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Photoluminescence of GaN grown by molecular-beam epitaxy on a freestanding GaN template

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Photoluminescence (PL) studies were performed on a 1.5-μm-thick GaN layer grown by molecular-beam epitaxy on a freestanding GaN template that in turn was grown by hydride vapor-phase epitaxy. PL spectra from both the epilayer and the substrate contain a plethora of sharp peaks related to excitonic transitions. We identified the main peaks in the PL spectrum. Taking advantage of the observation of donor bound exciton peaks and their associated two-electron satellites, we have determined the binding energies of two distinct shallow donors (28.8 and 32.6 meV), which are attributed to Si and O, respectively. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1421421]

The major obstacle to obtain high-quality III-nitrides materials and devices is the lack of native substrates. At present, sapphire is the most commonly used substrate for the GaN-based devices. However, because of large lattice mismatch between these materials and different thermal expansion coefficients, a high density of dislocations is typical for GaN regardless of the growth technique employed. Recently, several attempts have been made to grow homoepitaxial GaN by molecular-beam epitaxy (MBE) (Ref. 1) and metalorganic chemical-vapor deposition (MOCVD) (Refs. 2–5) on bulk GaN single crystals prepared by a high-pressure, high-temperature method[1–4] and on quasibulk GaN grown on sapphire by hydride vapor-phase epitaxy (HVPE) and then separated by laser lift-off.[5] The obtained high-quality layers allowed observation of numerous sharp excitonic features in the photoluminescence (PL) spectrum. Several PL peaks in the excitonic spectrum of GaN are unambiguously identified, while attributions of others still remain controversial.

In this letter, we report the PL study of homoepitaxial GaN grown by MBE on a 200-μm-thick freestanding GaN template. We have determined the binding energies of two shallow donors in undoped GaN, attributed to silicon and oxygen. A nominally undoped 1.5 μm layer was grown by MBE on a Ga face of freestanding GaN template. The template in turn was grown by HVPE on a *c*-plane sapphire substrate and separated from the substrate by laser lift-off. Before the overgrowth, the GaN template was mechanically polished, dry etched, and finally etched in molten KOH. A 30-nm-thick undoped $Al_xGa_{1-x}N$ cap layer with $x=12\%$ has been deposited on top of the 1.5 μm GaN layer. Part of the 10×10 mm surface of the sample was mechanically shuttered during the MBE process, so that both the GaN substrate and MBE-overgrown layer could be studied under the same experimental conditions.

Steady-state PL was excited with a He–Cd laser (325 nm), dispersed by a 1200 rules/mm grating in a 0.5 m monochromator and detected by a photomultiplier tube. The best resolution of the PL setup was about 0.2 meV, the photon energy was calibrated with a mercury lamp accounting for the refraction index of air.

The structural properties of the GaN template and overgrown MBE epilayer were characterized by high-resolution x-ray diffraction. The full widths at half maximum (FWHM) of the omega scan (rocking curve) for the [002], [102], and [104] directions are 53, 145, and 54 arc s, respectively, for the MBE-grown area and 52, 137 and 42 arc s, respectively, for the GaN substrate. The similar characteristics of the substrate alone and the substrate with MBE overgrowth indicate a similar crystal quality of GaN both in the substrate and overgrown layer. A comprehensive characterization of the high-quality GaN templates has been reported elsewhere[6] and will not be repeated here.

Excitonic PL spectra of the substrate and MBE-overgrown area are shown in Fig. 1. The main features of the PL spectra are similar, yet a few distinctions can be noticed. A peak at 3.4673 eV is attributed to the *A*-exciton bound to an unidentified shallow acceptor $(A^0,X_A^{n=1})$.[4] The most intense peaks at 3.4720 and 3.4728 eV are attributed to the *A*-exciton bound to two neutral shallow donors, D_1 and D_2: $(D_1^0,X_A^{n=1})$ and $(D_2^0,X_A^{n=1})$. The FWHM of these peaks is 0.7 meV at 15 K and their positions are the same with an accuracy of 0.2 meV for the substrate and different points of the overgrown layer. The ratio between the intensities of the $(D_1^0,X_A^{n=1})$ and $(D_2^0,X_A^{n=1})$ peaks is different in the substrate and overgrown layer (Fig. 1). This feature helped us to identify four other peaks related to the excitons bound to the same shallow donors. Namely, the peaks at 3.4758 and 3.4766 eV, having the same intensity ratio and energy sepa-

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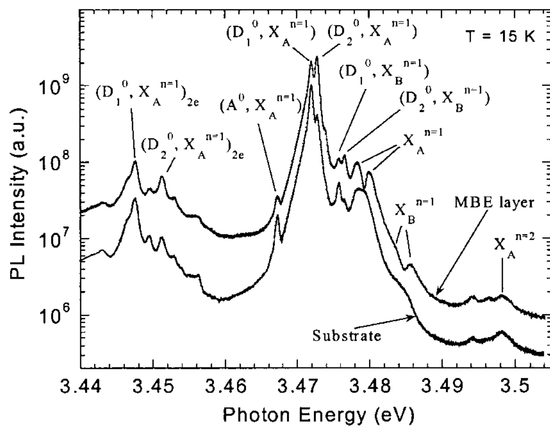

FIG. 1. Excitonic PL spectrum for GaN in the area of substrate and in the MBE-overgrown part. Excitation density is 100 W/cm^2.

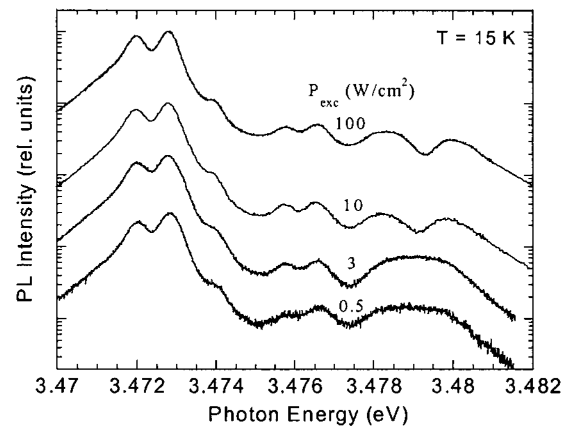

FIG. 2. PL spectrum of MBE-overgrown GaN at different excitation densities ($P_{\rm exc}$).

ration as the $(D_1^0,X_A^{n=1})$ and $(D_2^0,X_A^{n=1})$ peaks are attributed to the B-exciton bound to the D_1 and D_2 donors: $(D_1^0,X_B^{n=1})$ and $(D_2^0,X_B^{n=1})$, in agreement with Refs. 4 and 7. Note that in the previous works only a single peak was observed in this region (3.476 ± 0.002 eV) of the PL spectrum.[2–4,7,8] Our data rule out the alternative assignment relating this peak to the A-exciton bound to an ionized donor $(D^+,X_A^{n=1})$.[3,8] Indeed, the energy separation between the $(D_1^0,X_B^{n=1})$ and $(D_2^0,X_B^{n=1})$ peaks observed in our study is only 0.8 meV, whereas the peak separation of the $(D_1^+,X_A^{n=1})$ and $(D_2^+,X_A^{n=1})$ excitons should be equal to the difference between the ionization energies of the donors, which is about 4 meV, as will be estimated below.

Two other peaks, also related to donor bound excitons (DBEs), are observed at 3.4475 and 3.4512 eV and attributed to the so-called two-electron transitions: $(D_1^0,X_A^{n=1})_{2e}$ and $(D_2^0,X_A^{n=1})_{2e}$. This type of DBE recombination, first observed in GaP,[9] involves radiative recombination of one electron with a hole leaving the neutral donor with second electron in an excited state. One of these peaks (3.451 eV) has previously been reported[4,8,10] and attributed to Si.[10] In the effective-mass approximation, the donor excitation energy from the ground to the $n=2$ state equals $\frac{3}{4}$ of the donor binding energy E_D. Consequently, from the energy separation between the principal DBE line and the associated two-electron satellite, we can find the binding energies of two shallow donors: $E_{D_1}=4/3\times24.5=32.6$ meV, $E_{D_2}=4/3\times21.6=28.8$ meV. It appears reasonable that the peak at 3.443 eV is the two-electron transition related to the second excited state ($n=3$) of the D_1 donor since its separation from the $(D_1^0,X_A^{n=1})$ peak is $8/9\times32.6=29.0$ meV.

Free excitons (FEs) related to the A and B valence bands ($X_A^{n=1}$ and $X_B^{n=1}$) are identified at about 3.479 and 3.484 eV, respectively, in the PL spectrum of the GaN substrate (Fig. 1). The $X_A^{n=1}$ peak has an asymmetrical shape, and the $X_B^{n=1}$ peak is seen as a shoulder. In the MBE-overgrown epilayer these peaks are split: a doublet with maxima at 3.4782 and 3.4799 eV and a doublet with the high-energy maximum at 3.4856 eV (the low-energy maximum is seen as a shoulder in Figs. 1 and 2). Similar splitting has been observed earlier and attributed to a manifestation of the polariton branches.[2]

From the separation between the FE and DBE peaks we find the binding energies of the DBEs related to the D_1 and D_2 donors as 7.0 and 6.2 meV, respectively. According to the empirical Haynes rule, the binding energy of the DBE is proportional to the binding energy of the corresponding donor. The proportionality constant (α) for the D_1 and D_2 donors is found to be 0.215, which is close to the result of Meyer ($\alpha=0.2\pm0.01$).[7] In addition to the dominant DBE doublet, we observed a weak peak at 3.474 eV (Figs. 1 and 2). Assuming that this peak is the DBE $(D_3^0,X_A^{n=1})$ with the localization energy of 5.0 meV, we can estimate the binding energy of the corresponding donor, D_3, to be $E_{D_3}=5/\alpha=23.3$ meV. Furthermore, a weak peak at about 3.456 eV can be attributed to the two-electron satellite of the $(D_3^0,X_A^{n=1})$ peak. The origin of the weak peaks at 3.4496 and 3.4529 eV remains unclear. These peaks may be two-electron satellites of some unresolved DBE lines or excitons bound to deeper acceptors.[11]

With increasing temperature, all peaks related to the bound excitons quench, while the quenching of the free excitons is negligible up to 50 K (Fig. 3). This result supports the above assignments of the peaks. Excitons bound to the D_1 donor quench faster than the excitons bound to the D_2 donor, which is consistent with their binding energies.

In the range from 3.49 to 3.50 eV, we resolved three peaks (Fig. 1), which are often observed in this region, and sometimes denoted as X_1, X_2, and X_3.[4,8,12,13] It is believed that they all are related to the free A exciton and the highest-

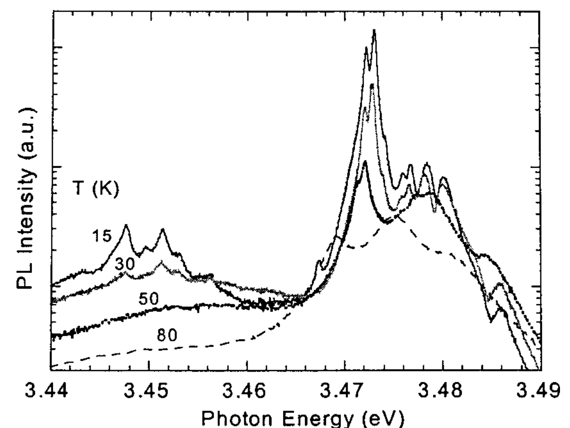

FIG. 3. PL spectrum of the GaN substrate (dashed line) and MBE-overgrown layer (solid line). Inset shows in more detail the exciton-related region.

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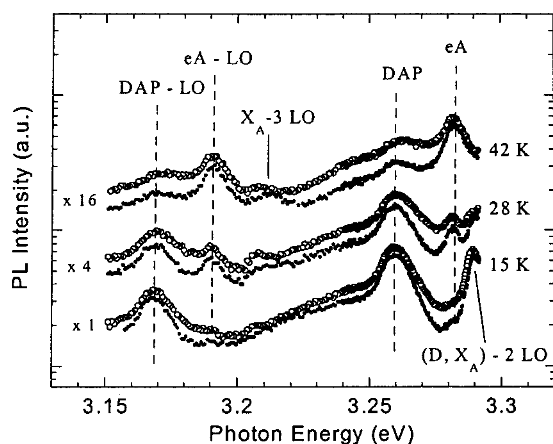

FIG. 4. PL spectrum of the shallow DAP band at different temperatures in the area of the substrate (empty circles) and in the MBE-overgrown part (filled circles). Excitation density is 100 W/cm^2.

energy one (X_3) is clearly established to be the $n=2$ excited state of the A exciton ($X_A^{n=2}$).[8,12,13] From the energy positions of the $X_A^{n=1}$ and $X_A^{n=2}$ peaks (3.479 and 3.4983 eV, respectively), we can find the A-exciton binding energy in the hydrogen model as 25.7 meV and the band gap $E_g=3.5047$ eV. Note that the observed positions of the PL peaks from the substrate and the overgrown epilayer are the same with an accuracy of 0.2 meV. As compared to the PL spectra from the strain-free GaN,[4] the PL peaks observed in our sample are shifted to higher energy by about 1 meV, indicating small residual strain in the GaN template.

The PL spectra of the substrate part and MBE-overgrown area are very similar in a wide range of the photon energies. Besides multiple sharp peaks related to the above-discussed excitonic transitions and their less-resolved LO phonon replicas at energy separations that are multiples of 92 meV, the spectra contain much weaker shallow donor–acceptor pair (DAP) emission with the main peak at about 3.26 eV, which is related to transitions from a shallow donor to unidentified shallow acceptor. With increasing excitation power, the maximum of the shallow DAP band shifted from 3.255 to 3.260 eV, which can be related to the saturation of emission from distant pairs having longer lifetimes. With increasing temperature from 15 to 60 K, the shallow DAP band quenches giving way to transitions from the conduction band to the shallow acceptor ($e-A$ transitions) with the main maximum at about 3.282 eV (Fig. 4). From the separation between the DAP and $e-A$ peaks in the low-excitation limit, one can estimate the ionization energy E_D of the shallow donor predominantly participating in the DAP transitions. Accounting for the average kinetic energy ($kT/2$) of free electrons (1.5 meV at 35 K) and the Coulomb interaction in the DAP of about 7.5 meV,[14] we obtained $E_D=32$ meV. This value is very close to the binding energy of the D_1 donor obtained above from the analysis of the excitonic spectrum. Note that position of the DAP band is the same in the substrate and overgrown layer within an accuracy of about 0.5 meV. This result may be explained by the fact that at low-temperature and low-excitation intensity the occupation of the deeper D_1 donor with electrons is more favorable.

It is commonly believed that Si and O are the dominant shallow donors in undoped GaN grown by different techniques.[7,10] The binding energy of the Si donor of about 29 meV has been extrapolated from the magnetic-field dependence of the infrared absorption in Si-doped GaN.[15] Mireles and Ulloa calculated the value of 30.4 meV for Si in GaN using an effective-mass theory approach that accounts for the central cell corrections.[16] These values are close to the binding energy of our D_2 donor (28.8 meV), and thus we assigned it to Si, although a shallower binding energy of Si donors (22 meV) has been reported.[17] Our D_3 donor is presumably the same defect observed in Si-doped GaN by Jayapalan *et al.*[17] Since oxygen is expected to be a somewhat deeper donor than silicon,[10] we attribute the D_1 donor (32.6 meV) to oxygen. This result is consistent with the calculated binding energy of oxygen donor (31.4 meV).[16]

In summary, homoepitaxial GaN layer grown by MBE on a freestanding GaN template has excellent crystalline and optical quality. The PL spectrum contains a plethora of sharp exciton peaks, as well as defect-related green and shallow DAP bands. Based on the fine structure of the excitonic PL spectra, we determined the donor binding energies to be 28.8 and 32.6 meV. These donors are attributed to silicon and oxygen, respectively.

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