field intensity for (b) $M_1$ mode and (c) $M_2$ mode.

Lindium, and ammonia (NH₃) are used as the precursors of Ga, Al, In, and N, respectively. For the active layers, bis(n-propyltetramethyl-cyclopentadienyl)europium (EuCp₂) and argon-diluted O₂ sources are used to dope the samples with Eu and O. Basically, growth proceeds under atmospheric pressure with an H₂ ambient.

After initial growth of a 30-nm-thick low-temperature GaN buffer layer (LT-GaN) at 500 °C, a 2.5-μm-thick undoped-GaN (ud-GaN) layer is subsequently grown at 1180 °C. This is followed by the growth of a 625-nm-thick sacrificial layer and a 220-nm-thick GaN:Eu,O active layer. The sacrificial layer consists of 12 periods of Al₀.₈₂In₀.₁₈N/Al₀.₁₅Ga₀.₈₅N with thicknesses of 2 and 50 nm, respectively. The thin Al₀.₈₂In₀.₁₈N layers are grown to prevent desorption of In atoms from the Al₀.₈₂In₀.₁₈N layers and to suppress surface degradation during the epitaxy of the thick Al₀.₈₂In₀.₁₈N layers. For the sacrificial-layer growth, the carrier gas is changed from H₂ to N₂, and the reactor pressure is decreased to 10 kPa. The Al₀.₈₂In₀.₁₈N layers and GaN:Eu,O active layer are grown at 790 °C and 960 °C, respectively. The Eu concentration is approximately $7 \times 10^{19}$ cm⁻³.

D. Lithography and side-wall treatment

Prior to lithography, 350-nm-thick SiO₂ films are deposited on the grown samples using an electron-beam evaporator and subsequent spin-coating of a resist. The patterns of the L7-type 2D-PhC nanocavities are drawn with an electron-beam lithography system and are subsequently transferred to the SiO₂ films using CHF₃/Ar reactive-ion etching (RIE). The nitride-based layers are etched down to the underlying ud-GaN by Cl₂-induced coupled plasma RIE to fabricate deep air holes. To form clear {1100} side walls of the hexagonal holes, we chemically etch the samples for 10 min at 85 °C using tetramethylammonium hydroxide (TMAH). The sacrificial Al₀.₈₂In₀.₁₈N layers are selectively wet etched with hot nitric acid for 2 h at 120 °C through the fabricated air holes. Then, the SiO₂ films are chemically removed with HF.

III. RESULTS AND DISCUSSION

A. Structural characterization and cathodoluminescence mapping

Figure 3(a) shows a scanning-electron-microscope (SEM) image of a fabricated 2D-PhC structure. Crystallographically stable {1100} side walls of the hexagonal holes are clearly obtained, and L7-type 2D-PhC patterns with good hole periodicities are successfully fabricated. We characterize the size-related fabrication errors of the etched air holes from the SEM images, assuming a Gaussian distribution. The estimated standard deviations of the radii ($\Delta r$) are 1.6–2.2 nm, corresponding to 1.9%–7.1% of $r$ for 2D PhCs with $r/a$ values of 0.15–0.38 [Fig. 3(b)]. The
relative standard deviations of the hole radii ($\Delta r/r$), which reflect the fabrication errors, are smaller for larger air holes because the accuracy of the side-wall etching using TMAH may be degraded for smaller holes due to the viscosity of the etchant.

To confirm light confinement in the fabricated L7 nanocavities, we perform cathodoluminescence (CL) measurements at room temperature. The acceleration voltage of the electron beam is adjusted to 5 kV, which is low enough to obtain CL signals from only the GaN:Eu,O layer. The CL signals are detected with a photomultiplier through an optical-fiber bundle and a monochromator. Figure 4(a) shows a CL intensity map of an L7 nanocavity with $r/a = 0.27$ acquired at a wavelength of 622 nm. The GaN:Eu,O emission inside the PhC-patterned area is enhanced compared with that from the nonpatterned area. Typically, strong inhibition of coupling to two-dimensional slab modes degrades the overall efficiency in 2D PhCs, whereas the LEE for spontaneous emission in the vertical direction increases [30]. Hence, the CL intensity enhancement in the PhC-patterned area outside of an L7 cavity may be attributed to LEE enhancement due to photonic-band-gap formation around the wavelength of the Eu emission. On the other hand, the further increase in the GaN:Eu,O emission inside the L7 cavity indicates a light-confinement effect within the cavity [33]. In fact, a CL intensity map of an L7 nanocavity with $r/a = 0.15$, which is less than the value of $r/a$ of 0.19 required to form a photonic band gap, does not show LEE enhancement and a light-confinement effect [Fig. 4(b)].

**B. Photoluminescence spectra and $Q$-factors of nanocavities**

To precisely characterize the optical properties of the L7-type 2D-PhC nanocavities without the influence of charge-up, carbon contamination [34], and impact excitation [35] of Eu$^{3+}$ ions due to electron-beam irradiation, microscopic photoluminescence (PL) measurements are performed at room temperature using a He-Cd laser [$\lambda = 325$ nm, continuous wave (cw)] as an excitation source. A microscope objective (40×, NA = 0.47) focuses the excitation laser on the sample and collects the PL signal. From a knife-edge characterization, the estimated laser-spot diameter is approximately 3.2 μm. The PL is focused on the entrance of an 80-cm spectrometer, and the detection is performed by a thermoelectrically cooled CCD camera. The spectral resolution is about 0.02 nm.

Figure 5(a) shows the PL spectra of L7-type 2D-PhC nanocavities with $r/a$ values of 0.27 and 0.32 under 80.8 mW/cm$^2$ excitation. The black dotted curve is a 2.1-times-enlarged PL spectrum of a nonpatterned GaN:Eu,O film area. The spectral shape is that of a typical GaN:Eu,O emission, which consists of multiple narrow-band peaks arising from eight types of Eu center with different local structures [36] (see Appendix A). The respective emissions have narrow line widths of approximately 0.5 nm even at room temperature, as we have previously reported [27,37]. For each L7 nanocavity for which simulations are shown in Fig. 2(a), two obvious resonant peaks, corresponding to the fundamental mode ($M_1$) and the second mode ($M_2$), are observed. The energy separation between the $M_1$ and $M_2$ modes (about 15 meV) indicates that the respective cavity modes are basically coupled to different Eu centers [36]. Moreover, the resonant peaks move to shorter wavelengths as $r/a$ increases.

Considering the size of the excitation spot, the PL signals are expected to be detected not only from the L7 cavities but also from the PhCs outside of the cavities. Therefore, the PL intensity ($I_{PL}$) obtained should be expressed using the PL intensities of GaN:Eu,O coupled to the $M_1$ ($I_{PL}^{M_1}$) and $M_2$ ($I_{PL}^{M_2}$) modes as

$$I_{PL}(\lambda) = I_{PL}^{M_1}(\lambda) + I_{PL}^{M_2}(\lambda) + I_{PL}^{off}(\lambda) + I_{PL}^{out}(\lambda) \simeq I_{PL}^{M_1}(\lambda) + I_{PL}^{M_2}(\lambda) + \alpha I_{film}(\lambda),$$

where $I_{PL}^{out}$ indicates the off-resonant PL intensity for outside of the cavity area, and $\alpha$ is the modulation factor. Note that the off-resonant GaN:Eu,O emission should be
FIG. 5. (a) PL spectra of L7-type 2D-PhC nanocavities with r/a values of 0.27 and 0.32 under 80.8 mW/cm² excitation. The black dotted curve is a 2.1-times-enlarged PL spectrum of a nonpatterned GaN:Eu,O film area. (b) PL intensity ratio (I_{PL}/I_{film}) obtained from an L7 nanocavity with r/a = 0.32 under 16.2 mW/cm² excitation. The solid lines are fitted Lorentzian curves for the two cavity peaks, and the estimated Q-factors are 5400 for the M1 mode and 1800 for the M2 mode.

The black dotted curve is a 2.1-times-enlarged PL spectrum for the M1 mode (I_{cav}^{M1}/I_{film}) at a wavelength of 623.62 nm. At the same time, a 4.1-fold-enhanced emission at 617.60 nm coupled to the M2 mode (I_{cav}^{M2}/I_{film}) is also observed. The respective resonant peaks are fitted with Lorentz curves, which are depicted as solid lines in Fig. 5(b), and the line widths (Δλ) of the resonant peaks of the M1 and M2 modes are 0.12 and 0.35 nm, respectively. The line widths are one order of magnitude wider than the spectral resolution in this study.

The Q-factors of the M1 and M2 modes (Q_{ave} and Q_{ave}') are experimentally estimated from the relationship \( Q = \lambda/\Delta \lambda \) to be 5400 and 1800, respectively, as average values for various excitation-power conditions. The Q-factor of 5400 is comparable to those of state-of-the-art nitride-based 2D-PhC nanocavities with embedded active layers for use in the blue-ultraviolet region [21–23]. Comparing these values with the calculated Q-factors of 28 000 for the M1 mode and 1800 for the M2 mode [Fig. 2(a)], it is clear that Q_{ave}' agrees well with the designed Q-factor, whereas Q_{ave} is around one fifth of the designed value. In general, the experimentally obtained Q-factor (Q_{exp}) is determined by

\[
\frac{1}{Q_{exp}} = \frac{1}{Q_{des}} + \frac{1}{Q_{fab}} + \frac{1}{Q_{other}},
\]

where Q_{des} and Q_{fab} are related to the pure radiation losses predicted by the FDTD simulations and the optical losses induced by fabrication disorder, respectively. Q_{other} accounts for all other optical losses, such as light absorption and surface scattering. Thus, Q_{exp} should be dominated by the lowest Q-factors in Eq. (2), and we conclude that Q_{ave}' is determined by Q_{des} for the sample. On the other hand, Q_{ave} may be limited by Q_{fab}. The fabrication errors observed in the SEM images become larger for 2D PhCs with a smaller r/a value [Fig. 3(b)]. The fact that Q_{ave} for a nanocavity with r/a = 0.27 is degraded to 1200 also supports the speculation that Q_{ave} is limited by Q_{fab} in this study.

C. Excitation-power dependence of luminescence

After the determination of \( \alpha \) and the Lorenz fittings of the cavity modes, the PL signals for all the terms in Eq. (1) can be obtained separately. We investigate the excitation-power dependence of the wavelength-integrated PL intensities for the nanocavity with r/a = 0.32 [Figs. 6(a) and 6(b)].

For strong excitation, the emission intensity of GaN:Eu,O is typically saturated due to the limited number of Eu centers, and the PL intensity increases sublinearly with the excitation power [38]. This is because the...
long relaxation lifetime of the dominant $^5D_0 - ^7F_2$ transitions in Eu$^{3+}$ ions, approximately 250 μs, which is much longer than the typical carrier recombination lifetime in GaN, limits the excitation rate of Eu$^{3+}$ ions. Therefore, strong excitation can easily saturate the Eu-related centers with photoexcited carriers, and other nonradiative recombination processes become more effective. In Fig. 6(a), a sublinear slope of 0.74 is obtained for the integrated PL intensity from a nonpatterned film area. The off-resonant PL intensity of the PhC yields a slightly smaller slope of 0.69. The slope variation should reflect the power dependence of $\alpha$, which is the result of a balance of LEE enhancement and IQE degradation. Assuming that the LEE is almost independent of the excitation power density, the slope variation is attributed to further degradation of the IQE of the PhC under strong excitation conditions. The IQE degradation is discussed in detail later in this section.

Figure 6(b) depicts the excitation-power dependence of the Eu luminescence coupled to the M1 mode. Unlike the typical situation for GaN:Eu,O, it is noteworthy that a linear increase with a slope of 1.0 is obtained for weak excitation conditions with an excitation power density less than 30 mW/cm$^2$. However, the slope decreases drastically for power densities greater than 100 mW/cm$^2$ and reaches 0.22, which is less than one third of the slope for the off-resonant PhC emission. The slope decrease is not attributed to radiation division among the cavity modes, because the respective cavity modes are coupled to the emission from different Eu centers. In fact, we also confirm that the M2 mode exhibits the same tendency (see Appendix B).

To elucidate the mechanism of such distinctive behavior, we calculate the enhancement of the integrated PL intensity for the resonant peaks per unit area ($E_{\text{cav}}^{MN}$) with respect to a GaN:Eu,O film as:

$$E_{\text{cav}}^{MN}(P) = \frac{S_{\text{spot}}}{S_{\text{cav}}} \frac{\int I_{\text{cav}}^{MN}(\lambda, P) d\lambda}{\int I_{\text{film}}(\lambda, P) d\lambda} \approx \frac{S_{\text{spot}}}{S_{\text{cav}}} R_{\text{LEE}}^{MN} R_{\text{IQE}}^{MN}(P),$$

where $S_{\text{spot}}$ and $S_{\text{cav}}$ represent the areas of the excitation spot and of the resonant space of an L7 cavity, respectively. For simplicity, $S_{\text{cav}}$ is effectively calculated as the mode volume divided by the slab thickness, and the ratio $S_{\text{spot}}/S_{\text{cav}}$ is approximately 64. $N$ is equal to 1 and 2 for the M1 and M2 modes, respectively. $R_{\text{LEE}}^{MN}$ and $R_{\text{IQE}}^{MN}$ are the ratios of the LEE and IQE, respectively, for the cavities to those for the film. Similarly, the enhancement for the off-resonant Eu emission from the PhC ($E_{\text{PhC}}^{\text{off}}$) is calculated as:

$$E_{\text{PhC}}^{\text{off}}(P) = \frac{S_{\text{spot}}}{(S_{\text{spot}} - S_{\text{cav}})(1 - F) + S_{\text{cav}}} \alpha(P),$$

where $F$, which is expressed as $3(r/a)^2$, is the filling factor of the hexagonal air holes in the triangular lattice pattern. Figure 7(a) shows the enhancement of the PL intensity as a function of excitation power density. Reflecting the aforementioned linear increase in the PL intensity of the cavity modes for a 2D PhC with $r/a = 0.32$, $E_{\text{cav}}^{M1}$ and $E_{\text{cav}}^{M2}$ increase with excitation power up to around 30 mW/cm$^2$, reaching maxima of 12 and 6.2, respectively. For higher excitation conditions with an excitation power density above 100 mW/cm$^2$, however, both $E_{\text{cav}}^{M1}$ and $E_{\text{cav}}^{M2}$ decrease significantly due to the drastic saturation of the PL intensities of the cavity modes, as indicated in Fig. 6(b).

According to Eq. (4), the $R_{\text{IQE}}^{MN}$ term should dominate the variation of the PL ratio for the cavity modes because the excitation power density should have a negligible impact on the area and $R_{\text{LEE}}^{MN}$ should be fairly constant. Hence, the Purcell effect may enhance the transition probability for...
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FIG. 7. (a) Enhancement of integrated PL intensity per unit area, expressed as $E_{\text{cav}}^{1M_1}$, $E_{\text{cav}}^{2M_2}$, and $E_{\text{off}}^{\text{PhC}}$ in Eqs. (4) and (5), as functions of the excitation power density. (b) Resonant-wavelength shift of the $M_1$ mode in an L7 cavity with $r/a = 0.32$ as a function of the excitation power density.

the $^5D_0\rightarrow^7F_2$ transitions of Eu$^{3+}$ ions in GaN:Eu,O coupled to cavity modes, effectively suppressing the saturation of the Eu emission (IQE degradation) for lower excitation conditions.

On the other hand, the drastic degradation of the PL ratio under strong excitation conditions is attributed to IQE degradation in the L7 cavity. A similar degradation behavior was observed for PhC nanocavities with Er-doped Si nanocrystals [39]. We consider that one possible reason for the IQE degradation is laser-induced sample heating. The heating effect induced by a cw laser is especially severe for 2D-PhC nanocavities because the aligned air holes adjacent to a cavity impede heat dissipation from the cavity area. Furthermore, PhC slabs with many etched air holes have an increased surface-to-volume ratio, implying more pronounced surface recombination at higher temperatures compared with typical film samples.

Such IQE degradation due to laser heating has been previously reported for InAs QDs embedded in a 2D-PhC cavity [40]. In the case of rare-earth-doped semiconductors, moreover, sample-heating-induced thermal quenching may be promoted not only by surface recombination of carriers but also by energy back-transfer from excited rare-earth ions to carrier traps [41]. As estimated from Fig. 7(a), the threshold excitation power density around 30 mW/cm$^2$ for the IQE degradation and the slope of the degradation are almost independent of the cavity-mode type, resonant wavelength, and $Q$-factor. These results suggest that quenching is dominated by the pronounced surface recombination in GaN:Eu,O 2D-PhC nanocavities. In fact, the resonant wavelength of the cavity modes gradually redshifts under stronger excitation conditions with a power density above 30 mW/cm$^2$ [Fig. 7(b)]. The redshift may be attributed to the increased refractive index of GaN in a 2D PhC, and the results also support a heating effect of the cw-laser excitation. Although other origins of redshifts in cavity modes, such as oxygen desorption and carbon adsorption on GaN slabs induced by ultraviolet laser pumping, have recently been reported [42,43], the excitation power density used in this study was two orders of magnitude lower than those under the conditions reported. Moreover, the redshift in this study is reversible in the excitation-power range, and hence the redshift is attributed to sample heating. For off-resonant emission from the PhC, the laser-induced heating effect should be smaller than that for the cavity area because, unlike the cavity area, most of the off-resonant PhC areas are off-center from the excitation spot. We actually confirm that only a slight IQE degradation is observed for the off-resonant emission compared with that for the cavity modes [Fig. 7(a)].

To suppress the sample-heating effect, we additionally perform PL measurements under pulsed laser excitation with a duty cycle of 5% and actually observe a slight intensity enhancement for strong excitation conditions (see Appendix C). However, a drastic IQE degradation is also found even under pulsed excitation. In addition, from a combinational analysis of the thermo-optic coefficient of GaN [44] and FDTD simulations, the estimated temperature elevation due to laser heating is at most 10 K, considering the small size of the redshift in Fig. 7(b). Therefore, it is plausible as another possibility that the IQE degradation originates from a more severe saturation of Eu centers inside the L7 nanocavity than in typical GaN:Eu,O films. As described above, only limited numbers of Eu$^{3+}$ ions with electric dipoles, coupled to cavity modes, can show resonant peaks. For weak excitation conditions, the limited number of resonant Eu$^{3+}$ ions in an L7 cavity have a higher IQE compared with typical GaN:Eu,O due to the Purcell effect, whereas the threshold carrier density for filling the resonant Eu centers may become smaller.

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Assuming ultrafast carrier trapping rates (approximately 85 ps) for Eu-related defects [45], the threshold excitation power density of 30 mW/cm² can be converted to a density of fully excited Eu ions of 1.2 × 10¹⁸ cm⁻³ using the penetration depth of the excitation light (approximately 100 nm) and the typical lifetime of ⁵D₀⁻→F₂ transitions in Eu³⁺ ions (approximately 250 μs). The calculated density corresponds to 1/60 of the total number of Eu ions incorporated into the GaN. This ratio may indicate the coupling factor of Eu³⁺ ions to an L7 cavity. Thus, the IQE degradation for the cavity peaks may also be attributed to a pronounced saturation effect originating from the limited number of Eu centers coupled to cavity modes as well as to thermal quenching due to the sample-heating effect. Direct lifetime measurements under various excitation conditions will be necessary to further elucidate the impact of the Purcell effect and radiative carrier recombination.

Finally, we investigate the PL enhancement for an L7 nanocavity with \( r/a = 0.27 \), where the \( Q \)-factor is lower than that of the cavity with \( r/a = 0.32 \) due to larger fabrication errors. For this L7 cavity, the GaN:Eu,O emission is mainly coupled to the M₂ mode [Fig. 5(a)]. \( Q_{M}^{L7} \) is 1200, which is slightly smaller than the \( Q \)-factor of the M₂ mode of the cavity with \( r/a = 0.32 \), and the PL enhancement also decreases slightly, with a similar tendency. Although \( Q_{M}^{L7} \) is only 470, the PL enhancement is much larger than that for the cavity with \( r/a = 0.32 \), as depicted in Fig. 7(a). Both L7 nanocavities exhibit similar excitation-power dependences, whereas a 54-fold enhancement is achieved at the maximum for the L7 cavity with \( r/a = 0.27 \). The PL enhancement for the M₂ mode is around one order of magnitude higher than that for the nanocavity with \( r/a = 0.32 \) even under strong excitation conditions. Thus, we conclude that this remarkable PL enhancement can be attributed to the coupling of various types of Eu center emitting at various wavelengths to the M₂ mode due to the lower \( Q \)-factor, and many Eu centers may be widely influenced by the Purcell effect.

When the central wavelength of a resonant mode corresponds to that of an emitter, the Purcell factor, considering spectral overlaps among emitters and cavity modes, can be expressed as

\[
F_P = \frac{3Q_{exp} \left( \lambda/n_{GaN:Eu,O} \right)^3}{4\pi^2V} \frac{\Delta f_r}{\Delta f_r + \Delta f_e} \xi^2, \tag{6}
\]

where \( \Delta f_r \) is the line width of the resonance (emitter) in terms of frequency [37,46,47]. The line width of a single type of Eu center at room temperature is approximately 0.5 nm (\( \Delta f_e = 36 \) GHz). The polarization mismatch between the excited emitter dipole and the resonant-mode field is defined as the factor \( \xi^2 \). For the simplified discussion here, we assume that \( \xi^2 \sim 1 \) for sufficiently weak excitation conditions, where Eu centers coupled to cavity modes are not fully excited, because preferential carrier diffusion and energy transfer to such efficient Eu centers may occur.

For the M₂ mode of the L7 cavity with \( r/a = 0.27 \), the volume of the simulated mode is approximately \( 1.49 \lambda^3/n_{GaN:Eu,O}^3 \). In order to precisely calculate the Purcell factor, we need to clarify further how many types of Eu center are coupled to the cavity mode and how large the degree of polarization matching is between the Eu ions and the resonant-mode field. However, the situation for this material system is complicated, and the method to determine precisely the actual coupling conditions in GaN:Eu,O is still under debate. In this case, the M₂ mode is coupled to most of the dominant peaks of the Eu emission. So, as a simplification, to roughly estimate the Purcell factor using Eq. (6), we assume that every Eu center is coupled to the cavity mode. Similarly to calculations in a previous report [37], we estimate the Purcell factor as 23, using the experimental \( Q \)-factor of the L7 cavity with \( r/a = 0.27 \) based on the above assumptions. In addition, the LEE is estimated from the PL enhancement for the off-resonant emission to enhanced by a factor of approximately 2.5. Therefore, we can expect a total PL enhancement by a factor of 58. The value is comparable to the experimental 54-fold PL enhancement, even though it is a rough estimation.

As we have previously reported, macroscopic GaN:Eu,O-based resonant-cavity LEDs with distributed Bragg reflectors have achieved a 4.8-fold luminescence enhancement [48]. However, the enhanced Eu luminescence is mostly attributed to the LEE enhancement, and the IQE enhancement based on the Purcell effect is only a factor of 1.1. \( Q_{M}^{L7} \) for the L7 cavity with \( r/a = 0.27 \) in this study is 5.6 times as large as the \( Q \)-factor of the macroscopic cavity with reflectors, whereas a Purcell factor of around 20-fold is estimated experimentally. These findings clearly indicate that the small mode volumes of the 2D-PhC cavities effectively enhance the radiative transitions of Eu ions. In general, the Purcell factor should be high for 2D-PhC cavities with higher \( Q \)-factors, and the roughly estimated Purcell factor (neglecting spectral overlaps) of the M₁ mode of the cavity with \( r/a = 0.32 \) (\( Q_{M}^{L7} \sim 5400 \)) is approximately 200 based on Eq. (6). However, the PL enhancement is only 12 for the M₁ mode in the experiment. Therefore, the assumptions made for our rough estimation of the Purcell factor are not satisfied for a cavity with a high \( Q \)-factor. These results indicate that detuned Eu centers do not contribute to the actual Purcell factor, and the total Eu emission is not sufficiently enhanced. To obtain highly enhanced spontaneous emission from GaN:Eu,O using a 2D-PhC nanocavity, the design of a 2D PhC with an effective \( Q \)-factor needs to be further investigated, considering the number of types of Eu center and the line widths. Furthermore, to achieve a strong Purcell effect using a 2D-PhC nanocavity with an ultrahigh \( Q \)-factor, the formation of a single type of Eu center is also desired.
IV. CONCLUSION

We present a demonstration of nitride-based 2D-PhC nanocavities with a GaN:Eu,O active layer aimed towards unexplored red regions, fabricated using simplified selective wet etching of an Al$_{0.82}$In$_{0.18}$N sacrificial layer. The GaN:Eu,O active layer, grown by OMVPE, is embedded in an L7-type 2D-PhC nanocavity with a triangular lattice pattern of hexagonal air holes. The 2D PhCs are designed by use of FDTD simulations to form a photonic band gap with an energy corresponding to the dominant $^5D_0-^7F_2$ transitions of Eu$^{3+}$ ions. SEM images of the fabricated L7-type 2D-PhC nanocavities confirm that the structures are well organized, and clear $\{1\bar{1}00\}$ side walls of the hexagonal air holes are obtained after a TMAH etching process. CL intensity maps clearly indicate that the 2D-PhCs strongly confine the Eu luminescence within the cavity area. PL spectra of the 2D-PhC nanocavities show obvious cavity modes coupled to the Eu emission, and the maximum $Q$-factor of the fundamental mode is 5400, which is comparable to those of state-of-the-art nitride-based 2D-PhC nanocavities with embedded active layers for use in the blue and ultraviolet regions. Consequently, the IQE of the resonant Eu emission is remarkably improved as the excitation power increases under weak excitation conditions with an excitation power density of less than 30 mW/cm$^2$. On the other hand, it degrades gradually under strong excitation conditions with an excitation power density of more than 100 mW/cm$^2$. The IQE enhancement may originate from the Purcell effect, whereas the degradation may be attributed to a laser-heating effect and a pronounced Eu saturation for the cavities. We achieve a 54-fold increase in the integrated PL intensity per unit area at the maximum with respect to a typical GaN:Eu,O emission, and it is clear that the small mode volumes of the 2D-PhC cavities significantly enhance the radiative transitions of the Eu ions in GaN. GaN:Eu,O embedded in an appropriately designed 2D-PhC nanocavity shows remarkably enhanced red emission. It should be an efficient light source not only for highly efficient emitters but also for next-generation optical applications such as fluorescence-based nano- and micro-optoelectromechanical systems.

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APPENDIX A: ENLARGED PL SPECTRUM OF GaN:Eu,O FILM

In the main part of the paper, we state that the spectral shape of the GaN:Eu,O emission consists of multiple narrow-band peaks from eight types of Eu center with different local structures [36]. Figure 8 shows an enlarged PL spectrum of a nonpatterned GaN:Eu,O film area, and we can clearly confirm that the Eu emission is composed of many sharp emission lines even at room temperature.

APPENDIX B: INTENSITY CORRELATION AMONG CAVITY MODES

To be able to discuss the excitation-power dependence of Eu emission coupled to cavity modes, we perform micro-PL measurements on an L7 cavity with $r/a = 0.32$. As described in Sec. III C, we assume that the radiation from the Eu ions is not divided between the two cavity modes ($M_1$ and $M_2$) even though both resonant modes
overlap with the emission spectrum. This is because the broad emission we observe in Fig. 5(a) is formed from multiple narrow peaks based on eight different types of Eu transition [36], and each type of Eu center has a narrow line width (approximately 0.5 nm) even at room temperature [27,37]. Therefore, the different cavity modes (M1 and M2) are basically coupled to spectrally or structurally different Eu centers, and the radiation division is not severe for this material system.

Figure 9 shows the excitation-power dependence of the wavelength-integrated PL intensities for the respective cavity modes and their sum. Intensity-division correlation between the cavity modes is not observed, and all the excitation-power dependences show almost the same tendencies. The results also support the assumption that radiation division between cavity modes does not occur, and it is not the reason why intensity saturation is observed under strong excitation conditions.

**APPENDIX C: PULSED LASER EXCITATION OF NANOCAVITY**

We additionally perform micro-PL measurements using pulsed laser excitation to avoid sample-heating effects induced by cw excitation. A pulsed He-Cd laser is generated by use of an acousto-optic modulator, and we set the pulse width and the repetition rate to 50 μs and 1 kHz, respectively (duty cycle 5%). The excitation-power dependence of the integrated PL intensity for the M1 mode of an L7 cavity with r/a = 0.32 under both excitation conditions (cw and pulsed) is shown in Fig. 10. To compare the PL intensities under both excitation conditions, the intensities are divided by the duty cycle. Although a slight intensity enhancement (approximately twofold) is observed for strong pulsed excitation, a tendency to saturation of the intensity is also observed similarly to cw excitation. The PL improvement may be attributed to the suppression of sample heating. In fact, the resonant wavelengths under pulsed excitation are quite stable over the entire excitation region, as shown in Fig. 11, and there are no sample-heating-induced redshifts, unlike the case for cw excitation. Therefore, we find that the efficiency degradation under strong excitation as shown in Fig. 7(a) is mainly caused by the number of Eu ions coupled to the cavity modes regardless of the duty cycle, whereas the PL intensity decrease is partly attributed to sample heating.


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