Study of the dominant luminescence mechanism in InGaN/GaN multiple quantum wells comprised of ultrasmall InGaN quasiquantum dots

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High quality green (508 nm) and blue (424 nm) light emitting diodes (LEDs) from InGaN/GaN multiple quantum wells with stable ultrasmall indium-rich clusters of 2 nm and 3 nm from two different nominal indium contents have been grown by metalorganic chemical vapor deposition. Comprehensive calculations including polarization, piezoelectric field, and size effect help derive an indium composition of 59% and 31% for the In-rich clusters of 2 nm and 3 nm, which agrees amazingly well with the asymmetric phase diagram for phase separation. From this model, we can further demonstrate that the dominant emitting mechanism for green LED is the polarization field, however, for blue LED, both the size effect and polarization effect are equally important. © 2005 American Institute of Physics. [DOI: 10.1063/1.1891291]

Due to their large spectrum, InGaN multiple quantum wells (MQWs) have been extensively employed as the active layers in light emitting diodes (LEDs) and laser diodes. However, the large lattice mismatch between InN and GaN lattices causes difficulties in their growth while film instability against spinodal decomposition often causes nonuniform distribution of indium-rich aggregates, behaved as quantum dots. In addition, owing to the presence of the clusters, the emitting mechanisms for the InGaN/GaN superlattices have not yet been completely identified. The factors arising from quantum dots include (i) quantum confinement effect, (ii) composition of the dots, and (iii) internal electric field, which should all be considered in any accurate discussion of the transition behaviors of carriers. However, while indium concentrations of InGaN quantum wells can be estimated experimentally, the true indium content of small In-rich clusters is still difficult to determine due to the shape and small sizes of clusters. On the other hand, large internal electric fields due to spontaneous polarization and piezoelectric fields are the consequences of the lack of inversion symmetry in the wurtzite structure and the strain at heterointerfaces. Theoretical calculations have shown that redshift can be as large as 0.208 eV for In0.2Ga0.8N quantum dots of 2.08 nm in height caused by the piezoelectric field. Therefore, for higher In content of InGaN on GaN, a piezoelectric field as high as several MV/cm is expected. In addition, over the past few years, it has been controversial to whether the dominant luminescence mechanism in InGaN/GaN originates from the presence of the In-rich cluster or from the internal electric field.

In this paper, we report on a successful growth of highly stable ultrasmall clusters in high quality InGaN/GaN superlattices, which emit blue and green light. The underlying light emitting mechanism can be fully understood by a complete analysis of all effects and factors. In addition, the indium content inside the dots can be inferred from the calculations.

Two samples were characterized in the study. Samples were grown on c-plane sapphire substrates by metalorganic chemical vapor deposition. Sample A consists of seven periods of InGaN/GaN multiple quantum wells sandwiched between n-GaN doped with Si and p-type GaN doped with Mg. The growth temperatures for the barrier and well were 760 °C and 860 °C, respectively. The structure and MQW growth conditions of sample B were the same as sample A, except that the growth time for the well and barrier was different, and the indium flow rate was half that of sample A. Light emitting quality was examined by micro photoluminescence (μPL) with a He–Cd laser (325 nm). High resolution transmission electron microscopy (HRTEM) and x-ray diffraction (HRXRD) were used to analyze the microstructure of the samples, and the cross-sectional TEM samples were prepared using traditional mechanical polishing methods followed by low temperature Ar+ ion milling.

Figures 1(a) and 1(b) show HRTEM bright-field images under a (0002) two beam condition for samples A and B. The barriers and wells in the MQW can be easily distinguished by fluctuations in the indium composition. In addition, there exists a uniform and dense distribution of blobs with strong black and white contrast inside the wells in both images, implying strong strain contrast resulting from coherent dots imbedded in the wells. The dot size and in-plane density were measured to be about 2±0.1 nm and 9×10^{12} cm^{-2} for sample A, while for sample B they were 3±0.1 nm and 4×10^{12} cm^{-2}. For a clear diagram of the dots, an enlarged view of the energy-filtered HRTEM image of sample A is shown in inset of Fig. 1(a). Serious distortion of lattice planes, which is the typical characteristic of dots, associated with strong dark contrast seen in some regions within the InGaN layer (dashed circles), is taken as direct evidence for strong aggregation of indium atoms. The thicknesses of the barrier and well for samples A and B were 22 nm, 2 nm, and 9 nm, 2 nm, respectively. Since the sizes of the dots are extremely small compared to self-assembled quantum dots by the S–K growth mode for the same lattice mismatch, the dots here should correspond to In-rich clusters due to spinodal...
main peaks located at 2.8 eV from simulations to be 33±2% and 9±1%, respectively, in the quantum wells of sample A and B can be estimated peaks for good layer quality and the average indium content to the higher growth temperature or higher indium flux. Both those dots should be thermodynamically stable, probably due samples A beam-damage or beam-induced effects, indicating that from fresh areas and within a reasonably short time to avoid decomposition. Importantly, the images were always taken because of lower 

FIG. 1. HRTEM bright-field images under a (0002) two beam condition for samples A (a) and B (b). The inset in (a) is an enlarged view of the energy-filtered HRTEM image of sample A.

decomposition. Importantly, the images were always taken from fresh areas and within a reasonably short time to avoid beam-damage or beam-induced effects, indicating that those dots should be thermodynamically stable, probably due to the higher growth temperature or higher indium flux. Both HRXRD rocking curves (not shown) exhibit a few satellite peaks for good layer quality and the average indium content in the quantum wells of sample A and B can be estimated from simulations to be 33±2% and 9±1%, respectively.

PL measurement from sample A in Fig. 2 reveals two main peaks located at 2.8 eV (442 nm) and 2.44 eV (508 nm), which are believed to be emitted from the quantum wells and dots, respectively. The peaks at 2.8 eV and 2.44 eV correspond to average In composition of 40% and 64% in the wells and dots, respectively, if they were in bulk form. However, due to the uncertainty surrounding the piezoelectric and quantum effects, the exact In composition derivation is difficult, though important to measure. The PL result from sample B is shown as the dashed line in Fig. 2, which also shows two main peaks but is blueshifted to 3.37 eV (369 nm) and 2.93 eV (424 nm) because of lower nominal In content. PL results stay exactly the same after the samples have been annealed at 900 °C for 30 min, proving that those quantum dots are stable.

In order to visualize the dominating factors, we performed a theoretical calculation comprised of all factors affecting the band structure of InGaN quantum dots and the transition energy, \( E_t \), which is defined as

\[
E_t = E_g + E(\text{conf}) - E_p,
\]

where \(-E_p\) is the decrease in energy due to the polarization field and \( E_g \) is the bulk InGaN band gap energy. Furthermore, the confinement energy, \( E(\text{conf}) \), from the size effect was evaluated by the effective mass model derived by Brus as

\[
E(\text{conf}) = \frac{\hbar^2 \pi^2}{2r^2} \left( \frac{1}{m_e \times m_0} + \frac{1}{m_h \times m_0} \right) - \frac{1.8e^2}{4 \pi \varepsilon_0 r}
- \frac{0.124e^4}{\hbar^2 (4 \pi \varepsilon_0)^2} \left( \frac{1}{m_e \times m_0} + \frac{1}{m_h \times m_0} \right)^{-1},
\]

where \( r \) is the particle radius and the other parameters have their standard definitions. The effective masses of electron and heavy hole and the permittivity constant of InGaN were linearly extrapolated from the atomic ratio of InN and GaN by Vegard’s law. The material parameters used are listed in Table I. We adopted 1.9 eV for InN band gap energy since Shubina et al. recently demonstrated that 0.7 eV was linked to Mie resonance and surface/gap states associated with In precipitates. The last term in Eq. (1), \( E_p \), consists of spontaneous and piezoelectric polarization. Bernardini et al. proposed a model based on random mixing in ternary nitride alloy and applied pertaining \textit{ab initio} method to derive the equation of spontaneous polarization for InGaN in C/m² as

\[
P_{\text{In,GaN}}^{\text{SP}} = -0.042x - 0.034(1-x) + 0.038x(1-x).
\]

As for piezoelectric polarization, Saito et al. performed a theoretical appraisal for InGaN quantum dots of various

![FIG. 2. Micro PL spectra from samples A (solid line) and B (dashed line).](image)

![TABLE I. All material parameters employed in the calculation of the transition energy.](table)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>GaN</th>
<th>InN</th>
<th>In_{0.5185}Ga_{0.4815}N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk band gap energy (eV)</td>
<td>3.4</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>Lattice constant (nm)</td>
<td>0.3189</td>
<td>0.3545</td>
<td></td>
</tr>
<tr>
<td>Effective mass of electron</td>
<td>0.5185</td>
<td>0.5703</td>
<td></td>
</tr>
<tr>
<td>Effective mass of hole (m_0: free electron mass)</td>
<td>1.61 m_0</td>
<td>1.68 m_0</td>
<td></td>
</tr>
<tr>
<td>Relative permittivity</td>
<td>10.4</td>
<td>14.6</td>
<td></td>
</tr>
</tbody>
</table>

\[a\] Reference 15.  
\[b\] Reference 16.  
\[c\] Reference 17.
shapes using an $sp^3$ tight-binding model and found that the lateral component of piezoelectric polarization is insignificant. Vincenzo et al.\textsuperscript{11} have given an explicit prescription for the calculation of the linear piezoelectric field of InGaN as below in C/m$^2$:

$$p_{X_1}^{\text{PZ}}(x) = x P^{\text{PZ}}_{XN}[\varepsilon(x)] + (1 - x) P^{\text{PZ}}_{YN}[\varepsilon(x)],$$

$$P_{\text{GaN}}^{\text{PZ}} = -0.918\varepsilon + 9.541\varepsilon^2,$$

$$P_{\text{InN}}^{\text{PZ}} = -1.373\varepsilon + 7.559\varepsilon^2.$$  

The above formulas express the convenient all-inclusive dependence of polarization on basal strain. The total polarization leads to the appearance of an electrostatic piezoelectric potential.

Figure 3 shows our calculated results of transition energy with indium composition for the cluster sizes of 2 nm (sample A) and 3 nm (sample B). The solid lines mark the theoretical energy band gaps for materials in bulk form. However, the calculated band gap energy for quantum dots decreases rapidly even below $E_g$ for bulk InN. Horizontal dashed lines A and B represent the experimental PL peak positions, which intersected with two calculated lines at indium content of 59% and 31% for samples A and B, respectively. To verify the validity of our calculations, we compared our calculated results (closed circles) with experiments (open circles) from published results\textsuperscript{12,13} and found good agreement between them. Due to their tiny size, the indium content in the dots is almost inaccessible by any current technique but can be reliably derived by our method. These two indium contents in quantum dots agree amazingly well with the phase diagram, which proves the phase separation obeys an asymmetric curve, where the nominal indium composition of 10% and 29% decompose into two phases of 9%, 30% and 27%, 27%, respectively.\textsuperscript{14} In the region of low indium content, the strain from InGaN dots is small and the size effect would dominate the transition energy, resulting in blueshift. However, with increasing indium concentration, accompanied with the enhancement of piezoelectric polarization, the carriers are separated and the energy band gap is redshifted, which causes the transition energy to decrease quickly. Therefore, the crossover indium composition can be found for samples A and B, which are 54% and 30%, respectively, where the blueshift from the size effect is balanced by the redshift from the polarization effect. Sample A exhibits 0.13 eV of redshift, indicating that the polarization field dominates the transition of carriers. On the other hand, the transition energy of sample B is close to the crossover point. We have shown that the emitted wavelength in the full visible light spectrum can be effectively controlled by controlling the quasidot size in the active layers.

In summary, we have successfully grown high quality green and blue InGaN/GaN superlattices by using the phase separation method, and have been able to attribute the emission mechanism to the ultrasmall quasidots in the samples observed by HRTEM. In addition, we have performed theoretical calculations taking all contributory effects into account to derive the indium content of 59% and 31% for the two samples. Therefore, the dominant emitting mechanism for sample A (green) is the polarization field, while for sample B (blue), both the size effect and the polarization effect are equally important.

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