BAlGaN light emitting diode emitting at 350 nm

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Abstract

In this work, we report the first demonstration of an ultraviolet light-emitting diode (LED) with boron-containing multiple quantum wells. Electroluminescence emission from the BAlGaN LED was observed at 350 nm, with higher intensity compared to the AlGaN reference LED. A higher operating voltage compared to the reference LED was also observed which may be attributable to a nanomasking behaviour of boron in (Al)GaN alloys.

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In this work, we report the first demonstration of an ultraviolet light-emitting diode (LED) with boroncontaining multiple quantum wells. Electroluminescence emission from the BAlGaN LED was observed at 350 nm, with higher intensity compared to the AlGaN reference LED. A higher operating voltage compared to the reference LED was also observed which may be attributable to a nanomasking behaviour of boron in (Al)GaN alloys.

Introduction: III-Nitride ultraviolet (UV) light sources are in increasing demand to replace mercury-based lamps owing to potentially higher efficiencies, smaller footprints, and tunable wavelengths [1]. While significant developments have been made over the past two decades, the performance of AlGaN-based light-emitting diodes (LEDs) still lags behind visible (In)GaN-based devices [2, 3]. Some of the major challenges are the crystalline quality of initial substrates/templates, light absorption within the LED heterostructure (due to p-GaN contact layers), lack of reflective contacts, and large intrinsic polarisation fields across the active region [4]. These fields originate from a combination of the ionicity of the bonds in the wurtzite lattice and the lattice mismatch in the crystal, which result in a separation of the electron and hole wavefunctions in the quantum wells (QWs), along with a redshift in the emission spectrum. This effect is more commonly known as the quantum confined Stark effect (QCSE) and is detrimental to the internal quantum efficiency (IQE) of the device.

Wurtzite boron nitride is an ultra-wide indirect bandgap material with a bandgap of $\tilde{}$ 6.7 eV, while the bandgap estimate for a direct transition is $\tilde{}$ 13 eV [5, 6]. The relatively small BN lattice constant of a [?] 2.5 Å allows for the possibility of lattice-matching between well and barrier/buffer material [7]. Therefore, the addition of small amounts of BN to the (Al)GaN QWs has the potential to negate the polarisation field across the well and reduce the QCSE, thereby increasing the IQE. However, boron-containing QWs have to

overcome many practical challenges in order to demonstrate experimentally their potential. In this Letter, we report, to our knowledge, the first UV LED with B-containing QWs.

Growth and fabrication: A BAIGaN MQW UVA LED was grown by metalorganic chemical vapor deposition (MOCVD) in an AIXTRON $3\times2"$ close coupled showerhead reactor. A 2-inch c -plane sapphire wafer with 25 nm sputtered AlN (Kyma Technologies) was used as the substrate, onto which a 200 nm AlN connecting layer was grown. This was followed by 400 nm u -Al_{0.35}Ga_{0.65}N, 1.8 µm Al_{0.350.22}Ga_{0.650.78}N (upper 0.9 µmn -doped) graded composition layer, five QW/QB B_x (Al_{0.06}Ga_{0.94})_{1-x} N (3.5 nm)/Al_{0.16}Ga_{0.84}N (10 nm), 30 nm Al_{0.35}Ga_{0.65}N electron blocking layer (top 20 nm p -type doped), 50 nmp -Al_{0.350.00}Ga_{0.651.00}N, and 10 nm p -GaN contact layer. The growth temperature of the active region was 1160°C. Trimethylgallium, trimethylaluminum, triethylboron (TEB), and ammonia were used as the main precursors. The TEB/III ratio for the QW was 1%. Disilane and bis-cyclopentadienyl magnesium were used as the n - and p -type dopants, respectively. A reference LED was also grown, with the exact same structure as above, but with no TEB flowing during QW growth.

After growth, both samples were processed into individual LEDs. First, a surface clean consisting of buffered oxide etchant, HCl:DI 1:1 and 45% KOH at 100°C was carried out to prepare the p-GaN surface for processing. Pd was evaporated as the p-metal, followed by the formation of 100 μ m diameter circular mesas by inductively-coupled plasma etching with a Cl₂-based plasma. Finally, Ti/Al/Ti/Au was evaporated to form the n-metal.

Effects of boron incorporation: Test MQW stacks consisting of B_x (Al_{0.05}Ga_{0.95})_{1-x} N/Al_{0.16}Ga_{0.84}N with different TEB/III ratios were grown by MOCVD, and a transmission electron microscopy (TEM) image revealed the presence of nanopipe-shaped voids in the active region for a low TEB/III ratio (< 1%). This effect has been attributed to boron surface segregation during growth [8]. It is proposed that boron acts as a surfactant, reducing the surface energy of the semipolar and nonpolar planes to below that of polar c-plane. In between the nanopipes, the QWs are undisturbed and show high uniformity. For the sample prepared with a higher TEB/III ratio (3%), the QWs disappear completely due to a high concentration of voids. Hence, for this LED experiment the TEB/III was set to 1%, using a QW growth temperature of 1160°C.



Fig 1 SEM image from FIB cut of BAlGaN LED material. Voids can be seen in the active region of the LED (some of them are highlighted by the red arrows), showing an effect of boron.

Fig 2 Room temperature PL of the LEDs. The BAlGaN LED shows a reduction in intensity compared to the AlGaN reference LED.

Figure 1 shows a scanning electron microscopy (SEM) image of a focused ion beam (FIB) cross-section through the BAlGaN LED. The 'jagged' Pt interface is due to initial e-beam Pt evaporation and surface

roughness. Voids can be seen in the active region of the LED, confirming the same mechanism of boron incorporation as observed in the BAlGaN test MQW sample preparation [8]. The AlGaN reference LED showed no such disturbance of the active region (not shown). These voids could explain the reduced intensity of the BAlGaN LED in the photoluminescence (PL) as seen in Figure 2. For these measurements, a frequencydoubled continuous wave Ar-ion 244 nm laser was used as the excitation source, and measurements were carried out at room temperature. The AlGaN LED MQW emission has a peak at around 344 nm, and there is a slight redshift of 2 nm in the BAlGaN LED. This is likely due to the significant bowing parameter of BGaN and BAlN alloys [5, 6]. The peak at 314 nm is attributed to emission from the buffer layer, while the broad peak centered around 400 nm is due to the p-type region. The PL shows a lower QW peak intensity with the addition of B. It is possible that the area of the active region capable of photoexcitation has been reduced because of these voids; however, more work is required to understand their impact on PL performance.

LED characterization and discussion: Figure 3a shows the IV characteristics of the LEDs. A noticeable increase in operating voltage upon addition of B in the QWs is clear. Inset is the IV on a semi-log scale, in which the BAlGaN LED demonstrates a higher turn on voltage. One possibility is that this phenomenon is due to the voids providing a more restricted path to carriers.

In the electroluminescence (EL) shown in Figure 3b, contrary to the PL, the BAlGaN LED shows an integral intensity almost 4 times higher than that of the AlGaN reference LED. This was consistent over multiple devices.

Fig 3 IV characteristics of the BAlGaN QW LED and AlGaN QW reference LED (a); their EL spectra measured at injection currents of 30 mA; and LI characteristics (c) (Inset shows the relative efficiencies in arbitrary units versus current).

The MQW peak from the BAlGaN LED (350 nm) shows a slight redshift compared the AlGaN LED (347 nm), similar to the PL. The exact reasons for this improvement in performance of the BAlGaN LED under electrical injection are not clear, but improved localization of carriers due to the presence of boron, light scattering from voids, as well as higher current density in the BAlGaN LED are all possible contributing factors. This latter point is worth further discussion: under electrical injection, the voids (assumed to be formed because of segregated BN [8]) likely act as insulating regions, forcing the carriers into the undisturbed areas of the active region. This has the effect of increasing the effective current density in the active region, resulting in an increase in operating voltage compared to the AlGaN reference but also a more favourable ratio between radiative recombination and Shockley-Reed-Hall non-radiative recombination [9], which could explain the higher EL intensity from the BAlGaN LED. This is supported by the LI characteristic in Figure 3c. At lower currents, the BAlGaN LED has a higher intensity, however it then shows an increased droop in output power at significantly lower injection currents than the AlGaN reference LED. This droop is likely due to increased Joule heating in the device. In addition, this droop could be related to non-radiative Auger recombination beginning to dominate with higher current density (C term in the 'ABC ' recombination model proportional ton³) [10].

A relative wall plug efficiency (WPE) of the LEDs is plotted against current in the inset of Figure 3c. While the boron-containing LED has a higher operating voltage, it has a peak efficiency value approximately 3 times higher than that of the AlGaN reference LED. This suggests that the IQE of the LED has been improved with the addition of small amounts of BN, although the potential effects of light scattering on extraction efficiency must be considered.

Conclusion: We report the first demonstration of a UV LED containing BAlGaN QWs. EL shows QW emission at around 350 nm with diode-like IV behaviour. SEM images revealed the presence of voids in the active region of this LED, as seen in previous test MQW samples. While there are other potential effects of these voids, we postulate that they act as insulating regions, forcing the current into the undisturbed areas of the active region. This ultimately increases the current density, resulting in higher EL intensity compared to the AlGaN reference LED for the same drive current. The observed increase in the operating voltage

would also tend to support this theory. LI characteristic shows a drop in output power at lower currents in the BAlGaN LED, however, a relative WPE plot shows that it is around 3 times more efficient, indicating potential beneficial effect of BN in the QWs. Further work is required to better understand the mechanism of these voids in the active region and how to control them with growth conditions. This work demonstrates successful operation of a boron-containing LED, although the question of benefits in terms of mitigating QCSE in III-Nitride based UV LEDs – or even boron incorporation in the undisturbed parts of BAlGaN QWs remains open.

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