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The authors observed a drastic reduction of the yellow luminescence (YL) intensity in carbon-doped semi-insulating GaN in air or oxygen ambient as compared to the intensity in vacuum. The YL intensity dropped about 300 times while the exciton emission remained almost unchanged. The authors assume that the donor-acceptor-pair transitions involving a gallium vacancy complex in a thin near-surface region cause the strong YL. Oxygen molecules or ions induce the surface states acting as a very efficient channel of nonradiative recombination. The results indicate that carbon may not be involved in the acceptor responsible for the YL band in GaN:C. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2400074]

In spite of considerable attention to the yellow luminescence (YL) in GaN, the origin of the deep acceptor responsible for this broad band remains unknown.[1] In high-purity freestanding GaN, the YL band and the green luminescence band were assigned to transitions from the conduction band or shallow donors to two charge states of the same deep-level defect: a complex involving a gallium vacancy (V_{Ga}) and a shallow donor (O_N), i.e., $V_{Ga}O_N$, having a concentration of about 10^{15} cm^3.[2] It is very likely that in less pure GaN the YL band is caused by V_{Ga}-related point defects trapped at structural defects. However, there are numerous works (see, for example, Ref. 3 and references in Ref. 1) in which the authors insist on observation of a correlation between doping with carbon and the intensity of the YL band and attribute the YL band to a defect containing carbon. Armitage *et al.*[3] suggested that C-related defects cause the YL band in C-doped GaN, while a gallium vacancy is responsible for the YL band in undoped GaN. On the other hand, first-principles calculations of Wright[4] showed that the YL band is unlikely to be caused by a carbon-related defect. Recently, we studied low-temperature photoluminescence (PL) in a set of C-doped GaN layers and have not found a correlation between the concentration of C and the intensity of the YL band.[5] However, we have noticed that at room temperature the PL intensity greatly changes in some GaN:C samples when air is evacuated. In this letter we report on a striking effect of the ambient on the YL band in one of the C-doped GaN samples.

A high-resistivity C-doped 2.3-μm-thick GaN layer was grown by metal organic chemical vapor deposition method on *c*-plane sapphire substrate by EMCORE Corporation and studied within the Wood-Witt Initiative "Defects in GaN" (Sample No. EM7053 for internal reference). Concentrations of Si, C, and O in the bulk part of the sample have been estimated as about 7×10^{15}, 1×10^{17}, and 5×10^{16} cm^{-3}, respectively, by the secondary ion mass spectrometry (SIMS).[6] Steady-state PL was excited with an unfocused He–Cd laser (55 mW, 325 nm), dispersed by a 1200 rules/mm grating in a 0.3 m monochromator and detected by a cooled photomultiplier tube. Calibrated neutral-density filters were used to attenuate the excitation power density (P_{exc}). An optical cry-

ostat was used as a chamber with a basic vacuum in mid 10^{-6} mbar.

At room temperature the PL spectrum of the GaN:C sample placed in air ambient contained an exciton emission with the main peak at 3.42 eV and a broad YL band peaking at about 2.2 eV (Fig. 1). The external quantum efficiency (QE) of PL was about 0.001%. Remarkably, evacuation of air resulted in drastic increase of the YL band intensity while the exciton emission intensity remained nearly the same (Fig. 1, curve "vacuum-1"). Annealing of the sample in vacuum at 400 °C for about 1 h under the laser illumination with P_{exc} =0.3 W/cm^2 and subsequent cooling to room temperature resulted in further increase of the YL intensity (Fig. 1, curve "vacuum-2"). The effect was reversible insofar as allowing air into the chamber restored the PL signal to its original level. We repeated this cycle several times, and the results were reproducible. The decrease of the YL intensity upon transition from vacuum to air ambient was fast (Fig. 2), while the inverse process was extremely slow. Under the laser illumination with P_{exc}=0.003 W/cm^2 there was no noticeable change of the YL intensity after 1 h of air evacuation. At P_{exc}=0.3 W/cm^2 the YL intensity increased in vacuum about ten times in 30 min, and the rise apparently
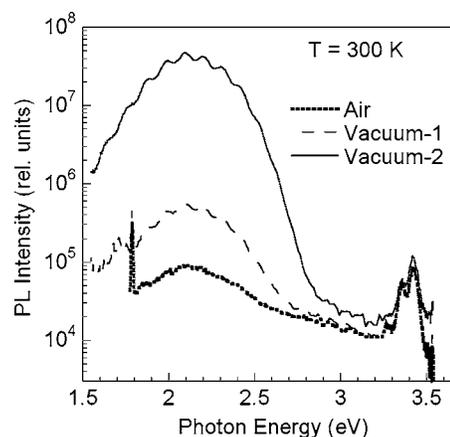

FIG. 1. Room-temperature PL spectrum from a GaN:C layer in vacuum and air ambient. The transition from "vacuum-1" to "vacuum-2" state took place after annealing the sample in vacuum at 400 K and subsequent cooling down to room temperature. The QEs of the YL band are 0.001% in air and 0.3% in vacuum after the annealing. P_{exc}=0.003 W/cm^2.

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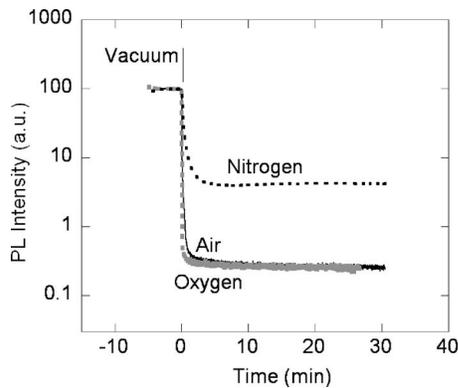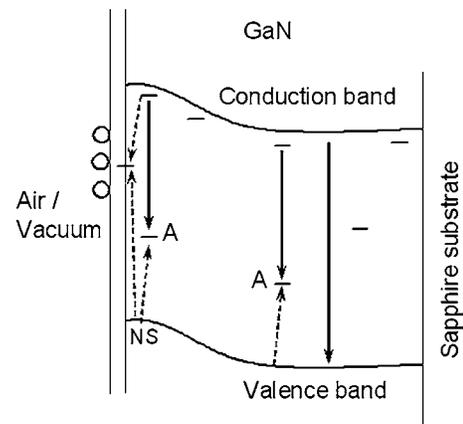FIG. 2. Evolution of the YL intensity under different ambient conditions.

FIG. 3. Schematic of band potentials and main transitions in GaN:C layer grown on sapphire substrate. The solid and dashed arrows indicate radiative and nonradiative transitions, respectively. A very thin oxide layer at GaN surface, as well as adsorbed oxygen species on it, is also schematically shown. NS denotes a thin near-surface region where potentials are nearly flat. A denotes deep acceptor states responsible for the YL band.

saturated. Only after annealing the sample at 400 K under UV illumination for several hours the YL intensity returned to its highest level in vacuum. To check if the decrease of the YL intensity in air ambient is caused by oxygen or, for instance, by water vapor we repeated the experiment with 0.9999-pure oxygen and industrial-grade nitrogen instead of air. Oxygen decreased the PL exactly to the same level as air, while the decrease in nitrogen atmosphere was significantly smaller (Fig. 2). Moreover, the PL intensity regained its original vacuum level after nitrogen evacuation in a few minutes at room temperature, whereas restoration of the PL intensity after oxygen ambient was very slow, even slower than after air. We conclude that the adsorption of oxygen is responsible for the reduction of the YL intensity, and that the PL decrease in nitrogen atmosphere is apparently due to its contamination with oxygen.

Previously we observed the decrease of PL intensity in undoped GaN placed in air or oxygen atmosphere.[7] After brief study of this effect in about 50 undoped GaN samples we concluded that the exciton emission intensity typically decreases by 1.5–3 times in air ambient, while the YL intensity decreases less or even remains the same in the majority of the samples. Such behavior has been attributed to either oxygen-related nonradiative recombination at the surface or just to oxygen-induced additional negative charge at the surface causing the rise of upward band bending and widening of the depletion region.[7] Exciton emission should be more sensitive to the electric field in the depletion region than the YL. The characteristic time of the exciton formation and the average time of the hole capture by the YL-related acceptors in GaN are about the same—of the order of 10^{-10} s.[8] However, even if the excitons are formed, they would be ionized in the electric field of about 10^5 V/cm,[9] the value typical for the depletion region in undoped GaN. In contrast, the electrons trapped at shallow donors can still recombine with the holes captured by deep acceptors in the depletion region via the donor-acceptor-pair (DAP) mechanism and cause the YL. Therefore, we expect that the luminescence from the depletion region (both exciton and YL) is substantially suppressed due to the fast separation of photogenerated carriers and reduced probability of their capture by defects or formation of excitons. At the same time, the excitonic emission intensity is more sensitive to the value of the electric field in the depletion region since the formed excitons may be ionized by a high electric field.

The results obtained in this work are very unusual. Indeed, nearly unchanged in shape and intensity exciton emis-

sion indicates that the depletion region is almost invariant under the change of ambient. Therefore, the drastic change of the YL intensity in different ambients should be attributed to a competition between two channels *in a thin near-surface layer*: radiative and nonradiative recombinations of photogenerated carriers, and not to variation of the depletion region width. Figure 3 illustrates the proposed model. To explain very low QE of PL in air ambient, we assume that a negative charge at the surface causes an upward band bending. The depletion region is wide since the electron concentration is very low. The electric field in this region sweeps photogenerated electrons towards the sapphire substrate and holes towards the surface. Due to the separation of the charges the band bending in conditions of PL is reduced, yet only partially.[10] An important feature of this model is that in a thin (1–10 nm) near-surface region (NS region, thereafter) the potentials are relatively flat (Fig. 3). Such a shape of the potentials near the surface may be realized when free holes on the way to the surface are trapped by deep acceptors near the surface, while trapping of free electrons by shallow donors in the depletion region is less efficient since they may be easily ionized at room temperature. Then a photoinduced positive charge would accumulate not only at the surface but also in the NS region.

About 1%–10% of the laser light is absorbed in the NS region, and almost all the other photons are absorbed in the wide depletion region. The recombination of holes trapped at deep acceptors in the NS region with electrons trapped at shallow donors via the DAP mechanism causes the YL. The observed nonexponential decay of the YL after pulsed excitation with a nitrogen laser (337 nm) supports the DAP nature of the YL band. In a vacuum, the NS region is by far the major source of the YL. Assuming that the QE of the YL in this region is of the order of 10%, the value typical for undoped GaN,[8] we obtain that recombination via deep acceptors in just ~3-nm-thick NS region can explain the QE of 0.3% observed in vacuum. In air or oxygen ambient, the adsorption of oxygen ions or molecules induces surface states that apparently are very efficient in recombination of photogenerated carriers. The nonradiative recombination via the surface states competes with the radiative recombination channel in the NS region and causes the drastic reduction of

the YL when oxygen is present at the GaN surface (Fig. 3). This model qualitatively explains all the characteristic features of the PL behavior in different ambients.

As for the origin of the YL band, at this stage of knowledge we are still unable to give a conclusive answer. It is unlikely that the YL-related acceptor states are located directly at the surface or that the deep acceptor in C-doped GaN is different from the acceptor in undoped GaN for the following reasons. The shape and position of the YL band in the GaN:C sample in vacuum were identical to the characteristics of the YL band in a large number of undoped GaN samples in which the YL was nearly insensitive to air evacuation. Furthermore, we studied the thermal quenching of the YL band in the GaN:C sample in vacuum. Between 400 and 550 K the YL intensity dropped about 1000 times exhibiting the activation energy of 1.0 ± 0.1 eV, very similar to the results for undoped GaN,[8] where the YL was attributed to a deep acceptor in bulk. We assume that the bulk acceptor responsible for the YL band in both undoped and C-doped GaN samples is a bulk-type V_{Ga}-based complex.[1] The properties of this defect would be significantly altered if the defect was located at the surface or if the origin of the defect was completely different.

It is not clear what the role of carbon is in the observed effects. It may not be directly involved in PL but only in trapping holes, creating a potential profile shown in Fig. 3. It is known that carbon introduces acceptors that compensate shallow donors and lead to high resistivity. However, the question of where the energy level of these acceptors is in wurtzite GaN remains open. It is very unlikely that carbon creates a shallow acceptor.[5] If carbon in a Ga site forms a complex with V_{Ga}, the properties of such complex should not be much different from the $V_{Ga}O_N$ complex; however, theoretically such a complex was not considered. In undoped GaN (with high concentration of free electrons), air evacuation causes much smaller effect on the YL because the depletion region and the flat-potential region near the surface are much narrower than those in GaN:C. That is why PL from the bulk part of a layer has the main contribution in undoped or n-type doped GaN.

In conclusion, we observed an unusually large change in intensity of the YL band in carbon-doped high-resistivity GaN sample at room temperature when the air or oxygen ambient was replaced by a vacuum. The observed effect is attributed to photoinduced desorption of oxygen from GaN or its native oxide surface. The surface states introduced by adsorbed oxygen in GaN are very efficient in nonradiative recombination of photogenerated carriers which otherwise recombine predominantly via deep acceptors in a thin near-surface region and cause the strong YL band when air is evacuated. The acceptor responsible for the YL band in C-doped GaN is apparently the V_{Ga}-related complex and may not be associated with carbon. The role of carbon in the observed unusual effects is not clear enough.

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