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ABSTRACT

Zincblende GaN has the potential to bridge the “green gap” due to the absence of internal electric fields with respect to wurtzite GaN. However, at present, the quality of zincblende GaN light emitting diodes (LEDs) is not yet sufficient for useful efficient green devices. One of the major challenges is the poor spectral purity of the emitted light. A multimicroscopy approach, combining scanning electron microscopy-cathodoluminescence (SEM-CL), scanning transmission electron microscopy (STEM), and scanning electron diffraction (SED), is applied on a single feature to enable cross correlation between techniques and to investigate the possible causes for the broad optical emission of a zincblende GaN LED structure. This investigation demonstrates that SEM-CL on a site-specific TEM cross section prepared by focused ion beam (FIB) microscope can provide access to nanoscale light emission variations that can be directly related to structural differences seen in STEM. We demonstrate that the general large quantum well (QW) emission peak width relates to quantum well thickness and In content fluctuations. Multiple low-energy QW emission peaks are found to be linked with stacking fault bunches that intersect the QWs. Splitting of the QW emission peak is also found to be caused by the formation of wurtzite-phase inclusions associated with twins formed within the zincblende matrix. Our characterization also illustrates the quantum well structure within such wurtzite inclusions and their impact on the optical emission.

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INTRODUCTION

Most of the research effort on III-nitride materials has been devoted to the wurtzite structure, stimulated by the realization and success of blue and violet c-plane light emitting devices. However, for longer-wavelength light emission, c-plane quantum wells (QWs) with higher In content and, therefore, higher strain, produce large in-built electric fields that separate the wavefunctions of electrons and holes, leading to a radiative recombination efficiency that rapidly declines with increasing wavelength. Fortunately, other conventional light emitting diode (LED) systems (based on AlGaInP) also exhibit a very low efficiency in the green-yellow spectral region due to a change from a direct to an indirect bandgap. Overall, the difficulties of achieving high LED efficiencies in this spectral region are often referred to as the “green gap.”

One of the main reasons for the research effort on zincblende GaN LEDs is to close the “green gap.” The optical properties of zincblende GaN are expected to present some advantages over its wurtzite counterparts due to the absence of an in-built electric field along the [001] growth direction. In addition, zincblende structures might offer a new opportunity for the integration of nitride LEDs with conventional GaAs and Si electronic devices. In this work, we focus on the properties of a zincblende GaN LED structure. Therefore, all III-nitrides described here are in the zincblende structure unless explicitly stated otherwise.

Although some optical properties of zincblende GaN have been characterized, such as its optical bandgap (3.30 eV), the emission of zincblende GaN LED has rarely been characterized in correlation with its structure. In this work, the emission properties of a LED heterostructure sample are measured on the nanoscale by...
cathodoluminescence (CL) in a scanning electron microscope (SEM), applied on a focused-ion-beam (FIB)-prepared TEM cross-section specimen, which is later characterized by scanning transmission electron microscopy (STEM). By applying multiple microscopy techniques on the same specimen (multimicroscopy), we are able to utilize the advantages of both the TEM for structural analysis and of SEM-CL for optical analysis, which includes a higher available current, resulting in higher e–h pair generation, as well as a lower acceleration voltage reducing potential beam damage.5–7

**EXPERIMENTAL**

The LED sample was grown in a 6 × 2 in. Thomas Swan close-coupled showerhead MOVPE reactor on a 3C-SiC/Si substrate provided by Anvil Semiconductors Ltd. A schematic of the sample structure is shown in Fig. 1. The LED heterostructure is deposited on a 460 nm Si-doped GaN epilayer (GaN:Si) grown in a H2 environment. Five 3 nm InxGa1−xN QWs separated by 14 nm GaN barriers were grown using N2 as the carrier gas. The growth continued with a 10 nm undoped GaN layer after the last barrier, followed by the growth of 15 nm Mg-doped AlGaN, designed to function as an electron blocking layer (EBL). The whole structure was capped by a 180 nm Mg-doped GaN layer (GaN:Mg). An annealing treatment was performed at the end of the growth process in a N2 atmosphere at 700 °C to activate the Mg dopants. The structure of the investigated sample has been characterized previously in another paper,8 which revealed that stacking faults (SFs) can cause alloy segregation in the QWs and EBL, resulting in local In-rich and Al-rich nanostructures, respectively.

The cross-sectional specimen was prepared in the [-110] zone using the standard FIB (FEI Helios NanoLab™) preparation technique for STEM samples, closely following the manufacturer’s guidelines. In brief, samples were initially protected with a Pt coating and prepared using a FIB employing standard in situ lift-out methods and adhered to a three post-lift-out Cu grid via Pt deposition. Sequential FIB cleaning milling at an acceleration voltage of 30 kV was used to mill down to a ~100 nm thick lamella, followed by a 5 kV treatment to reduce ion damage. The final specimen thickness is 95 nm – 120 nm, based on a STEM electron energy loss spectroscopy measurement. A FEI Tecnai Osiris, operating at 200 kV, with a beam current of 80 pA and a high angle annular dark field (HAADF) collection semi-angle range of 65 mrad – 200 mrad was used for the structural analysis. Compositional characterization of this sample was done using a SuperX EDS system. Scanning electron diffraction (SED) was conducted using an FEI F20 with a Nanomegas DigiSTAR diffraction system running at 200 kV and processed using Pyxem.9 Crystal phase mapping was determined using a pattern matching indexation algorithm, and a defective material was determined by the reliability of phase identification.

The CL measurements were performed on the FIB lamella specimen using an Allalin 4027 Chronos SEM-CL system with a 150 l/mm grating (blazed at 500 nm), a 1024px CCD detector and a Horiba IHR 320 spectrometer with a focal length of 319.76 mm. The excitation energy was 5 kV, the beam current was 10 nA, and the acquisition time was 20 ms. The slit width was optimized to minimize acquisition time while maintaining a spectral resolution of 2 nm. A helium cryostat is used to maintain the temperature of the sample, during all CL measurements, at 10 K. Monte Carlo Casino software10 was used to estimate the interaction volume of the incident e-beam. Considering only the GaN matrix, the incident electrons lose 90% of their energy in the first 100 nm, meaning that the electron interaction volume is mostly contained within the FIB lamella.

**RESULTS AND DISCUSSION**

**SEM-CL characterization**

To examine the CL emission properties, a cross-section secondary electron (SE) image and a CL hyperspectral map of the lamella specimen were taken concurrently and are shown in Fig. 2. For this purpose, the specimen was rotated by 90°, so that it is examined with the fast scan direction across the individual layers of the GaN LED heterostructure. An electrical charge accumulated within the specimen which caused sample drift during the measurement. This drift is reflected in the appearance of the SiC/GaN interface, which appears to meander despite the fact it is almost atomically flat (see Fig. 3) and hence expected to be observed as a straight line without any drift.

Figure 2(a) shows the SE image of the investigated lamella specimen. The various layers of the LED structure are marked by blue and red lines in the images. The identification of the layers was done utilizing both the optical response from the samples as

![FIG. 1. A schematic diagram of the sample structure.](image-url)
well as STEM images, which will be discussed later in the Nanoscale characterization section. The multiple quantum well (MQW) stack is marked by the two red dashed lines labeled in Fig. 2(a). The panchromatic CL image, shown in Fig. 2(b), reveals that most of the CL luminescence originates from the GaN:Si and the MQW layers with minimal luminescence originating from the GaN:Mg layer. We identified several possibilities for the strong reduction in intensity from the Mg doped layer. The main explanation is likely to be the lower optical quality of the Mg doped layers, as Mg doped GaN layers are known to be associated with an increased incorporation of point defects in the hexagonal crystal system.\(^1\)\(^1\) Additionally, we acknowledge that other effects may contribute to the problem, such as surface damage by the FIB preparation and carrier depletion by the Pt protective layer. However, we note that in SEM-CL on the FIB lamella, we are able to image bright and consistent luminescence from the QWs which are the main focus of this study.

The mean CL spectrum of the lamella specimen in Fig. 2(c) shows two peaks at 3.27 eV and 2.71 eV, respectively. The emission peak at 3.27 eV correlates well with the free exciton (X) peak in 2b-GaN measured at low temperature by other groups.\(^1\)\(^2\)\(^-\)\(^1\)\(^6\) Notably, although the first GaN epilayer is Si doped, we cannot observe a clear DAP peak in the mean spectra. This indicates that a lower density of the unintentional acceptor and thus, a different impurity incorporation is present in our sample when compared to the samples reported in Refs. 17 and 18. The peak at 2.71 eV in the mean spectra is caused by luminescence from the In\(_x\)Ga\(_{1-x}\)N MQW.

Spatially averaged spectra are used to examine the emission of the sample at different positions of the heterostructure. Figure 3 shows such representative CL spectra taken from 4 × 126 pixel (about 37 × 1162 nm\(^2\)) areas near the SiC/GaN interface (a), in the GaN just below the In\(_x\)Ga\(_{1-x}\)N/GaN MQWs (i.e., the GaN grown just prior to the first In\(_x\)Ga\(_{1-x}\)N QW) (b), and at the In\(_x\)Ga\(_{1-x}\)N MQW layers (c).

Comparing the spectra taken near the SiC/GaN and the GaN/In\(_x\)Ga\(_{1-x}\)N interfaces in Figs. 3(a) and 3(b), we find significant differences in the optical properties. While in both spectra, the excitonic emission lines are the dominant feature of the spectra, the spectrum taken at the SiC/GaN interface shows a significant shoulder on the higher energy side, emitting at 3.37 eV. We attribute this peak to a high density of crystal defects close to the interface, with both wurtzite inclusions and closely spaced \{111\}-type SFs\(^1\)\(^9\) being possible candidates for emission energies above 3.30 eV. Previous research has shown that the SF density in cubic GaN is strongly reduced with increasing sample thickness due to reaction and annihilation of SFs on different inclined \{111\} planes of a tetrahedron.\(^2\)\(^0\)\(^-\)\(^2\)\(^1\) We find that the same happens in our sample (see Nanoscale characterization section), explaining the strong improvement in the optical quality of the GaN:Si layer along the growth direction evident by the reduced linewidth in line spectra (see in the supplementary material). The high energy shoulder in Fig. 3(a) is, therefore, most likely due to closely spaced SFs.

In Fig. 3(c), the averaged luminescence from the In\(_x\)Ga\(_{1-x}\)N MQW displays a large FWHM (~280 meV), indicating inhomogeneities in the local QW properties. In order to have a more detailed analysis of the spatial variation, Gaussian fits were applied to the hyperspectral map. This allows us to treat the near band edge (NBE) and the MQW emission separately by fitting the spectra at each point of the map with two Gaussian functions centered around 3.27 eV and 2.71 eV, respectively, after removing the constant background generated by thermal noise. The Gaussian fits are
applied to the first 600 nm of the LED structure, covering the GaN:Si layer and the active MQW region, but very little of the GaN:Mg layers as the emission from the GaN:Mg layers is too weak. It is worth noting that a single Gaussian fit fails to accurately describe the luminescence behavior at locations with more than two emission peaks (i.e., multiple peak). We, nonetheless, utilized a single peak to describe the QW behavior as the double peak is highly localized and using two Gaussians to describe the QW behavior for the whole sample would lead to overfitting. Nevertheless, they provide a useful overview of the variations in GaN NBE and MQW emission energies. Figure 4 demonstrates the fitting results and a spectrum of the selected area, where a single Gaussian does not fully describe the complex MQW behavior. Figures 4(a) and 4(b) show the variations in the emission energies of the GaN NBE peak and the QW emission peak, respectively. The maps are masked in areas where the fitted peak emission intensities are below 6% of the maximum. The masked areas appear as solid white in the figure. The red dashed lines are used to indicate the position of the MQW layer.

From the fitted emission energy map of Fig. 4(a), the GaN NBE exhibits a slight red shift as the distance from the SiC/GaN interface increases from left to right. The change is consistent with...
the difference observed between the local emission spectra in Figs. 3(a) and 3(b), which results from the reduction of SF density and its accompanied peak narrowing effect.

A relatively large variation in emission energies is observed for QW emission in Fig. 4(b), which we attribute mainly to changes in QW thickness and \( \text{In}_x \text{Ga}_{1-x} \text{N} \) alloy fluctuation. The QW emission recorded outside of the marked MQW region is a result of excited carriers diffusing into the MQWs in addition to the ca. 100 nm wide interaction volume of the electron probe. Figure 4(c) shows the spectrum of a strongly red-shifted signal from a region highlighted by the black box region in Fig. 4(b). The red shift in the QW emission energy is caused by sharp peaks that decorate the low-energy flank, marked by the red box. These sharp peaks can be produced by local In enrichment, which was observed as a result of SF induced alloy segregation in this sample.\(^8\) Additionally, bunches of SFs could potentially lead to the formation of wurtzite-like inclusions in the QWs for which the resulting quantum confined Stark effect would also lower the emission energies.\(^{22}\)

**Nanoscale characterization**

For the plan-view CL measurements (paper in preparation), QW emission peak splitting has been observed regularly over distances of a few hundred nanometers, where a single QW emission peak becomes two separate peaks. To study the In\(_x\)Ga\(_{1-x}\)N QW emission peak splitting found locally in the plan-view measurements, a multimicroscopy experiment combining STEM and CL, focusing on such a feature, is taken on the FIB lamella specimen. The result is demonstrated in Fig. 5. This experiment also demonstrates the possibility to obtain a clear SEM-CL signal from a specimen prepared for the STEM purpose, a result that was also recently achieved by Dimkou *et al.* by studying optically active atom probe tips.\(^{23}\)

Figure 5(a) shows a cross-sectional STEM image, with a CL image of the same area inset, with both datasets reoriented to a direction where [001] is pointing upward. The positions of features on the two images have been correlated by noting that at the location labeled A, the CL image reveals an approximately 200 nm step in the QW structure. This protrusion in the QW CL is associated with a similar excursion in the bright lines associated with QWs in the STEM image. Both the region labeled A and an adjacent region labeled B in the figure will be discussed here in more detail. Region A is the structural anomaly, and the STEM data show that the QWs were grown on steeply inclined facets. Region B represents a reference region, in which QWs were grown on a surface that is relatively flat and parallel to the (001) plane with only a few SFs intersecting the QWs. Structures similar to feature A have been found in multiple lamella specimens. The CL spectra obtained at region A and region B are presented in Figs. 5(b) and 5(c), respectively. The spectrum of reference region B shows two emission peaks at 2.78 eV and 3.26 eV, which are the QW emission peak and the GaN NBE peak, respectively. In comparison, the CL spectrum of region A exhibits two distinct QW-related emission peaks at around 2.59 and 2.85 eV, while the GaN NBE peak is absent from its spectrum.
In order to examine the structural properties, SED measurements were taken, and a phase analysis was performed. The phase analysis around region $A$ is shown in Fig. 6 while the phase analysis for region $B$ showed that it is zincblende GaN with a high phase purity (see Fig. S3 in the supplementary material). In the virtual bright field image in Fig. 6, a boundary between region $A$ and the surrounding matrix is visible as a curvy line of dark contrast. The nanobeam electron diffraction patterns, on the right of the figure, were taken at several locations at and around the feature. The diffraction pattern of area 1 shows a pattern characteristic of zinc-blende GaN in the $\langle -110 \rangle$ zone and with $\langle 001 \rangle$ growth orientation. The absence of any diffuse striation in the diffraction pattern along the $\langle 111 \rangle$ directions indicates that this region of the specimen is free from $\langle 111 \rangle$-type SFs. The electron diffraction pattern taken from the lower part of region $A$ (area 2) shows a typical pattern of the wurtzite GaN phase in the $[1\overline{1}0\overline{2}]$ zone, revealing that region $A$ is a wurtzite inclusion in the surrounding zincblende film. The diffraction patterns from area 3 taken at ca. 130 nm below region $A$ reveal a highly defective area, showing the typical streaky patterns caused by SFs in the zincblende matrix. The electron diffraction pattern of the boundary region surrounding region $A$ (area 4) leads to a combination of the diffraction patterns of both phases, with the $[0001]_{wz}$ of wurtzite GaN and the $[001]_{zb}$ of zincblende GaN misoriented by about $16^\circ$, which reveals the orientational relationship between the wurtzite inclusion and the matrix.

The higher-magnification STEM image in Fig. 7(a) reveals the detailed structure of region $A$. The QWs in feature $A$ exhibit mirror symmetry around its $[0001]_{wz}$ growth direction (marked by the purple arrow), which is $15.9^\circ$ inclined to the $[001]_{zb}$ axis of the surrounding zincblende material. The QWs are tilted at an angle of about $25^\circ$ to $[0001]_{wz}$, sitting approximately on the $\langle -1011 \rangle$ and $\langle 1011 \rangle$ planes of the wurtzite inclusion. In feature $A$, certain facets appear to have grown faster than others, which leads to pronounced $\langle 10\overline{1}\overline{1} \rangle$ planes on which the QWs (referred to as $\langle 10\overline{1}\overline{1} \rangle$ QWs below) and the EBL have formed. $\langle 10\overline{1}\overline{1} \rangle$ planes are well-known stable low index facets in wurtzite GaN and are often found as the facets of V-pits in (0001) surfaces or are sometimes used as the surface plane for the growth of semi-polar LEDs. The apex of each pair of $\langle 10\overline{1}\overline{1} \rangle$ QWs (referred to as apex QWs below) and the $\langle 10\overline{1}\overline{1} \rangle$ EBL pair exhibits a very small region of the c-plane growth. Several SFs, shown as dark line contrast, can also be observed below the onset of feature $A$ and are highlighted in a red circle.

The formation of such a feature can be explained when assuming the following consecutive steps:

1. A group of SF bunches causes the formation of a crystal twin embedded within the zincblende film. This crystal twin is...
formed by reversing the stacking order of the {111} bilayers from –AaBbCc– to –CcBbAa–, as illustrated in Fig. 6(b). The twin boundaries (111)_zb || (111)_twin highlighted in red lines show where the stacking changes compared to the surrounding material.

(2) The upper (−1−11)_twin facet of the twin forms an interface 15.9° away from the (001)_zb of the zincblende matrix.

(3) A wurtzite inclusion with the (−1−11)_twin || (0001)_wz interface (green line) is then formed on the upper (−1−11)_twin facet of the twin. From Fig. 6(a), it appears that once the wurtzite inclusion has formed, it forms boundaries such as (−1−11)_zb, (111)_zb, (112)_zb, and (−4−41)_zb, with the surrounding zincblende matrix.

It is worth noting that due to the lower formation energy of the wurtzite phase compared to the zincblende phase, the onset of the wurtzite GaN growth can be very easy so that any zincblende crystal twin, which initiates wurtzite growth might be only a few atomic layers thick. The diffraction pattern of a zincblende crystal twin is thus not observed perhaps due to the relatively small size of the relevant region or a projection effect of the twin in the lamella. The inset of Fig. 7(a) shows the same STEM image overlayed by colors, indicating the positions of different regions involved in the formation process of feature A.

Wurtzite GaN has a higher bandgap than zincblende GaN by about 210 meV. The emission of [10−11] QWs is thus expected to have slightly higher energy than the emission of the surrounding zincblende QWs. From Fig. 7(a), carriers within the [10−11] QWs are seen to be confined in a thinner region (~1 nm) than normal zincblende QWs, which may also lead to high emission energy due to a stronger quantum confinement effect. Compositional analysis provides another perspective to the high-energy emission from the [10−11] QWs. Figure 8 shows an energy dispersive x-ray spectroscopy (EDS) map of In around feature A. The In_xGa_{1−x}N MQWs in the wurtzite inclusion are observed to have a lower In content than those in the zincblende matrix. (However, we note that since the wurtzite QWs are thinner, the EDS signal may have led to an underestimation of their composition due to beam spreading effects.) Therefore, the 2.85 eV high-energy MQW emission present in the CL spectra in Fig. 5(b) is attributed to the [10−11] QW emission.

However, the apex QWs, grown on the polar (0001) c-plane of the wurtzite inclusion, exhibit a higher In incorporation than the QW parts on the {10−11} facets in Fig. 8. These apex QWs are expected to have a lower bandgap than the [10−11] QWs due to a slightly higher In content. Carriers within [10−11] QWs can thus easily diffuse to and get trapped inside these apexes, leading to a strong emission from the apex QWs, despite their relatively small sizes. Additionally, the apex QWs have a relatively large thickness [3 nm – 4 nm as shown in Fig. 7(a)], which reduces the blue shift arising due to energy quantization. Furthermore, both the polar orientation and the increased thickness will lead to an increased red-shift due to the QCSE in this region. All these effects (higher composition, higher thickness, and increased QCSE) will result in lower emission energy, compared to the emission of the adjacent semi-polar [10−11] QWs. The low-energy 2.59 eV peak observed by SEM CL is hence attributed to the emission of the apex QWs.
Further study outside the scope of this paper will be undertaken to investigate the In content and the strain state to model the band structure of feature A.

CONCLUSIONS
In this work, we demonstrate that the emission of a FIB lamella specimen of a research zincblende GaN LED sample can be characterized by SEM-CL. The CL emission wavelengths from the GaN:Si layer and In\(_x\)Ga\(_{1-x}\)N MQW layer are at 3.27 eV and 2.71 eV, respectively. The QW emission is not homogeneous throughout the sample. Low-energy QW emission peaks can be produced by stacking faults intersecting with QWs. Correlated STEM and SED experiments also reveal that QW emission peak splitting is produced by small wurtzite inclusions, which can be formed from crystal twins. The \(10\{\overline{1}1\}\) QWs and the apex QWs within wurtzite inclusions are the origins of the high and low-energy emission peaks, respectively.

SUPPLEMENTARY MATERIAL
See the supplementary material for the CL line spectra along the growth direction across the GaN:Si layer and the MQW layer.

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DATA AVAILABILITY
The data that support the findings of this study are openly available in the University of Cambridge repository at https://doi.org/10.17863/CAM.69599.

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