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Reactive Ion Beam Etching of GaN and AlGaN for Nanostructure Fabrication Using Methane-Based Gas Mixtures

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Abstract: The basic characteristics of ECR-reactive ion beam etching (RIBE) of GaN and AlGaN using methane-based mixtures was studied for nanowire fabrication is studied. Both of GaN and AlGaN/GaN heterostructure can be etched by using a gas mixture of $CH_4/H_2/Ar$ at a low etching rate of about 10nm/min giving nm accuracy. <-1100> and <2-1-10> line pattern etching showed {0-110} and {11-21} sidewall facets, respectively, indicating its chemical reaction dominant low-damage nature. By conventional CH_4-based gas mixture, the etching saturates at a depth of a few 100 nm and roughness of surface increases with time, since the surface reaction produced Ga rich surface and this disturbs the etching process. By adding nitrogen into the gas mixture ($CH_4/H_2/Ar/N_2$ = 5/15/1.5/4.5 sccm), surface stoichiometry is dramatically improved. This also gives smooth etched surface with roughness of 2 nm enough for nanostructure fabrication. By using the optimized etching condition with nitrogen addition to the gas mixture, an AlGaN/GaN nanowire structure with a wire width of 110 nm has been successfully fabricated.

Keywords: Reactive ion beam etching (RIBE), methane-based gas mixture, nitrogen gas, gallium nitride (GaN), aluminum gallium nitride (AlGaN), nanostructure

1. Introduction

Availability of a large conduction band discontinuity and high carrier densities in the AlGaN/GaN heterostructure system is attractive not only to high electron mobility transistors (HEMTs), but also to various quantum devices having nanostructures.

In order to fabricate nanostructures, dry etching turns out to be a key process for GaN-based materials because of the difficulty of wet chemical etching in these materials. Previously, Cl-based gas systems containing CCl_2F_2 [1], BCl_3 [2] etc. were used for dry etching of GaN, and efforts have been made to achieve high etch rates with vertical etch profiles.

However, requirements for nanostructure fabrication are somewhat different. 1) The etch rate must be slow enough to achieve nm-scale accuracy. 2) The etching damage must be small. 3) The process that reveals crystalline facets is more desirable in many cases such as preparation of patterned substrates for selective epitaxial growth of nanostructures and wrap gate formation [3] for gate-control of nanostructures.

In this paper, we characterize and optimize ECR-reactive ion beam etching (RIBE) etching process of GaN-based materials using methane-based gas mixtures for nanostructure fabrication. The advantages of methane-based gas mixtures are low corrosion and toxicity, slow etching suitable for nanostructure fabrication process.

2. Experimental

The sample structures are shown in **Fig.1**. Si-doped GaN samples and $Al_{0.25}Ga_{0.75}N$/GaN heterostructure samples both grown by metalorganic vapor phase epitaxy (MOVPE) on (0001) sapphire substrates were used. As the etching mask, line-and-space masks either using a vacuum deposited Cr metal film or using a sputter deposited thin SiO_2 film (30 nm) were used. Patterns were formed by conventional photolithography.

Etching was performed in an ECR-RIBE chamber (Eiko Engineering-ERI-3000) which is connected to a UHV multi-chamber system.

The standard $CH_4/H_2/Ar$ mixture (= 5/15/6 sccm) was used for etching. The microwave power was 200 W and the acceleration voltage was 300 V. The chamber pressure was kept at 0.4mTorr during etching. The sample was not intentionally heated during etching.

The etching profiles and morphology were characterized by AFM (Digital Instruments-Nanoscope IIIa) and SEM (Hitachi-S4100). The surface chemistry was characterized by the in-situ XPS analysis chamber (Perkin-Elemer PHI 1600C, Monochromatic) using. After etching, the sample was transfer to the XPS chamber through the transfer chamber without air exposure of the sample.

3. Results and discussion

3.1 Basic etching properties of Methane-based RIBE

Two directions of mask stripe along <-1100> and <2-1-10> directions were prepared. **Figures 2(a)** and **(b)** show the cross sectional SEM images of GaN and AlGaN/GaN heterostructure samples after methane-based dry etching for 40 minutes, respectively. They show successful selective etching with the etching depths of 448 nm and 252 nm for GaN and AlGaN/GaN heterostructure, respectively. Both GaN and AlGaN could be etched by using the methane-based gas mixture. The smaller etching depth of the AlGaN/GaN sample is due to lower etching rate of AlGaN than that of GaN. No appreciable undercut was observed. It was also seen that the cross section was not vertical, but mesa shapes.

The angle of the sidewalls was 73 ° and 62 ° for the mask stripe directions of <-1100> and <2-1-10>, respectively, for both GaN and AlGaN/GaN heterostructure. The angle of the sidewall was kept constant even increasing the etching time.

The observed angles of the sidewall of 73 ° and 62 ° for <-1100> and <2-1-10> direction line mesas correspond to the {11-21} and {01-11} facet, respectively. The present facet revealing etching strongly indicates that the etching is dominated by chemical reaction rather than physical bombardment, leading to small process-induced damage.

Figure 3 shows the measured etching depth of the GaN and the AlGaN/GaN heterostructure as a function of the etching time. The initial etching delay seems to be due to slow etching of surface oxidized layer and AlGaN layer. Both materials showed the same average etching rate of 13nm/min for GaN layer. However, the etching depth saturated at about 400-500 nm in both cases. Smoothness of the etched surface was investigated by atomic force microscopy. RMS roughness increased as increase of etching time, and it reached 6.1 nm in the case of 60 minutes etching.

In order to understand the mechanism of the etching saturation, in-situ analysis of the etched surface was carried out. The measured Ga3d core level spectra before and after etching are shown in **Figures 4 (a)** and **(b)**, respectively. After etching, a large amount of Ga-Ga bonding component appeared. This indicates that the etching process changed surface stoichiometry and produced Ga rich surface. Most likely chemical reactions during methane-based dry etching are shown in **Fig.5**. Removal of Ga from surface thought formation of the Ga containing volatile component in the etching reaction seems to be slower than desorption of N atom through formation of NH_3. This faster desorption of nitrogen from GaN leads to Ga rich surface, and disturbs the etching process. Increase of surface roughness with time as observed by AFM seems to show nonuniformity of such reaction process.

3.2 The effect of nitrogen addition to the gas mixture

In order to improve the surface stoichiometry, we modified gas mixture by adding nitrogen gas, which compensates the over desorption of N during etching. The mixture with nitrogen of $CH_4/H_2/Ar/N_2$ = 5/15/1.5/4.5 sccm was used. The measured XPS spectra of the etched surfaces without and with nitrogen addition are shown in **Figures 6 (a)** and **(b)**. It is clearly seen that addition of nitrogen reduces the Ga-Ga bonding peak dramatically as expected. **Figure 7** shows the measured etch depth as a function of the etching time for the AlGaN/GaN heterostructure for two cases of without and with nitrogen addition. The nitrogen addition to the gas mixture suppress saturation of etching, and the etch depth increased linearly with time which enable deep mesa etching. The etching rate was 9.2 nm/min, and this value is not so different from that of the etching without nitrogen gas. **Figures 8 (a) and (b)** show AFM images of the etched surface using the gas mixtures without and with nitrogen. Very smooth and flat surface could be obtained by nitrogen addition. **Figure 8 (c)** compares the measured AFM rms roughness with time for two cases of without and with nitrogen addition. Clearly, the roughness became much smaller by nitrogen addition, and was kept less than 3 nm even increase of etching time.

3.3 Fabrication of AlGaN/GaN nanowire structure

Finally, we attempted to fabricate a nanowire structure on an AlGaN/GaN heterostructure wafer, using the optimized etching process with addition of nitrogen. **Figure 9** shows schematically a SEM image of the intended structure. The direction of the wire was chosen to be <-1100> direction. As the etching mask, a sputter deposited SiO_2 film with a thickness of 30 nm was used. The nanowire pattern was formed by conventional electron beam lithography in first, and the pattern was transferred to the SiO_2 film by wet chemical etching. This SEM image shows the fabricated GaN-based nanowire. As shown in **Fig. 9**, a nanowire structure with a very smooth etched surface could be fabricated. According to AFM line profile measurements, the width of the nanowire was as narrow as 110 nm. Unfortunately, the wire did not allow appreciable electrical conduction, being buried in the leakage currents through the buffer layer, which is unavoidable for present GaN based materials. Fermi level pinning at the sidewall may be playing a role to deplete carriers from the wire. Further investigation of damage and its effect on nanostructures is needed.

4. Conclusion

The basic characteristics of ECR-reactive ion beam etching of GaN and AlGaN/GaN heterostructure using methane-based mixtures are studied GaN-based nanostructure fabrication process. Methane-based ECR reactive ion beam etching was studied for GaN and AlGaN at etching rates was suitable for nanostructure formation. Both of GaN and AlGaN can be etched by using a gas mixture of $CH_4/H_2/Ar$ at a slow etching rate of about 10 nm/min suitable for nanostructure fabrication. The etching is a facet-revealing process, indicating its chemical reaction dominant low-damage nature. However, the etching saturates at a depth of a few 100 nm and roughness of surface increases with time. XPS study indicated formation of Ga droplet due to unbalanced removal of Ga and N atoms from the surface. By adding nitrogen gas mixture, Ga droplet formation is dramatically suppressed. This avoids saturation of etching with time, and smoothness of etched surfaces is very much improved. Stoichiometry deterioration and etching saturation can be substantially improved by N_2 addition to the gas mixture. By using the optimized etching condition with nitrogen addition to the gas mixture, an AlGaN/GaN nanowire with width of 110 nm has been successfully fabricated.

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Figure caption

Fig.1 (a) GaN and (b) AlGaN/GaN heterostructure sample structure used in this study

Fig.2 Cross sectional SEM images of (a) GaN and (b) AlGaN/GaN heterostructure after dry etching

Fig.3 Etching depth of GaN and AlGaN/GaN as a function of the etching time

Fig.4 Ga3d core-level XPS spectra from GaN surface (a) before etching and (b) after etching for 20 minutes

Fig.5 Most likely chemical reaction during methane based dry etching of GaN

Fig.6 Ga3d core-level XPS spectra from GaN surface after etching by (a) without N_2 and (b) with N_2 = 5/15/1.5/4.5 sccm for 20 minutes

Fig.7 The measured etch depth as a function of the etching time for the AlGaN/GaN heterostructure for two cases of without and with N_2 addition

Fig.8 AFM images of the etched surface using the gas mixtures (a) without N2 and (b) with N_2 addition, and (c) comparison the measured AFM rms roughness with time for two case of without and with N_2 addition

Fig.9 A SEM image of a fabricated AlGaN/GaN nanowire structure

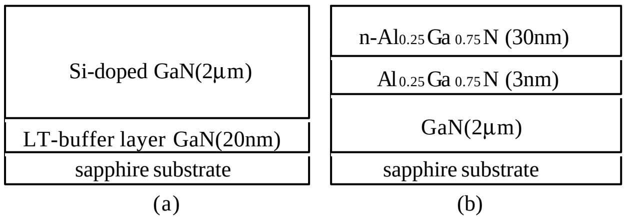


Fig.1 (a) GaN and (b)AlGaN/GaN heterostructure sample structures used in this study.

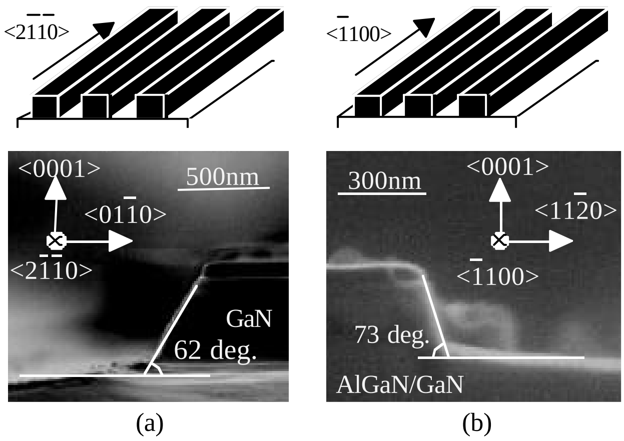


Fig.2 Cross sectional SEM images of (a) GaN and (b) AlGaN/GaN heterostructure after dry etching by ECR-RIBE.

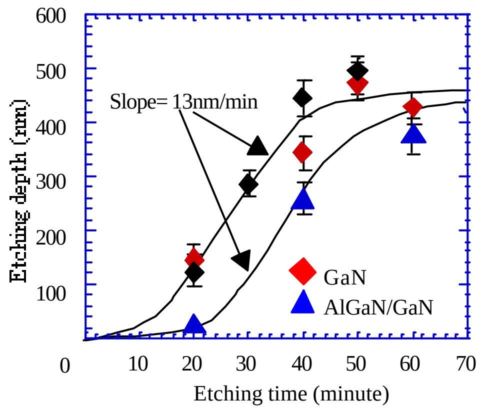


Fig.3 Etching depth of GaN and AlGaN/GaN as a function of the etching time.

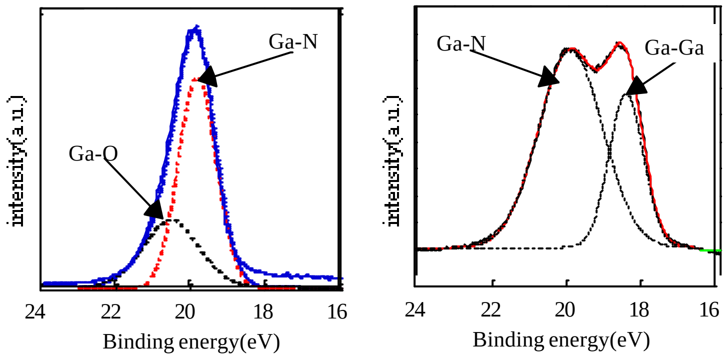
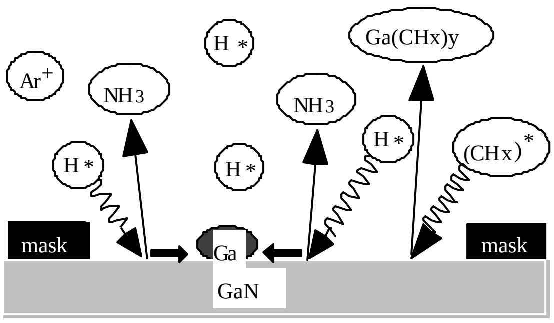


Fig.4 Ga3d core-level XPS spectra from GaN surface (a) before etching and (b) after etching for 20 minutes



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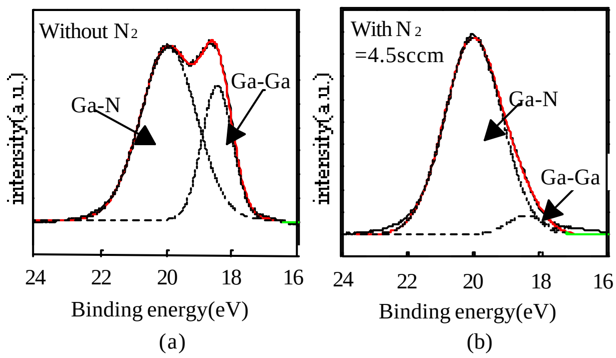


Fig.6 Ga3d core-level XPS spectra from GaN surface after etching by (a) without N_2 and (b) with N_2 = 4.5sccm for 20 minutes.

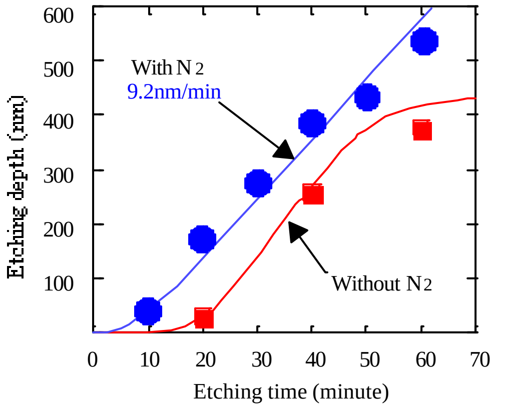
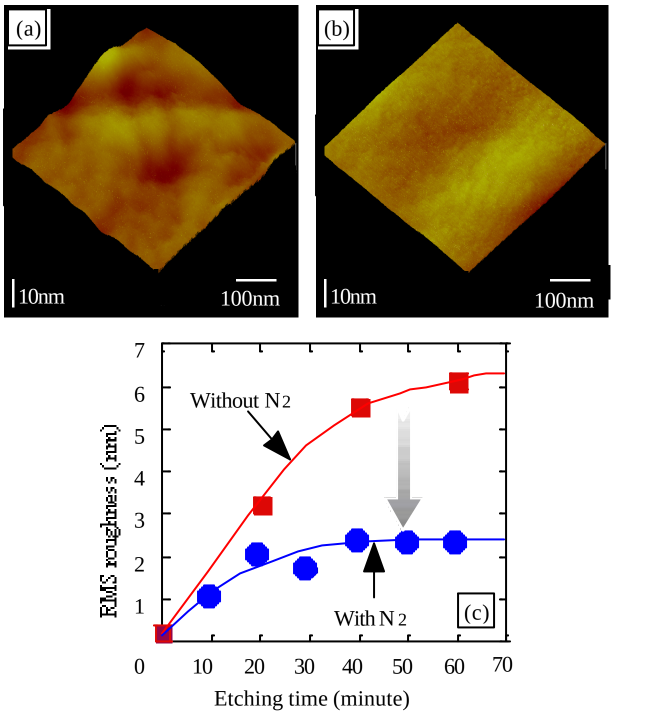


Fig.7 The measured etch depth as a function of the etching time for the AlGaN/GaN heterostructure for two cases of witout and with N_2 addition



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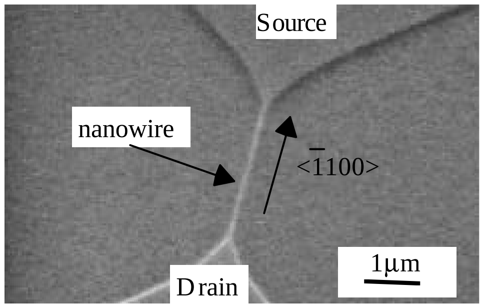

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