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Reactive ion etch-induced effects on the near-band-edge luminescence in GaN

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GaN grown on *c*-plane sapphire substrates has been reactive ion etched successfully in a SF_6 plasma with an etch rate of 29 nm/min. The etch rate does not change with substrate temperatures between 10 and 50 °C. Optical transitions have not been destroyed after etching, instead, two additional lower energy transitions appear close to the band-edge luminescence. The two additional transitions are related to defect states that bind excitons. The defect-bound states exhibit different behavior compared to the free excitonic states in that their normalized intensities decrease more rapidly as temperature increases, the peaks exist only up to 80 K, and their line energies show no temperature dependence. © *1999 American Institute of Physics.* [S0003-6951(99)04121-2]

Dry etching is used widely and routinely in semiconductor device fabrication due to its ability to produce high spatial resolution structures with controllable and uniform etch rates. Group III nitrides have attracted much attention recently because of their wide spectrum of potential applications ranging from optoelectronic devices for the blue-ultraviolet spectral region[1] to high temperature devices.[2] The high bond strength of gallium to nitrogen presents a challenge to achieving good etching characteristics in GaN. A number of methods have been employed to etch GaN and its related compounds, including photochemical wet etching,[3] dry etching utilizing high density plasmas,[4] and conventional reactive ion etching.[5] However, introduction of defects after etching, via a number of possible mechanisms,[6,7] can degrade the materials optical and electronic properties.[8,9] Therefore, the identification and reduction of etch-induced damage is critical in device applications. While Pearton *et al.*[10] assessed electrical damage in indium-containing nitrides after dry etching and concluded that the nitrides may be more resistant to damage introduction than other III–V semiconductors, no studies of etch-induced effects on the optical properties of GaN have been reported. In this letter, we present a reactive ion etching process using SF_6 as the dry etch gas and examine in detail the changes in the near-band-edge luminescence of GaN before and after etching.

The material used is nominally undoped 2.5-μm-thick GaN with good surface morphology grown by metalorganic vapor-phase epitaxy (MOVPE) on *c*-plane sapphire substrates. The samples have been reactive ion etched in an Oxford Plasmalab 80 system. The substrate temperature for etching was varied between 10 and 50 °C. Plasma conditions of 0.45 W/cm^2 power density, 15 mTorr etch pressure, 40 sccm SF_6 flow rate, resulting in a dc bias of -440 V have been employed. Photoluminescence experiments have been carried out using an argon-ion laser operating at a wavelength of 333.8 nm as the excitation source. At this wavelength, the penetration depth of the laser beam is estimated to be ≈100 nm from existing absorption data.[11] The laser light with incident power of 3 mW was focused normally to the sample plane in a backscattering geometry. Luminescence was collected by quartz optics and focused to the entrance slit of a 0.75 m SPEX model 1700 spectrometer with the signal detected by a thermoelectrically cooled photomultiplier tube. The samples were mounted in a closed cycle helium cryostat and variable temperature experiments were performed between 24 and 250 K.

Figure 1 shows a scanning electron micrograph of GaN reactive ion etched at 50 °C in a SF_6 plasma. An etch rate of about 29 nm/min, has been achieved. Generally, fluorinated plasmas tend to produce isotropic profiles due to the dominance of chemical reactions during the etching process. In this case, near anisotropic sidewalls can be seen clearly. Fur-

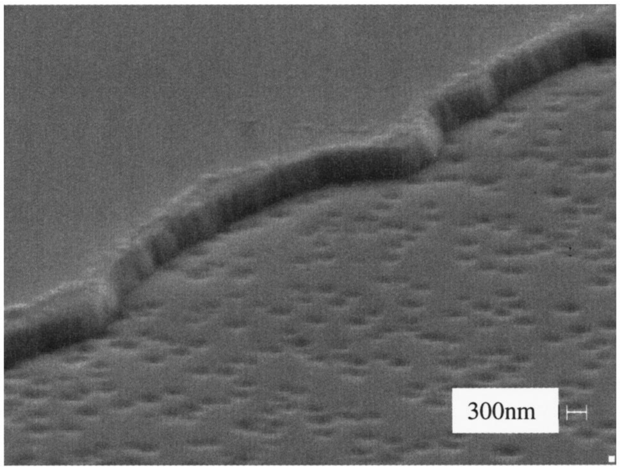

FIG. 1. Scanning electron micrograph of GaN reactive ion etched in SF_6 plasma at 50 °C for 17 min.

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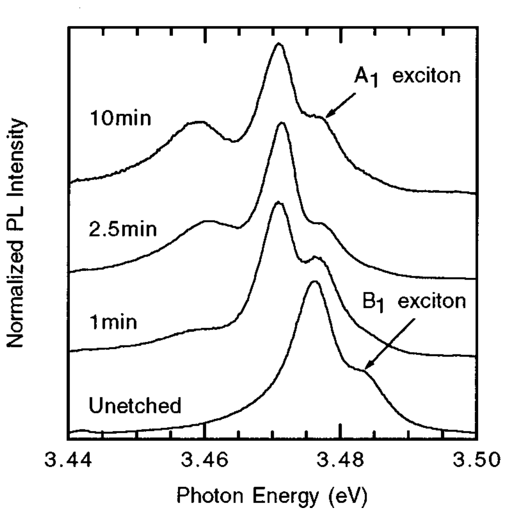

FIG. 2. Photoluminescence spectra at 24 K of unetched GaN and GaN etched in SF_6 plasma for 1, 2.5, and 10 min.

thermore, the etch rate of GaN has been found to be independent of substrate temperature between 10 and 50 °C. These observations illustrate the dominance of the physical mechanism in the etching regime considered. It is clear from Fig. 1 that there is some degree of pitting in the surface etched for 17 min. The surfaces etched for 10 min or less do not show pitting behavior and are the subject of the photoluminescence study discussed below.

Photoluminescence results obtained at 24 K from an unetched, and GaN reactive ion etched for 1, 2.5, and 10 min under the conditions developed are shown in Fig. 2. In the unetched sample, two peaks are seen at energies of 3.477 and 3.483 eV, respectively. The spectra of the etched samples are markedly different from the unetched sample. First, we notice that all the GaN samples continue to luminesce after etching. The peak at 3.477 eV is still clearly visible. The peak at 3.483 eV weakens and becomes a high energy shoulder while two additional peaks emerge at 3.471 and 3.460 eV. In addition, the intensity of the low energy shoulder at 3.460 eV increases relative to the 3.471 eV peak as the etching time increases.

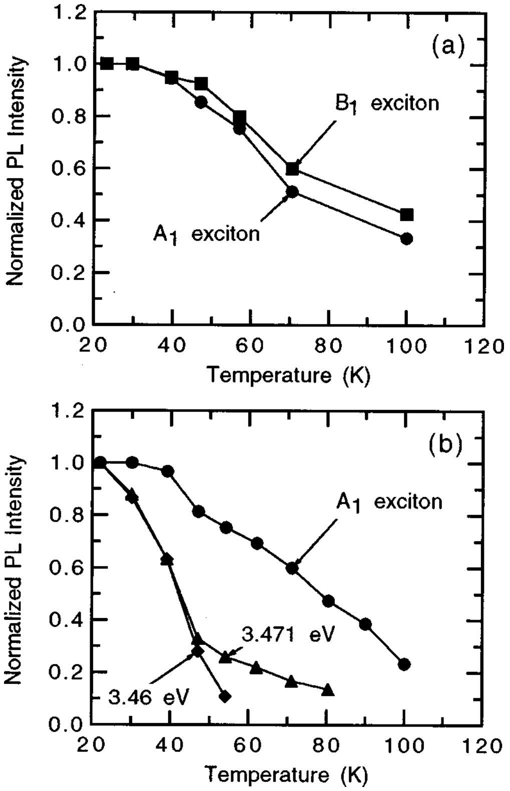

FIG. 3. Temperature dependence of normalized PL intensity ratios for the band-edge peaks in (a) unetched GaN, and (b) GaN etched in SF_6 plasma for 2.5 min. Lines are drawn as a guide to the eye.

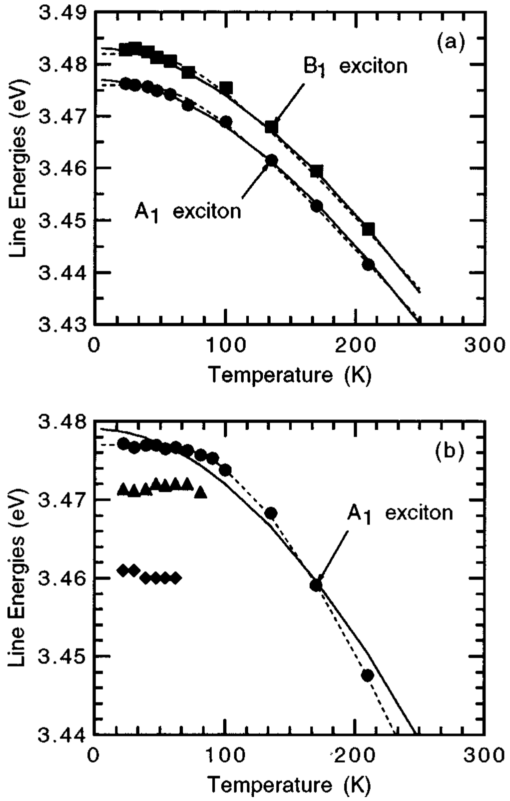

FIG. 4. Temperature dependence of the band-edge energy peaks in (a) unetched GaN, and (b) GaN etched in SF_6 plasma for 2.5 min. Solid and dotted lines are fits to the Varshni (see Ref. 16) and Korona (see Ref. 17) formulas, respectively.

The normalized ratio of luminescence intensities for the transitions from the unetched and 2.5 min etched GaN are plotted as a function of temperature in Figs. 3(a) and 3(b). The intensities of the 3.483 and 3.477 eV peaks from the unetched sample show a temperature dependence that identifies them as B_1 and A_1 excitonic peaks, respectively.[12–14] In the etched sample, the temperature dependence of the intensity of the 3.477 eV peak is unchanged showing that the A_1 exciton is observed at the same energy as in the unetched sample. The intensities of the peaks at 3.471 eV and at 3.460 eV weaken much faster with increasing temperature compared to the A_1 exciton line. The temperature dependence of the peak at 3.471 eV and the 6 meV separation below the A_1 exciton line at 3.477 eV indicate that this line is a donor-bound exciton.[12,15] The separation of the 3.460 eV line from the A_1 peak (17 meV), and the quicker decrease in intensity of this line above 40 K compared to the donor-related line, are consistent with the identification of the lower energy line with an acceptor-bound exciton.[13]

Figures 4(a) and 4(b) show the temperature dependence of the line energies of the unetched and 2.5 min etched GaN

TABLE I. Least-square fitted parameters: α, β, and E_0 in the Varshni[a] formula; and λ, β, and E_0 in the Korona[b] formula.

	Unetched	2.5 min etched
Varshni[a] (solid line)	$\alpha = 6.7e^{-4}$ (eV/K)	$\alpha = 1.0e^{-3}$ eV/K
	β=645 K	β=1331 K
	$E_{0B1}(0\ \text{K}) = 3.483$ eV	$E_{0A1}(0\ \text{K}) = 3.479$ eV
	$E_{0A1}(0\ \text{K}) = 3.477$ eV	
Korona *et al.*[b] (dotted line)	$\lambda = 0.069$ eV	$\lambda = 0.175$ eV
	β=232 K	β=406 K
	$E_{0B1}(0\ \text{K}) = 3.482$ eV	$E_{0A1}(0\ \text{K}) = 3.477$ eV
	$E_{0A1}(0\ \text{K}) = 3.476$ eV	

[a] See Ref. 16.

[b] See Ref. 17.

between 22 and 250 K. The shift of the A_1 and B_1 exciton to lower energies corresponds to band gap shrinking as the temperature increases. In general, such temperature dependence of the free excitonic energies can be described by Varshni's empirical relationship.[16] Korona *et al.*[17] used another relationship and obtained a better fit to their data from homoepitaxial (unstrained) GaN layers. We have fitted our data using both relationships (see Table I). It is possible to fit the data from our unetched sample with both formulas while data for the 2.5 min etched sample are described much better with Korona's formula. Although it may be possible to reason that strain relaxation exists on the surface of the GaN after etching, an extended interpretation of this result is not possible at present due to the inherent difficulties in acquiring a detailed knowledge of the strain field and its temperature dependence.[15,18] The two low energy lines at 3.471 and 3.460 eV only exist up to 80 K and show no temperature dependence.

The appearance of the donor- and acceptor-bound transitions is believed to be a result of defects introduced into the semiconductor by the etching process. These defects bind excitons at low temperatures. Etch-induced native defects, impurities, and self-compensation,[19,20] within the top 100 nm of the GaN surface, may explain the emergence of the additional luminescence lines after etching.

In summary, we have demonstrated the use of SF_6 plasma to reactive ion etch GaN with an etch rate of 29 nm/min. The etching rate does not change with substrate temperatures between 10 and 50 °C. Our photoluminescence data give strong evidence that after reactive ion etching in SF_6 plasma, defect-related states cause free excitons to be bound. These defect-bound excitons show significantly different behavior from free excitons.

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