PATTERNING III-N SEMICONDUCTORS BY LOW ENERGY ELECTRON ENHANCED ETCHING (LE4)

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ABSTRACT

Fabricating device structures from the III-N wide bandgap semiconductors requires anisotropoic dry etching processes that leave smooth surfaces with stoichiometric composition after transferring high-resolution patterns with vertical sidewalls. The purpose of this article is to describe results obtained by a new low-damage dry etching technique that provides an alternative to the standard ion-enhanced dry etching methods in meeting these demands for processing the III-N materials.

INTRODUCTION

The Group III nitride wide bandgap semiconductors hold the potential for important technological innovations in optoelectronics and in high power, high frequency microelectronics.[1] [2] [3] Blue and green Light Emitting Diodes (LEDs) are available,[4] [5] and blue Laser Diodes have been reported.[6] Moreover, transistors fabricated from the III-N materials operate at much higher temperatures and under more adverse conditions than similar devices based on more familiar materials, because of the combination of wide bandgap, strong chemical bonds, and relative chemical inertness.[7] These same properties of high chemical bond energies and relative chemical inertness lead to difficulties in processing the III-N materials by standard lithographic and etching processes.[8] Since only very limited wet etching reactions have been identified for these materials,[9] [10] fabrication of even large structures requires dry etching. Reactive Ion Etching (RIE) gives very slow rates and requires unusually high ion energies; the results are ion bombardment damage, modified stoichiometry in surface and near-surface regions, and a tendency toward the overcut

etch profiles and trenching effects familiar in ion-dominated dry etching processes. [11] [12] [13] [14] High-density Electron Cyclotron Resonance (ECR) microwave plasmas at modest power, sometimes accompanied by heating the sample to 200°C, produce acceptable etch rates; however, further increase of plasma power and rf bias on the sample to increase etch rate again creates ion-induced damage, alters stoichiometry, and roughens the surface.[15] [16] [17] Depending on plasma power and rf bias, ECR etching of GaN produces RMS surface roughness from 4 nm to 85 nm.[18] Chemically Assisted Ion Beam Etching (CAIBE), in which Ar^+ ion beams at 500 eV are directed to the etching surface through a background pressure of reactive gases, has produced vertical profiles on features 2.0 μm wide (but not on sub-micrometer features), but with N depletion at the etched surfaces.[19] [20] [21] [22] Two recent comprehensive reviews summarize results achieved for the III-N materials with these standard *ion-enhanced* dry etching techniques and provide references to numerous specific studies.[23] [24]

The difficulties faced by the ion-enhanced dry etching techniques trace largely to the need for energetic ions to overcome the strong chemical bond energies in the III-N materials. Alternative dry etching techniques that avoid energetic ions must then be considered, especially to achieve surface smoothness and selectivity between different III-N films.

A very attractive alternative is the new, low-damage dry etching technique called *Low Energy Electron Enhanced Etching (LE4)* in which electrons at energies 1-15 eV and reactive species at thermal velocities arrive at the surface. These electrons impart negligible momentum to the etching surface, and thereby avoid the ion bombardment damage intrinsic to RIE, ECR, and CAIBE, while "enhancing" the etch chemistry to give anisotropic pattern transfer. In earlier work, we demonstrated LE4 of Si(100)[25] and GaAs(100)[26] in a DC hydrogen or hydrogen/chlorine plasma with good anisotropy, high selectivity relative to the masking materials, and very smooth surfaces; the etch rate ranged from 20 $nm \cdot min^{-1}$ to 5 $\mu m \cdot min^{-1}$ depending on the reactive gas composition and temperature.

The first studies of LE4 on GaN demonstrated anisotropic pattern transfer, smooth surfaces, and stoichiometric surfaces for 1.0 μm thick films of GaN on Si(100) substrates, [27] and for 2.0 μm thick films of GaN(0001) deposited on α(6H)-SiC(0001) with a buffer layer of AlN(0001) between film and substrate.[28] Results reported here illustrate the capability of LE4 to produce anisotropic etching and smooth surfaces in samples with stacked interfaces.

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EXPERIMENTAL METHODS

LE4 was conceived as a damage-free alternative to RIE and ECR for fabricating nanostructures in Si and compound semiconductors. The feasibility of LE4 was first demonstrated in UHV surface science type experiments with a beam of molecular hydrogen and a beam of low energy electrons simultaneously incident on an atomically clean, non-masked sample, with *in situ* mass spectrometry and surface spectroscopy.[29] Recently LE4 has been used to transfer a hexagonal array of 18-nm holes on a 22-nm lattice constant from a biologically derived pattern into Si(100). [30] High resolution cross-sectional transmission electron microscopy showed Si lattice fringes at the perimeter of the etched holes. TEM images of identical samples intentionally briefly ion bombarded with 2 keV Ar ions before LE4 showed an amorphous damaged layer surrounding the perimeter of the etched holes. These experiments together demonstrate that LE4 does not inflict lattice displacement damage on the substrate. For device applications, as described here, LE4 is carried out by placing the sample on the (grounded) anode of a DC glow discharge. Temperature of the sample is controlled by and measured at the sample stage. The apparatus is described in moderate detail in References 25 and 26. Typical process pressures were 2 - 10 Pa; pure chlorine, pure hydrogen, or mixtures of chlorine and hydrogen were studied, at flow rates of 10 - 30 sccm.. GaN samples were masked by deposition of a 200 nm SiO_2 film [by plasma enhanced chemical vapor deposition (PECVD)]. Patterns were defined in the oxide mask layer by standard photolithography techniques followed by either wet etching or RIE through the oxide layer.

RESULTS

Etch Profile.

Figure 1 shows an SEM image of the edges of lines 2 μm wide on a 2.5 μm thick single crystal GaN(0001) sample patterned by RIE of the oxide layer, and etched at 6.6 Pa pure chlorine and 150 $mA \cdot cm^{-2}$ discharge current**.** The result is highly anisotropic etching, as evidenced by straight side walls, no overcut, no trenching, and no "pedestal" at the base of the line. The etched open field areas between lines appears quite smooth in the SEM image. The samples patterned by photolithography and wet etching of the oxide layer showed mask undercutting during wet etching, which led to mask edge erosion and mask edge roughness. These imperfections in the mask were faithfully transferred to the sample during LE4, and did not show anisotropy comparable to that in Figure 1.

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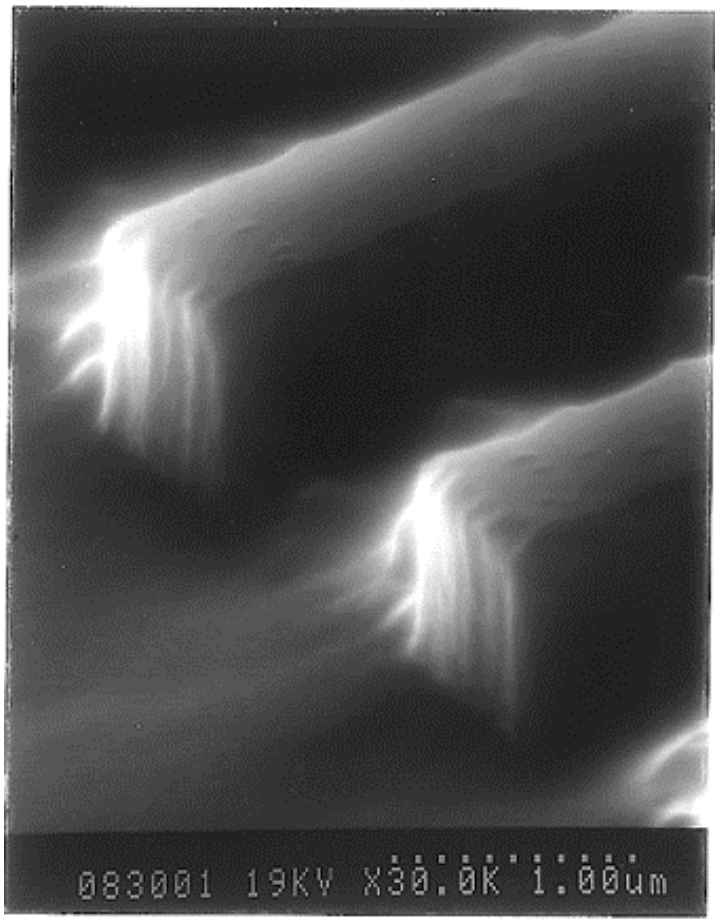

Fig.1. Anisotropic etching of GaN film with SiO_2 mask patterned by RIE. The sample was etched in 6.6 Pa of chlorine for 20 minutes at a current density of 150 mA/cm^2. (Ref.28)

Surface Morphology.

AFM of this sample before etching showed RMS surface roughness was 8.5 - 10 Å. After LE4, RMS surface roughness is 2.5 Å, and the difference between highest and lowest features is 2.2 nm. Nearly identical images were obtained at several locations on the etched surface. By comparison, ECR etching of GaN produces RMS surface roughness from 4 nm to 85 nm, depending on plasma power and rf bias.[31]

It is significant that LE4 smoothened the surfaces of the as-grown GaN material in these experiments. Similar experimental conditions in our earlier LE4 studies of Si(100) and GaAs(100) cited above produced measured RMS surface roughness of 2 - 3 Å after LE4, nearly identical to the values measured on the polished wafers from which the samples were cut. Under these intermediate conditions of pressure and current density, LE4 can accomplish surface

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polishing as well as etching. This result is not seen in ion enhanced etching, which roughens surfaces during etching. The mechanism of the smoothening process remains to be explained.

Figure 2 shows results of etching such a sample to a depth of 2.75 μm. In this case the etch passed completely through the GaN layer and the AlN buffer layer, exposing the SiC substrate. It is notable that LE4 produced reasonably anisotropic (clearly limited by the mask) and clean sidewalls and a very smooth etched surface while passing through three such disparate materials separated by two very challenging interfaces. This result suggests that LE4 processes can be designed to produce vertical, smooth, and damage-free sidewalls for edge-emitting complex multi-layer structures such as LEDs or laser diodes in which the active layer is a multi-quantum well structure.

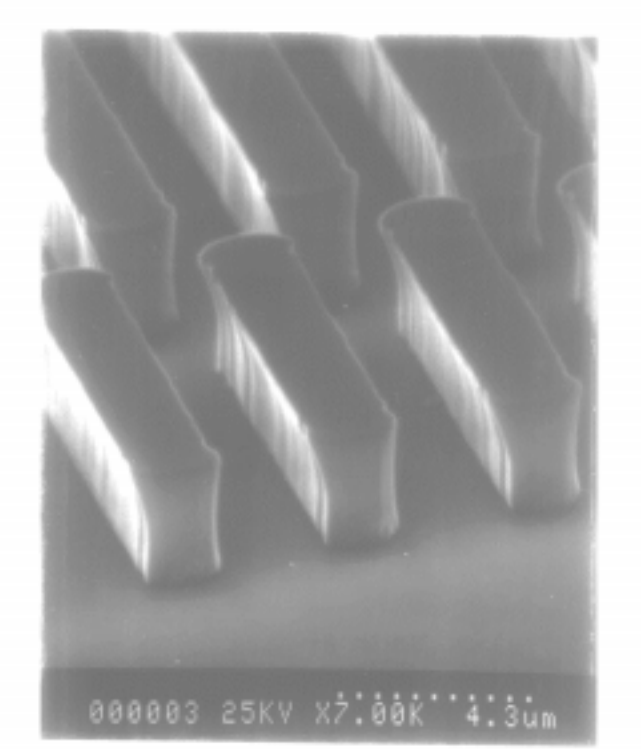

Fig.2 Deep etching of GaN film with SiO_2 mask defined by photolithography and wet etching. The sample was etched in 6.6 Pa of chlorine, with current density of 150 ma/cm^2.

Surface Composition.

Using the GaN/Si(100) samples grown by MOMBE in LE4 with pure hydrogen plasma, we qualitatively evaluated the effects of different LE4 conditions on surface composition by Auger electron spectroscopy. The lack of reliable GaN standards for comparison precludes rigorous quantitative Auger analysis, and roughness of the samples makes questionable any semi-

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quantitative analyses based on tabulated Auger sensitivity factors. Thus our qualitative estimates of surface composition were obtained by comparing the *relative intensities* of the gallium $L_3M_{45}M_{45}$ line at 1068 eV and the nitrogen $KL_{23}L_{23}$ line at 384 eV measured on samples before and after etching. Within the limits of this comparison method, the stoichiometry of etched surfaces is essentially the same as for unetched samples. In other studies, this simple qualitative comparison method has shown that ion-enhanced etching processes deplete N relative to Ga at the surface.[32]

Etch Rate.

We observed a strong temperature dependence of the GaN/Si(100) etching rate in hydrogen plasma, ranging from 70 Å/min at 50°C to 525 Å/min at 250°C; details are presented in Reference 27. The Arrhenius plot is fit by a single straight line with activation energy of 160 meV. Temperature dependence of the etch rate for III-V compounds usually gives Arrhenius plots with double slopes when both group III and group V elements are solids at the process temperature, signifying the need for two independent reactions to volatilize the III and V atoms.[33] At present, we do not know the chemical identity of the actual etch products in the LE4 of GaN. But since the temperature dependence appears to determine the activation energy for a single chemical reaction, and since nitrogen does not need to form a compound to become volatile, we speculate that the products are GaH_3 or $GaCl_3$and N_2.

All GaN(0001)/SiC samples in the present study were etched in pure chlorine plasma at room temperature at moderate etch rates of 50 - 70 nm·min^{-1} in order to ensure controllable etch results on the thin film materials. Nonetheless, the LE4 apparatus allows the plasma current density to be increased by an order of magnitude. Besides this, according to our previous experiments on GaAs, anisotropic etching is maintained up to 30 Pa of the process pressure while the etch rate increases substantially at higher pressures due to the greater density of the reactive species. According to our estimates, it is therefore possible to achieve LE4 rates exceeding 150 nm·min^{-1} *at room temperature* while maintaining good etch results such as anisotropy, surface morphology and stoichiometry. Preliminary results indicate that the rate increases substantially with temperature. Quantitative studies and process optimization have yet to be carried out.

SUMMARY AND DISCUSSION

The results obtained to date indicate that, within the moderate ranges of gas pressure and current density used here, LE4 of GaN samples is intrinsically anisotropic, with the quality of etched profiles determined primarily by the quality of the SiO_2 mask material and sharpness of the

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mask edges. In all our studies of LE4 on Si, GaAs, and GaN samples, we have never observed trenching effects or overcut profiles, which are associated with ion-induced degradation of the mask in ion-enhanced etching processes. This excellent result is inherently characteristic of LE4, since LE4 was developed specifically to achieve anisotropic etching without ion bombardment, in order to eliminate ion bombardment damage to both mask and substrate during etching.

Excellent anisotropy has been achieved at the same time as acceptable rate, and with no etch-induced surface roughening or degradation of surface stochiometry. The vertical, smooth, damage-free sidewalls should serve as excellent laser cavity mirrors, and the smooth, stoichiometric etched surfaces are well suited for ohmic contacts.

However, several questions remain to be studied. It is necessary to extend these results systematically to a wider variety of III-N materials (including alloys and heterostructures) grown on different substrates. Etch rate, surface roughness, etch profile, and surface composition must be explored over broad ranges of process chemistry and temperature. Since LE4 presumably proceeds via material-specific energy thresholds for electron energy transfer instead of the indiscriminate momentum transfer of ion-surface collisions, LE4 processes that are highly selective between materials can be designed. This will require careful consideration of temperature to guarantee that the necessary reactants can be adsorbed and the resulting products removed while the electron energy is in the appropriate range for a particular material.

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