Electronic Supplementary Information (ESI)

Disentangling the effects of nanoscale structural variations on the light emission wavelength of single nano-emitters: InGaN/GaN multiquantum well nano-LEDs for a case study

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Calculation of the in-plane strain and lattice parameters

The in-plane biaxial strain $\varepsilon_{//}$ in the primary film can be evaluated from the measured Raman shift of the E_2^h phonon mode $\Delta\omega$ according to the following equation

$$\Delta\omega = \left(2a_\lambda - 2\frac{c_{13}}{c_{33}}b_\lambda\right)\varepsilon_{||} \tag{1}$$

where $\Delta\omega = \omega - \omega_0$ with ω being the E_2^h peak position for the strained initial film and ω_0 that for the strain-free nanorods, $a_\lambda(E_2^H)$=-850 and $b_\lambda(E_2^H)$=-920 represent phonon deformation potentials, C_{13} and C_{33} are elastic constants with $2C_{13}/C_{33}$=0.6, these values being characteristic for GaN.[1]

The strain relaxation from epilayer to nanorod quantified by the in-plane strain $\varepsilon_{//}$ can be related to the corresponding lattice constants as described by[2]

$$\varepsilon_{||} = \frac{a_{Epi} - a_{NR}}{a_{NR}} \tag{2}$$

where we took a_{NR}=3.189 Å that equals the lattice constant of strain-free GaN in agreement with the Raman results and calculated a_{Epi}=3.179 Å. The positive sign of the Raman shift along with the negative sign of the in-plane strain support the compressive nature of the strain in the starting film, which forces the film lattice constant to decrease with respect to that of the strain-free reference, nano-LEDs in our case. Moreover, the in-plane strain between the InGaN/GaN layers can readily be computed using equation 2 applied to this layer structure as $(a_{Epi,\ GaN} - a_{InGaN})/a_{InGaN}$ and $(a_{NR,\ GaN} - a_{InGaN})/a_{InGaN}$ where $a_{Epi,\ GaN}$=3.179 Å, $a_{NR,\ GaN}$=3.189 Å, and a_{InGaN} for a particular In composition denoted x is given by[3]

$$a_{InGaN}(x) = xa_{InN} + (1-x)a_{GaN} \tag{3}$$

An a_{InGaN}=3.25 Å is obtained for x=0.18, which combined with a_{InN}=3.545 Å and a_{GaN}=3.189 Å give an in-plane strain of -2.27 % for the initial film that decreases to -1.97 % for the nanorods.

A_1(LO) mode

Although a similar tendency was also found for the E_2^h mode (see Figure 3b,d,f), the shift difference is smaller in the case of the A_1(LO) mode. The reason lies in the dissimilar atomic vibrations for the two modes with respect to the c-plane:[4, 5] since the E_2^h mode originates from the in-plane vibrations of the atoms in contrast to the A_1(LO) mode arising from the out-of-plane atomic oscillations, the former exhibits a higher sensitivity to the in-plane strain. This leads to a larger shift difference and to a pronounced peak splitting that can be used to quantify strain in nanostructured LEDs as demonstrated in the previous paragraph.

1.   Chen, L.-Y.; Huang, H.-H.; Chang, C.-H.; Huang, Y.-Y.; Wu, Y.-R.; Huang, J. *Opt. Express* **2011,** *19*, A900-A907.
2.   Jovanović, V. D.; Harrison, P., Strained Quantum Wells. In *Quantum Wells, Wires and Dots*, John Wiley & Sons, Ltd: 2006; pp 219-241.
3.   Christmas, U. M. E.; Andreev, A. D.; Faux, D. A. *J. Appl. Phys.* **2005,** *98*, 073522.
4.   Hiroshi, H. *J. Phys.: Condens. Matter* **2002,** *14*, R967.
5.   Choi, S.; Heller, E.; Dorsey, D.; Vetury, R.; Graham, S. *J. Appl. Phys.* **2013,** *113*, 093510.

Figure S1
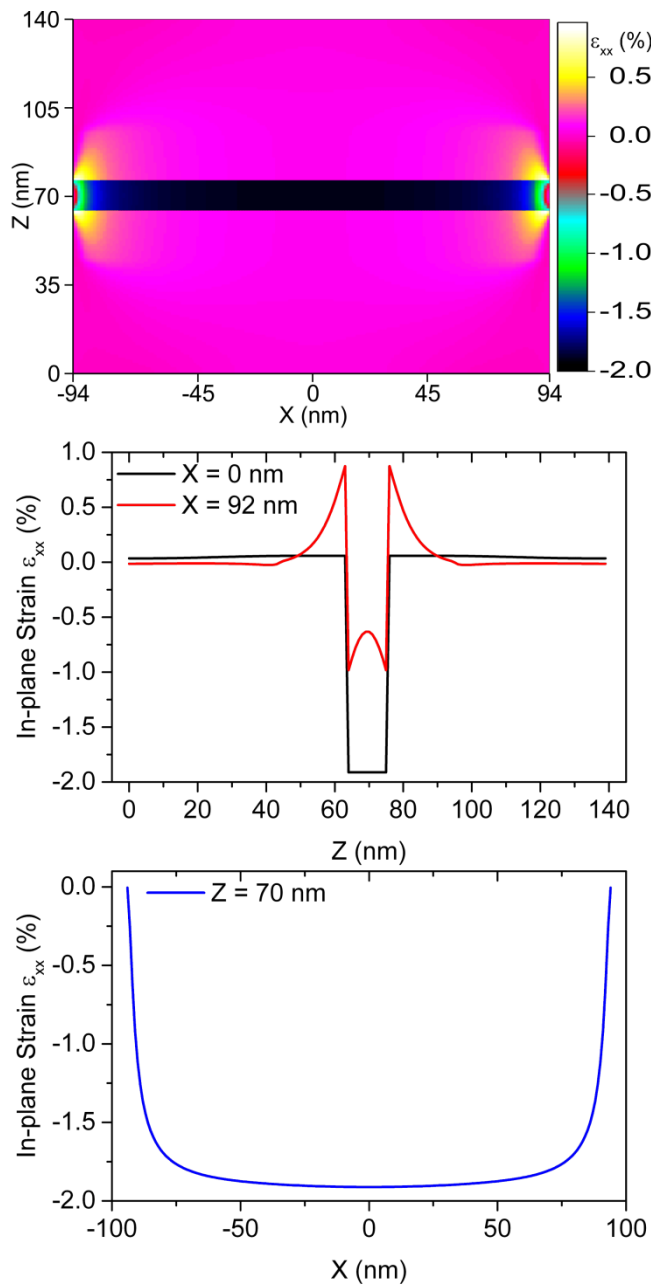
(Top) The 2D radial strain distribution for a 188 nm diameter nanorod containing a single 2.4 nm thick InGaN ($a_{In0.18Ga0.82N}$=3.25 Å) quantum well (QW) in between strain-free GaN barriers (a_{GaN}=3.189 Å) surrounded by air was calculated using the nextnano³ simulation package.

The external stress was assumed to be zero (freestanding nano-LED in air), while the in-plane strain ($\varepsilon_{||}$) profiles were calculated by assuming Neumann boundary conditions.

The tutorial used as the input file in the simulations can be found at http://www.nextnano.com/nextnano3/tutorial/3Dtutorial_GaNAlGaN_QW_strain_freestanding.htm

(Middle) Vertical strain profiles at the center and edge of the nanorod LED.

(Bottom) Horizontal strain profile at the middle of the QW region. A weighted mean in-plane strain of $\varepsilon_{||}$=-1.78 % was found when averaging over the entire QW area.

Figure S2
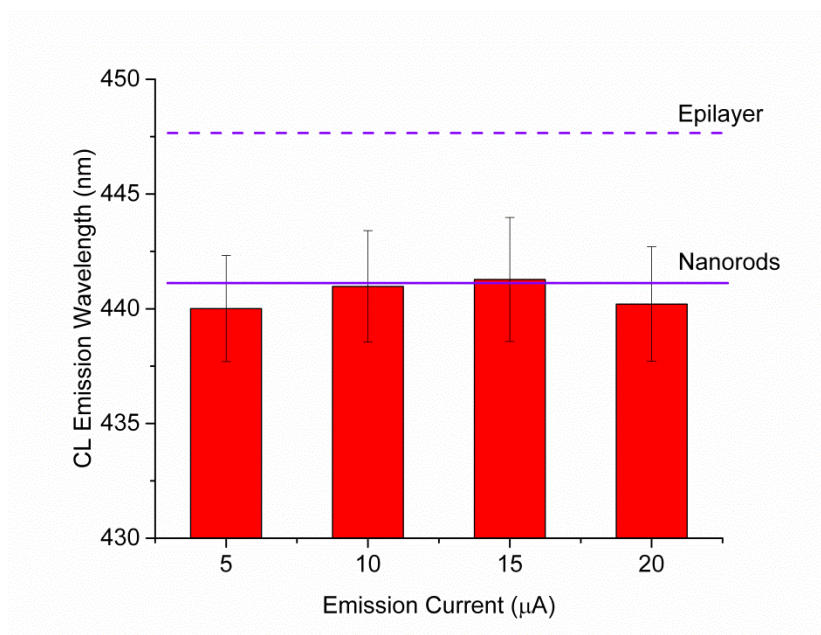
Mean CL peak position values function of the SEM emission current from 10 nanorod LEDs for each current (40 rods in total). The larger the current, the higher the electron density injected into the InGaN/GaN MQWs. The minor variations within the standard deviation with respect to the mean value indicated by the horizontal line from the 30 nanorods in Figure 5b excited at 15 µA demonstrates that a blue-shift induced by the band filling effect can be excluded in our case. Thus, the measured blue-shift of the QW emission wavelength of nano-LEDs with respect to that of the epilayer (mean value from 30 data points indicated by the horizontal dashed line) is attributed to the reduction of the piezoelectric-field induced QCSE due to the strain relaxation as a result of the rod formation upon nanopatterning.
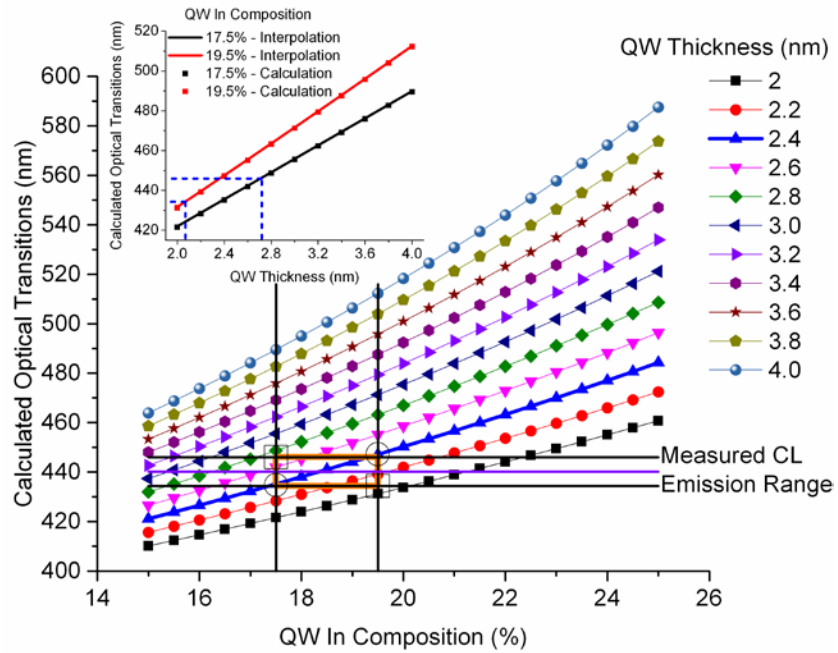
Figure S3
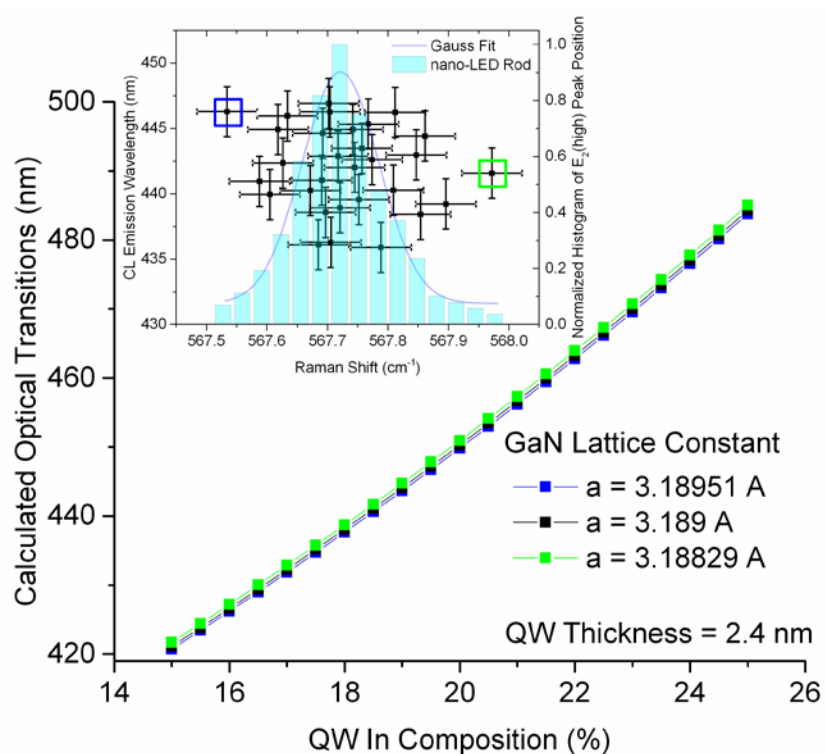
The squares in the inset highlight the two nano-emitters with the outermost detected strain states. Their GaN lattice constants were estimated to be 3.18829 Å and 3.18951 Å using the equations (1) and (2). Based on these values, the QW emission curves were calculated using the nextnano³ simulation package (details are given in the paragraph below). It can be seen that the emission wavelengths for the two nano-LEDs are very close to those of strain-free GaN with a lattice constant of 3.189 Å, the mean difference being only 0.55 nm.

For the 1D self-consistent Schrödinger-Poisson calculations in the QWs we used the effective mass approximation and the 6x6 **k•p** method for the electron and hole wavefunctions, respectively. The nanostructure was modelled as a superlattice, i.e., we applied periodic boundary conditions to the Poisson equation, while the growth direction was set along the hexagonal axis [0001] with the InGaN QWs being strained with respect to the GaN barriers. The band profiles were calculated including the effects of strain, piezoelectric, and spontaneous polarization. The Schrödinger equation is solved using Dirichlet boundary conditions for a region of 12.6 nm around a single QW from which the transition energies (as measured by Cathodoluminescence) can be estimated based on the confined electron and hole states.

The tutorial used as the input file in the simulations can be found at http://www.nextnano.de/nextnano3/tutorial/1Dtutorial_GaN_AlGaN_QW_dispersion.htm

Figure S4

This graph shows a 2D representation of the data from Figure 5c and describes how the experimental and calculated data can be used to define the limits of the projected white rectangle.

First, the QW In composition was defined by the intersection (marked by the two circles) of the calculated emission curve for the nominal QW thickness of 2.4 nm with the measured CL emission limits resulting in the 17.5 – 19.5 % range (marked by the two vertical lines). Second, the QW thickness was defined by the intersection (marked by squares) of the two vertical lines with the calculated emission curves leading to the 2.07 – 2.72 nm interval (obtained by interpolation, see inset). The combination of the QW In content and thickness boundaries gives rise to the orange rectangle, which is the same as the projected white rectangle in Figure 5c.