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Wet-chemical Cleaning of Epitaxial GaN(0001) Surfaces

L. Peng[1], A. Ohta[1], N. X. Truyen[1], M. Ikeda[1], K. Makihara[1], N. Taoka[2], T. Narita[3], K. Itoh[3], D. Kikuta[3], K. Shiozaki[4], T. Kachi[4], and S. Miyazaki[1]

[1]Grad. School of Eng., Nagoya Univ., Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan
[2]AIST GaN-OIL, Akasaki Institute 4F, Furo-cho, Chikusa-ku, Nagoya, Aichi, 464-8601, Japan
[3]Toyota Central R&D Labs., 41-1, Yokomichi, Nagakute, Aichi 480-1192, Japan
[4]IMaSS, Nagoya Univ., Furo-cho, Chikusa-ku, Nagoya, 464-8601, Japan

Abstract

The influence of wet-chemical treatments of homo-epitaxial GaN(0001) surface using H_2O_2 and/or NH_4OH on its surface morphology and chemical states have been systematically investigated. We have demonstrated that the addition of slight amount of NH_4OH in H_2O_2 is effective to obtain a flat surface with low hydro-carbon contaminants and low surface state density.

1. Introduction

Surface cleaning of GaN is generally crucial from viewpoints of controllability and reproducibility in device fabrication processes involving device performance and its reliability [1]. However, standard cleaning method of preparing the GaN surface has not been established well.

In this work, to get a better understanding of GaN surface cleaning, we have studied the changes in the surface morphology, chemical bonding features, and filled electronic states of homo-epitaxial GaN surface by wet-chemical treatments using H_2O_2 and/or NH_4OH.

2. Experimental Procedures

A ~2 μm-thick n-type GaN(0001) with a Si concentration of 5×10^{16} cm^{-3} was grown on a free-standing GaN substrate by MOCVD. Then, the wafer dicing was performed after resist coating. For resist removal from the surface, ultrasonic cleaning of acetone and IPA solutions was carried out and followed by deionized pure-water rinse. After that, the GaN(0001) surface was immersed in any of different chemical solutions such as NH_4OH, H_2O_2, and NH_4OH + H_2O_2 at 80 ºC. Subsequently, pure water rinsing for 5 min and drying by N_2 gas blow were carried out.

3. Results and Discussion

AFM images of the GaN(0001) surface before and after H_2O_2 and NH_4OH treatments at 80 ºC for 10 min were taken in a tapping mode using a Si cantilever with a tip apex of ~7 nm at a scan rate of 1 Hz as shown in Fig. 1. For the initial surface before wet-chemical treatment, a clear step-terrace structure with a root mean square (RMS) roughness of ~0.1 nm was clearly observed (Fig. 1(a)). With the treatment in the NH_4OH solution, no significant change in the surface morphology was observable (Fig. 1(b)), which suggests that GaN etching in such an alkaline solution proceeds uniformly. A similar result was observed from the sample treated in a solution of NH_4OH: H_2O = 4: 6 (data not shown). On the contrary, in the case of H_2O_2 treatment (Fig. 1(c)), protrusions with an areal density of ~1.7×10^{10} cm^{-2} and an average height of ~1.3 nm were clearly observed, which results in an increase in the RMS value from 0.1 nm to 0.3 nm. And, protrusions were located mostly at step edges, implying that chemical reactions of H_2O_2 with GaN (0001) surface proceed from the step edges preferentially.

In Fig. 2, chemical bonding features at GaN surface for the samples shown in Fig. 1 were evaluated from the XPS measurements under monochromatized AlKα radiation (1486.6eV). It should be noted that Ga $2p_{3/2}$ signals in the higher binding energy side originating from Ga-O bonding units were slightly decreased by the wet chemical treatments. And, these Ga-O signals taken for the sample after H_2O_2 treatment were larger than that after NH_4OH treatment, which was also confirmed from the analysis of O 1s signals. In addition, decrease in the surface carbon contaminants were hardly detected. Considering that H_2O_2 acts as an oxidant, the observed protrusions on AFM images are likely to be Ga oxide. From these results, H_2O_2 treatment of GaN surface induces a formation of protrusions involving in oxidation reaction.

To suppress the formation of surface protrusion by enhancing the Ga oxide etching, effect of NH_4OH addition in H_2O_2 solution were systematically investigated. Figures 3 and 4 show the AFM topographic images of GaN surface after the wet-treatment of NH_4OH: H_2O_2: H_2O = 0.05~3: 3: 7 at 80 ºC for 10 min and the density of surface protrusion as a function of the concentration of NH_4OH, respectively. In the case of NH_4OH addition at the amount of 0.010% in a solution of H_2O_2, areal density of the protrusions was markedly decreased down to ~0.5×10^{10} cm^{-2} compared to that of H_2O_2 treatment, presumably due to the etching reaction of Ga oxide as well as GaN by NH_4OH [2]. And, the changes in the O 1s and C 1s signals from native oxide and carbon contaminants by wet treatment were also plotted as a function of the concentration of NH_4OH as shown in Fig. 5. It was found that lower intensity of either C 1s or O 1s was acquired by the treatments of H_2O_2+NH_4OH solution compared to single solution treatments, indicating that H_2O_2+NH_4OH solution resulting in a surface with less oxide and hydro-carbon contaminants.

PYS measurements were carried out to evaluate the energy distribution of defect states on GaN surface (Fig. 6). In the PYS measurements, photoelectron yields from the sample were measured as a function of photon energy in the region of 3.0~7.8 eV [3]. The yield from filled defect density of GaN surface in the energy region of valence (E_V) edge (~6.75 eV) was significantly decreased by H_2O_2 and NH_4OH treatments,

which was responsible for the removal of surface native oxide. In addition, further decease in the yield intensity in the region near the E_V by $NH_4OH+H_2O_2$ treatment was observed. Also, the yield intensity near to the conduction band (E_C) edge was increased, which was due to release of the band bending and/or passivation of conduction band defects.

4. Conclusions

H_2O_2 treatment of GaN(0001) induces surface protrusions involving in oxidation reaction and demonstrated that the addition of slight amount of NH_4OH is quite effective to suppress such protrusions in H_2O_2 cleaning. Slight addition of NH_4OH in H_2O_2 is a promising for removal of surface carbon contaminants on GaN.

Acknowledgements

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References

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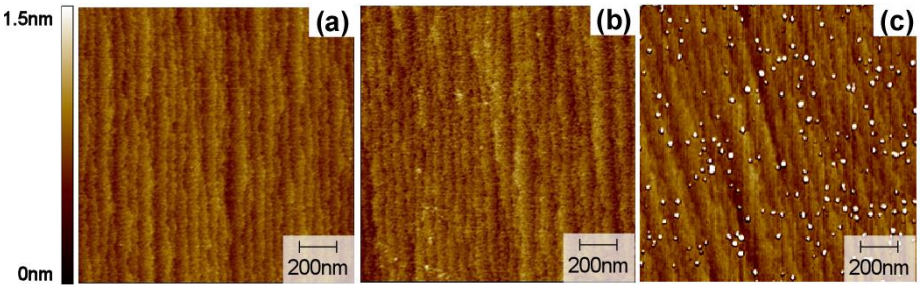

Fig. 1. AFM topographic images taken for GaN(0001) surface (a) before and after wet-chemical treatments of (b) NH_4OH and (c) H_2O_2 at 80ºC for 10 min.

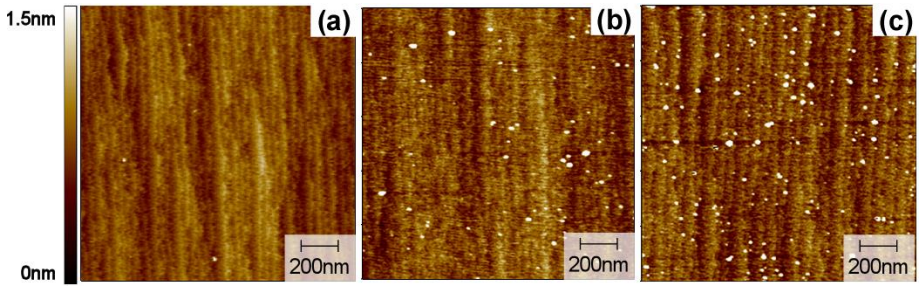

Fig. 3. AFM topographic images taken for GaN surface after $NH_4OH+H_2O_2$ treatment with different NH_4OH concentration ($NH_4OH : H_2O_2 : H_2O = x : 3.0 : 7.0$, (a) x=0.1, (b) 1.0, .and (c) 3.0).

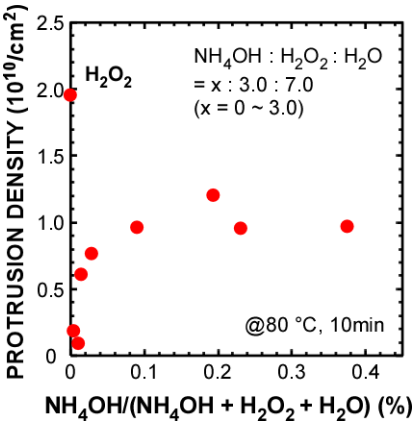

Fig. 4. Protrusion density on GaN surface after $NH_4OH+H_2O_2$ treatments as a function of the NH_4OH concentration.

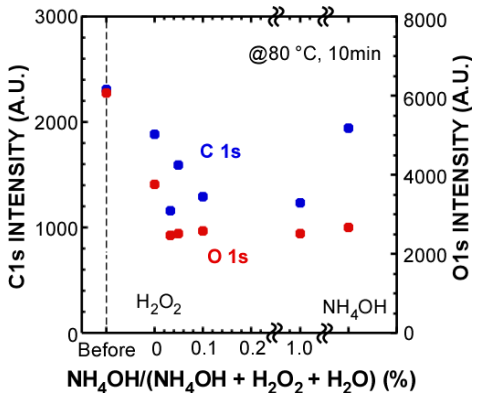

Fig. 5. Integrated intensity of C 1s and O 1s XPS core-line signals from surface carbon contaminants and oxide after $NH_4OH+H_2O_2$ treatments as a function of the NH_4OH concentration. Intensity was normalized by Ga $2p_{3/2}$ signals from Ga-N bonding units.

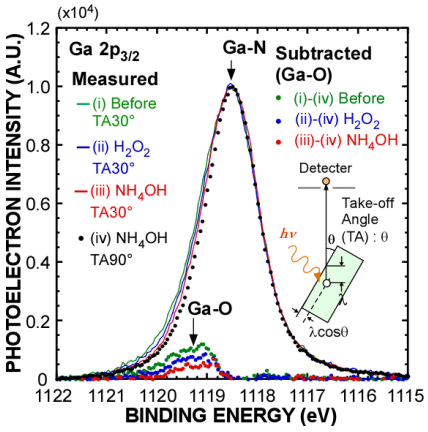

Fig. 2. Chemical bonding features at GaN surface evaluated from Ga $2p_{3/2}$ Core-line Spectra. Intensity normalization and energy calibration were made by Ga-N bonding units from Ga 2p signals.

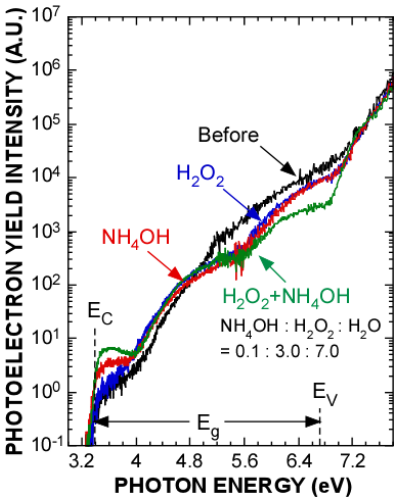

Fig. 6. PYS spectra taken before and after wet chemical treatments of H_2O_2, NH_4OH, and H_2O_2+ NH_4OH. The observed photoelectron yields from the sample were attributed to the emission from the filled defects and valence electrons. E_C and E_V denoted with conduction band bottom and valence band top of GaN.