Light-emitting diode development on polar and non-polar GaN substrates


A3. Metalorganic Vapor Phase Epitaxy
B1. Nitrides
B3. Laser diodes
B3. Light emitting diodes

ARTICLE INFO

Available online 14 June 2008

Keywords:
A3. Metalorganic Vapor Phase Epitaxy
B1. Nitrides
B3. Laser diodes
B3. Light emitting diodes

ABSTRACT

GaN/NaN multiple quantum well light-emitting diode structures in polar c-axis and non-polar m-axis growth have been compared in terms of luminescence properties. Grown under identical conditions, under low excitation density the c-axis structure has a luminescence maximum at 558 nm while the m-axis structure shows a maximum at 488 nm and shows superluminescence at 485 nm under high photoexcitation density. Under the same conditions, on increasing the excitation power, the peak intensity increases 40 fold in the m-axis structure without any variation of the emission wavelength. In similar but separately grown c-axis structures without a p-side, luminescence shifts from 555 nm at low excitation density to superluminescence at 485 nm under high excitation. The coincidence, of the superluminescence wavelength in the polar structure with the stable peak wavelength in the non-polar one, suggests that the wavelength shift in the polar structure is due to its piezoelectric polarization. The absence of such effects in the m-axis-grown structure therefore suggests a stronger dipole matrix element, potentially enabling higher quantum efficiencies and suitability for high efficiency light-emitting diode and laser diode designs in the green spectral region.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Light-emitting diodes (LEDs) employing heterostructures of group-III nitrides are a prime contender for the realization of energy-efficient solid-state lighting [1,2]. As a direct bandgap material, alloys of Ga1−InN can be tuned to emit light covering every portion of the visible spectrum. White light of good color-rendering quality (additive white) requires a more or less continuous spectrum and can be obtained by the combination of various such light sources. On the other hand, image information encoded in red–green–blue (RGB) colors can be reproduced by three highly monochromatic light sources of red, green, and blue. Current best practices in LED lighting employ blue or near-UV LEDs to excite a phosphor that downconverts those photons into longer wavelength light dependent on the phosphor chemistry and composition. The more efficient approach employs LEDs that emit directly at the target wavelength and thereby bypass the energy loss of downconversion. Even in the ideal case of 100% quantum efficiency this downconversion from the blue to the green amounts to a 20% energy loss. Of particular interest therefore are high efficiency LEDs in the green (525 nm) and deep green (555 nm) spectral region.

Current technology primarily employs heteroepitaxial metalorganic vapor phase epitaxy (MOVPE) of AlGaN alloys on dissimilar substrates like sapphire or SiC. This typically results in high densities of threading dislocations that are extremely difficult to prevent from penetrating the active quantum well (QW) region. The considered roles of those defects range from electrically active donor centers [3], highly active non-radiative recombination centers [4], over mid-gap trap states assisting charge tunneling [5], and seeds for V-defects [6], to pathways of metal impurity electromigration and acceptor diffusion. Our previous work finds a correlation of V-defect density in the active region and the efficiency of LEDs, particularly in the green spectral region [7].

Promising therefore are freestanding GaN templates or bulk wafers that can be grown by hydride vapor phase epitaxy with threading dislocation densities as low as mid–10^6 cm^-2 [8]. Grown at a high growth rate, in inexpensive processes, such substrates could alleviate the need for elaborate multi-step growth processes in expensive MOVPE. c-Axis-oriented wafers up to a diameter of 2" are commercially available at this time. For other crystallographic orientations, thick c-axis-grown material can be sliced and cut in other directions. Such pieces typically result in narrow slices of 5–10 mm width. Here we compare emission properties of c-axis and m-axis-oriented multiple QW (MQW) structures.
Piezoelectric polarization in group-III nitrides follows from the uniaxial lattice geometry of the wurtzite lattice structure in combination with partially ionic bonding properties in the diatomic point group that lacks inversion symmetry [9]. Hence heteroepitaxy along the unique c-axis induces discontinuities of the (pyroelectric) polarization component and pseudomorphic heteroepitaxy adds piezoelectric components due to induced biaxial strain. Such polarization localized within a bipolar LED structure can cause a range of dynamic instabilities when electrons and holes are injected in regular device operation. In the past, primarily a reduced interband dipole matrix element [10] and emission wavelength shift [11] have been attributed to the presence of piezoelectric polarization within the QW.

For this reason, Takeuchi et al. [12] proposed to orient QWs along directions other than the c-axis of the lattice. For a uniform slab, directions including combinations of the m- and a-axes only are free from polarization components. In heterostructures, however, due to the asymmetric strain and polarization tensors, directions of minimum polarization vary with the actual structure and may involve higher indices of all three lattice eigenvectors. For simplicity of nomenclature, here polar and non-polar growth direction refers to the simple slab geometry, typically that of the thick GaN epilayer.

Fig. 1 depicts the c-plane (Fig. 1b), m-plane (Fig. 1d), and a-plane (Fig. 1f) of the crystal and their relations to the hexagonal crystal cell. Schematically shown are also conduction and valence band edges across a typical type-I QW grown along the respective c-axis (Fig. 1a), m-axis (Fig. 1c), and a-axis (Fig. 1e). The vector of net polarization $P$ is indicated. The polarization leads to a separation of electron and hole wave functions. The dipole matrix element is lowered and the radiative transition will be a slow process as indicated in Fig. 1a.

Growth along a direction that does not induce a net polarization leads to symmetric wave functions and associated fast radiative transitions. The situation is sketched for the cases of m-axis (Fig. 1c) and a-axis (Fig. 1e) growth. The separation of mobile charges along the field leads to a lowering of the interband transition energy, which can be well approximated by the quantum confined Stark effect. Our previous experimental evidence suggests an even larger red shift $\Delta E = L P / \hbar e$, where $L_{z}$ is the full width of the QW [13,14]. A third aspect of the net polarization of the QW is its local interaction with the screening pair of mobile charges. This, under high carrier injection conditions, is considered to lead to a partial screening and an effective wavelength blue shift. None of this should occur in a polarization-free QW, promising a more stable emission wavelength.

The actual polarization conditions in the QWs, as a function of crystal orientation, are a convoluted function of deformation potentials and piezoelectric constants, the latter of which show quite some discrepancy throughout the literature. Based on the respective information available, Takeuchi et al. [12] predicted vanishing polarization in wells grown along the (1120) m-axes and the (1010) a-axes, but also along the (1124) axes. A more recent analysis predicts this latter minimum near an angle 45° off the c-axis [15]. Consequently, growth along the m- and a-axes should provide vanishing polarization and a big increase in the interband dipole matrix element and quantum efficiency.

2. Experimental procedure

n-Type GaN templates were grown on sapphire along the c-axis. A 6 μm GaN c-plane template was prepared in MOVPE and a second, 10 mm thick sample was prepared in HVPE. The latter typically shows a threading dislocation density in the mid to low $10^6 \text{ cm}^{-2}$. It was cut into individual freestanding 300 μm thick slices along the m-plane and electromechanically polished for epitaxial overgrowth. Wafer pieces of both crystal orientations were mounted side to side for simultaneous overgrowth. After 1 μm n-type GaN overgrowth along the c- and m-axes, Ga$_{1-x}$In$_x$N/ GaN QW structures were grown in MOVPE at temperatures above 650°C using TMGa, TMIn, and NH$_3$ precursors. Some samples were capped off with a p-type AlGaN electron blocking layer and a p-type GaN contact layer to form an entire LED structure. For
comparison, additional c-axis-oriented MQW structures were grown on sapphire without a p-side [7,16,17].

Continuous wave (cw) and 10 ns pulsed photoluminescence (PL) experiments were performed at room temperature using the 325 nm line of a HeCd laser and the 337 nm line of a N2 laser, respectively. Power density readings are those of the focused laser beam at the location of the sample. They have not been corrected for flux losses for entering the samples. Cathodoluminescence was performed at 20 kV.

3. Discussion

The crystalline perfection of the m-axis-oriented LED structure has been analyzed in cross-sectional transmission electron microscopy (TEM; Fig. 2). The image shows portions of the sample with high structural regularity and reveals wide areas without any structural defects propagating along the m-growth axis. The transition from the m-oriented bulk substrate to the n-GaN overgrown layer should lie outside of Fig. 2a on the left. Apparently, homoepitaxial overgrowth occurred without generation of significant concentrations of defects and without producing any TEM contrast. In the middle of the figure, a set of 10 QWs can be identified as dark lines perpendicular to the m-axis. Barriers identified as light bars separate the QWs. Some structural defects appear to connect some of the wells. On the right hand side of the image, the p-AlGaN layer, identified as a lighter thin layer, and the p-GaN layer can be distinguished by comparison with the growth protocol. Apparently, very regular QW structures can be achieved also along the m-axis growth. Widths of wells and barriers, as derived from these results, are very close to those obtained in the c-axis-grown structure. Without developing any specific epi methods to reduce threading dislocation densities in m-axis growth, low-dislocation-density active regions can be obtained by our approach of homoepitaxy on reoriented low-dislocation-density c-axis-grown bulk GaN from HVPE. This approach therefore should be the preferred approach to evaluate the potential for the development of light emitters grown along this crystal orientation.

The optical properties of this m-axis-oriented LED structure in comparison with the simultaneously grown c-axis structure are shown in Fig. 3. In cathodoluminescence at room temperature, the c-axis sample shows a strong peak emission at 558 nm—well into the deep green. At the same excitation, the m-axis sample exhibits a peak at 363 nm and a predominant one at 488 nm. The first stems from the GaN band edge, most likely in the p-layer and the latter is from the QW. Apparently, despite identical offered growth conditions, emission in the m-axis structure is at a substantially shorter wavelength. Without any indication that the actual structure was any different, we have to assign the differences to the respectively used growth directions. Indeed, as argued above, well and barrier growth rates are found to be identical for both crystal growth directions. A value that we cannot assert yet is the actual InN fraction in the Ga1-x InN wells. It has been argued that In incorporation should be significantly smaller in the m-axis growth [18]. This could also be the case here. On the other hand, the lower density of dislocations in the homoepitaxial structure should enable a higher incorporation, since In is not consumed in clusters at the defects. While having no direct means yet to determine the actual InN fraction, we want to offer a second plausible explanation.

In our previous study of the electronic bandstructure in piezoelectric c-axis-oriented Ga1-x InN/GaN QWs, by comparing optical absorption and light emission properties with bandstructure calculations [13], we find a gaping discrepancy between the calculated first electron–hole transition (N2) and the observed light emission peak energy (N3). This discrepancy, \( A_{\text{well}} = E(N_2) - E(N_3) \), is the equivalent of the well-known experimentally observed Stokes shift in a wide range of studies [10,19]. We developed an explanation by which this offset is a replication of the polarization dipole across the QW—an effect that largely exceeds the quantum confined Stark effect [13,14,20,21]. Fig. 4 summarizes the model. While neglecting possible fields in the barriers, the electronic bandstructure in Ga1-x InN/GaN QWs for a typical well of \( x = 0.18 \) and width \( L_z = 3 \) nm is shown. Due to the piezoelectric polarization of electric field strength \( F \), a polarization dipole of \( A_{\text{barrier}} = F L_z \) is induced across the well. Accordingly, + and – states are distinguished depending on their location left or right of the dipole. Associated possible transitions involving the barrier band edges are shown in Fig. 4a. The calculated single-particle states of the electron (\( e_1 \)) and first heavy (\( h_1 \)) and light hole (\( lh_1 \)) in the well are shown with their corresponding transition N2 in Fig. 4b. The resulting joint density of states (J-DOS) as a function of transition energy is shown in Fig. 4c and
the apparent term scheme in Fig. 4d. The latter includes the experimentally found low-excitation-density luminescence emission $N_2$. In experiment, transition $N_2$ appeared as a replica to $N_1$ with a separation of $A_{\text{well}}$, which is very close to $A_{\text{barrier}} = FeL_2$. The replication of the polarization dipole in the well can be tentatively explained by a coupling of the electron–hole pair to the local polarization dipole of the QW.

On the basis of such a model, any avoidance of the piezoelectric polarization, e.g. by growth along non-polar directions, should avoid the reduced wave function overlap and dipole matrix elements in transition $N_2$. More importantly, however, it should also get rid of the large Stokes shift between $N_2$ and $N_1$ as $F = 0$. As a result, the discrepancy between emission wavelength and absorption band edge on the one hand, but also bandstructure calculation on the other hand, should vanish. Our experimental data and models in Refs. [10,13] can be used to estimate the polarization dipole for a polar QW structure with an emission line at 558 nm. In extrapolation, we find that in this case, $A_{\text{well}} = FeL_2$ should amount to 440 meV. In the absence of polarization in non-polar-oriented QWs of the same composition, an emission beyond 465 nm cannot be expected.

Based on these considerations, it does not come as a surprise that even in the presence of identical QW geometry and alloy compositions, both systems exhibit different emission wavelengths. According to our explanation, just the fact of reduced polarization in the well should explain the significantly shorter emission wavelength in the $m$-axis structure when compared to the $c$-axis QWs.

The second aspect of polarization in the QW is the instability of the emission wavelength. On a logarithmic intensity scale, Fig. 5 shows examples of $c$-axis-oriented MQW structures as used in our sapphire-based green LEDs (note, these MQW structures differ from the full LED structures shown in Fig. 3). A structure with a surface emission at 500 nm under a low-density cw excitation at 325 nm is depicted in Fig. 5a. Under pulsed excitation at 337 nm, detected in emission from the cleaved edge, the maximum shifts toward shorter wavelengths. At a further increased excitation density of 2.9 mJ/cm², a line narrowing to 6 nm FWHM at 457 nm is observed, which is typical for superluminescence. Superluminescence is spontaneous emission amplified by stimulated emission in a gain medium. In contrast to laser operation, superluminescence shows very short coherence times and a large emission linewidth [22]. The line narrowing indicates progressive mode discrimination under the gain curve as the condition for lasing develops. The case for an even longer wavelength emitting $c$-axis-oriented MQW sample is presented in Fig. 5b. Surface emission under low-density 325 nm cw excitation occurs at 555 nm. With higher excitation density and switching to the cleaved edge detection, emission intensity increases, the peak moves to shorter wavelengths, and an emission mode narrowing

---

**Fig. 4.** Bandstructure schematic based on realistic modeling of 3 nm Ga0.82In0.18N/GaN QW inducing a polarization dipole $FeL_2$ across the QW. (a) The resulting transition scheme involving barrier states. (b) Single-particle states and corresponding transition $N_2$ in the well. A schematic of the joint density of states (c) and the terms scheme (d) as observed includes an additional transition $N_3$. It appears to split from $N_2$ by the same amount of the polarization dipole. A coupling to the local polarization state is the likely reason (after Refs. [10,13]).

**Fig. 5.** Surface and edge luminescence in $c$-axis-grown polar MQW structures under various photoexcitation densities. (a) Structure emitting at 500 nm under low excitation shows superluminescence at 457 nm under high excitation. (b) In a structure emitting at 555 nm under low excitation, superluminescence occurs at 485 nm at high excitation.
is observed at 2.9 mJ/cm². At these conditions, superluminescence becomes evident at a wavelength as long as 485 nm, yet still at a substantial blue shift of 70 nm or 323 meV over the low-excitation-density luminescence peak.

This large blue shift by more than 300 meV exemplifies the challenge to develop green laser diodes, emitting at wavelengths beyond 500 nm, in such material. The strong wavelength shift also, however, is very close to the value of the well-described Stokes shift and the quantity of the polarization dipole across the QW, lending clues to the detrimental effects of the piezoelectric polarization in the development of laser diodes.

Applying the same excitation range to the non-polar m-axis-oriented MQW LED structure (including p-side) results in the spectra of Fig. 6—again on a log-intensity scale. At a low excitation density of 20 W/cm² at 325 nm, the emission peak occurs at 488 nm in surface emission. On switching to edge emission detection and increasing the excitation density from 0.03 to 2.9 mJ/cm², emission intensity increases by a factor of 40 while well maintaining the peak emission at 488 nm. Apparently, in this m-axis structure, where net polarization in the QW should be eliminated, a wavelength shift, as described in the c-axis material, does not occur. On the contrary, the emission spectrum remains extremely stable over a large range of excitation; yet indications of superluminescence or stimulated emission do not occur. We tentatively attribute this to the fact that the QWS in this structure are covered by a p-AlGaN and p-GaN layer, reducing the effectiveness of external photoexcitation. However, other factors may play a role in this early stage of growth optimization.

4. Conclusions

GaN/InGaN MQW LED structures grown simultaneously on both, c-axis-oriented GaN/sapphire template and m-axis-oriented bulk GaN substrate have been compared in terms of their luminescence properties. At low excitation density, the c-axis structure shows a PL maximum at 555 nm while the simultaneously grown m-axis-oriented structure shows PL at 488 nm. On increasing the excitation power density, PL peak intensity increases 40 fold in the non-polar structure without any variation of the emission wavelength. In contrast, separately grown c-axis structures without a p-side exhibit a strong blue shift of the emission and superluminescence in the range (e.g. at 485 nm) where the m-axis structure emits independent of excitation density. The substantial blue shift in the c-axis structure therefore must be directly attributed to the piezoelectric dipole across the QWs.

According to this model, the absence of piezoelectric polarization in the m-axis growth requires significantly higher InN fractions in the GaInN QWs to reach green emission than in the polar c-axis growth. At the same time, suppression of polarization also shows avoidance of the wavelength blue shift under high excitation density. From both it may also be anticipated that the reduction of interband transition matrix elements should also be avoided in the m-axis structure. Altogether, substantially higher efficiency LEDs and laser diodes may become possible using a non-polar growth geometry.

Acknowledgment

This work was supported by a DOE/NETL Solid-State Lighting Contract of Directed Research under DE-FC26-06NT42860.

References