Electronic structure of a single-layer InN quantum well in a GaN matrix

M. S. Miao, Q. M. Yan, and C. G. Van de Walle
Materials Department, University of California, Santa Barbara, California 93106-5050, USA

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Using first-principles methods and 8-band $k \cdot p$ simulations, we study the electronic structure of an ultrathin quantum-well system consisting of a single layer of InN inserted in GaN matrix. Experimental photoluminescence and electroluminescence emission peaks for such structures have been reported in the wavelength region between 380 to 450 nm. In contrast, our calculations show an energy difference between the electron and hole states around 2.17 eV (573 nm). Possible origins of the experimental light emission are examined. We suggest that the experimental emission may be due to recombination of electrons (holes) in GaN with holes (electrons) in the quantum well. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4794986]

InN has been attracting attention as an important nitride semiconductor because of its low band gap (less than 0.7 eV). Combined with the large gaps of GaN and AlN, it enables the band gaps of nitride alloys to cover the entire visible spectrum and reach well into the infrared. Compared to GaN, InN is more difficult to grow due to its low dissociation temperature. To date, the most important applications are ultraviolet (UV) to green light emitting diodes (LED) and lasers that use InGaN alloys with fairly low In concentrations. Growing high-quality InGaN layers with high In content on GaN is difficult due to the large lattice mismatch between InN and GaN and the tendency for phase separation. One proposal to overcome these problems is to use ultrathin layers of InN sandwiched between GaN. Yoshikawa et al. reported that high quality InN layers with an atomically sharp and flat interface could be fabricated at growth temperatures as high as 650 °C. Light emission from the recombination of electrons and holes in such InN/GaN monolayer quantum wells (MLQWs) was observed in both photoluminescence (PL) and electroluminescence (EL). The emission peak ranged from 380 nm to 425 nm, corresponding to a cutoff energy of 300 eV and a $k \cdot p$ mesh of $4 \times 4 \times 1$ centered at the $\Gamma$ point are used. The InN layer is assumed to be pseudomorphically grown on GaN, i.e., the lattice constant in the plane of the interface is that of GaN, while the lattice constant along the $c$ direction is allowed to relax.

According to the macroscopic theory of elasticity, within the linear regime, the strain in the perpendicular direction is related to the biaxial strain by $e_{zz} = -2 \frac{C_{13}}{C_{33}} e_{xx}$, in which $C_{13}$ and $C_{33}$ are the elastic constants. Using $2 \frac{C_{13}}{C_{33}} = 0.821$ (Ref. 19), we plot $e_{zz}$ as a function of $e_{xx}$, together with the calculated strains in a MLQW and in bulk InN subject to the same in-plane biaxial strain as the MLQW. As shown in Fig. 2, the calculated $e_{zz}$ for bulk InN is lower than that predicted from macroscopic elasticity, which is due to the nonlinearity at

![FIG. 1. Calculated atomic structure of an InN single layer inserted in a GaN matrix. Large (green) balls represent Ga, large darker (purple) balls In, and the small (grey) balls N. Bond lengths (in Å) are indicated.](image-url)
such a large strain. However, the strain in the very thin MLQW is quite different from that in strained bulk InN and actually compares remarkably well with the macroscopic theory.

Figure 1 shows the optimized structure of the InN layer embedded in a GaN matrix. The In-N bonds are severely distorted, resulting in very different bond lengths for bonds between In and N in the same bilayer (2.056 Å) versus In and N in adjacent bilayers (2.182 Å). For comparison, the bond lengths in bulk InN are 2.155 Å and 2.161 Å. There are also two different N-In-N angles, one formed by N atoms in the same bilayer and the other by N atoms in adjacent bilayers ([N-In-N]). These two angles are very close in value in bulk InN (110.2° and 108.7°), but in the MLQW, the N-In-N angle decreases to 101.4° while the N-In-N angle increases to 116.7°. The distortion is partially due to the large strains that are present in the MLQW, but also to the different bonding features of the N atoms bonded to In in different layers: the N atoms in the same bilayer as In bond to three In and to one Ga, while the N atoms in the adjacent bilayer bond to three Ga and one In. To provide insight in these contributions, we performed a calculation for bulk InN strained with the same εxx and εzz as the MLQW. We found In-N bond lengths of 2.093 Å in-plane and 2.125 Å along c. This bond-length difference is significantly smaller than the difference in bond lengths found for the MLQW, showing the important impact of the specific bonding environment (partial bonding to Ga atoms).

Accurate results for the electronic band structure of the InN/GaN MLQW are obtained here by employing a hybrid functional. The calculated energy difference between the electron state (lowest unoccupied orbital) and the hole state (highest occupied orbital) is 2.17 eV. This energy (corresponding to a wavelength of 573 nm) is much higher than the fundamental gap of InN, indicating that quantum confinement is significant. However, the energy is much below the emission peaks (above 2.92 eV) observed in PL or EL experiments.

One potential explanation for this discrepancy is that the inserted layer is not pure InN but actually consists of InGaN. In order to examine this hypothesis, we simulated the electronic structure of GaN/InGaN/GaN quantum wells using the 8-band k · p method, as shown in Fig. 3. Reassuringly, we found that the k · p simulation yields a band gap for the pure InN MLQW of 1.97 eV, close to the first-principles result. The recombination energy increases with decreasing In concentration, but reaches the values that are observed in PL and EL experiments only when the In concentration is less than about 35% In. If the QW is actually more than one ML thick (which would result from interdiffusion), then even lower In concentrations would be required to produce the experimental emission peaks. Assuming that the experimental growth indeed results in high-In layers on a monolayer scale, we cannot attribute the emission to recombination within an InGaN QW.

Here, we propose an alternative explanation for the observed emission peaks. As shown in Fig. 4, the observed light emission may originate from the recombination of carriers located in different spatial regions, i.e., from the GaN barrier to the InN quantum well. Our first-principles calculations produce energy differences between the highest occupied state (hole state) and the three lowest unoccupied states (electron states) at the Γ point of 2.17, 2.71, and 2.97 eV; the latter two energies actually correspond to electron states that are mainly localized in GaN. We also find that the energy differences between the lowest unoccupied state (electron state in the MLQW) and the second- and third-highest occupied states (hole states in the GaN region) are 2.57 and 2.71 eV.

In order to examine the likelihood of this mechanism, we plot the wave functions of the electron and the hole states in the InN quantum well in Figs. 4(b) and 4(c). Not surprisingly for such a thin QW, the wave functions spread out into the neighboring GaN barrier layers. The hole state is localized not only on N atoms within the InN layer but also on N atoms in the underlying GaN layer [Fig. 4(b)]; electrons, on the other hand, spill over into the GaN overlayer [Fig. 4(b)].
The relative spatial locations of the electron and hole states are consistent with the polarization field evident in Fig. 4(a).

The spillover of the QW wave functions into the barrier layers facilitates recombination of carriers in the QW with carriers in the GaN barrier. Recombination of electrons in GaN with holes in the QW gives rise to an emission energy $E^R_{eb} = 2.71$ eV; recombination of electrons in the QW with holes in GaN barrier emits light at $E^R_{eh} = 2.57$ eV. Capture of carriers in nitride QWs is known to be imperfect; strategies for addressing electron overshoot, in particular, have been widely discussed. This illustrates that trapping of carriers in this ultrathin well may be a bottleneck, leading to suppression of the lowest-energy recombination channel and favoring recombination involving carriers in the barriers. We also note, however, that the energy region corresponding to our calculated lowest-energy emission (2.17 eV) was not explored in the PL and EL studies to date. The remaining difference between our calculated recombination energies ($E^R_{eh}$ and $E^R_{eb}$) and the observed PL energies in the 2.92–3.26 eV range could be due to the composition of the MLQW, which may not consist of pure InN as discussed above.

In summary, we have studied the structural relaxation and the electronic structure of a monolayer InN quantum well embedded in GaN, using both first-principles density functional theory and the 8-band $k \cdot p$ method. Our calculations show that recombination between electrons and holes in the MLQW results in light emission around 573 nm. Such recombination may be suppressed due to difficulties in carrier capture. We propose that the reported emission peaks in the blue and UV originate from recombination involving carriers in the neighboring GaN barrier regions.

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