Investigation on the origin of luminescence quenching in N-polar (In,Ga)N multiple quantum wells

Caroline Chèze
TopGaN sp. z.o.o., al. Prymasa Tysiąclecia 98, 01-424 Warszawa, Poland

Marcin Siekacz
TopGaN sp. z.o.o., al. Prymasa Tysiąclecia 98, 01-424 Warszawa, Poland and Institute of High Pressure Physics, Polish Academy of Sciences, ul. Sokolowska 29/37, 01-142 Warszawa, Poland

Grzegorz Muzioł and Henryk Turski
Institute of High Pressure Physics, Polish Academy of Sciences, ul. Sokolowska 29/37, 01-142 Warszawa, Poland

Szymon Grzanka
TopGaN sp. z.o.o., al. Prymasa Tysiąclecia 98, 01-424 Warszawa, Poland

Marcin Kryško and Jan L. Weyher
Institute of High Pressure Physics, Polish Academy of Sciences, ul. Sokolowska 29/37, 01-142 Warszawa, Poland

Michał Boćkowski
TopGaN sp. z.o.o., al. Prymasa Tysiąclecia 98, 01-424 Warszawa, Poland and Institute of High Pressure Physics, Polish Academy of Sciences, ul. Sokolowska 29/37, 01-142 Warszawa, Poland

Christian Hauswald, Jonas Lähnemann, and Oliver Brandt
Paul-Drude-Institut für Festkörperelektronik, Hausvogteiplatz 5–7, 10117 Berlin, Germany

Martin Albrecht
Leibniz-Institut für Kristallzüchtung, Max-Born-Strasse 2, 12489 Berlin, Germany

Czesław Skierbiszewski
TopGaN sp. z.o.o., al. Prymasa Tysiąclecia 98, 01-424 Warszawa, Poland and Institute of High Pressure Physics, Polish Academy of Sciences, ul. Sokolowska 29/37, 01-142 Warszawa, Poland

(Received 21 November 2012; accepted 10 April 2013; published 29 April 2013)

The growth of N-polar (In,Ga)N structures by plasma-assisted molecular beam epitaxy is studied. (In,Ga)N multiple quantum well samples with atomically smooth surface were grown and their good structural quality was confirmed by x-ray diffraction, scanning transmission electron microscopy, and defect selective etching. The In incorporation was higher in the N-polar than in the Ga-polar oriented crystal, consistent with previous reports. However, despite the good morphological and structural properties of these samples, no photoluminescence signal from the (In,Ga)N wells was detected. In contrast, a thick N-polar (In,Ga)N layer exhibited a broad peak at 620 nm in good agreement with the In content determined by x-ray diffraction. The potential source of the luminescence quenching in the N-polar (In,Ga)N multiple quantum wells is discussed and attributed either to a strong nonradiative recombination channel at the surface promoted by the electric field or to the high concentration of point defects at the interfaces of the quantum well structures. © 2013 American Vacuum Society.

I. INTRODUCTION

Nitrogen-polar (N-polar) group III-nitrides spontaneously form during molecular beam epitaxy (MBE) on bare (0001)-sapphire or C-face SiC substrates. However, the N-polar [0001] orientation was rather disregarded for device prospects. This mainly lies in the fact that compared to the metal-polar [0001] direction, growth along the N-polar [0001] direction usually yields poorer surface morphology and p-type doping, and higher sensitivity toward impurity incorporation. Yet, N-polar nitrides have redrawn an increasing interest thanks to recent breakthroughs in the field of transistors and green emitters. More precisely, N-polar green light emitting diodes grown by MBE have also been demonstrated and this result has been made possible by two beneficial effects of the N-polarity. The first one is related to the more efficient In incorporation during growth of (In,Ga)N along the N-polar direction thanks to the higher thermal dissociation limit of N-polar InN. The second effect is the reversed direction of the spontaneous and piezoelectric polarization fields in N-polar compared to that of Ga-polar III-nitrides, which should yield better device performance. Still, a much poorer photoluminescence (PL) was reported for N-polar multiple quantum wells (MQWs) grown by metal organic chemical vapor deposition (MOCVD) compared to Ga-polar ones. Concerning MBE growth, no direct comparison on the PL of (In,Ga)N MQW structures of both polarities is available. Therefore, the quenching of the
PL of N-polar MQWs compared to Ga-polar ones is an important question that needs to be clarified for further optical device development.

In this work, we study the growth and properties of (In,Ga)N layers and MQWs on N-polar GaN by plasma-assisted MBE (PAMBE). We have grown an (In,Ga)N layer and MQW samples in the metal-rich regime on free-standing substrates from Saint-Gobain polished on the N-polar side. During some of these experiments, Ga-polar GaN substrates were also mounted as reference to allow for a direct comparison. The growth under metal-excess yielded atomically smooth surfaces for the N-polar MQW structures. Nevertheless, a PL signal could be measured only from a thick N-polar (In,Ga)N layer, and not from the N-polar (In,Ga)N MQWs. We discuss several effects which could be responsible for the luminescence quenching in our (In,Ga)N heterostructures. These effects are as follows: First a high density of dislocations acting as nonradiative recombination centers, second a higher O incorporation, third the formation of a surface depletion layer induced by the electric fields, and fourth the presence of a high concentration of point defects at the well interfaces. Finally, we conclude that the last two effects are most likely causing the luminescence quenching of our N-polar MQW structures.

II. EXPERIMENT

All the samples were grown by PAMBE in a custom-designed V90 VG Semicon MBE system under In-rich conditions on N-polar c(0001) and Ga-polar c(0001) substrates, which were mounted with indium onto a 2 in. GaN/sapphire template. The N-polar and the Ga-polar substrates were produced by hydride vapor phase epitaxy (HVPE, St Gobain), except for the Ga-polar substrate of the first experiment (A), which was produced by high nitrogen pressure solution (HNPS) synthesis (Institute of High Pressure Physics PAS). The Ga- and N-polar HVPE substrates had comparable dislocation densities ranging from 10^7 to 10^8/cm^2 while the HNPS substrate had 10^5 dislocations/cm^2. Before growth, the N-polar substrates were cleaned in successive lukewarm piranha solution and HF. The N- and Ga-polar substrates were outgassed for 60 min at 650°C. The Ga-flux (see Table I) was set to 0.34 μmol/h and the QWs were formed by adjusting the Ga-flux (see Table I). The surface morphologies were investigated by atomic force microscopy (AFM) in tapping mode and the root mean square (rms) roughness of these samples was measured over an area of 5 × 5 μm^2. The sample composition and thicknesses were determined by x-ray diffraction (XRD) assuming fully strained structures, unless specified otherwise, and compared with PL measured at room temperature. Cathodoluminescence (CL) was also carried out at room temperature on sample D. Finally, defect selective etching (DSE) and scanning transmission electron microscopy (STEM) studies were performed to assess the structural quality of the samples. To this aim, cross-sectional TEM specimens were prepared by mechanical tripod polishing followed by Ar⁺ milling down to electron transparency.

Table I. Growth parameters of the (In,Ga)N structures and In content x in the MQW structures determined by XRD simulations. The values in parenthesis correspond to the In content estimated from the PL results as described in Ref. 10.

<table>
<thead>
<tr>
<th>Sets</th>
<th>N-rate QWs (μmol/h)</th>
<th>N-rate QBs/layer (μmol/h)</th>
<th>Ga-rate QWs (μmol/h)</th>
<th>Ga-rate QBs/layer (μmol/h)</th>
<th>x N-face QWs (%)</th>
<th>x N-face QBs/layer (%)</th>
<th>x Ga-face QWs (%)</th>
<th>x Ga-face QBs/layer (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.82</td>
<td>0.33</td>
<td>0.61</td>
<td>&lt;0.33</td>
<td>23.0</td>
<td>0.5/0.2</td>
<td>13.2 (16.4)</td>
<td>0.6/0.6</td>
</tr>
<tr>
<td>B</td>
<td>0.34</td>
<td>0.34</td>
<td>0.27</td>
<td>0.33</td>
<td>17.0</td>
<td>0.8/1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.34</td>
<td>0.34</td>
<td>0.28</td>
<td>0.33</td>
<td>16.0</td>
<td>0.2/0.3</td>
<td>9.2 (11.0)</td>
<td>1.5/2.0</td>
</tr>
<tr>
<td>D</td>
<td>—</td>
<td>0.34</td>
<td>—</td>
<td>0.13</td>
<td></td>
<td>34–40</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

FIG. 1. (Color online) Details of the different sets of N- and Ga-polar structures grown by PAMBE.
Conventional STEM observations were performed on an aberration corrected FEI TITAN 80-300 electron microscope operated at 300 keV.

III. RESULTS

The experimental results presented in the following are divided into three subsections. In the first subsection, we assess the structural and optical properties of the N-polar (In,Ga)N MQW samples. We show that despite their good crystalline and interface quality, the N-polar (In,Ga)N MQWs do not emit light. The second subsection deals with an N-polar (In,Ga)N layer that does exhibit a characteristic PL peak. In the last subsection, we examine and discuss the origins of the luminescence quenching in the N-polar (In,Ga)N MQW samples.

A. N-polar (In,Ga)N MQWs

1. Morphology of the samples

The surface of all the MQW samples, N- or Ga-polar, was atomically smooth, and single atomic steps were resolved. Their rms roughness was lower than 1 nm, the highest value being 0.84 nm, which was obtained for the N-polar sample from set B. Figure 2 presents the AFM measurements of the N-polar MQW samples from the sets A, B, and C after lukewarm piranha cleaning in order to remove the excess metal. Threading dislocations (TD) in Fig. 2(b) and other defects pinning the steps [inset in Fig. 2(b)] were as dense as $1 \times 10^{5}$/cm$^2$ for the N-polar sample of set B. Particularly for the N-polar sample from set C, we have also observed hexagonal defects [inset in Fig. 2(c)], the sides of which were rotated by 30° to 1010. However, the defect density directly resolved by AFM after growth was still in agreement with the nominal density of the substrates. In addition, the step-flow morphology evidenced the high quality of the growth.

2. X-ray diffraction

Complementary XRD measurements confirmed the good structural quality of the growth of sets A, B, and C. Figure 3 presents the XRD measurements for the samples from set C. We stress that we observed satellite peaks for all the MQW samples. These measurements clearly revealed a higher In content in the N-polar (In,Ga)N QWs than in the Ga-polar ones. The N-polar samples from sets B and C had very similar content. Also, it seemed that the trend was reversed for the QBs and layers (see Table I). However note that the uncertainty in the estimation of the In content was at least 1%; therefore, the In content in the QBs and layers is found to be equivalent for samples of both polarities belonging to the same set.

3. Photoluminescence

Figure 4 presents the room temperature photoluminescence spectra from the N-polar MQW samples. Figure 4(a) compares the intensity of the samples from set C. For the N- and Ga-polar samples, a peak at 367 nm was observed with comparable intensity. This peak was red-shifted by about 4 nm compared to the GaN near band-edge (NBE) emission at 363 nm and could be possibly attributed to the (In,Ga)N layers with an In content of about 1% or less, superimposed
onto the GaN NBE peak from the substrate. The spectrum of the Ga-polar sample was dominated by a strong and well defined peak at 422 nm characteristic for (In,Ga)N wells with 11% In, according to our calculations \(^1\) and in good agreement with the XRD results (see Table I). In contrast, we could not observe any signal from the N-polar (In,Ga)N QWs despite their apparent good structural quality confirmed by AFM and XRD \([\text{Fig. 3(a)}]\). Moreover, the luminescence of all the N-polar samples was even lower than the one of the bare substrate before growth \([\text{Fig. 4(b)}]\), evidencing strong absorption of the epitaxial structures. Besides the luminescence quenching, the only signal for the growth on N-polar samples was a faint shoulder at about 445 nm attributed to a defect peak that we have often observed for growth on Saint-Gobain substrates.\(^1\) For an In content of 16–23% in 3 nm thick N-polar QWs, one would expect a luminescence peak in the range of 440–500 nm. Thus, this peak could have been overlapped or masked by the observed 445 nm peak or the shorter wavelength side of the wide yellow luminescence (YL) band. However, no studies have been carried out so far on the effect of the N-flux on the homogeneity of the In content in N-polar (In,Ga)N, which may not be the same as for Ga-polar (In,Ga)N. This issue would require further investigation.

4. Scanning transmission electron microscopy and defect selective etching

As it has been established for Ga-polar GaN that a strong quenching of the luminescence occurs for threading dislocation densities above \(10^{10}/\text{cm}^2\),\(^1\) we wanted to have a more precise estimation of the dislocation density in our N-polar samples to exclude this effect. Therefore, we have carried out STEM and DSE studies on our samples. STEM micrographs of the N-polar sample from set A, displayed in \(\text{Fig. 5}\), confirm the nominal and XRD measured layer sequence. Furthermore, quite sharp interfaces are evidenced, and neither dislocations nor stacking faults could be found over an area of 3 \(\mu\text{m}^2\). This result corresponds to a local dislocation density lower than \(3.4 \times 10^7/\text{cm}^2\). It thus demonstrates the suitability of the growth conditions to achieve MQWs with good microstructural quality. In agreement with this result, DSE revealed the formation of hexagonal pits associated with dislocations with density of \(2 \times 10^7/\text{cm}^2\) for the same sample \([\text{Fig. 6(a)}]\). The depths of these pits matched the depths of different heterostructure interfaces \([\text{Fig. 6(b)}]\), i.e., at the interface between the GaN and the (In,Ga)N buffer layers, during the break in the buffer layer, and at the interface between the buffer layer and the first QW. The etch pit densities of the N-polar samples from sets B and C were about \(5 \times 10^7/\text{cm}^2\). Depending on the area observed, we estimated that the uncertainty of these values is not higher than a factor 2, and therefore, these defect densities are found in agreement with the nominal defect densities of the substrates and with the one observed directly after growth by AFM.
Nevertheless, the different pit depths measured after etching revealed that defects were also introduced by the interfaces during growth. However, we estimated an uppermost dislocation density of $1 \times 10^{8}/cm^2$ in these samples, that is comparable to the one in Ga-polar samples.

B. N-polar (In,Ga)N layer

Finally, we have grown an N-polar (In,Ga)N layer in the metal-rich regime. Figure 7(a) is an AFM scan of this nominally 150 nm thick layer from set D (Table I), with In content ranging from 34% to 40% as determined by XRD. The surface of this sample was completely covered by hexagonal hillocks and the rms value was 6.03 nm. The reciprocal space map (rsm) depicted in Fig. 7(b) indicates that in fact this layer was relaxed to a degree of 46–78%. The simulation of the 2-Theta/Omega scan presented in Fig. 7(c) was made assuming parameters for the layer taken from the peak maximum of the rsm corresponding to 35.8% In and a relaxation of 59.7%. Nevertheless, despite its very poor structural quality, this layer showed a broad luminescence peak at 620 nm with full width at half maximum of 78 nm [Fig. 7(d)]. This emission corresponds to an In content of about 39% (Ref. 14), which agrees well with the XRD data. Importantly, for this layer, we did not observe any peak related to the NBE of the GaN substrate, further indicating that the emission at 620 nm really stemmed from the (In,Ga)N layer. The observation of luminescence from this layer may be related to carrier localization attributed to strong inhomogeneities in the In content. In fact, preliminary cathodoluminescence measurements (Fig. 8) indicated granular luminescence with very inhomogeneous wavelength in agreement with the very broad linewidth of the PL. The hillock border exhibited a shorter wavelength than their center. This result is possibly related to the differences in the In content or relaxation state. Based on these results, we now discuss the possible causes of the absence of luminescence in the N-polar (In,Ga)N MQWs.

C. Discussion: Why is the N-polar MQW luminescence quenched?

The problem of the poor PL intensity in N-polar (In,Ga)N MQW structures compared to Ga-polar ones has already
been reported for (In,Ga)N-GaN heterostructures grown by MOCVD and was attributed to a higher TD density and impurity or defect concentrations. Mainly four different effects may be at the origin of luminescence quenching. The first one is a high dislocation density acting as nonradiative recombination channel. However, we found that the structural quality of our N-polar MQW structures is as good as the one of Ga-polar MQW structures. Thus, if we assume that the diffusion length of the carriers in the (In,Ga)N QWs is the same for both polarities, the quenching of the PL by threading dislocations in our N-polar MQW structures should still be moderate. Therefore, we think that the observed quenching cannot be attributed solely to dislocations. Second, a higher impurity level, namely O and C, in N-polar compared to Ga-polar GaN grown by MBE has also been reported. Indeed, secondary ion mass spectrometry revealed an O level in the N-polar sample from set A in the order of $10^{18}$ at/cm$^3$, which was at least an order of magnitude higher than in the Ga-polar sample from the same set. This value is high, but still comparable to data available in the literature. Moreover, O is a shallow donor and should lead to an increase of the intensity of the bound exciton line. Only paired with point defects like Ga vacancies, O donors could give rise to strong YL in GaN. Concerning the C level in our samples, we have no data available. Nevertheless, C is amphoteric and its dominant behavior as acceptor in GaN may be self-compensated. In addition, the thick (In,Ga)N layer grown at the same temperature and about half the rate of the MQWs should contain even more impurities. However, the characteristic (In,Ga)N PL is not quenched for this layer. Yet, as the volume contributing to radiative recombination is much bigger for layers than for MQWs, one cannot unambiguously conclude on this effect. The third source of luminescence quenching may be the formation of a surface depletion layer caused by the electric field. In N-polar GaN, the polarization field is directed from the substrate toward the surface and leads to the gathering of free carriers at the surface. Thus, the probability of radiative recombination may be reduced by the capture of carriers by surface defects or adsorbates. Note, however, that the difference in the cap layer thickness of the N-polar samples from sets A, B, and C may be too small compared to the depletion layer thickness to limit this effect since the upper limit for the carrier diffusion length in GaN and (In,Ga)N is about 200 nm. In addition, the formation of a p-type cap on top of the structure in the N-polar sample of set C would further increase this trend since, in this case, the built-in electric field has the same direction as the polarization field. At this point, it would be also pertinent to consider the surface band bending for N-polar GaN, but the data available are rather scattered and strongly depend on sample preparation and processing. However, we cannot discriminate this effect from the fourth one which is the presence of high concentrations of point defects at the MQW interfaces, likely related to N-vacancy defects. Indeed, the volume concentration of such traps in n-type N-polar GaN grown by MBE was found to be as high as $2 \times 10^{14}$/cm$^3$, and was one order of magnitude higher than in equivalent Ga-polar samples. This high concentration of traps is most probably present in both our N-polar (In,Ga)N layer and MQWs. However, the successive changes in the III:V ratio applied during the MQW growth may modulate their concentration level. They may particularly gather at the interfaces of the heterostructures and efficiently reduce the radiative recombination.

IV. SUMMARY

In conclusion, we have grown atomically smooth N-polar (In,Ga)N MQWs and an N-polar (In,Ga)N layer by PAMBE. The layer shows a clear (In,Ga)N related peak at 620 nm while the (In,Ga)N MQWs of high structural quality do not emit luminescence. While the effect of a higher impurity level present in N-polar samples compared to the Ga-polar ones cannot be disregarded, the formation of a surface depletion layer induced by the electric fields, or the presence of a high concentration of point defects at the heterostructural interfaces is considered as the most likely origin of the quenched MQW PL.

ACKNOWLEDGMENTS

The authors are thankful to A. Feduniewicz-Zmuda and B. Grzywacz for their help in sample preparation, to G. Cywinski for discussion, and to T. Remmele and J. Smalc-Koziorowska for their help in STEM experiment preparation. This work was supported partially by the Polish Ministry of Science and Higher Education Grant No. IT 13426 and the European Union within European Regional Development Fund, through Grant Innovative Economy (POIG.01.01.02-00-008/08) and within FP7-PEOPLE-IAPP-2008 through Grant SINOPLE 230765.

11. S. Grzanka, private communication (10 February 2012).