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Characterization of Red Emission in Nominally Undoped Hydride Vapor Phase Epitaxy GaN

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We report characterization of the red emission band in hydride vapor phase epitaxial GaN using cathodoluminescence spectroscopy and imaging and time-resolved photoluminescence. The observed properties of the emission are consistent with recombination of excitons bound at close donor-acceptor pairs. The time evolution of the emission signal during electron beam irradiation supports the association of the red emission with charged centres.

1 Introduction

Light emission from GaN films is a sensitive probe of defects and impurities present in the material and the associated radiative and nonradiative processes. In addition to the band edge emission, deep emission bands frequently observed in this material continue to be a subject of intensive studies. The yellow band with the peak at about 2.2 eV, common in wurtzite GaN, has attracted a significant research effort as it was considered to compete with the technologically desirable edge emission [1]. Its red counterpart in cubic GaN was examined as well [2]. In this work we concentrate on the red emission band present in wurtzite GaN films grown by hydride vapor phase epitaxy (HVPE). The HVPE technique often yields films with a broad emission band similar in appearance to the yellow band, but with the maximum at about 1.8-1.9 eV. The purpose of this paper is to examine its properties so that a framework can be established for the microscopic picture of the relevant defects.

Relative to the band edge emission, the red band is weaker than the yellow band. The strength of the red band varies from sample to sample; this study was carried out on films selected for the high intensity of the red band. Measurements reported by other authors on HVPE grown films indicate a sporadic coexistence of the yellow and red bands [3] [4]. In our films, however, the yellow band was absent. The red emission band discussed here should be distinguished from other bands also referred to as "red", these include the red emission in cubic GaN examined by the present authors [2], and the red band in GaN codoped with Mg and Si [3].

The red emission is observed both in nominally undoped HVPE GaN films grown on *a*- and *c*-oriented sapphire substrate without buffers (for details of growth procedures see Ref [5]), and in HVPE films grown on GaN templates prepared by metalorganic chemical vapor deposition [6]. The latter layers show a much higher degree of structural quality than the films simply deposited on sapphire, thus suggesting inadvertent defect incorporation in the growth process.

2 Experiments

The GaN films were grown on a-sapphire without any buffers, but using pre-nitridation of the substrate prior to growth by hydride vapour phase deposition. The substrates were heated to growth temperature followed by nitridation in a 20 % NH_4 flow for 15 min and GaN growth was initiated by introducing HCl. Growth was carried out at 1080 °C at a growth rate of about 30-50 μm/h. The thickness of the samples was in the range of 20-85 μm and their structural quality was assessed using x-ray diffraction [7]. Cathodoluminescence (CL) images, spectra and kinetics and scanning electron microscope images (SEM) were taken at room temperature in a JEOL35C scanning electron microscope with a MONOCL2 system by Oxford Instruments and in a LEO 1550 system. The PL kinetics measurements were performed at 2K using a photon counting system. The pulsed excitation was provided by either a mode-locked Ti:sapphire solid-state laser, frequency doubled to 340 nm with 2 ps pulses, or a frequency-tripled Nd:YAG laser at 350 nm with 2 ns pulses at a varying repetition rate.

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3 Results and Discussion

The examined HVPE films typically show smooth surface morphology, with a small number of hexagonal pits as shown in an SEM image (Figure 1a). These pits originate at the large scale columnar assemblies of structural defects close to the film-substrate interface [8]. An AFM image typically shows a terrace structure and the small defects recently linked with threading dislocations [9]. (Figure 1b). A photoluminescence emission spectrum taken at 2K at the top surface of such films is usually dominated by a strong excitonic emission (Figure 2). In the films selected for this work the red emission band peaking at ~1.9 eV is also present. The surface nonuniformities shown in Figure 1a offer a useful tool for characterization of the emission properties. We have earlier reported spatial nonuniformities of the band edge emission [8], particularly at the hexagonal pits. Similar spatial nonuniformities are present in the examined films as presented in Figure 3a,b. The monochromatic CL maps taken at an accelerating voltage of 35 kV for the band edge emission peak, (Figure 3a) and for the peak of the red emission (Figure 3b) clearly show that the two emissions behave in an opposite way - the edge emission is enhanced at the center of the hexagonal pit, while the red emission is uniformly suppressed across the entire hexagon. The enhancement of the edge emission at the hexagons is attributed to doping nonuniformities, with the high electron concentration localized at the columnar structures which terminate at the hexagonal pits [8].

The red band has been previously associated with oxygen. For example, Hofmann *et al*. [10] report that the red band is observable in epitaxial GaN which is highly doped with carbon and/or oxygen, with doping values in the high 10^{19} cm^{-3} as measured by secondary ion mass spectrometry (SIMS), regardless of the growth method. To verify this we carried out studies of oxygen content in HVPE GaN by secondary emission mass spectroscopy (SIMS) imaging (Figure 4). The results indicate clear nonuniformities of oxygen distribution with oxygen concentration significantly increasing at hexagonal pits. However, we did not find a similar enhancement of the red emission in the proximity of the pits. On the contrary, we observed a strong decrease of the red emission.

The monochromatic CL images show also some nonuniformities other than those observed at hexagonal features. Between the hexagonal defects both the edge and the red emission show spatial intensity variations (Figure 3a and Figure 3b). Such nonuniformities were earlier reported for edge emission wavelengths only [2] and attributed to threading dislocations. In the present films we have observed these micrometer scale variations for the red emission wavelengths as well.

We have explored the evolution of the red emission band as a function of the excitation current. The corresponding spectra taken for varying current are shown in Figure 5a. Within the accuracy of our experiment the shape of the red band does not change with an increase in current. The peak intensity of the red band was plotted as a function of the current varying over five orders of magnitude (Figure 5b) and it shows power dependence with the power of 0.79. The evolution of the red emission band was also followed as a function of the accelerating voltage at constant current conditions (Figure 6). As the voltage is increased the deeper sections of the film are accessed, and at 35 kV the layers up to 5 micrometers deep can be probed. At lower voltages, the band is relatively narrow and blue-shifted. At increasing voltages the band broadens and shifts to the red.

We have also monitored the changes in the red emission intensity following an intense electron beam irradiation. This method was earlier used for characterization of the yellow emission in MOCVD GaN [11]. The technique is based on an observation that a very intense electron beam leads to local charging, even in a relatively conducting material. This excess of charge causes strong localized electric fields that are capable of causing electromigration of charged defects. The signatures of emission bands associated with the charged defects can be then monitored to confirm that the defects have indeed moved either away or towards the point of impact of the beam. Prior to the irradiation experiment we have irradiated a single spot on the sample for 5 minutes at 35 keV at a current of $8x10^{-8}$ A, the highest achievable in our system. The result of this irradiation on the CL image at 352 nm is a black dot about 2 micrometers in size. However the corresponding SEM image of the same area did not indicate any deposits, for example from surface contamination due to the build up of hydrocarbons on the surface (images not shown). This confirms that the effects discussed below are intrinsic to the film. We have carried out a similar irradiation in a number of locations on the sample, both inside and outside of the hexagon. The detailed evolution of the time-dependent red emission signals at 620 nm is shown in Figure 7a,b. Each trace was taken at a different spot to ensure compatibility. Both inside (Figure 7a) and outside of the hexagon (Figure 7b), the red emission decreases by about 50 percent over 1000 seconds, and, concurrently, the band edge emission shows a consistent and strong decrease at most of the locations.

Further, we have carried out the time-resolved photoluminescence measurements at several selected wavelengths within the red emission band. The

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photoluminescence decay at all these wavelengths is exponential and the decay time of 12 ns +/- 0.5 ns is observed for each of the studied wavelengths within the band (the decay characteristic at 650 nm is shown in Figure 8). This behavior is distinctly different from that reported for the yellow band in MOCVD GaN, and red band in cubic GaN where either non-exponential or energy-dependent decay is observed [2] [12]. The independence of the decay time on energy may be indicative of two possible mechanisms [13]. In the case of the emission being due to the donor-acceptor pair recombination, at a high concentration of one impurity, an impurity band is formed. In such circumstances the recombination process resembles the free-to-bound process rather than the DAP recombination. The second option involves donor and acceptor impurities forming close pairs (such as for example Mg-O pairs in p-GaN). These pairs are neutral centres, but may still be capable of binding the carriers. In this case the recombination process is typical of an exciton bound at a neutral centre. In our films the first possibility should be ruled out, as the red emission is more intense outside of the hexagons, in the region where the band gap emission indicates low electron concentration and high film quality. The formation of impurity bands is very unlikely in these regions.

The red emission measured on the cross-sections of the HVPE films grown on the MOCVD templates shows some degree of optical polarization with the dominant contribution polarized parallel to the *c*-axis [14]. This behavior is opposite to that of the yellow emission observed in the same cross-sectional studies and is coming possibly from the template. The yellow emission is preferentially oriented perpendicular to the c-plane. The degree of polarization varies with structural quality (details are discussed in Ref. [14]).

The polarization properties reported by Shubina *et al.* [14] provide support for our interpretation, as they indicate preferential orientation of the centres responsible for the red emission. Our interpretation does not rule out the one proposed by Shubina, that the red emission is associated with certain types of dislocations. The red emission can, for example, be associated with a particular neutral centre which is preferentially formed in the presence of certain dislocations. The excitonic mechanism is also consistent with the excitation current dependence observed in this work. A large spectral width of the emission can be explained by strong coupling to phonons. The ODMR measurements provide arguments in support of the proposed mechanism [10] [15]. The measurements within the range of the red emission band reported in [10] reveal two superimposed signals which have different relaxation times and thus can be separated, with g = 1.98 and 2.01, respectively. The g = 1.98 resonance is commonly attributed to the deep (300 meV) donors that are tentatively identified as the centres responsible for the red emission [16].

4 Conclusion

We have characterized, by means of photo- and cathodoluminescence spectroscopy and imaging, the red emission band commonly appearing in HVPE grown GaN. The spatially-resolved monochromatic cathodoluminescence images indicate that the emission band shows an anticorrelation with the band edge emission, suggesting a competing recombination channel. The emission is also non-uniform across the film cross-section, and it broadens and red-shifts when the deeper layers of the film are excited. The energy-independent time-resolved PL measurements indicate that the band is not due to pair recombination, instead, a mechanism based on a recombination of excitons bound to a neutral centre is proposed. The emission is progressively quenched during intense electron beam irradiation, consistent with charged centres being associated with the emission.

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FIGURES

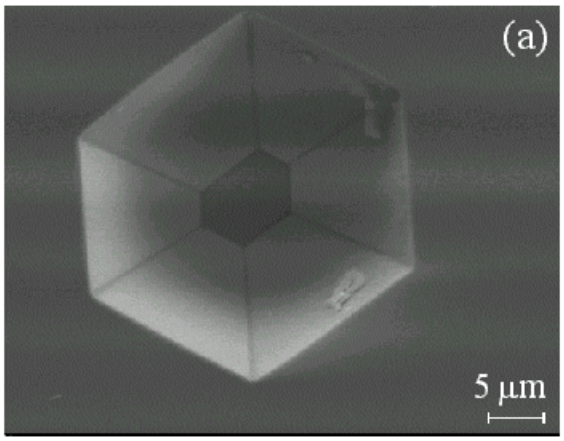

Figure 1a. A SEM image of the surface of the HVPE-GaN film.

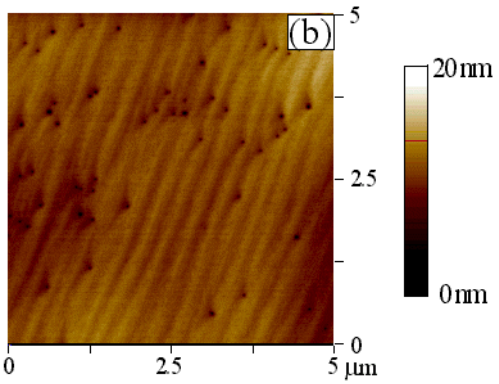

Figure 1b. An AFM image of the surface of the HVPE-GaN film.

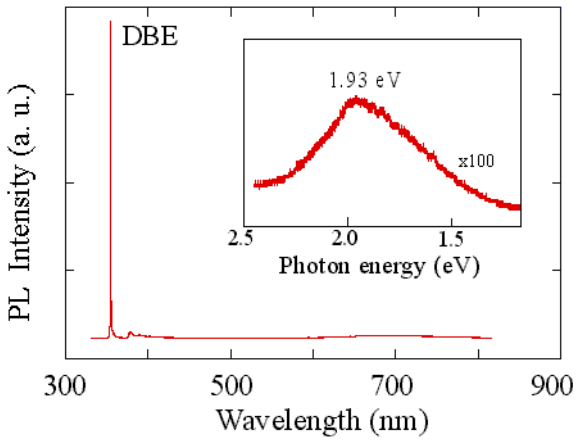

Figure 2. A photoluminescence spectrum taken at 2K.

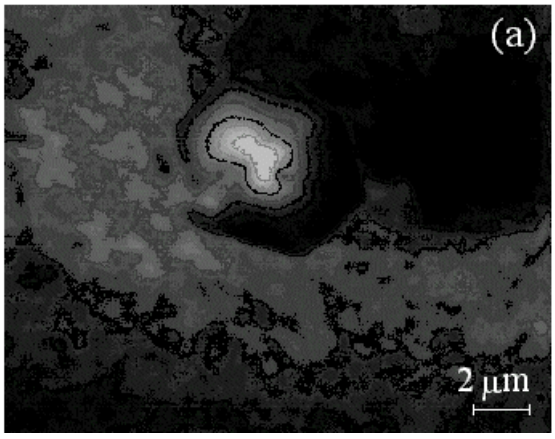

Figure 3a. Monochromatic cathodoluminescence image taken at the peak of the edge emission - 360 nm.

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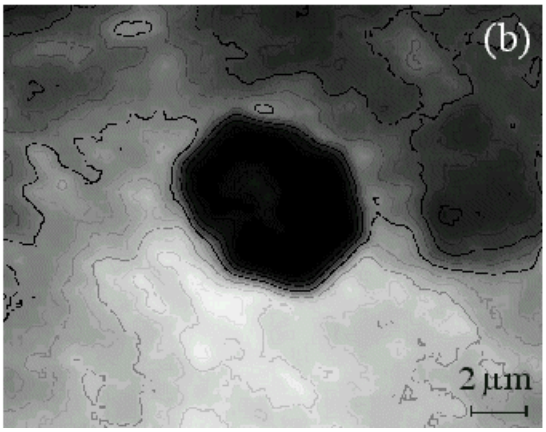

Figure 3b. Monochromatic cathodoluminescence image taken at the peak of the red emission - 620 nm (b).

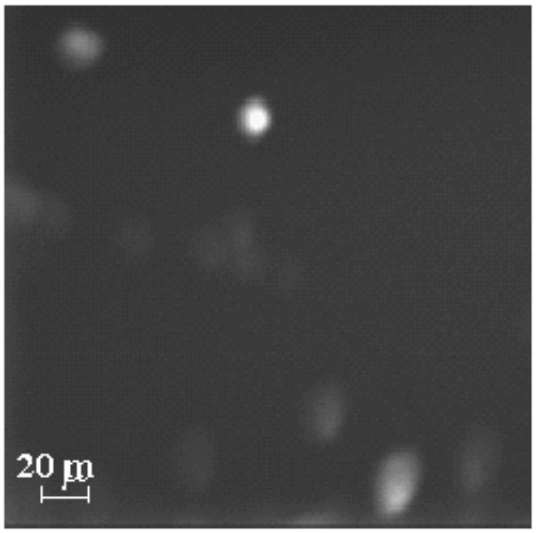

Figure 4. A SIMS image showing nonuniformities of oxygen distribution on the film surface.

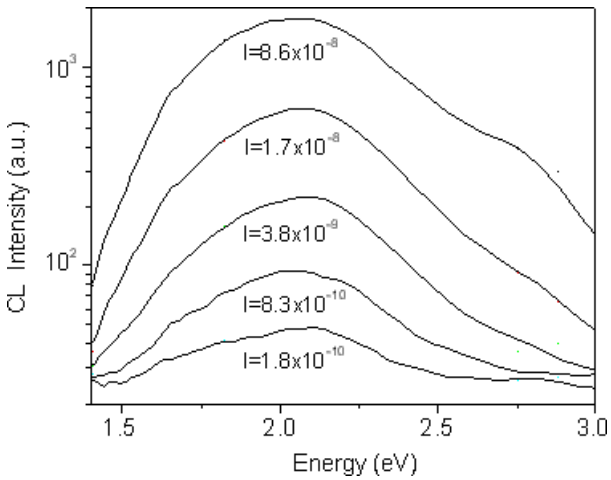

Figure 5a. The evolution of the red emission spectra as a function of current.

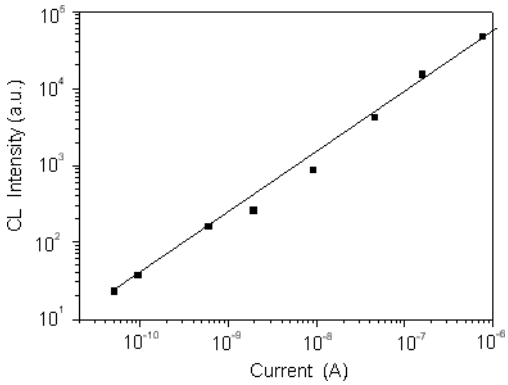

Figure 5b. The integrated intensity of the red emission as a function of current.

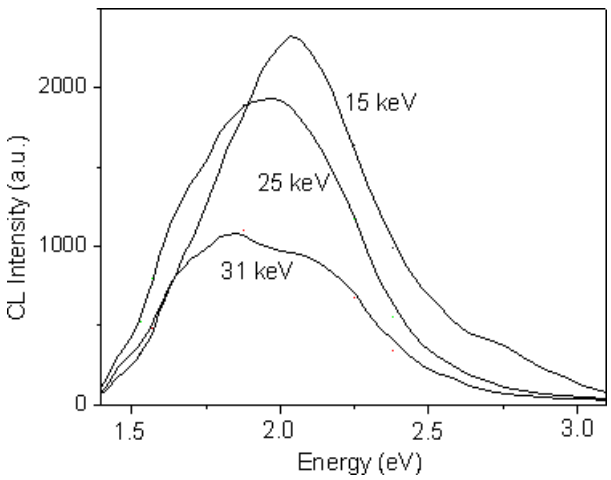

Figure 6. The evolution of the red emission band as a function of accelerating voltage.

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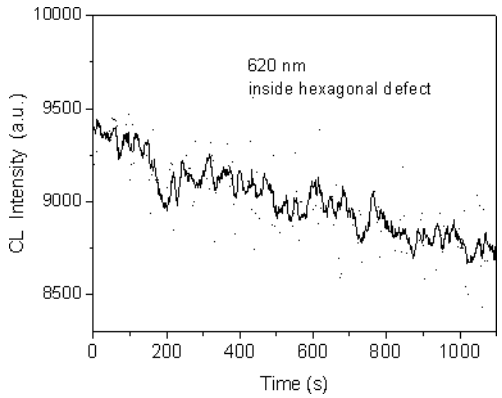

Figure 7a. The CL signal as a function of time at 620 nm at high current inside of a hexagonal defect.

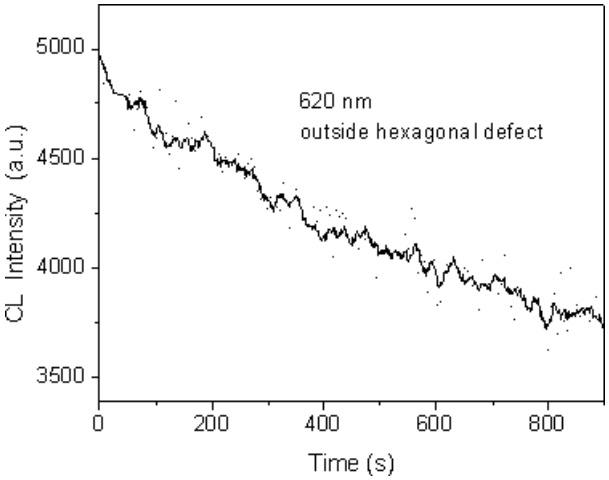

Figure 7b. The CL signal as a function of time at 620 nm at high current outside of the same defect.

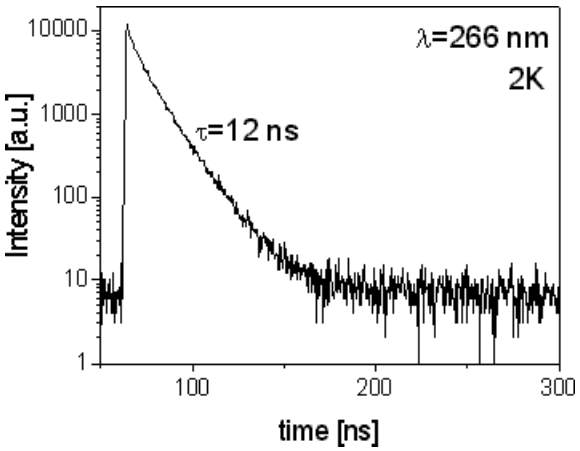

Figure 8. The PL decay characteristics at 650 nm.

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