Investigation of etch characteristics of non-polar GaN by wet chemical etching

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\textbf{A R T I C L E  I N F O}

\textbf{Article history:}
Received 30 March 2010
Received in revised form 30 July 2010
Accepted 3 August 2010
Available online 7 August 2010

\textbf{Keywords:}
Gallium nitride
Non-polar
Wet chemical etching
X-ray photoelectron spectroscopy

\textbf{A B S T R A C T}

We characterized the surface defects in a-plane GaN, grown onto r-plane sapphire using a defect-selective etching (DSE) method. The surface morphology of etching pits in a-plane GaN was investigated by using different combination ratios of H\textsubscript{3}PO\textsubscript{4} and H\textsubscript{2}SO\textsubscript{4} etching media. Different local etching rates between smooth and defect-related surfaces caused variation of the etch pits made by a 1:3 ratio of H\textsubscript{3}PO\textsubscript{4}/H\textsubscript{2}SO\textsubscript{4} etching solution. Analysis results of surface morphology and composition after etching by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) demonstrated that wet chemical etching conditions could show the differences in surface morphology and chemical bonding on the a-plane GaN surface. The etch pits density (EPD) was determined as 3.1 \times 10^{8} \text{cm}^{-2} by atom force microscopy (AFM).

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1. Introduction

Group III-nitride-based materials have many applications in optoelectronic devices [1]. The wurtzite structured nitride material has strong piezoelectric and spontaneous polarization along the c-axis, resulting in a clear quantum-confined Stark effect. The non-polar (a-/m-axis) nitrides have a crystal structure with the c-axis lying parallel to the quantum well, and this has attracted considerable interest during the past few years, for their absence of any polarization field [2]. However, non-polar gallium nitride contains high density of threading dislocations (TD) (between 10\textsuperscript{8} and 10\textsuperscript{10} cm\textsuperscript{-2}) and stacking faults (SF) (10\textsuperscript{2} cm\textsuperscript{-1}) owing to the planar anisotropic nature of its crystal growth. Dislocations limit the lifetimes and performances of nitride-based devices [3].

Therefore, DSE plays an important role in the characterization of crystalline gallium nitride materials. The commonest DSE technique for surface defect investigations is wet chemical etching. Hot phosphoric acid (H\textsubscript{3}PO\textsubscript{4}), mixed in a H\textsubscript{3}PO\textsubscript{4}/H\textsubscript{2}SO\textsubscript{4} solution, molten potassium hydroxide (KOH), and photo-electrochemical etching (PEC) have been shown to etch pits at defect sites on the GaN c-plane [4]. This method shows promise, because data acquisition is a fast, simple process, and uses inexpensive equipment. Recently, research groups reported the other applications for the DSE technique, such as reducing film dislocations [5] and enhancing the performance of light emitting diodes (LED) [6–8]. There are many reports investigating defects in c-plane GaN using the DSE technique [9,10], but only few investigations of dislocations in a-plane GaN are reported [11]. In this study, we focus on discriminating between surface defects in a-plane GaN, from those in c-plane GaN.

We used the DSE approach to understand surface defects of “non-polar” a-plane GaN layers, grown onto r-plane sapphire by metal organic chemical vapor deposition (MOCVD). We investigated the characteristics of etch pits by changing the etching compound, and evaluated the EPD by exploiting the differing local etching rates of different surface morphologies using specific wet-chemistry. We focused on a comparison of etching behaviors between mixtures of two acids, H\textsubscript{3}PO\textsubscript{4} and H\textsubscript{2}SO\textsubscript{4}, on a-plane GaN with the aim of finding an optimum mixture ratio of the two acids that would best characterize the surface defect types in a-plane GaN samples. Examination of surface morphologies using SEM and XPS showed that different etching solution compositions produced characteristic etching morphologies. An optimal acid mix ratio would allow us to more easily distinguish the types of dislocations that were present prior to etching. Detailed information of surface composition and the electronic structure of GaN layers are essential for understanding the formation of interfaces between layers, and for optimizing device performance.

2. Experiment procedure

All a-plane GaN films were grown on r-plane sapphire (within ±0.5°) using a MOCVD reactor. The precursors were trimethylgal-
from that of defect-free regions, thus revealing defects by exploiting different local etching rates. Such DSE produces etch pits or hillocks on a film surface, due to the inhomogeneous nature of defects compared with the crystal matrix. We examined the acid mixture ratio to obtain etch characteristics of a-plane GaN film.

Fig. 2 shows plane-view SEM images of the surface morphologies of a-plane GaN after etching with various ratios of acid mixtures. The temperature (160 °C) and time (20 min) were both fixed. After etching the a-plane GaN layer with H3PO4/H2SO4 at the ratio of 1:0 (pure H3PO4), the shape of the etch pits presents a stripe-like pattern along the c-axis. The etched-stripes are composed of two (10T0) facets and the direction is along the c-axis, as shown in Fig. 2(a). The figure shows that a-plane GaN etch pits are very distinct from those of the c-plane GaN reported in previous studies [13]. The c-plane GaN etch pits were formed as nanopipes in hexagonal geometry composed by (110T0) faceted planes. Compared to c-plane GaN, the etch pits of a-plane GaN are more like nanobubbles, which start at the N-facet (000 T) and terminate at the Ga-facet (000 1), but laid on the surface along the c-axis. Thus, pure H3PO4 solution etches N-polarity GaN films very quickly, resulting in the complete removal of surface morphology [14]. Li et al. concluded that the different etching characteristics of Ga-polar and N-polar crystals are due to different surface bonding states, and are only dependent on polarities, not on surface morphology, or growth methods [15]. Thus, the surface defects of a-plane GaN etched by pure H3PO4 solution are not suitable to calculate the etch pit density (EPD) and obtain the information about various types of dislocations. Furthermore, the etch chemistry should be developed for observing other defect-related etch pits, for example, edge and mixed dislocations. To optimize the etch chemistry for determining various dislocations present, the ratio of etchants was optimized by mixing the H3PO4 and H2SO4 [16]. Fig. 2(b) and (c) are the plane-view SEM images of a-plane GaN films, etched by the acid with mixture ratios at 1:0.5 and 1:3. These two figures show that the shape of etch pits are composed of two long (10T0) facets, as shown in Fig. 2(b). The length of (10T0) facets is shorter as the proportion of H2SO4 in etchant mixtures is increased. When the film is etched by pure H2SO4, the shape of etch pits changes to rhombus-like with no (10T0) facets present, as shown in Fig. 2(d). From these images, it was found that the etch rate of these facets is altered by changing the H3PO4/H2SO4 ratio. From Fig. 2(c), we see that a different size of etch pit forms when etching with H3PO4/H2SO4 in a 1:3 ratio. These observations suggest that variation in pit size follows the size of Burgers dislocation vectors in GaN [17]. However, we need to correlate etched pit size and morphology with a-plane GaN dislocation features, as observed by TEM. Based on our experimentation, we recommend the optimal etching solution composition for observing surface defects is H3PO4/H2SO4 at a 1:3 ratio.

Fig. 3(a) and (b) show the AFM images (3 μm × 3 μm) of a-plane GaN before and after wet-etching for 5 min with a 1:3 H3PO4/H2SO4 ratio. From the AFM image, it was found that dark spots of post-etched film are more distinct than that of non-etched film. The EPD of etched-GaN surface is approximately 6.1 × 10^9 cm^-2. An EPD value of 10^9 cm^-2 is far below dislocation density (10^10−10^11 cm^-2) of the a-plane GaN epi layer grown on r-plane sapphire). In c-plane GaN film, this 2–3 orders of magnitude difference between plan-view TEM and EPD counts is attributed to screw dislocation and mixed dislocations, which are not the dominant kind of TDs in GaN film [14]. On contrary, the most common dislocation type for a-plane GaN are threading dislocations, which corresponds to 1–2 orders of magnitude between XTEM and EPD counts.

The surface chemical composition was also investigated by XPS measurements at 45° take-off angle. Fig. 4 shows the XPS spectra of Ga 3d core levels to compare four different surfaces, namely as-grown, pure H2SO4, H3PO4/H2SO4 (1:3), and pure H3PO4 treated...
GaN thin film. In order to determine the amount and composition on GaN surface and chemically treated samples, the peak fitting procedure using Gaussian–Lorenzian line shapes was applied to the experimental spectra (solid lines). In the procedure, three peaks, namely Ga–O, Ga–N, and Ga–Ga, were used to fit the Ga 3d experimental spectra [18]. As seen in the bottom trace of Fig. 4, the Ga 3d surface spectrum prior to etching was toward to the higher binding energy side, due to the presence of natural oxidation products of gallium nitride (Ga2O3). Note that the Ga 3d core level peak near 19.9 eV is mainly assigned to bulk GaN (Ga–N) based chemical bonding [19]. In addition, the native oxide thickness is less than the XPS sampling depth ($t = \lambda \sin \theta$; $\lambda$ and $\theta$ are IMFP of photoelectrons and take-off angle; for instance $t = 4$ nm for Ga 3d) [20] of the core level in GaN layer so that the contribution of the bulk GaN was detectable. After etching by different acids, the shifts of the Ga 3d peaks tend toward lower binding energy. Compared to as-grown GaN film, the shifts in binding energies after etching by different acids (H2SO4, H3PO4/H2SO4, and H3PO4) are 0.23, 0.44, and 0.71 eV, respectively. It indicates that the atom Ga tends to form Ga–N rather than Ga–O bonding on the surface after wet chemical treatment and the damage surface was refreshed [21].

After etching by pure H2SO4, the amount of surface oxide can be reduced but only up to certain extent. Furthermore, a significant amount of aforementioned native oxides can be removed by adding H3PO4 in the etching media. Considering the improved removal of oxide compounds, it can be concluded that pure H3PO4 treatment is faster and much more aggressive than pure H2SO4. However, it is also seen that large amounts of Ga–Ga metallic components appeared. On the other hand, the participation of H3PO4 to the etch solution can largely contribute the formation of metal clusters, as can be seen clearly in the top trace in Fig. 4. The possible mechanism can be explained as follows. In the etching process of III–V materials, the removal rate of group III-related products of etching reaction must be balanced with that of group V-related products, unless the etching product itself contains group III and group V atoms in a one-to-one ratio [18]. In the present case, the etchants are likely to react with nitrogen atoms at the GaN surface, resulting in leaving Ga metallic clusters on the surface. After etching by pure H3PO4, the amounts of Ga metal clusters on the surface were more than those after etching by other etchants. It’s due to the fast etching rate of pure H3PO4 on N-polarity GaN films.

**Fig. 2.** Plane-view SEM images of etched-GaN layer with the mixed H3PO4/H2SO4 ratio of (a) 1:0, (b) 1:0.5, (c) 1:3, and (d) 0:1.

**Fig. 3.** Plane-view AFM images of (a) before and (b) after wet-etching GaN layer with 1:3 ratio mixture of H3PO4/H2SO4.
Fig. 4. XPS spectra of Ga 3d core levels from as-grown GaN, and different acid treated GaN surfaces.

4. Conclusion

The surface defect of a-plane GaN grown on r-plane sapphire by MOCVD was evaluated using the DSE technique. From SEM images of GaN films etched by different ratio acid mixtures (H₃PO₄/H₂SO₄), we demonstrated well-controlled crystallographic etching of a-plane GaN by altering the H₃PO₄/H₂SO₄ ratio. It appears that the different types of dislocations can be determined from observing the various sizes of etch pits using a 1:3 ratio of H₃PO₄/H₂SO₄ etching solution. The EPD of etched-GaN was approximately 6.1×10⁸ cm⁻², as calculated by AFM. The XPS spectra of Ga 3d core level shows that the GaN film treated with pure H₃PO₄ had the largest shift in binding energy (0.71 eV) compared with as-grown GaN film. It indicated that the damage surface was refreshed after chemical treatment. Wet chemical etching is a viable process to improve the properties of a-plane GaN related devices.

Acknowledgments

The authors would like to thank National Science Council, the Bureau of Energy, Ministry of Economic Affairs, Taiwan, for the financial support under Contract no. 98-D0204-6, TDPA program nos. 97-EC-17-A-07-S1-105, NSC 97-2623-E-168-001-IT, and the assistance in material characterization provided by the LED Lighting and Research Center, NCKU are also appreciated.

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