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Unusual luminescence lines in GaN

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A series of sharp intense peaks was observed in the low-temperature photoluminescence spectrum of unintentionally doped GaN in the photon energy range between 3.0 and 3.46 eV. We attributed the majority of these peaks to excitons bound to unidentified structural and surface defects. Most of the structural- and surface-related peaks (at 3.21, 3.32, 3.34, 3.35, 3.38, and 3.42 eV) were observed in Ga polar films. In N polar GaN, we often observed the 3.45 eV peak attributed to excitons bound to the inversion domain interfaces. © 2003 American Institute of Physics.
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I. INTRODUCTION

Structural and surface/interface defects are known to affect markedly electrical and optical properties of semiconductor devices. In GaN, the effect of structural defects on optical properties is not yet well established. It is commonly accepted that dislocations act as nonradiative recombination centers in GaN.^{1,2} However, it is well known that dislocations can bind excitons.³ In general, excitons can be bound to various point and extended defects, such as shallow and deep donors and acceptors,^{4,5} stacking faults,⁶ surface adatoms,⁷ and acceptor-like surface defects.⁸

In high-quality undoped GaN, only free excitons and excitons bound to shallow donors and acceptors comprise the low-temperature photoluminescence (PL) spectrum at photon energies between 3.0 and 3.5 eV,^{9,10} along with the characteristic series of peaks due to shallow donor-acceptor pair (DAP) transitions.¹¹ However peaks with unusual properties are often observed in the range of 3.0–3.46 eV^{12–39} in addition to the well-identified transitions. The origin of these peaks is controversial. For example, the commonly observed 3.42 eV peak^{12–21} has been attributed to recombination between electrons bound to oxygen donors and free holes,^{12,13} DAP-type transitions involving a very shallow unidentified acceptor,¹⁴ and exciton bound to structural defects,^{10,15–20} in particular to stacking faults^{17,19} and *c*-axis screw dislocations.²⁰ Even less is known about the other peaks. The purpose of this article is to catalogue these unusual PL lines in GaN and establish their characteristics.

II. EXPERIMENTAL DETAILS

Most of the undoped GaN layers in this study (with thickness from 1 to 2 μm) were grown on *c*-plane sapphire by molecular beam epitaxy (MBE). Some of the films were grown on 10- μm -thick GaN buffer layers prepared by hydride vapor phase epitaxy (HVPE) on sapphire or on the 200- μm -thick freestanding GaN templates. Among several hundred of undoped GaN samples, we have selected some 20 samples exhibiting pronounced sharp peaks in the range between 3.0 and 3.46 eV for a detailed investigation. The quality of the layer structure was examined by high-resolution x-ray diffraction (XRD) and atomic force microscopy (AFM). Chemical etching in H_3PO_4 at various conditions was used to reveal pits originating from threading dislocations and to analyze transformation of the surface morphology with etching. Dislocations and inversion domains in the selected samples were studied by cross-sectional transmission electron microscopy (TEM). Polarity of the samples was established from etching characteristics, surface morphologies, TEM, and XRD data.⁴⁰ To eliminate the effect of any nonuniformity, the 2 in. wafers were cut into $\sim 5 \times 5$ mm pieces and for each treated sample a reference sample was taken from the adjacent area of the wafer. The uniformity within each sample was also checked.

PL experiments were carried out in the temperature range of 15–300 K using a closed cycle optical cryostat. The luminescence was excited with the 325 nm line of a He–Cd laser, dispersed using a 0.5 m grating monochromator and detected with a Hamamatsu photomultiplier tube. Particular attention was given to any possible artificial peaks from laser lines or oil contamination.

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FIG. 1. Low-temperature PL spectrum from two characteristic areas of GaN layer grown by MBE on a freestanding GaN template.

III. EXPERIMENTAL RESULTS

A. “Usual” and “unusual” PL peaks in GaN

Low-temperature PL spectra from good-quality GaN layers grown by MBE under various conditions contain the following main features: (i) free exciton (FE) and neutral shallow donor bound exciton (DBE) peaks near 3.478 and 3.472 eV, respectively, with a few longitudinal optical (LO) phonon replicas spaced by 91–92 meV, (ii) very weak DAP band with the main peak at 3.26–3.29 eV and a few LO phonon replicas, and (iii) weak yellow luminescence band with a maximum at about 2.2 eV. In better-quality GaN films more peaks could be resolved in the exciton emission spectrum, in particular two-electron satellites at about 3.45 eV (solid curve in Fig. 1). The set of exciton peaks and their phonon replicas in the range of 3.0–3.5 eV (solid curves in Figs. 1 and 2) refer to usual exciton peaks or a “pure” exciton spectrum observed in high-quality GaN.^{9,10} However in some 70 GaN samples, out of several hundred, we detected a set of sharp peaks in the range 3.0–3.46 eV, in addition to the FE,

FIG. 2. Low-temperature PL spectra from different GaN layers grown on sapphire by MBE. The spectra are normalized at maximum and shifted along the energy axis (from 1 to 7 meV) so that the DBE peak position is the same for all samples (3.470 eV).

DBE, and DAP peaks and their phonon replicas (Figs. 1 and 2). The relative intensity of these peaks varied from sample to sample. After a careful analysis of the peak positions, shapes and changes caused by etching, and by temperature and excitation power variations, we classified the “unusual” peaks and labeled them as Y_i with i starting from 1 for the peak with the highest photon energy and increasing for the peaks with lower photon energies (Table I). Some of these peaks appear as doublets. Typically, in as-grown Ga polar films we observed the peaks Y_2 , Y_4 , Y_6 , and Y_7 . In N polar films with high density of inversion domains we often observed only the Y_1 peak in addition to the usual DBE emission, but some N polar films contained also other Y_i peaks. At the moment we cannot establish any clear correlation between the surface morphology or crystal structure (obtained from AFM and TEM data) and the appearance of the Y_i peaks. We rule out the possibility that these peaks arise from inclusion of the zinc-blende (cubic) phase of GaN because the position, shape and behavior of these peaks with respect to temperature and excitation intensity are very different

TABLE I. Classification and typical characteristics of the Y_i peaks in GaN.

Group label	Subgroup label	Nominal position (eV)	Huang–Rhys factor	Comments, Properties	Tentative identification
Y_1	Y'_1	3.45	0.02	Observed only in N polar films with high density of inversion domains	Exciton bound to inversion domain interface
	Y''_1	3.46			
Y_2	Y'_2	3.41	0.05	Disappeared after hot wet etching. Shifted with P_{exc} in some samples	Exciton bound to structural defect at the surface
	Y''_2	3.42			
Y_3	Y'_3	3.37	<0.2	Observed only in the samples 495 and 770.	Exciton bound to structural defect (?)
	Y''_3	3.38			
Y_4	Y'_4	3.350	0.01	Evolved with UV exposure. Memory effect at 15 K.	Exciton bound to structural defect at the surface
	Y''_4	3.362			
Y_5	...	3.34	...	Observed in a few samples.	Exciton bound to structural defect (?)
Y_6	...	3.32	~0.1	Evolved with UV exposure. Memory effect at 15 K. Large shift with P_{exc}	Surface donor–acceptor pair
Y_7	Y'_7	3.21	0.06	The most common peak in the studied samples.	Exciton bound to structural defect
	Y''_7	3.23	...		

from the features observed in cubic GaN (see Sec. IV B). To make certain that these PL peaks are not related to contamination of the sample surface, we cleaned the selected samples in boiled aqua regia ($\text{HNO}_3:\text{HCl}=1:3$), or etched them in hot phosphoric acid. Below we present a detailed account of influence of the sample treatment and variation of PL measurement conditions on Y_i peaks in GaN.

B. Effect of sample treatment and experimental conditions on Y_i peaks

1. Effect of etching

Many of our Ga polar films had columnar- or bubble-like surface that remained unchanged after etching in boiled aqua regia, whereas the surface became relatively flat with hexagonal-shaped pits after etching in hot H_3PO_4 . Note that the depth of the pits did not increase with increased etching time, remaining under 30 nm, and we could not detect any reduction of the layer thickness even after 1 h of etching or more. Cleaning of the sample in aqua regia resulted in a marked enhancement of the DBE and FE emission but it barely affected the rest part of the PL spectrum. Etching in hot phosphoric acid for a time from a few seconds to few minutes decreased slightly intensities of the DBE, FE, Y_4 , and Y_7 peaks and drastically reduced intensities of the Y_2 and Y_6 peaks (see Fig. 3 in Ref. 38).

The surface morphology of the as-grown N-polar GaN layers represented large columns with small roughness in the short-range scale.⁴¹ Etching for only 10 s in H_3PO_4 at 100 °C removed the substantial part of the layers, and at higher temperatures the films were completely etched off in a period less than 1–2 min. The intensity of the Y_1 peak increased markedly after etching in H_3PO_4 in the samples where this peak dominated. In the N polar films exhibiting the Y_2 – Y_7 peaks, the etching process usually reduced the Y_2 and Y_6 peaks markedly, similarly to the etching results in Ga polar GaN.

2. PL bleaching and memory effect

We have noticed that the Y_4 and Y_6 peaks in Ga polar films evolved with duration of the ultraviolet (UV) laser exposure, while the rest of the peaks, including the DBE peak remained essentially unchanged as shown in Fig. 3 (see also Fig. 5 in Ref. 38). The effect was irreversible at low temperatures. Even after 1 h of keeping the sample in dark, the intensity of the Y_4 peak remained approximately the same as that immediately after the UV exposure, demonstrating an optical memory effect (Fig. 4).

3. Effect of excitation intensity

We examined the evolution of PL spectrum with increasing excitation intensity in a set of samples exhibiting Y_i peaks. The PL intensity of most of the Y_i peaks increased almost linearly in a wide range of excitation densities (10^{-4} – 300 W/cm^2) similar to the increase of the FE and DBE peaks (see Fig. 2 in Ref. 38 and Fig. 5 in Ref. 39). The Y_3 , Y_4 , Y_5 , and Y_7 peaks did not shift with the excitation intensity. The Y_6 peak in all samples shifted to higher photon energies by up to 20 meV, the Y_2 peak shifted by about 2

FIG. 3. Transformation of PL spectrum with exposure time of He–Cd laser at 15 K. $P_{\text{exc}}=200 \text{ W/cm}^2$. The sample was etched in H_3PO_4 for 1 min at 160 °C and subsequently exposed to air for 20 d.

meV in Ga polar layers, and by up to 8 meV in N polar layers, and the Y_1 peak usually shifted by about 1–2 meV to higher photon energies (Fig. 5).

4. Effect of temperature

The effect of sample temperature on PL was studied in nine samples including Ga and N polar films with different contributions of the Y_i peaks. The DBE peak quenched fast giving way to the FE peak at temperatures above 35 K in all the samples, thus confirming the identification of the FE and DBE peaks. At temperatures below 100 K, all the Y_i peaks quenched similar to the DBE and FE peaks with activation energies in the range between 10 and 30 meV. A typical transformation of the PL spectrum in Ga polar film is shown in Fig. 6 (see also Fig. 4 in Ref. 39). The Y_7 peak transformed with temperature in a very similar fashion in all the samples studied, namely, its Y_7' component at 3.21 eV quenched first, giving way above 120 K to the Y_7'' component at about 3.23 eV that quenched above 150 K. In Fig. 7(a), we

FIG. 4. Intensity of the Y_4 peak across the sample after exposure of three points to UV light by He–Cd laser beam having a diameter of $\sim 0.1 \text{ mm}$ and excitation power density of 200 W/cm^2 followed by storage in dark for 1 h. The central point was exposed for 2 h, and the other two for 20 min.

FIG. 5. Dependence of the PL peak shift on excitation density at 15 K.

plotted the intensities of the Y'_7 and Y''_7 components versus inverse temperature and fitted the experimental data to the well-known expression⁴²

$$I(T) = \frac{I_0}{1 + C \exp(-E_a/k_B T)}, \quad (1)$$

where I_0 and C are constant parameters, k_B is the Boltzmann constant, and E_a is the activation energy. The fit yields $E_a = 15 \pm 5$ meV for quenching of Y'_7 component below 120 K and $E_a = 120 \pm 20$ meV for quenching of Y''_7 component above 120 K. Note that above 120 K the Y'_7 peak quenched at the same rate or even faster than the Y''_7 peak. This behavior is similar to the interplay between the DBE and FE peaks⁴³ observed also in the samples studied, which confirms that the Y'_7 and Y''_7 peaks have a common origin.

FIG. 6. PL spectra at different temperatures and $P_{\text{exc}} = 100$ W/cm². FIG. 7. Temperature dependence of two components of the Y_7 peak (a) and the Y_4 peak (b). Solid curves are fits using Eq. (1) with $E_a = 15$ meV (Y'_7), 120 meV (Y''_7), 18 meV (Y'_4), and 42 meV (Y''_4).

In the Ga polar films exhibiting an intense and well-defined Y_4 peak (samples 426, 605, 845, and 1107), we have noticed a shoulder at the high-energy side of the peak about 12 meV from the main Y_4 peak, which evolved into a separate peak with increasing temperature (see Figs. 4 in Refs. 38 and 39). Although these peaks may be independent, we assume a common nature and labeled them as Y'_4 and Y''_4 . The thermal behavior of these peaks [Fig. 7(b)] was similar to that of the Y_7 doublet. Quenching of the PL intensity could be fitted using Eq. (1) with $E_a = 18$ meV for the Y'_4 peak and $E_a = 42$ meV for the Y''_4 peak.

A typical transformation of the PL spectrum with temperature in N polar films exhibiting the Y_2 – Y_7 peaks is shown in Fig. 8. In N polar films exhibiting an intense Y_1

FIG. 8. Temperature dependence of PL spectrum at $P_{\text{exc}} = 0.2$ W/cm² for N polar GaN film grown on sapphire substrate.

FIG. 9. PL spectrum of N polar sample 627 at $P_{\text{exc}} = 10^{-3} \text{ W/cm}^2$ (a) and 100 W/cm^2 (b) at different temperatures in the range between 15 and 100 K. Dashed vertical lines show the low-temperature positions of the peaks: Y_1' —3.445 eV (a), 3.453 eV (b); Y_1'' —3.4596 eV (a), (b); DBE—3.4702 eV (a), 3.4712 eV (b); FE—3.478 eV (a), (b).

peak, the low-energy component Y_1' gave way to the high-energy component Y_1'' (Fig. 9). Note that the position of the Y_1' component depended on the excitation intensity. Despite the apparent difference in the quenching behavior at low and high excitation intensities, quenching of the Y_1' and Y_1'' peaks in both cases takes place with the same activation energy of about $23 \pm 5 \text{ meV}$.

We plotted the positions of the FE (DBE) and some of the Y_i peaks versus temperature (Fig. 10) in order to compare the peak shifts with reduction of the GaN band gap. All shifts in the Y_i peaks are consistent with the temperature shrinkage of the GaN band gap,⁴⁴ supporting our assumption that the Y_i peaks originate from GaN layer.

FIG. 10. Temperature dependence of positions of the FE and Y_i peaks in GaN samples. For sample 605 the DBE and FE peaks were unresolved and the position of their common maximum is plotted. Solid curves reproduce the temperature dependence of the GaN band gap (Ref. 44) shifted vertically to fit the data for the Y_i peaks.

IV. DISCUSSION

A. Oil-related 3.31 and 3.36 eV lines

There are numerous reports regarding the 3.36 and 3.31 eV lines in GaN.^{22–34} The actual position of these sharp lines falls into the range of 3.358–3.370 and 3.298–3.313 eV in these studies. Usually these lines were detected in undoped GaN where no emission typical for GaN was observed^{22–28} or in *p*-type GaN where the near-band-edge emission was absent or very weak.^{29–31} A few clearly observed phonon replicas of the 3.31 eV line (separated by about 70 meV which is lower than LO phonon energy in GaN by about 20 meV) were reported.^{22–25,29} No shift in the position of the 3.36 eV line was observed under a hydrostatic pressure up to 4.4 GPa, while the band gap of GaN increased by about 190 meV.²³ The lines were most commonly attributed to the cubic phase inclusions formed by stacking faults^{26,32} or to excitons localized at extended defects in GaN.^{22,23,29,33}

The unusual properties of the 3.31 and 3.36 eV lines (zero pressure coefficient, lower than LO phonon energy separations between phonon replicas, appearance of these lines in the samples with very weak or zero background from the usual excitonic emission) lead one to consider the possibility of an artifact of measurements. We observed these lines of questionable origin with the same positions, shapes, and *properties* in the PL spectrum of GaN only when we used oil-based thermal compound for affixing the samples to the sample holder.³⁸ In particular, three pronounced phonon replicas of the 3.31 eV peak separated by about 70 meV were observed (see Fig. 1 in Ref. 38). Almost identical PL spectra were obtained from a droplet of mechanical pump oil. We assume that the 3.31 and 3.36 eV peaks, observed in Refs. 22–34, are related to some kind of oil contamination. To eliminate these sorts of artifacts in our experiments, we used an oil-free pump system and chose to clip the samples to the holder without any glue or paste. Despite these precautions, we did observe PL peaks at about 3.30–3.33 and 3.35–3.36 eV (the Y_4 , Y_5 , and Y_6 peaks). However their *properties* and shapes were different from those of the oil-related 3.31 and 3.36 eV lines.

B. Emission from cubic inclusions

In order to ascertain whether the observed Y_i peaks are due to the cubic phase inclusions in wurtzite GaN or not, we will briefly review the selected optical studies on cubic GaN. It is well established that the low-temperature PL spectrum of zinc-blende (cubic) GaN grown on GaAs contains two intense peaks: a peak at $3.27 \pm 0.01 \text{ eV}$, attributed to exciton (FE and DBE) emission, and a peak at 3.13–3.18 eV, attributed to the DAP-type emission involving shallow donors and acceptors.^{45–48} Much weaker features were detected in the PL spectrum of cubic GaN below 3.1 eV.^{45,47,48} Very similar results were obtained for GaN grown on *c* plane of sapphire when a minor amount of cubic phase formed in hexagonal GaN.^{49–51} It was demonstrated that the peak position of the 3.27 eV line is independent of excitation intensity and follows the band gap with increasing temperature.^{45–48} The DAP emission shifted markedly to higher photon energies

with excitation intensity^{45–49} and with temperature^{45–48} demonstrating a behavior typical of the DAP-type transitions.

The positions and properties of the 3.27 and 3.15 eV peaks from cubic GaN or cubic inclusions in hexagonal GaN do not match any of the Y_i peak studied in this work. It is also doubtful that nanometer-size cubic inclusions may be responsible for the sharp and intense PL peaks observed in this study, as was suggested in Ref. 26 for explaining the 3.31 and 3.37 eV peaks in GaN. Indeed, fluctuations in the shift due to the quantum size effect should be large enough for such small inclusions, resulting in substantial broadening of the emission peak and different peak positions in different samples.

C. Characteristics of the Y_i peaks

1. The 3.45 eV peak (Y_1)

The 3.45 eV peak, denoted in this work as Y_1 , appeared only in our N polar films containing a high density of inversion domains ($\sim 10^{11} \text{ cm}^{-2}$) and relatively low density of dislocations ($\sim 10^9 \text{ cm}^{-2}$).^{52,53} Although the position of the Y_1 peak is about the same as that for the two-electron satellites of the DBE in GaN,⁵⁴ we rule out such identification in our N polar GaN samples because the ratio between the intensities of the main DBE peak and its two-electron satellite should not be sample dependent, whereas the relative intensity of the Y_1 peak changed at least 100 times among the samples. Previously this peak was detected in GaN samples with columnar structure as a doublet with maxima at 3.452 and 3.458 eV and was attributed to an exciton bound to a donor or acceptor involving a hole from the *A* or *B* valence subbands, respectively.¹⁶ Recent high spatial resolution PL studies demonstrated that the bright emission at 3.45–3.46 eV originates from the inversion domain boundaries and this peak was attributed to a shallow trap.³⁵ Our results are consistent with the results of Ref. 35 since the 3.45 eV peak dominated in the PL spectrum of our N polar samples having a high density of inversion domains. However we would argue with the assumption made in Ref. 35 that the corresponding transition is from the conduction (or valence) band to a shallow trap. The intensity of the Y_1 peak in our sample 627 did not show any saturation behavior up to 300 W/cm² and even increased superlinearly in the range of 0.3–300 W/cm², rather implying an excitonic nature. A very small Huang–Rhys factor⁵⁵ for the Y_1 peak (about 0.02) also supports the assumption about its excitonic nature. We assume that the Y_1 peak is related to excitons bound to inversion domain boundaries. Narrow Ga polar domains in N polar media may create high and narrow potential humps near the surface due to essentially different band bending near the surface in Ga and N polar films.⁵⁶ The height of these potential humps may be sample dependent, dictated by adsorbing ability and the extent of surface oxidation, etc. This would explain the slightly different positions of the Y_1 peak in different samples. The shift of the peak position with excitation intensity may be due to partial screening of potential variation near the surface. It is unlikely that the two components of the Y_1 peak (Y'_1 and Y''_1) are due to location of the hole in the *A* and *B* valence subbands, as it was proposed in Ref. 16,

because the separation between the components in the doublet depends on excitation intensity (Fig. 9). They rather reflect contributions from the bulk and surface regions of the sample. The position of the surface-related component (Y'_1) is sample-dependent since the potential at the surface is affected, for example, by oxidation and adsorption.

2. The 3.42 eV peak (Y_2)

Extensive studies of the 3.42 eV peak in GaN have been undertaken previously. The exact position of this peak was sample-dependent, spaced from the DBE peak by a distance of about 40–65 meV.^{12,16} Sometimes a doublet structure of this peak was observed.^{15,18,20} The relative intensity of this peak increased after annealing, especially in water vapor atmosphere.³⁶ It was noted in Ref. 16 that the 3.42 eV emission dominated in columnar GaN and that cathodoluminescence (CL) images at 3.42 eV revealed bright spots corresponding to the column sites. A shift of this peak to higher photon energies was observed with increasing temperature or excitation intensity and interpreted as manifestation of the DAP transitions involving unknown shallow acceptor.^{14,18,21} Others attributed the 3.42 eV peak to a transition from a donor to the valence band where the donor was assumed to be oxygen.^{12,13} Some investigators suggested that the 3.42 eV peak is related to structural defects,^{10,15–20} in particular to cubic inclusions or stacking faults in the wurtzite GaN^{10,18,19} or to *c*-axis screw dislocations.²⁰

The 3.42 eV peak, denoted in this study as Y_2 , appeared in many of our as-grown GaN samples with Ga and sometimes N polarity. The separation between the DBE and Y_2 peak ranged from 50 to 70 meV in different samples. We observed a doublet nature of the Y_2 peak in N polar samples (Fig. 8) with a separation between the components of about 7–9 meV, whereas in Ga polar samples it always appeared as a single peak. The Y_2 peak was detected only in as-grown samples with columnar- or bubble-like surface morphology, and it never appeared in the samples with flat surface (samples 605, 1107 exhibiting Y_4 and Y_7 peaks and in many other samples not containing any Y_i peaks). The Y_2 peak disappeared or drastically decreased after etching in hot phosphoric acid, which removed the top bubble-like layer. With increasing excitation intensity, the Y_2 peak typically did not shift (with accuracy of 1–2 meV) in Ga polar films representing a single peak, but it shifted to higher energies (both Y'_2 and Y''_2 components) in the N polar films. The Huang–Rhys factor of this emission was estimated as 0.05. All the above-mentioned observations allow us to conclude that the Y_2 peak is related to excitons bound to some surface defects rather than to dislocations.

3. The 3.38 eV peak (Y_3)

The 3.38 eV peak, denoted as Y_3 , appeared only in two of the samples investigated: 495 (N polar) and 770 (Ga polar). The relative intensity of this peak was usually small which hampered its investigation to some extent. The Y_3 peak could be confused with LO phonon replicas of the DBE or FE emission. However, in some cases the Y_3 peak clearly appeared as an independent peak with behavior different

TABLE II. Positions of the main Y_i peaks in selected samples, as-grown and etched in phosphoric acid (with suffix “e”).

Sample	Polarity	Position of PL peak (eV)							
		DBE	Y_1	Y_2	Y_3	Y_4	Y_5	Y_6	Y_7
215	Ga	3.471	—	3.410	—	—	—	—	—
243	Ga	3.476	—	3.42	—	3.463	3.342	3.312	3.212
426	Ga	3.474	—	3.415	—	3.356	—	3.319	3.207
426-e		3.473	—	—	—	3.356	—	3.306	3.206
429	Ga	3.472	—	3.412	—	?	—	3.305	3.205
452	Ga	3.477	—	3.425	—	3.365	—	3.32	3.218
455	Ga	3.477	—	3.426	—	3.365	—	3.333	3.214
455-e		3.483	—	—	—	3.367	—	3.326	3.214
460	Ga	3.478	—	—	—	3.365	—	?	3.220
471	Ga	3.477	—	3.428	—	3.367	—	3.334	3.212
471-e		3.475	—	—	—	3.362	—	3.324	3.215
605	Ga	3.462	—	—	—	3.348	—	—	3.192
605-e		3.462	—	—	—	3.348	—	—	3.193
750	Ga	3.477	—	—	—	—	—	—	?
770	Ga	3.477	—	3.422	3.374	3.362	—	?	3.217
770-e		3.478	—	—	3.374	3.360	—	?	3.216
845	Ga	3.472	—	3.412	—	3.357	3.340	3.310	3.212
847	Ga	3.469	—	~3.4	—	3.350	3.332	?	?
1107	Ga	3.472	—	—	—	3.351	—	—	3.213
495	N	3.472	—	3.410	3.381	3.356	3.342	3.314	3.220
495-e		3.469	3.451	3.410	?	3.353	3.339	3.305	3.216
618	N	3.471	3.455	—	—	—	—	—	—
622	N	3.469	3.450	—	—	—	—	—	—
627	N	3.471	3.458	—	—	—	—	—	—
627-e		3.471	3.458	—	—	—	—	—	—
688	N	3.471	—	3.408	—	?	?	3.315	3.221
688-e		3.476	3.455	?	—	3.354	3.339	3.310	3.216
692	N	3.470	3.455	3.416	—	3.355	3.340	3.310	3.217

from the DBE and FE emission (see Fig. 2 in Ref. 38). In contrast to the FE and DBE emission, the intensity of this peak saturated with excitation intensity, however no shift was detected in a wide range of excitation intensities. With increasing temperature, the Y_3 peak quenched in a fashion similar to the quenching of the DBE emission and disappeared above 50 K due to a large contribution of the Y_2 , Y_4 and FE emissions at this photon energy (Fig. 8). A peak with a similar position (at about 3.38 eV), along with other peaks, similar to our Y_2 , Y_4 , and Y_7 peaks, was observed recently in the CL spectrum of a GaN sample grown by MBE on sapphire.¹⁷ Due to the absence of any shift of the Y_3 peak with excitation intensity, we rule out the possibility of DAP-type nature for this peak and attribute it to excitons bound to some unknown defects. The observed saturation of the peak intensity with excitation intensity can be explained by a low concentration of these defects.

4. The 3.35 eV peak (Y_4)

The 3.35 eV peak, denoted in this study as Y_4 , could be confused with the oil-related 3.36 eV line, and only a comprehensive study including variation of temperature and excitation intensity, cleaning and etching, etc., could pave the way to distinguish this PL line from that associated with oil contaminants. We suggest that, a peak with similar position observed in Refs. 22–34 is oil related, whereas the 3.35–3.36 eV lines observed in Refs. 17 and 37 may have the same origin as the Y_4 peak in our samples. The peak at about 3.37 eV observed by Kornitzer *et al.*¹³ is different from our Y_4 or

Y_3 peaks because the temperature quenching of the 3.37 eV peak in Ref. 13 is much slower than that for our Y_4 or Y_3 peaks.

We note that the Y_4 peak appeared only in Ga and N polar samples exhibiting a strong Y_7 peak, even when there were no other Y_i peaks (see Table II). This peak, having a full width at half maximum (FWHM) of 8–10 meV in representative samples, never shifted with excitation intensity and its shift with temperature was similar to the reduction of the band gap. It also never saturated with variation of the excitation intensity in a wide range. These are strong arguments in support of its excitonic nature. Etching the sample generally led to an increase of intensity of this peak. A very interesting effect is the evolution of the Y_4 peak intensity, observed in several Ga polar samples. The detailed study showed that while its intensity increased (sometimes up to a factor of 5) after several hours of UV exposure, the peak position shifted to lower photon energies by almost 1 meV. After interruption of the UV exposure, the intensity of the Y_4 peak decreased very slowly at low temperatures (about 10% decrease in 1 h), but after heating the sample to room temperature the initial PL intensity was restored. The Y_4 peak is due to an exciton bound to some surface defects, because UV illumination may affect the surface condition (for example, photoinduced desorption may charge or discharge surface states). Its excitonic nature is supported also by a very small FWHM (8–10 meV in representative samples) and a very small Huang–Rhys factor (0.01). The LO phonon replica of

this peak was clearly seen at a distance of about 90 meV in the samples with well-defined Y_4 peak (Fig. 4 in Ref. 38).

5. The 3.34 eV peak (Y_5)

The peak with a maximum at about 3.34 eV (the Y_5 peak) was observed only in a few samples: 495, 688, 692 (N polar films) and 243, 845 (Ga polar films). The relative intensity of this peak was usually small, hampering its study. The Y_5 peak was relatively sharp in all the above samples. Its position did not shift and its intensity did not saturate with increasing excitation intensity (see Fig. 2 in Ref. 38). With increasing temperature this peak quenched similar to other Y_i peaks at low temperatures and it disappeared above 30–50 K under the wing of the Y_6 peak at this photon energy. Similarly to the Y_3 peak, we attribute the Y_5 peak to exciton bound to some unidentified defect.

6. The 3.32 eV peak (Y_6)

The 3.32 eV peak, denoted in this study as Y_6 , could be confused with the oil-related 3.31 eV line. However, its properties are very different from those of the 3.31 eV peak studied in Refs. 22–34. The Y_6 peak was detected in most of the studied samples, both in Ga and N polar GaN films (see Table II). In the samples exhibiting the Y_i peaks, the Y_6 peak was not detected only in N polar films containing solely the Y_1 emission in the PL spectrum (samples 618, 622, and 627) and in Ga polar films with very flat surface (samples 605 and 1107). Unlike most of the Y_i peaks (and in contrast to the oil-related line), the Y_6 peak shifted substantially with excitation intensity in all the studied samples and was relatively broad. The character of the shift is typical for the shift of the DAP emission including a relatively deep donor.⁵⁷ We observed also a small “blue” shift of the Y_6 peak at low excitation intensities (Fig. 8) and “red” shift at high excitation intensities (Fig. 4 in Ref. 39) with increasing temperature, which is consistent with the attribution of this peak to a DAP-type transition, similar to the observations made in Ref. 58 for the DAP including a deep donor. With increasing temperature the Y_6 peak quenched (Figs. 6 and 8) with an activation energy of about 30 meV. We speculate that this is the binding energy of the donor involved in the DAP.

The attribution of the Y_6 peak to a DAP transition may seem to contradict the premise that the most shallow acceptor in undoped GaN has an activation energy of about 180 meV⁵⁹ and the corresponding DAP peak is some 40–50 meV deeper than the Y_6 peak.⁵⁴ We propose that the shallow donor and acceptor responsible for the Y_6 peak are located on the GaN surface. The binding energy for the donors and acceptors on the surface is reduced.^{60,61} The surface-related shallow DAP band has been previously identified in CdS at photon energies higher than the bulk shallow DAP band.⁶² Additional evidence supporting the surface origin of the Y_6 peak follows from the intensity evolution of the Y_6 peak with UV exposure time (Fig. 5 in Ref. 38). The intensity of the Y_6 peak increased by up to two times in some Ga polar samples and the peak shifted by about 5 meV to higher photon energies during this exposure. Similar to the Y_4 peak, the intensity of this peak stayed nearly unchanged for quite a long

time after the termination of UV exposure. One possible reason of the PL intensity evolution may be photo-induced desorption of some species from the surface. This process may cause a variation in band bending and, as a result, variation of the DAP transition energy since the energy of the spatially separated transitions depends on the slope of the bands.

7. The 3.21 eV peak (Y_7)

The 3.21 eV peak, denoted here as Y_7 , with a few LO phonon replicas has been observed in several studies.^{13,16,17,21,37} Sometimes the 3.2 eV peak appeared as a doublet with a separation of about 20–25 meV between its maxima.^{13,21} This peak was attributed to an unknown acceptor²¹ or to structural imperfections.³⁷

We observed the Y_7 peak in most of the studied samples (see Table II). With increasing temperature, the main component of the Y_7 peak (denoted Y_7') quenched, giving way to the high-energy component, Y_7'' (Figs. 6 and 8). A very similar transformation of the Y_7 peak has been observed in all samples measured in a wide temperature range (totally nine samples). The distance between the Y_7' and Y_7'' components was usually about 16 meV. The intensity of both components quenched with temperature [Fig. 7(a)] with quite small activation energy (about 120 meV) pointing to an excitonic origin of the Y_7 peak. This assumption is supported by its behavior with variation of excitation intensity in wide range (linear increase of the PL intensity without saturation and absence of the peak shift) and a very small Huang–Rhys factor (about 0.06). We assume that the Y_7 peak is related to excitons bound to some type of dislocations or other structural defects in GaN.

D. About identification of the Y_i peaks

Narrow luminescence lines with unusual properties have been originally found in ZnSe⁶³ and Si,⁶⁴ and since then there were numerous reports about unusual lines in ZnSe,⁶⁵ CdTe,⁶⁶ ZnTe^{65–67} (Y and Z lines) and in silicon (the so-called $D1$ – $D12$ lines).^{68–70} These lines in II–VI compounds and silicon are commonly attributed to excitons bound to extended structural defects,⁷¹ although the exact nature is controversial.⁷⁰ The question as to whether point defects are involved in this type of emission is also an open issue.⁶⁹ The majority of the Y_i lines in GaN, studied in the present work, are also related to extended structural defects. Below we present some arguments in support of our assertion.

The positions of the most frequently observed Y_i peaks were quite repeatable in a large set of GaN samples. They appeared at the following distances in energy from the DBE peak: 53 ± 3 meV (Y_2); 115 ± 1 meV (Y_4); 156 ± 5 meV (Y_6); and 262 ± 3 meV (Y_7). The Y_i peaks quench with rather small activation energies, much smaller than the binding energy of the shallowest known acceptor in GaN (note that quenching of the defect-related PL in n -type GaN is determined by escape of bound holes, not electrons).⁵⁹ However, the small activation energy can be explained by assuming that the Y_i peaks arise from recombination of excitons bound to some structural defects, such as dislocations, stacking faults, inversion domains, etc. Due to the one-dimensional strain field, the responsible defect may create a

strong local one-dimensional potential, which can strongly bind a hole, in turn attracting a loosely bound electron to form a bound exciton.⁷² Then the smaller activation energy observed at low temperatures may reflect the binding energy of the weakly bound electrons, whereas a deeply bound hole may be responsible for the larger activation energy at higher temperatures, observed in the quenching of the Y_4 and Y_7 peaks.

The high-energy components in several doublet peaks (Y_2 , Y_4 , and Y_7) can be also explained by the formation of complexes consisting of two holes bound to the structural defects and one electron bound to these holes by the Coulomb field (charged defect), as it was suggested earlier in explaining the doublet origin of the 364 nm line in GaN.²⁰ In contrast to the Y_2 , Y_4 , and Y_7 doublets, the separation of the Y_1 doublet components depended on excitation intensity which may be attributed to contributions from the surface and bulk regions of the sample.

In two recent articles,^{73,74} a correlation between the crystal quality, established by XRD, and the properties of the 3.42 eV peak has been reported. In particular, in a set of five GaN samples grown on SiC by MBE, the relative intensity of the 3.42 eV peak decreased less than two times with increasing FWHM of the (0002) GaN diffraction peak from ~ 12 to 16 arcmin,⁷³ indicating in the opinion of the authors of Ref. 73 that the 3.42 eV emission is related to the threading dislocations in GaN. In another study, it was noted that the 3.42 eV peak in GaN layers grown by HVPE on Si shifted from about 3.40 to 3.423 eV with an increase in the FWHM of the (0002) GaN diffraction peak from ~ 14 to 20 arcmin.⁷⁴ This led the authors of Ref. 74 to imply that the 3.42 eV emission is related to the crystal quality. We compared the peak positions and relative intensities of the Y_i peaks with the FWHM of the (0002) GaN diffraction peak in a large set of GaN layers grown by MBE on sapphire and could not find such correlation for any of the Y_i peaks (Fig. 11). Note that in a large set of reference GaN samples not containing the Y_i peaks, the FWHM of the (0002) diffraction peak also varied substantially, in the range from 1 to 50 arcmin. The broadening of the (0002) diffraction peak has been reported to relate to the density of screw dislocations.⁷⁵ The lack of a correlation between the appearance of the Y_i peaks and the FWHM of the (0002) GaN diffraction peak in the present work indicates that apparently none of the Y_i peaks is related to screw or mixed dislocations, in contrast to the assumption of Shreter *et al.*²⁰ on the origin of the 3.42 eV peak in GaN. Moreover, since the density of edge dislocations was not much different in our samples exhibiting strong Y_i peaks and reference samples containing no unusual peaks in the PL spectrum (in selective samples from both sets the density of edge dislocations varied from mid 10^9 to high 10^{10} cm⁻² according to the cross-sectional TEM data), we may also exclude the possibility that any of the Y_i peaks is related to the edge dislocations, as well. However we cannot exclude that the Y_i peaks are related to some point defects gettered by dislocations. As mentioned above, most of the Y_i peaks are most likely related to excitons bound to some structural or point defects, the nature of which is still not known. The fact that we do not observe unusual deep-level PL bands in

FIG. 11. Position of the DBE and Y_2 peaks (a) and ratio of PL intensities between the Y_i and DBE peaks (b) as a function of the FWHM of the (0002) XRD peak in a large set of thin GaN layers grown by MBE on sapphire substrate.

the samples with strong Y_i peaks may indicate that these point defects are nonradiative, even though they can bind excitons.

Despite the extensive list of samples and detailed PL investigations, aided by etching and XRD, additional studies would help narrow the possible origin of the Y_i peaks. In particular, secondary ion mass spectroscopy may establish possible correlation between the Y_i peaks and presence of impurities such as Si, C, or O. A detailed study of the GaN samples exhibiting strong Y_i peaks with TEM methods could also reveal some correlation between different types of structural defects (both bulk and surface) and Y_i peaks. Micro-PL and micro-CL studies could establish correlations between the surface defects and particular Y_i peaks. After obtaining the lifetimes of the Y_i peaks from the time resolved PL studies, one can estimate concentrations of the defects responsible for the Y_i peaks, using the method suggested in Ref. 59.

V. SUMMARY

We observed, studied, and classified the following unidentified peaks in the low-temperature PL spectrum of undoped GaN: Y_1 (3.45 eV), Y_2 (3.42 eV), Y_3 (3.38 eV), Y_4 (3.35 eV), Y_5 (3.34 eV), Y_6 (3.32 eV), and Y_7 (3.21 eV). Most of the peaks increased approximately linearly with increasing excitation density up to 300 W/cm² (except for the Y_3 and Y_6 peaks). The Y_3 , Y_4 , and Y_7 peaks did not shift with the excitation intensity, whereas the Y_6 peak shifted noticeably in all studied samples. The Y_1 , Y_2 , Y_4 , and Y_7 peaks appeared as doublets, at least under some experimental conditions. The Y_4 and Y_6 peaks evolved with duration of UV illumination.

Most of these peaks are related to excitons bound to structural defects in GaN yet to be identified. The Y_6 peak is attributed to the surface DAP-type transition. The Y_1 peak is related to the inversion domain boundaries.

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