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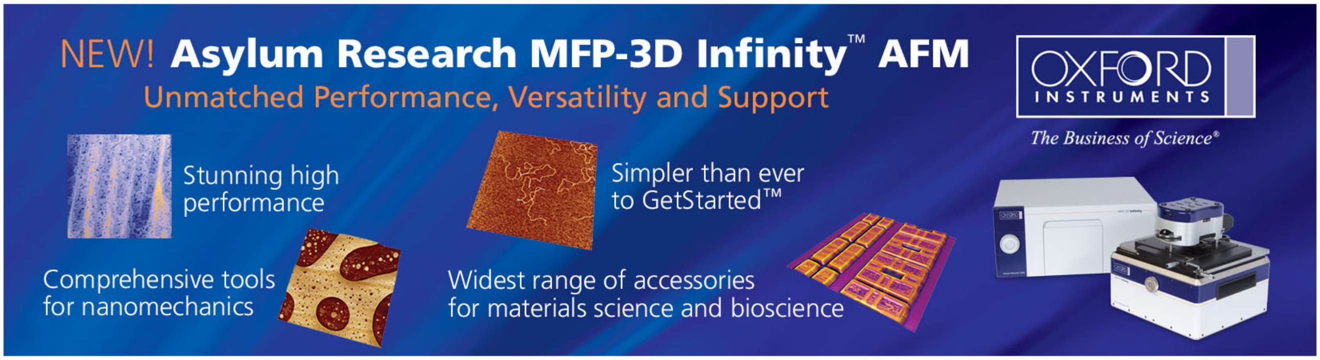

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Low-etch-pit-density GaN substrates by regrowth on free-standing GaN films

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In this study, GaN substrates with low-density etch pits were obtained by regrowth on free-standing GaN films (two steps) by hydride vapor-phase epitaxy (HVPE). The etch-pit density was lower than 4×10^4 cm^{-2} by atomic-force microscopy. The density is significantly lower than that of the HVPE-grown (one-step) GaN films (HVPE GaN), using sapphire as a substrate. The optical and electrical properties of the two-step HVPE-grown GaN substrates are superior to those of HVPE GaN. Temperature-dependent photoluminescence measurements reveal that thermal quenching behavior of the 2.9 eV band is possibly attributed to a shallow acceptor level at about 118 ±5 meV above the valence band.
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GaN is a promising material for optoelectronic device applications such as laser diodes and light-emitting diodes in the visible and ultraviolet spectrum as well as for electronic devices, due to its wide band gap and good thermal stability.[1] Because of lack of native substrates, these semiconductor devices have been grown on many alternative substrates such as sapphire and SiC. However, a large lattice mismatch is present between the GaN epitaxial layer and the foreign substrate, resulting in a large number of dislocations. Accordingly, sapphire and SiC give rise to a very large dislocation density, in the range of 10^8–10^{10} cm^{-2}.[2] In addition, the thermal expansion coefficient of the GaN film differs from that of the foreign substrate, giving rise to stress and bowing during heteroepitaxial growth. Using a GaN substrate would be a total solution to the problems mentioned above. Hydride vapor-phase epitaxy (HVPE), sublimation, and a high-pressure method have been applied to obtain GaN bulk crystal.[3–5] HVPE is so far the best of all these methods by which to grow thick GaN films because of its high growth rate. The extended defect density (etch pits) of a 300 μm GaN film grown by HVPE was recently reported to be 5×10^5 cm^{-2}.[6] Using GaN as a substrate yields a low threading dislocation density, and hence, improves the performance of the device.[7] In this work, we report on the properties of thick GaN substrates, obtained by regrowth on free-standing HVPE GaN.

Free-standing HVPE GaN films were obtained by HVPE growth and laser-induced lift-off. First, 2 μm templated GaN films (on sapphire) grown by metal–organic chemical-vapor deposition (MOCVD) were prepared. Next, thick GaN films, referred to as HVPE GaN, with a thickness in the range of 50–200 μm, were grown on these MOCVD templates using a conventional horizontal-type HVPE system. In this system, HCl reacted with liquid Ga (850 °C) to form GaCl gas and was then transported into the growth zone area where it directly reacted with NH_3 at a temperature of 1050 °C. The growth rate and V/III ratio varied between 50–150 μm/h and 10–100, respectively. The HVPE-GaN films were then separated from the sapphire by laser lift-off.[8] Following chemical cleaning of the surface, the two-step GaN, referred to as the GaN substrate, was obtained by regrowth at a rate of 100 μm/h on the free-standing HVPE GaN. GaN substrates have a maximum thickness of 500 μm and a typical sample area of 10×10 mm^2. Schematic diagrams of the MOCVD template, HVPE GaN, free-standing HVPE GaN, and the GaN substrate are shown in the inset of Fig. 1.

The GaN samples were first examined by double-crystal x-ray diffraction (DCXRD), as shown in Table I. The full

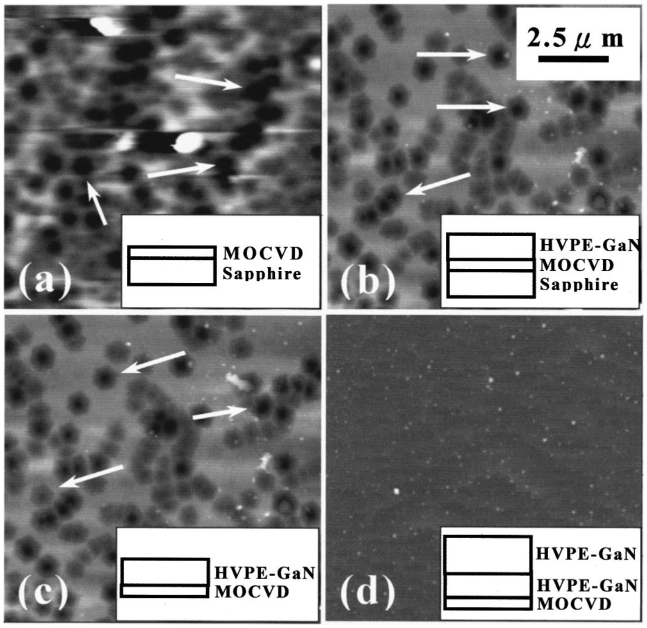

FIG. 1. AFM image of (a) MOCVD template, (b) HVPE GaN, (c) free-standing HVPE GaN, and (d) GaN substrate taken after chemical etching.

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TABLE I. Listed data of DCXRD and Hall measurements of the MOCVD template, HVPE GaN, free-standing HVPE GaN, and the GaN substrate.

GaN samples	FWHM of (0002) peak (arsec)	concentration (10^{16} cm^{-3})	mobility (cm^2/V s)
MOCVD template	200–300	5–15	150–250
HVPE GaN	120–200	1–12	200–800
Free-standing HVPE GaN	180–250	1–12	200–800
GaN substrate	180–250	0.8–10	700–1050

width at half maxima (FWHM) of the (0002) peak were 250, 160, 220, and 220 arcsec on average for the samples of the MOCVD template, HVPE GaN, free-standing HVPE GaN, and the GaN substrate, respectively. The FWHM of free-standing HVPE GaN is larger than HVPE GaN due to bowing of the GaN film after laser lift-off.[9] Following regrowth, bowing of the GaN film still exists, which makes the FWHM of the GaN substrate more than 200 arcsec.

Room-temperature Hall measurement was also performed to study the electrical properties of the GaN samples. Table I also shows the carrier concentration and carrier mobility of the GaN samples. Higher mobility can be achieved using the regrowth process on free-standing HVPE GaN. The mobility and the electron concentration are around 700–1050 cm^2/V s and 10^{16}–10^{17} cm^{-3}, respectively, due probably to the reduction of dislocation density and ionized impurity concentration.[10]

Prior to atomic-force microscopy (AFM) measurement, chemical etching[11] (H_3PO_4/H_2SO_4) was undertaken at 250 °C to reveal etch pits in these GaN samples. Figures 1(a)–1(d) show the AFM images obtained from the MOCVD template, HVPE GaN, free-standing HVPE GaN, and the GaN substrate, respectively. Figure 1(a) is a typical AFM image of an unintentionally doped MOCVD template. The density of the indicated etch pits is as much as 6×10^8 cm^{-2}. In our HVPE GaN samples, the etch-pit density (EPD) values were between 10^7 and 3×10^8 cm^{-2}, as shown in Fig. 1(b). Reynolds *et al.* stated that the defect density as a function of HVPE GaN thickness, declines significantly beyond a thickness of 75 μm.[12] For the 500-μm-thick GaN substrate, as shown in Fig. 1(d), no etch pits can be detected in the AFM image, even in the area of 50 μm$\times$50 μm. The EPD was estimated to be lower than 4×10^4 cm^{-2} which is a low reported density. The density could be tentatively explained as follows. First, the regrowth of GaN on free-standing HVPE GaN leads to a nearly stress-free homoepitaxy, and thus significantly reduces defect density. Second, the thickness of both HVPE GaN and the regrowth GaN films are strongly related to the defect density and the crystal quality.[12] For example, in order to obtain a high-quality GaN substrate, the defect density of HVPE GaN should be lower than 10^8 cm^{-2}, which corresponds to a thickness above 120 μm. Finally, the defect density also depends on the HVPE system used and the growth condition. The corresponding results will be published elsewhere.

Even though the GaN substrate sample shows an EPD lower than 4×10^4 cm^{-2}, an earlier report proved that no etch pits formed at the edge or at full core screw dislocations but could form at nanopipes (open-core screw dislocations).[13] In order to reconfirm the threading dislocation density of the GaN substrate, 60 and 150 K times plan-view transmission electron microscopy (TEM) was also observed by JEOL2000FSII. None of the detectable dislocations could be found from TEM, which are consistent with our AFM data.

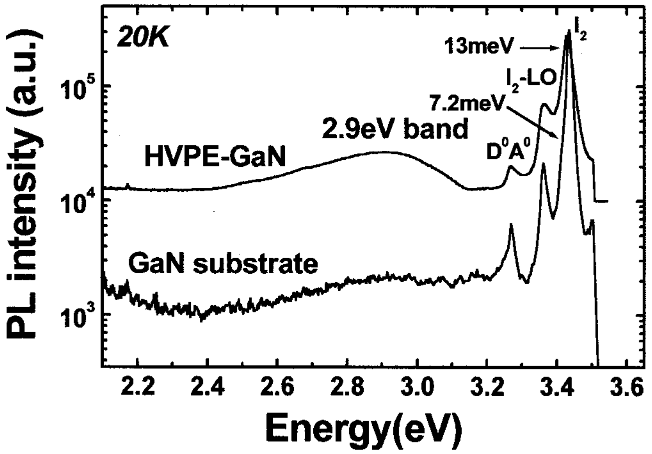

FIG. 2. Low-temperature (20 K) PL spectrum of HVPE GaN and the GaN substrate.

The surface roughness (after etching) was also determined from AFM data to be 12.034, 6.482, and 1.186 nm with respect to the samples of the MOCVD template, HVPE GaN, and the GaN substrate, as shown in Fig. 1. Among the three samples, the thick GaN substrate exhibits the smallest surface roughness, probably related to the presence of fewer EPDs and the good quality of the thick GaN film.

Photoluminescence (PL) measurements were obtained by exciting a 325 nm He–Cd laser on the GaN samples. Figure 2 displays low-temperature (20 K) PL spectra of HVPE GaN and the thick GaN substrate. The spectra of the samples demonstrate three peaks located at 3.44, 3.36, and 3.27 eV, which are related to the emission lines from natural donor-bound recombination (I_2 line), phonon replica of donor-bound exciton (I_2-LO), and natural donor–acceptor-pair recombination (D^0A^0), respectively.[14] The FWHM of the I_2 line at 3.44 eV, attributable to a transition of an exciton bound to a neutral shallow donor, are 13 and 7.2 meV for HVPE GaN and the thick GaN substrate, respectively. The spectrum also included a broadband with a peak at 2.9 eV, known as the 2.9 eV band, which is related to the defect level.[15] Following regrowth, the intensity of the 2.9 eV band decreases, implying that the regrowth of GaN on free-standing HVPE GaN can lower the defect density and result in enhancement of the emission line at 3.44 eV.

Temperature-dependent PL was also performed for the thick GaN substrate to examine the nature of the weak 2.9 eV band. As shown in Fig. 3, the PL intensity of the 2.9 eV band decreases gradually with increasing temperature from 20 to 150 K. However, the thermal quenching behavior of the 2.9 eV band is observed above 150 K. The activation energy was obtained from the best fit to the experiment data with an Arrhenius plot (inset in Fig. 3). The activation energy was then determined to be about 118±5 meV above the valence band. This is the thermal ionization energy of the shallow acceptor involved in the 2.9 eV band.[15] The PL quenching above 150 K is attributable to the thermal release of

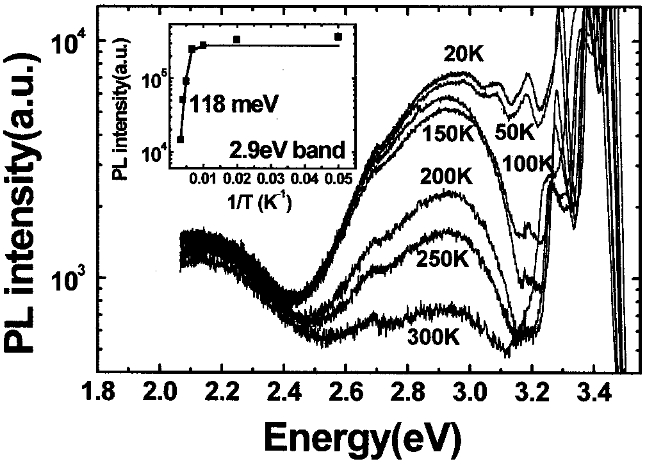

FIG. 3. Temperature-dependent PL spectrum of the GaN substrate.

holes trapped by the shallow acceptor. The result is different from that of earlier work,[15] and suggest that the 2.9 eV band involved a transition from a shallow donor level to a deep acceptor level located at 380 meV above the valence band. However, our fitting data suggest that the 2.9 eV band could possibly result from the transition between a deep donor level and a shallow acceptor level located at 118 meV above the valence band. A similar interpretation has also been suggested by Kaufmann *et al.*[16] The location of the shallow acceptor level is similar to that described in Ref. 17, wherein the two-hole (excited-state) transition of acceptor–bound excitons led to ground-state energies of 85 ± 1 and 115 ± 1 meV. Another group from the calculation of hole's effective mass indicated a level of $\mathbf{E}_A = 120$ meV.[18] Some more-detailed calculations further support the inference of the presence of a shallow acceptor level (100–130 meV).[19] However, the gallium vacancy V_{Ga} or any of its complexes with Si, O, and H could be another possible origin of the 2.9 eV band.[20]

In conclusion, GaN substrates were obtained by the regrowth process on free-standing HVPE-GaN films. The EPD was determined by AFM to be lower than 4×10^4 cm^{-2}. The electrical and optical properties of the GaN substrates are superior to those of HVPE GaN. The PL spectrum reveals the thermal quenching behavior of the 2.9 eV band. The behavior could be possibly related to the donor-to-acceptor transition involving a shallow acceptor level at 118 ± 5 meV above the valence band.

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