# Increasing the Luminescence Efficiency of Long-Wavelength (In,Ga)N Quantum Well Structures by Electric Field Engineering Using an (Al,Ga)N Capping Layer

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Despite the very high efficiency at blue wavelengths, nitride-based light-emitting diodes suffer from low efficiencies in the green and red spectral ranges. Different solutions have been proposed to mitigate the "green gap," including the addition of an (Al,Ga)N capping layer to the quantum well structure. In this work, we show how the increased polarization field due to such an (Al,Ga)N capping layer has profound effects on carrier location and recombination probabilities. The proper choice of (Al,Ga)N composition leads to an increased electron-hole overlap as well as an enhanced confinement in the quantum well region. Therefore, the combination of band structure and electric field engineering can be a promising approach to mitigate the green gap problem.

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## I. INTRODUCTION

Highly efficient red emission from (In,Ga)N/GaN quantum wells (QWs) is of fundamental importance for the fabrication of all-nitride-based microdisplays. Despite the very high efficiency of blue light-emitting diodes (LEDs), they suffer from very low yield at green and red wavelengths [1]. The low efficiency of high-In-content (In,Ga)N is attributed to many factors, the most discussed among them being low wave function overlap due to strong piezoelectric fields, localization issues due to alloy fluctuations [2], and the high number of (point) defects due to low growth temperatures [3]. Recently, David *et al.* [4] showed that defect-assisted nonradiative recombination can be a serious candidate for explaining the low recombination efficiency at high indium contents. In this nonradiative process, Auger electrons are scattered to a trap where they recombine by the Shockley-Read-Hall (SRH) process. This explanation leaves point defects as the main suspect for the "green gap." In 2012 Shioda *et al.* demonstrated enhanced emission efficiency in the green region using an (Al,Ga)N capping layer on top of (In,Ga)N QWs [5]. This is surprising, since (Al,Ga)N increases the polarization field across the QWs and therefore one would expect a reduced overlap between electron and hole wave functions. However, this additional polarization field enhances the quantum confined Stark effect (QCSE), which increases the redshift of the emission wavelength, and allows one to obtain the same emission wavelength using (In,Ga)N with lower indium content, as later demonstrated by the same group [6,7]. This permits growth of the QWs at higher temperatures, increasing the crystal quality and consequently the luminescence intensity [3]. However, there are still some disagreements as to what is the true effect of the (Al,Ga)N capping layer.

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## II. EXPERIMENT

In order to study the effects of (Al,Ga)N capping layers on the optical properties of the QWs, we grow several (In,Ga)N/GaN multi-QW undoped samples with and without an (Al,Ga)N capping layer by MOVPE in a $3 \times 2$ inch close-coupled showerhead reactor from EpiQuest on undoped 2 inch (0001) GaN on sapphire templates. The QW growth sequence is done following a modified Q2T growth [3,8], which consists of growing the capping layer at the same temperature as the QW. (In,Ga)N QWs (3–4 nm) are grown at 720 °C with TEGa and TMIn under $N_2$ carrier gas, followed by the growth of the (Al,Ga)N capping layer (5–12 nm) with TMGa and TMAl grown at the same temperature. We use TMGa for the capping layer in order to have more freedom on the vapor pressure ratio of Ga/Al for (Al,Ga)N and to reduce the effect of growth interruption during the switching of flows, since it is well known that interrupting the growth just after the QWs can have detrimental effects on In composition and interface sharpness [8]. After the (Al,Ga)N capping layer, the temperature is ramped up to 850 °C to grow the GaN barrier (6 nm) with TEGa and 1% of hydrogen in the $N_2$ carrier gas. This structure is repeated five times. Indium and aluminum contents, in the ranges 15%–25% and 0%–20%, respectively, are preliminarily calibrated by XRD on a series of (In,Ga)N/GaN and (Al,Ga)N/GaN QWs.

Room temperature photoluminescence (PL) is measured with a 10-mW HeCd laser emitting at 325 nm using a normalized CCD spectrograph as detector.

Finally, we calculate the optical properties of (In,Ga)N/GaN and (In,Ga)N/(Al,Ga)N/GaN QWs based on envelope function approximation and 8-band kp quantum simulations using TiberCAD [9]. Material parameters used in the simulations are taken from Ref. [10], except for polarization constants [11] and band offsets [12], which are obtained specifically for wurtzite structures.

## III. RESULTS AND DISCUSSION

### A. Experimental results

Figure 1(a) shows the PL intensity of a wide variety of (In,Ga)N/GaN and (In,Ga)N/(Al,Ga)N/GaN multi-QWs in which both compositions and thicknesses are changed. As can be seen, the PL intensity of the (In,Ga)N/GaN QWs decreases exponentially when moving towards longer wavelengths, which is typical for the green gap [13]. However, when an (Al,Ga)N capping layer is added on top of the QWs, the typical intensity drop of the green gap is shifted by 30–50 nm toward longer wavelengths. Interestingly, for wavelengths shorter than 560 nm the (In,Ga)N/GaN QWs seem to have higher PL intensities compared to (In,Ga)N/(Al,Ga)N/GaN QWs. This effect has been observed previously (Fig. 2 in Ref. [5] and Fig. 1 in Ref. [14]), where it was not shown directly but it can be easily inferred from the reported data. However, in those cases the crossing occurs at around 500–530 nm, thus at lower wavelengths compared to our case. Our explanation of this phenomenon is based on a trade-off between the increase of nonradiative defects and carrier confinement due to the (Al,Ga)N capping layer. The use of (Al,Ga)N as capping layer increases the polarization field in the QW, which in turn reduces the spatial extension of the wave function. Since the nonradiative lifetime steadily decreases with increasing wavelength [15,16], at wavelengths longer than 560 nm the density of nonradiative defects of the sample is expected to be high [3]. Therefore reducing the spatial extension of the wave function reduces significantly the electron-hole interaction volume with the surrounding defects. On the other hand, a better crystal quality at shorter emission wavelengths is expected due to higher growth temperatures, making wave function separation due to QCSE the (negative) dominant effect. Since this effect depends mostly on point defects, we expect it to happen at longer wavelengths for samples with a lower point defect density (which is dependent on growth conditions).

Figure 1(b) shows a subset of samples in which only the capping layer thickness and Al content are changed, keeping the same GaN barrier and (In,Ga)N QW (3.5 nm and 21% In). The capping layer of these samples is made of 5-nm GaN, 8-nm $Al_{0.18}Ga_{0.82}N$ (60-s deposition time), and 12-nm $Al_{0.18}Ga_{0.82}N$ (90-s deposition time). Quantum well thickness and indium concentration (3.5 nm and 21% In, respectively) are obtained from XRD analysis of the (In,Ga)N/GaN sample and assumed to be the same for all the samples. Figure 1(b) shows that the calculated transition energies (black arrows) are close to the observed center of emission wavelength, which confirms that the assumption of having identical QWs within the experimental uncertainties is reasonable. From the figure it is also possible to see that for a given QW, adding

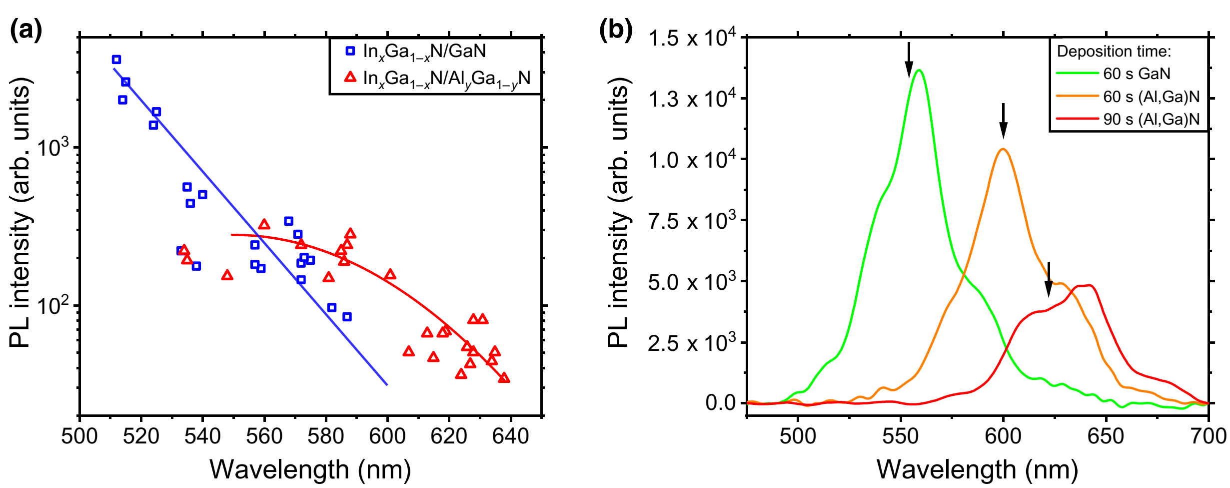


FIG. 1. (a) Room temperature photoluminescence intensity as a function of emission wavelength of the grown QWs with (△) and without (□) an (Al,Ga)N capping layer, in which both compositions and thicknesses are changed. The drop in intensity with the (Al,Ga)N capping layer is clearly shifted by about 50 nm to longer wavelengths compared to (In,Ga)N/GaN QWs. (b) Photoluminescence spectra of different samples with increasing (Al,Ga)N thickness, where the growth sequence of the QW and barrier is not changed. The black arrows indicate the calculated transition energies of the three different samples.

an (Al,Ga)N capping layer results in a clear redshift of the emission wavelength. Because no substantial change in QW In content between the samples is expected, the redshift of emission wavelength can be attributed to an increase in QCSE. This originates from the larger polarization charges at the (In,Ga)N/(Al,Ga)N interface compared to (In,Ga)N/GaN, with a consequent increase of electric field inside the QW.

### B. Simulated results

In order to understand the effect of the (Al,Ga)N capping layer on emission wavelength and intensity, we calculate the optical properties of (In,Ga)N/GaN and (In,Ga)N/(Al,Ga)N/GaN QWs. The simulated structure consists of a 10-nm GaN barrier surrounding a 3.5-nm (In,Ga)N quantum well and a 5-nm (Al,Ga)N capping layer. Periodic boundary conditions (PBCs) are imposed on the structure in order to mimic the behavior of multi-QWs. Indium composition of the QWs is varied between 20% and 30%. (Al,Ga)N thickness is kept fixed at 5 nm, while the Al content is increased in steps of 2% from 0% until the highest hole state moves outside of the QW due to the increased polarization field and low confining potential.

Figure 2(a) shows the optical matrix element ($|M|^2$) of the ground state transition as a function of emission wavelength for (In,Ga)N/GaN and (In,Ga)N/(Al,Ga)N/GaN QWs. Unlike wave function overlap, the optical matrix element takes into account the interaction of carriers with light and it is defined as $\langle\psi_f|\hat{\mathbf{a}}\cdot\mathbf{p}|\psi_i\rangle$, where $\psi_f$ and $\psi_i$ are the final and initial states, respectively, $\hat{\mathbf{a}}$ is the polarization vector, and $\hat{\mathbf{p}} = -i\hbar\nabla$ is the linear momentum operator [17]. For comparison, we perform the same theoretical analysis of a multi-QW system inserted in a *n-p* junction with an applied forward bias of 2 V. The emission wavelengths and optical matrix elements, calculated for the central QW, are shown in Fig. 2(b) ("biased LED") and are compared to the results obtained from the undoped structure with PBCs ("undoped") for the $In_{0.24}Ga_{0.76}N$/(Al,Ga)N/GaN case. As can be seen, the optical properties of the simulated QW with PBC structure are almost identical to the ones obtained for a full, biased LED structure, with much less computational effort. We obtain a similar agreement for LED structures with other In contents as the one shown in Fig. 2(a). This happens because in the yellow-red region, the polarization fields due to strain are much larger than the one imposed by the band bending from the biased junction.

The redshift of the emission wavelength can therefore be explained as an increase in QCSE. However, an increased QCSE usually leads to a decrease in electron-hole overlap, which is not observed for low aluminum contents. In all the simulations we can observe that adding some aluminum always increases $|M|^2$ until saturation and $|M|^2$ decreases at higher aluminum contents. The maximum increase in $|M|^2$ is found for the lowest indium concentration, which also shows the fastest reduction of intensity when further increasing Al content. Moreover, the peak of $|M|^2$ is found at higher redshifts for higher indium contents.

It is evident that the probability of finding electrons [Fig. 3(a)] and holes [Fig. 3(b)] in the QW region is affected by the change in aluminum content. As can be seen from Fig. 3(c), the probability of finding both electrons and holes in the QW resembles the behavior of

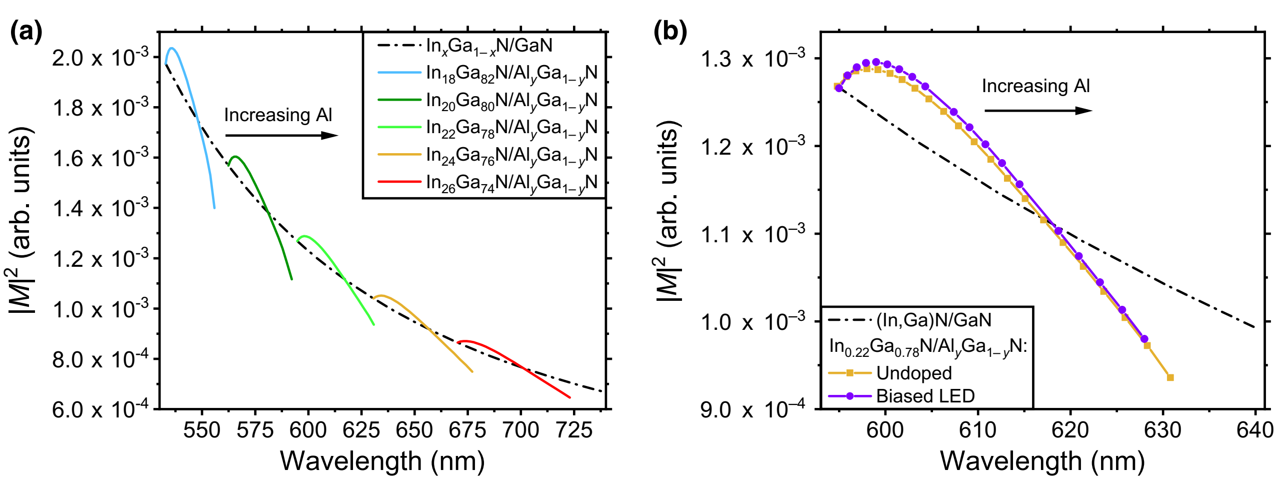


FIG. 2. (a) Calculated optical transition matrix element of the ground state ($|M|^2$) for various (In,Ga)N/(Al,Ga)N QWs with indium content ranging from 18% to 29% (on the black line). The emission wavelength increases when adding an (Al,Ga)N capping layer. (b) Magnification of the simulated $In_{0.24}Ga_{0.76}N$/(Al,Ga)N QW where each data point corresponds to a 2% increase in Al content. The result is compared with the simulation of the same structure in a biased *n-p* junction, from where it is possible to see that there is no substantial difference between the results.

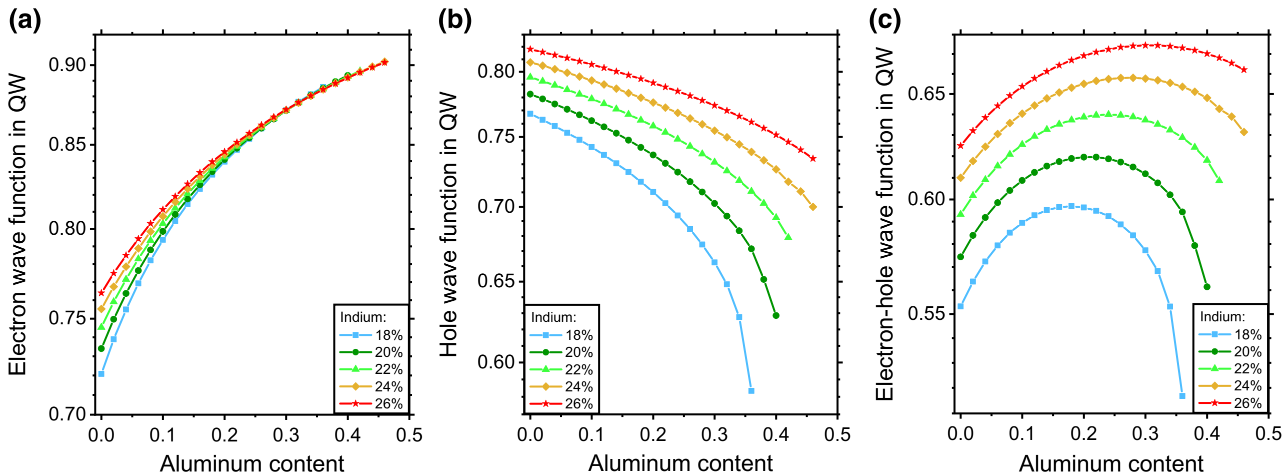


FIG. 3. Probability of finding an electron (a), hole (b), and both electron and hole (c) in the QW as a function of increase in aluminum content for (In,Ga)N/(Al,Ga)N/GaN QW. In the case of electrons, the increasing field enhances the confinement inside the (In,Ga)N QW. Hole confinement instead is strongly affected by initial indium composition and decreases with increasing Al content. The resulting combined probability shown in (c) resembles the behavior of the optical matrix elements, with an increase in confinement followed by a decrease.

the optical matrix elements, since a high probability of having carriers in the QW is required to increase the oscillator strength. Therefore, even if the physically relevant parameters are the optical matrix elements, the probability of finding the carriers inside the QW can be used to understand and explain the observed behavior. For (In,Ga)N/GaN QWs (i.e., no aluminum in the capping layer), the carrier position is only related to (In,Ga)N composition, which determines potential barriers and polarization field. As expected, for higher indium contents the wave functions are more strongly localized near the interfaces due to higher field and larger band offset. Despite the higher probability of finding electrons and holes in the QW region, the overlap decreases as a consequence of the increased QCSE. In fact, the higher field tends to separate electrons and holes, confining them at the opposite interfaces [holes at the GaN/(In,Ga)N one and electrons at the (In,Ga)N/(Al,Ga)N one], which can be seen from the band structure of Fig. 4.

When an (Al,Ga)N capping layer is added to the structure, the behavior of electrons and holes deviates significantly. In the case of electrons [Fig. 3(a)], the larger potential barrier combined with the higher field increases the fraction of the electron wave function inside the QW from around 72% to even 90%, regardless of initial indium concentration. On the other hand, holes [Fig. 3(b)] are confined at the GaN/(In,Ga)N interface. Therefore, they are only sensitive to the (In,Ga)N content and the change of the field in the GaN barrier. With increasing (Al,Ga)N content, the field across the GaN barrier decreases, causing the hole wave function to leak out from the QW. For the low-indium case, the probability of finding a hole inside the (In,Ga)N region decreases more than linearly with increasing field due to lower band offsets, while for high indium content the leakage is reduced by the higher confining potential.

The combination of the different responses to the increased aluminum content in the capping layer determines the unexpected behavior of the optical matrix element of Fig. 2(a).

To visualize how wave functions are affected by the (Al,Ga)N capping layer, Fig. 4 shows the band structures and electron and hole ground state wave function probability densities of $In_{0.24}Ga_{0.76}N$/GaN and $In_{0.24}Ga_{0.76}N/Al_{0.40}Ga_{0.60}N$/GaN QWs. The electron wave function is pushed further into the QW with increasing

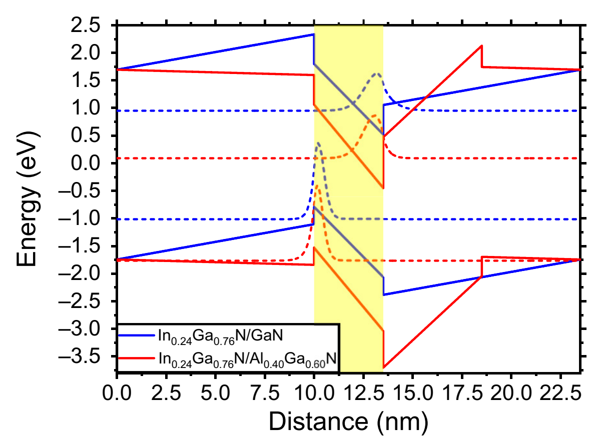


FIG. 4. Calculated band structure (solid lines) of $In_{0.26}Ga_{0.74}N$/GaN (red) and $In_{0.26}Ga_{0.74}N/Al_{0.40}Ga_{0.60}N$/GaN (blue) QWs with the electron and hole ground state wave function probability density shown as dashed lines. The QW region is highlighted for easier comparisons.

aluminum content in the (Al,Ga)N layer due to larger polarization field in the capping layer and the higher band offset at the (In,Ga)N/(Al,Ga)N interface. Both these effects contribute to increasing the confinement of the electron wave function in the QW. This explains the higher portion of the electron wave function in the (In,Ga)N QW of Fig. 3(a). At the same time holes, which are located at the GaN/(In,Ga)N interface, start to leak into the GaN barrier due to lower field in the GaN barrier until the highest hole state is almost entirely outside of the QW.

The observed maximum in $|M|^2$ is due to the different response of electron and hole wave functions to the increase in (Al,Ga)N composition. For low aluminum contents the fraction of electron wave function located in the QW increases faster than the decrease of hole wave function, leading to an overall increase of the overlap. On the other hand, for high electric fields (high aluminum content), hole wave function leakage into the barrier dominates and the overlap decreases again due to the increased carrier separation.

In the literature it is possible to find many different explanations of the increased emission intensity, such as improved smoothness of the interface [6,7,18] and increased crystal quality due to the strain-compensation effect of (Al,Ga)N [19,20], which reduces the total elastic energy in the structure, preventing the relaxation of the QWs. Also increased carrier localization has been discussed based on experimental data [21]. In this work we show that the observed increase in PL intensity can be explained as a consequence of the different response of carrier wave functions to the (Al,Ga)N capping layer, which has never been reported before.

We show that for moderate aluminum contents, carrier confinement in the well region is enhanced and in particular the location of electrons is strongly pushed inside the QW at the V-shaped potential barrier at the (In,Ga)N/(Al,Ga)N interface. Since electrons are the most mobile carriers, their stronger confinement may also lead to less interaction with surrounding point defects (like carbon or vacancies) originating from low-temperature growth, which make an important contribution to the green gap [15]. This is additionally important, since the (Al,Ga)N capping layer is grown at the same low temperature as the QW, which is not in the optimal growth conditions for (Al,Ga)N [22]. As a consequence, this effect could explain why the observed increase in PL intensity seems to be larger compared to the simulated results. This confinement effect could also explain the observed increase in nonradiative decay time observed by Ngo *et al.* [23] by time-resolved photoluminescence. Considering the recent work of David *et al.* [4], reducing the interaction of carriers with defects can effectively mitigate the green gap by reducing SRH and defect-assisted nonradiative recombination. Moreover, by carefully optimizing the aluminum content and engineering the band structure, hole leakage can be prevented leading to an even more pronounced increase in wave function overlap.

## IV. CONCLUSIONS

The lack of efficient emitters in green and red wavelength regions is a problem that has to be overcome in order to develop nitride-based full-color emitters. One possible approach to overcome the green gap problem is to use an (Al,Ga)N capping layer on top of (In,Ga)N QWs. We show that the addition of an (Al,Ga)N capping layer shifts the typical intensity drop toward longer wavelengths. From theoretical simulations we show that by proper selection of (Al,Ga)N composition it is indeed possible to increase both the optical matrix element and carrier confinement in the well region. The enhanced confinement, which reduces interaction of carriers with surrounding defects, is of particular interest considering the recent work of David *et al.* [4], who put a strong emphasis on the role of defects in the efficiency reduction at long wavelengths. As we show, electric field can have a positive effect on carrier recombination, unlike what has been thought up to now. We believe that this new understanding of electric fields as allies rather than enemies may open alternative paths to improve the efficiency of long-wavelength nitride-based emitters.


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