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Heteroepitaxial GaN films in general have very high concentration of defects and at the same time show broad photoluminescence (PL) peaks at energies below the band-gap energy (3.4 eV), i.e., the so-called yellow (YL) and blue luminescence (BL) centered at 2.2 and 2.9 eV, respectively. The origin of these PL peaks is commonly attributed to defects. The present paper studies the relationship of the yellow and blue luminescence with the defect structure by a combination of photoetching and photoluminescence. Nominally undoped (n-type) GaN layers were grown by metal organic chemical vapor deposition (MOCVD). By photoetching the perfect material between defects is removed and defect-related nanocolumns are formed. PL measurements of samples etched to various degrees allow the identification of the different PL features. A fully etched sample shows no PL signature related to any of the band edge features and BL is quenched completely, while the yellow luminescence is attenuated only to the degree to which the volume amount of GaN has been removed. Such behavior suggests that defects causing YL are not related to dislocations but are rather homogenously distributed throughout the layer in the form of point-like defects. The decrease of the BL intensity at 4.4 K with excitation dose (bleaching) and the simultaneous increase in YL intensity for as-grown samples and the lack of such effects for etched samples imply a direct connection between the defect centers responsible for YL and BL.

I. INTRODUCTION

Gallium nitride research and technology has progressed enormously over the past two decades resulting in large number of optoelectronic and high-power, high frequency devices.\textsuperscript{1} Despite the existence of operational GaN light emitting diodes (LEDs), laser diodes (LDs) and other devices,\textsuperscript{2} the III-nitride system is not yet flawless. Lack of commercially available free standing GaN substrates makes it necessary to use foreign ones such as sapphire or silicon carbide (SiC). Therefore, the resultant layers are characterized by large quantities of dislocations and other defects. Particular interest is concentrated around the origin of defect related luminescence bands, as they are natural competitors of the band-edge luminescence utilized in all GaN-based optoelectronic devices.

The bands in question are yellow luminescence (YL) centered around 2.2 eV and blue luminescence (BL) centered around 2.9 eV. The first of the two is quite commonly observed but it has never been attributed to any specific defect with certainty. Electron irradiation studies seem to suggest that the origin of YL is a gallium vacancy ($V_{Ga}$),\textsuperscript{3} or a $V_{Ga}$-Ga\textsubscript{N} Frenkel pair.\textsuperscript{4} Many reports suggest shallow donor-deep acceptor recombination as the cause of YL with the $V_{Ga}$ as the deep acceptor and an oxygen substitutional atom on a nitrogen site (O\textsubscript{N}) as shallow donor.\textsuperscript{8-10} The most commonly accepted cause for YL is thus a donor-acceptor recombination of $V_{Ga}$-O\textsubscript{N} defect.

BL is not as commonly observed as and such as its origins have not been studied in sufficient detail. Kang et al. suggest the same $V_{Ga}$-O\textsubscript{N} defect complex to be responsible for BL.\textsuperscript{11} Li et al., on the other hand, suggest a free electron to deep acceptor transition.\textsuperscript{12} Similar blue bands can be observed also in intentionally doped samples, but in that case their origin is believed to be of different nature.\textsuperscript{13}

There are also theoretical reports suggesting preferential incorporation of $V_{Ga}$-O\textsubscript{N} complexes into dislocation cores.\textsuperscript{14} Such an effect should result in YL or BL originating at dislocations, as was previously suggested by Ponce et al. for YL.\textsuperscript{15} The association of oxygen related defects with nanoropes has also been predicted theoretically\textsuperscript{16} and confirmed experimentally.\textsuperscript{17}

In this paper we present luminescence data for GaN samples which have been etched in a defect selective manner. The etching results in creation of nanocolumns which are formed around dislocation cores. By comparing the data obtained from unetched and etched samples we can verify the direct influence of dislocations on all photoluminescence bands.

II. EXPERIMENTAL DETAILS

The samples used in this investigation were Ga polar, nominally undoped GaN layers, which were grown on c-plane sapphire by MOCVD in a horizontal geometry reactor. The substrate was first cleaned in a HCl: HNO\textsubscript{3} solution outside the reactor, followed by an anneal in the reactor in a N\textsubscript{2} atmosphere at 500 mbar and at a temperature about 1000 °C. After this nitridation of the sapphire surface the substrate was cooled to 525 °C at which temperature a 20 nm GaN nucleation layer was grown at 500 mbar, followed by growth of the main n-type GaN layer at 1130 °C and 50 mbar. Trimethyl gallium and ammonia were used as precursors. The thickness of the GaN layers was typically.
about 2.5 μm with a carrier concentration of 6.5 ×10^{16} \text{ cm}^{-3} and a resistivity of 3.0 Ω cm, as obtained from Hall measurements. The overall crystalline quality is described by the FWHM of x-ray rocking curves and these were typically 259 and 136 arcsec for the (0002) and (0105) peaks, respectively.

The photoetching setup used in this study was an open-circuit version similar to that of Youtsey et al.\textsuperscript{18} The sample's area was ~0.5 cm\textsuperscript{2}, thereby ensuring homogenous illumination. Ohmic contacts to the GaN surface were made by evaporation of a 100 nm Ti layer covering area of 10%-20% of the total surface area. No additional heat treatment of the contacts was applied. The counter electrode was a PT coated plate with a surface area 50 times larger than that of the GaN electrode. The electrolyte used was a stirred KOH solution with a concentration of 0.004 M. The illumination was provided by 450 W UV enhanced Xe lamp equipped with water IR filter. The resultant power density was measured to be 300 mW cm\textsuperscript{-2}. It is important to note that only wavelengths below ~360 nm, i.e., the room temperature band gap of GaN, will contribute to photoetching. The photocurrent, which is a rough measure of the etch rate, was measured by a multimeter. As a function of time the photocurrent is rather constant (or slightly decreasing) until eventually a current collapse occurs. In this case the GaN layer (except the nanocolumns, see Sec. III) has been etched completely away. From integration of the photocurrent versus time plots of fully etched sample, time values for intermediate stages of etching, e.g., 1/4, 1/2, or 3/4 of the total layer can be estimated.

The morphology of samples after etching was examined by diffraction interference contrast (DIC) optical microscopy and scanning electron microscopy (SEM).

All PL measurements were performed at 4.4 K in a cold-finger continuous flow cryostat. Excitation was provided by the 325 nm line of HeCd laser with power density of 300 W cm\textsuperscript{-2}. Luminescence was analyzed using a 1 m long, Spex 1704 monochromator and a Jobin-Yvon backilluminated UV-enhanced CCD detector.

### III. RESULTS AND DISCUSSION

In order to recognize the origin of luminescence in this study, the effect of defect selective etching has to be understood. A sample submerged in a weak KOH solution equipped with a contact is illuminated by light with energy higher than that of the GaN band gap. The resultant photo-carriers are spatially separated by the electric field at the interface between the semiconductor and the electrolyte. In the case of n-type material the holes are forced towards the surface while electrons are forced away from it. Holes then take part in the etching process while electrons move through the sample and wiring to the counterelectrode where they complete the circuit by oxygen reduction.\textsuperscript{19}

Any kind of surface recombination will impede the etching by decreasing the number of available holes. Therefore, dislocations, which act as recombination centers, will not etch at all, leaving a sharp featured morphology. These nanocolumns have been proven to represent dislocations and nanopipes and their immediate vicinity.\textsuperscript{20,21} Figure 1 shows a SEM micrograph of the sample which has been etched for 1/4 of the time needed to etch the GaN layer completely. Each “whisker” represents a threading dislocation which might be either a screw, a mixed or an edge type as has been already proven by TEM measurements.\textsuperscript{22} The dislocation density measured for this sample is estimated at 6 \times 10^{9} \text{ cm}^{-1}, which is in line with the usual dislocation density for our samples and it is also comparable to the etch pit density (EPD) resulting from defect selective etching in molten KOH—NaOH mixture.

PL measurements have been performed with a spot diameter in the order of 30–50 μm, which is much larger than the average distance and diameter of individual nanocolumns. In this manner we obtain statistical PL data over a comparably large area. Figure 2 shows PL results for the band edge spectral range. The PL intensity is plotted in logarithmic scale to show low intensity features. The unetched sample shows a
clear donor-bound exciton (DBE) peak at 3.481 eV and free excitons A and B at 3.488 and 3.497 eV, respectively. Two peaks attributed to excitons bound on acceptors are visible at 3.460 and 3.466 eV. All these values are slightly shifted towards higher energies from the commonly known energies. This shift is attributed to the fact that at 2.5 µm thickness, the samples are compressively strained. The largest difference between the PL signal between the unetched and fully etched sample is the fact that all of the band edge luminescence is quenched. This is clear proof that dislocations are sources of ruinous recombination which is competitive to UV luminescence used for LED and LD operation.

The samples etched partially retain their band edge luminescence to a considerable degree with visible redshift. The luminescence is not quenched proportionally to the etched amount due to the fact that the absorption depth for excitation wavelength is only ~250 nm. After removal of some GaN during etching the remaining thickness remains larger than the absorption depth except for the fully etched sample. The signal thus obtained is therefore not considerably weaker than that from the unetched sample. The redshift of the luminescence peaks is caused by the fact that the etch rate is highest in the areas furthest away from dislocations. This results in the formation of nanocolumns and also rough morphology at their bases, causing, relaxation of strain, and the visible lowering of emission energies.

Figure 3 shows full emission spectra of the unetched and the fully etched samples in the range 1.9–3.35 eV. The unetched sample shows, apart from the previously mentioned band edge components, also a considerable blue luminescence (BL) centered around 2.9 eV and a strong yellow luminescence (YL) centered around 2.2 eV. After etching, the BL is completely extinguished while the YL considerably diminished. We have estimated that the complete etching removes between 85% and 95% of the material. The decrease in the YL intensity matches the decrease in the amount of GaN.

It has been suggested previously that the origin of yellow luminescence might be the $V_{Ga} - O_N$ defect complexes, which are predicted to accumulate at threading dislocation cores. Results described in this paper show that the YL has no correlation with threading dislocations other than that it is not quenched by nonradiative recombination occurring at dislocation sites. This indicates that defect centers responsible for YL are point defects homogenously distributed through the GaN layer and that they possess a higher recombination rate than that of dislocations. Therefore, either $V_{Ga} - O_N$ defects do not incorporate preferentially into dislocation cores, or such incorporation terminates their optical activity. Complete quenching of BL upon etching can be explained in two ways; either defects responsible for BL are not incorporated into the vicinity of dislocations or their recombination rate is much lower than that of dislocations and YL defect centers.

It has been previously reported, that BL and YL are involved in so called “bleaching” effect. A slow decay of the BL intensity under excitation is observed, accompanied by gradual increase of the YL intensity. Figure 4 shows such behavior for our samples with the BL decay matching the YL strengthening, suggesting a direct transfer of charge between the two defect complexes responsible for these PL bands. In agreement with other publications this metastable effect can be reversed by cycling the sample to room temperature within the confines of cryostat.

It is important to note that this behavior in our case is valid for as-grown samples as opposed to $H_3PO_4$-etched ones described by Reschikov et al. The bleaching times are much shorter compared to other reports, but it can be attributed to the fact that the excitation intensity used in this study was considerably higher, and according to Reschikov et al. it should have direct influence on the decay rate. No bleaching effect has been observed for the etched sample; lack of measurable BL being one of the reasons. However, YL in the same regime showed a completely constant intensity over time (see Fig. 4). This is another evidence that YL and BL are interconnected, most probably by different charge states of the same defect. However, the data collected do not allow us to state unambiguously which defects could be responsible.

IV. CONCLUSIONS

Measured PL data indicate that the presence of dislocations is destructive to the band-edge optical activity. Further-
more, it suggests that there is no spatial correlation between dislocations and yellow luminescence and that the YL is in fact caused by point-like defects homogeneously distributed in the GaN layer.

As mentioned in Sec. I, the YL is commonly believed to originate from $V_{\text{Ga}}\text{-O}_\text{N}$ complexes. Additionally, it has been suggested that these complexes incorporate preferentially into dislocations and in their vicinity. However, our results imply that YL is not directly related to the presence of dislocations. It is merely not diminished by their presence. One possible explanation is that the same $V_{\text{Ga}}\text{-O}_\text{N}$ defects have a different electronic signature when incorporated into dislocation-free GaN matrix in comparison with those incorporated into dislocation sites. In that case it is possible that they are indeed incorporated preferentially into dislocations but such an incorporation quenches their optical activity.

Defect centers responsible for the BL are either incorporated into the dislocation-free areas of the sample or they have a much lower recombination rate than that of nonradiative recombination on dislocation cores. The collected data also suggest a direct connection between YL and BL defect centers making it quite probable that they are different charge states of the same defect complex.

It is our belief that additional cathodoluminescence mapping and time-resolved photoluminescence studies would further contribute to answering the questions of spatial distribution and recombination rate of the defects responsible for YL and BL.

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