High resolution reactive ion etching of GaN and etch-induced effects

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We have developed a process using electron beam lithography and reactive ion etching for the high resolution pattern transfer of GaN. 150 nm dots have been fabricated in GaN successfully. Photoluminescence, scanning electron microscopy, and x-ray photoelectron spectroscopy have been employed to compare the damage inflicted on the GaN surfaces after SF_6 and Ar plasma exposures. Near-band-edge luminescence analysis indicates the existence of a higher concentration of donors on the top 100 nm of the GaN surface after Ar as supposed to SF_6 plasma exposure. An order of magnitude decrease in the ratio of the yellow to the band-edge luminescence intensity is found in the samples subjected to lower ion energies. Formation of pits is observed on the substrate surfaces after plasma treatment. Nitrogen deficient surfaces limited to the top few monolayers, as well as defect propagation down to 100 nm, exist in our plasma exposed GaN samples. © *1999 American Vacuum Society*. [S0734-211X(99)10006-4]

I. INTRODUCTION

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. However, introduction of defects after etching, via a number of possible mechanisms,[1–3] can degrade the material's optical and electronic properties. Therefore, the understanding of etch damage propagation mechanisms, as well as the identification and reduction of etch-induced damage are critical in device applications. 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[4] to high temperature devices.[5] Many dry etch techniques have been developed to process GaN.[6–9] We have chosen fluorine-containing plasma in our study because such gases are noncorrosive and have not been studied extensively for processing GaN.[10] Although the development of high etch rate processes in GaN is desirable for many applications, etch processes with a slow etch rate can be used for gate recess purposes in fabricating nitride-based transistors. While electrical damage in indium-containing nitrides after dry etching has been assessed previously,[11] few studies of etch-induced effects on the optical properties of GaN (Ref. 12) and no study on etch-induced changes of surface composition in GaN have been reported. In this article, we report the nanostructuring in GaN, and comparison of the changes in the optical properties and surface composition in exposing the GaN surfaces to chemical SF_6 and inert argon plasmas.

II. EXPERIMENTAL DETAILS

The material used is nominally undoped 2.5 μm thick GaN with good surface morphology grown by metalorganic vapor-phase epitaxy on *c*-plane sapphire substrates. To define the nanopatterns on the GaN, double layer poly(methy)-methacrylate (PMMA) resist and standard lift-off techniques have been used. The patterns have been defined in the PMMA layer using electron beam lithography in a converted Phillips PSEM 500 scanning electron microscope. 30 nm of NiCr alloy is used as the dry etch mask. The samples have

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[a)] Electronic mail: r.cheung@elec.canterbury.ac.nz been reactive ion etched in an Oxford Plasmalab 80 system, with plasma conditions of: 0.45 W/cm^2 power density, 15 mTorr etch pressure, and 40 sccm SF_6 flow rate, resulting in a dc bias of -440 V, and a substrate temperature of 50 °C.[12] An etch rate of 29 nm/min is measured. Using this process, GaN nanostructures are fabricated in the present experiments. In addition, to compare etch-induced effects by plasmas of different nature and ion energies, plain GaN surfaces have been subjected to chemical SF_6 plasma as well as inert argon plasma. Conditions of power and pressure in the argon plasma have been varied in such a way as to achieve a dc bias of -440 and -78 V on the substrate electrode. Etching with Ar plasma at -440 V results in an etch rate of 4 nm/min. All samples have been exposed to the plasmas for 2.5 min except for the fabrication of the nanostructures and etch rate measurements.

Band-edge and yellow photoluminescence (PL) experiments have been carried out on the plain etched surfaces 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.[13] 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 on 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.

X-ray photoelectron spectroscopy (XPS) experiments on the plain etched surfaces are performed using a PHI 5400 apparatus equipped with a dual anode (Mg/Al) x-ray source, a hemispherical analyzer, and a precision angle substrate stage. The Ga peak for GaN at 1117.8 eV is taken as a standard to correct for charging effects in the various samples, both in the Al $K\alpha$ and the Mg $K\alpha$ measurements. Taking into account the multiplet splitting due to spin orbit interaction, spectral analysis has been carried out based on mixed Gaussian/Lorentzian line shapes. The background intensity is corrected using the Shirley method.

III. RESULTS AND DISCUSSION

GaN structures in the nanometre scale have been fabricated successfully. Figure 1 shows GaN dots of 150 nm in diameter reactive ion etched using SF_6 plasma. The reactive ion etching process has been optimized to achieve the submicron resolution needed. Overcut profiles are still observed. This may be a result of the erosion of the NiCr mask during etching or the nature of the etching process itself.

We have examined the changes in the near-band-edge luminescence of plain GaN surfaces before and after etching. Figure 2 shows the spectra, taken at 25 K, of the photoluminescence intensity versus photon energy for unetched GaN and GaN exposed to SF_6 and Ar plasmas at -440 V for 2.5 min. All samples continue to luminesce after plasma exposure. 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. For the sample exposed to the SF_6 plasma, 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 the sample exposed to argon plasma, the peak at 3.477 eV is swamped by the 3.471 eV transition, which has increased in strength.

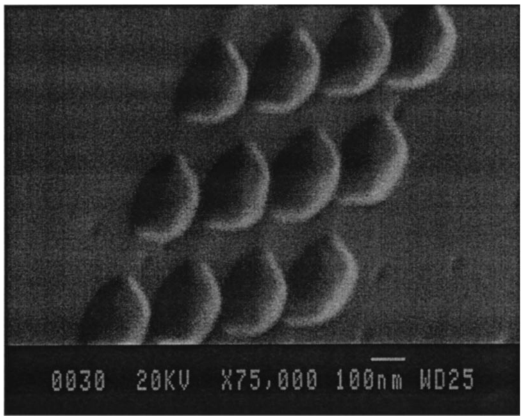

FIG. 1. 150 nm dots fabricated in GaN using electron beam lithography and reactive ion etching.

In order to identify the observed photoluminescence transitions, the dependence of the intensity peaks on temperature has been measured and is shown in Figs. 3, 4, and 5 for unetched GaN, GaN exposed to SF_6 plasma, and Ar plasma, respectively. The normalized ratios of luminescence intensities for the transitions are shown as insets. The intensities of 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.[12,14–16] For the sample exposed to SF_6 plasma, the intensities of the peaks at 3.471 and at 3.460 eV weaken much faster with increasing temperature compared to the A_1 exciton line and have been identified as donor-bound exciton and acceptor-bound exciton lines,

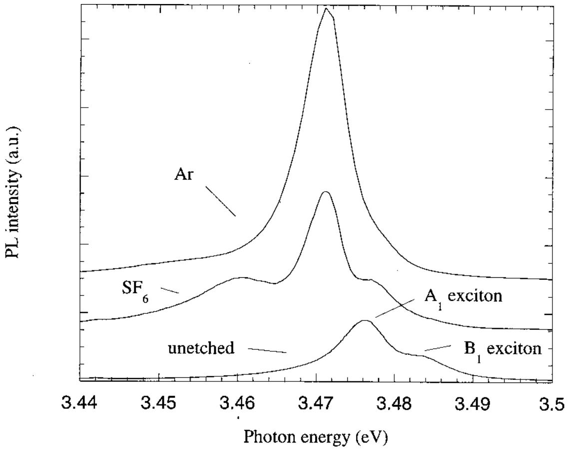

FIG. 2. Photoluminescence spectra for unetched GaN, and GaN exposed to SF_6 and Ar plasmas at -440V for 2.5 min. Spectra were taken at 24 K. Curves have been offset for clarity.

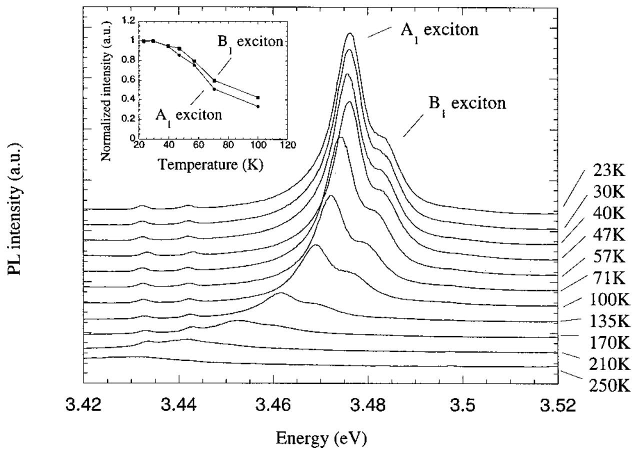

FIG. 3. Temperature dependence of PL spectra for unetched GaN between 23 and 250 K (curves are offset). (Inset) Normalized PL intensity vs photon energy for the A_1 and B_1 excitons.

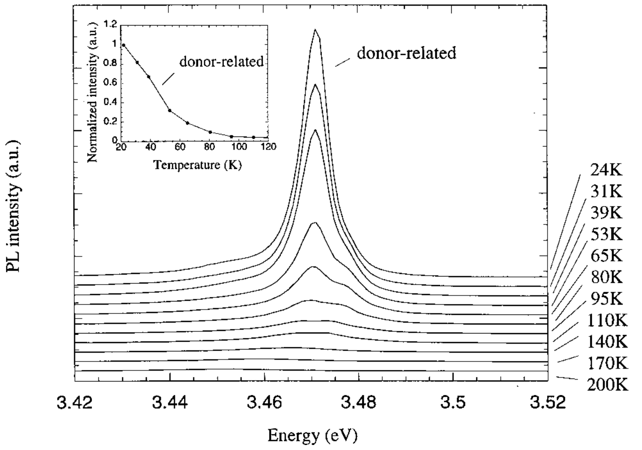

FIG. 5. Temperature dependence of PL intensity (a.u.) vs photon energy for GaN exposed to argon plasma at −440 V for 2.5 min between 24 and 200 K (curves are offset). (Inset) Normalized PL intensity vs photon energy for the main donor-related line.

respectively.[12,14,15,17] For the sample exposed to argon plasma, the peak at 3.471 eV is dominant, which we identify as a donor-related line since its intensity has a temperature dependence that is the same as the donor-bound exciton line in the sample exposed to the SF_6 plasma[12]. However, above 53 K, the donor-related transition has weakened sufficiently that the A_1 exciton can be observed at 3.477 eV. It is worth noting that the sample exposed to Ar plasma at −78 V shows similar luminescence peak positions but less absolute intensity compared to the one exposed at −440 V.

The dominance of the donor-related line intensity for the Ar bombarded sample as shown in Fig. 2 indicates that more donors have been introduced on the GaN surface compared to the sample exposed to SF_6 plasma. The larger molecular ions, more efficient removal of the surface material, and stronger chemical plasma–surface interaction in the SF_6 plasma may result in fewer donors introduced.

We now turn to a discussion of the yellow luminescence (at 2.2 eV) in these samples. The GaN sample exposed to Ar plasma at −440 V exhibits a much stronger yellow luminescence to the naked eye compared to all other samples. In addition, the intensity of the yellow peak from all the samples increases with increasing length of exposure to the ultraviolet laser beam.[18] The relative intensities of the yellow luminescence at 2.2 eV in relation to the band-edge luminescence at time = infinity and at 25 K has been monitored. We found that, for the unetched sample, the peak intensity of the yellow PL is about 2.5% of the band-edge PL, while for those GaN surfaces exposed to the SF_6 and argon plasmas (both at −440 V), this figure is about 30%. It is interesting to note that GaN exposed to −78 V argon plasma has the same yellow to band-edge peak intensity as the unetched sample. The yellow luminescence has been proposed to be a result of the presence of deep gap localized states,[19] which in this case, is likely to have been created by the energetic ion bombardment during the etching process. Coupled with the near-band-edge luminescence data, it is observed that etching at lower voltage introduces less defects.

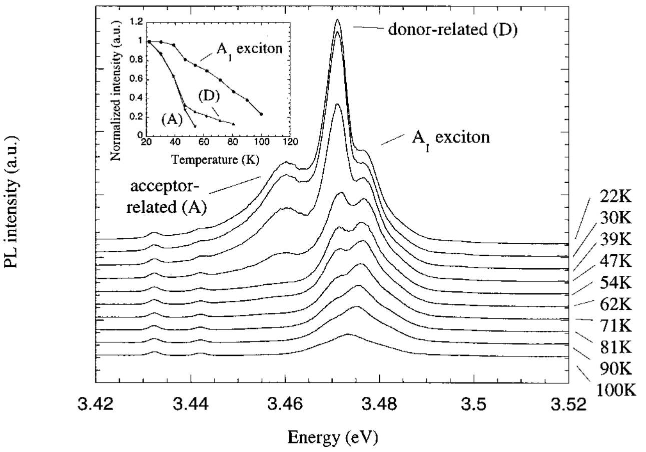

FIG. 4. Temperature dependence of photoluminescence intensity (a.u.) vs photon energy for GaN exposed to SF_6 plasma at −440 V for 2.5 min between 22 and 100 K (curves are offset). (Inset) Normalized PL intensity vs photon energy for the various excitonic lines (identified in text).

Figures 6(a)–6(c) show scanning electron microscopy (SEM) images of unetched GaN, and GaN exposed to SF_6 and argon plasmas. The unetched sample shows very smooth surface morphology while pits are observed in the samples exposed to the plasmas. The presence of pits after etching has been observed under different etching conditions.[9] In the present experiment, the formation of pits is similar for samples exposed to both chemical SF_6 and inert argon plasmas at −440 V. It is difficult to correlate this similarity with the differences observed in the near-band-edge luminescence of the SF_6 and argon exposed samples. However, the similar ratio of the yellow to band-edge luminescence between the plasma exposed samples at −440 V as compared to the unetched sample may relate to the pitted defects.

In order to gain insight into the surface composition change on the top few monolayers of the GaN after the plasma exposures, XPS has been performed on the unetched GaN, and GaN samples exposed to SF_6 and argon plasmas at −440 V. The relative Ga(2p)/N(1s) elemental concentra-

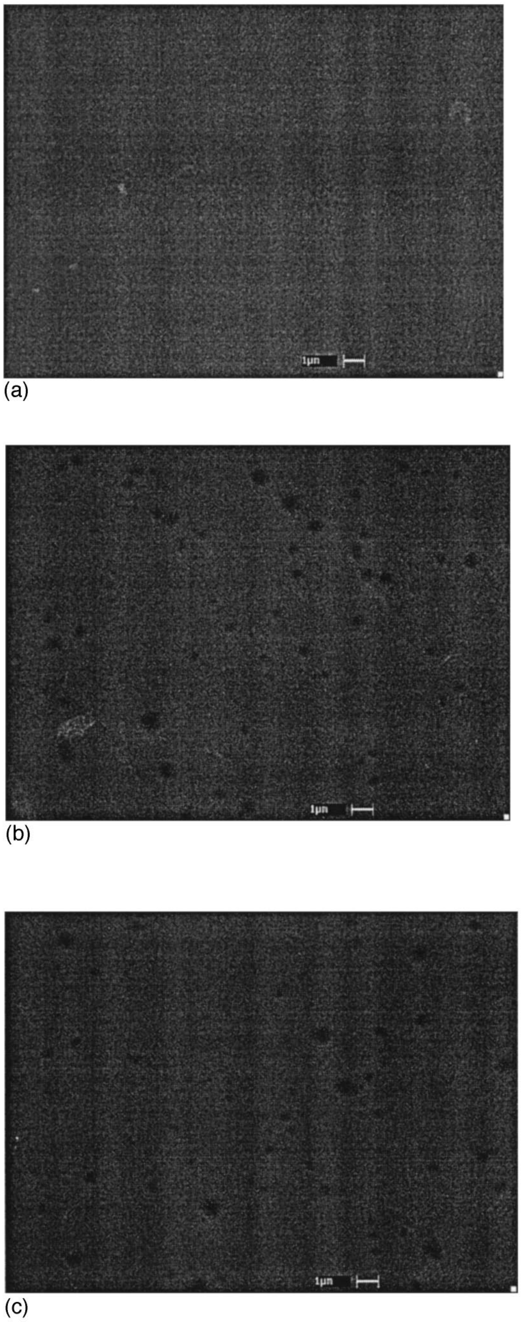

FIG. 6. SEMs of: (a) unetched GaN, (b) GaN exposed to SF_6 plasma at -440 V for 2.5 min, and (c) GaN exposed to argon plasma at -440 V for 2.5 min.

tion ratios for the 3 samples are 3.7, 13.9, and 18.3, respectively. It can be seen that a loss of nitrogen on the GaN surface is present after both SF_6 and Ar plasma exposures, more so after the Ar exposure. Nitrogen vacancies on the GaN surface behave as native donors[19] and could indeed contribute to the stronger donor peak observed in the near-band-edge luminescence. On the other hand, similar ratios in the yellow to band-edge photoluminescence intensity for the samples subjected to -440 V are observed. These results suggest the yellow luminescence is sensitive to defects created via ion bombardment during etching while the spectral components in the near-band-edge luminescence are also sensitive to the differences between the chemical plasma–surface interaction in the SF_6 and the inert nature of the Ar plasma exposures. Since our laser beam probes about 100 nm of the top GaN surface, a damage propagation depth of at least 100 nm is present after both SF_6 and Ar plasma exposures. At -440 V, the Ar exposure introduces more donors than the SF_6 exposure, down to 100 nm. Under similar etching conditions in GaAs/AlGaAs quantum wells using Ar ions, defect propagation as deep as ≈ 130 nm has been observed experimentally.[3] Radiation-enhanced diffusion[1] and ion channeling in the $\langle 110 \rangle$ direction for zincblende crystals[2] are possible mechanisms for defect propagation. We believe that in our plasma exposed GaN samples, effects of surface compositional change on the top few monolayers, coupled with defect propagation down to 100 nm, contribute to our experimental observations.

IV. CONCLUSIONS

We have developed a process for the high resolution pattern transfer of GaN. 150 nm dots have been fabricated in GaN successfully using electron beam lithography and reactive ion etching. From near-band-edge luminescence analysis, more donors have been introduced on the top 100 nm GaN surface after Ar as compared to SF_6 plasma exposure. Moreover, etching at lower voltages in Ar plasma introduces less defects. Formation of pits on the substrate surfaces after plasma exposure is evident. Nitrogen deficient surfaces limited to the top few monolayers, as well as defect propagation down to 100 nm, exist in our plasma exposed GaN. These results provide a basis for ways of damage reduction in the future dry processing of GaN.

ACKNOWLEDGMENT

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