Proc. Int. Workshop on Nitride Semiconductors
IPAP Conf. Series 1 pp. 778-781

Tree-like features formed on photoelectrochemically etched n-GaN surfaces
—— Revelation of threading dislocations in GaN ——

Akio YAMAMOTO, Katsuhiko AZUMA, Tomomi YASUDA and Akihiro HASHIMOTO
Department of Electrical & Electronics Engineering, Fukui University, 3-9-1 Bunkyo, Fukui 910-8507, Japan
e-mail: yamamoto@kyomu1.fuee.fukui-u.ac.jp

Electrochemical etching behavior of n-type GaN films grown on sapphire has been studied under UV (λ =325 nm) light illumination. As the cases for photoelectrochemical etching of n-type GaAs and InP, three different features appear on etched n-GaN surfaces depending on current density for etching; a high density (10^{10} cm^{-2}) of tree-like protrusions at a lower c—urrent density, a relatively flat surface at an intermediate current density, and peeling of the film from the substrate at a higher current density. From the shape and the density of tree-like protrusions, in addition to the analogy of these results with those for n-type GaAs and InP, it is reasonable to conclude that tree-like protrusions formed at a low current density are due to threading dislocations involved in n-GaN films. Thus, the photoelectrochemical etching is found to become a convenient method to detect dislocations in n-type III nitride materials.

KEYWORDS : GaN, photoelectrochemical etching, detection of dislocations, current density , tree-like feature

1. Introduction

Dislocation density is one of the important factors in the evaluation of crystalline quality of semiconductor materials. In order to reveal dislocations as etch pits, wet chemical etching is widely employed for Si and conventional III-V semiconductors. In contrast with those semiconductors, chemical stability for III nitrides makes it difficult to use wet chemical etching for etch pit formation. Therefore, a simple and rapid method to reveal dislocations is highly desirable for III nitrides. It has been demonstrated that dislocations in n-type semiconductor crystals can also be detected as protrusions or hillocks by photoelectrochemical etching [1, 2]. This method was successfully applied to n-InP [2], showing that this method has a higher resolution and a higher sensitivity for defect delineation than the conventional wet chemical etching. The mechanism for the dislocation detection as a protrusion is based on the recombination of photo-generated holes at dislocation sites. Since the electrochemical dissolution reaction needs holes, reduced concentration of holes at a dislocation site results in a reduced dissolution rate and, therefore, makes a protrusion there. If the dislocations in III nitrides act as recombination centers for holes, it is possible to apply photoelectrochemical etching in order to reveal dislocations in III nitrides. Recently, dislocations in III nitrides have been thought to act as recombination centers, although, in the early stage of the research, it was reported not to be the recombination centers because of the weak dependence of luminescence efficiency on dislocation density in GaN.

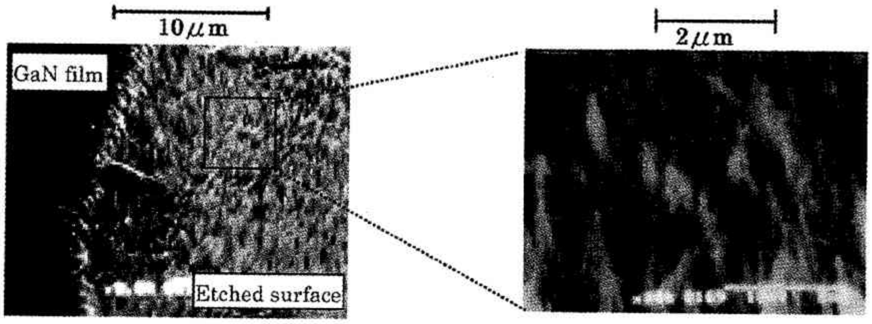
In this paper, we report electrochemical etching of n-GaN under UV light irradiation. Tree-like protrusions are formed on an n-GaN surface photoelectrochemically etched at a low carrier density. The density of protrusions is about 10^{10} cm^{-2}. From the analogy of the results for the present study with those for the photoelectrochemical etching of n-GaAs [1] and n-InP [2], protrusions are attributed to the threading dislocations involved in the sample. Thus, the photoelectrochemical etching is found to become a convenient method to detect defects in III nitrides, such as dislocations, which act as recombination centers of holes.

2. Experimental

Photoelectrochemical etching of n-type GaN was performed using a 0.1 mol/l NaOH solution at 20°C. N-type 2 μm-thick GaN films were grown at 1000 °C on α-Al_2O_3(0001) by the MOVPE method using TEGa and NH_3 as source gases and N_2 as a carrier gas. Grown GaN had a carrier concentration of $2x10^{17}$-$2x10^{18}$ cm^{-3}. Special procedures have not been done to reduce dislocation density in grown GaN films. The electrochemical etching was made galvano-statically with a current density of 0.5 –50mA/cm^2. A He-Cd laser with 325 nm wavelength and 100 mW output power was irradiated to the sample surface through the solution.

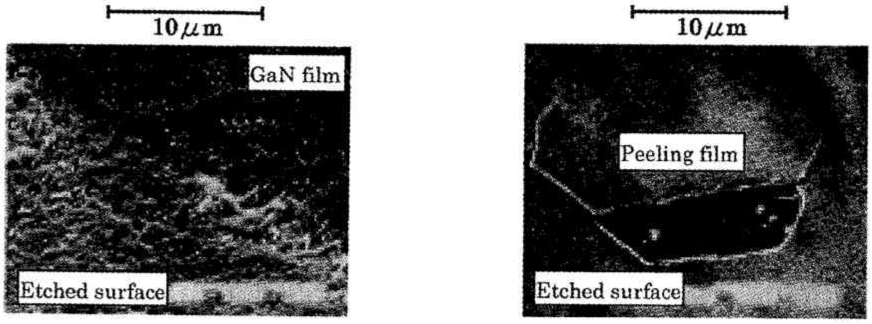
3. Results and Discussion

Figure 1 shows SEM images of typical GaN surfaces etched with a different current density under the constant light intensity. As shown in this figure, three different features appear on etched n-GaN surfaces, depending on the current density for etching. At low current densities, around 0.5 mA/cm^2, "tree-like" protrusions are formed on the etched surface (Fig. 1(a) and 1(b)). At a medium current density, around 15



(a) 0.5 mA/cm^2

(b) 0.5 mA/cm^2 (magnification of (a))



(c) 15 mA/cm^2

(d) 50mA/cm^2

Fig. 1. SEM images of photoelectrochemically etched n-GaN with a different etching current density.

mA/cm^2, a comparatively flat surface is formed (Fig. 1(c)). At high current densities, around 50 mA/cm^2, the sample surface is etched only slightly, and the remainder of GaN film is peeled off from the substrate (Fig. 1(d)). Figure 2 summarizes the current density dependence of etched GaN surface. As described above, current densities are roughly divided into three regions. The terms Region Ⅰ, Ⅱ, and Ⅲ will be used from now to refer the three regions, low, intermediate, and high current densities, respectively. It should be pointed out that the results in Fig. 2 are very similar to those for n-type GaAs [1)], except for the results in Region Ⅲ. Although the GaN film is peeled off from the substrate in Region Ⅲ in this case, deep etch pits are formed on n-GaAs [1)]. For n-GaAs [1)] and n-InP [2)], dot-like and line-shaped hillocks existed on the etched surface in Region I. They were proved to be due to the defects including dislocations, by clarifying one-to-one correspondence between hillocks and etch pits. The detection of defects as hillocks is enabled by a lower dissolution rate due to a lower density of photo-generated holes at defect sites as recombination centers. This is because only holes are concerned with anodic dissolution of semiconductors. This kind of defect detection by hillocks formation is possible under the condition that the consumption rate of holes as anodic current for dissolution is lower than the generation rate of holes by illumination [1, 2)]. From the analogy of the present results with those for n-GaAs and n-InP, it is reasonable to consider that the formation of "tree-like" protrusions is due to defects in GaN films. From the magnified image in Fig.1 (b), one can see that many trees are standing perpendicularly to the film surface. The density of trees is counted to be about 10^{10}/cm^2. The shape and the density of trees strongly suggest that they are due to the threading dislocations involved in n-GaN. Adesida et al. [3)] observed whiskers very similar to the trees obtained here. They also confirmed all whiskers to contain threading dislocations using TEM observation. The very fine structure of the trees is seen in Fig. 1(b). As reported previously [4)], fineness of formed protrusions should be governed by hole diffusion length. A shorter diffusion length gives a finer shape of protrusion. The existence of a thin needle with a diameter less than 0.1 μm in Fig. 1(b) suggests a very short diffusion length of holes in the sample.

With increasing anodic current density, sensitivity of defect detection by hillocks or protrusions formation becomes low because of electric field at the semiconductor/electrolyte interface, and there is a region where defects are not detected and a relatively flat

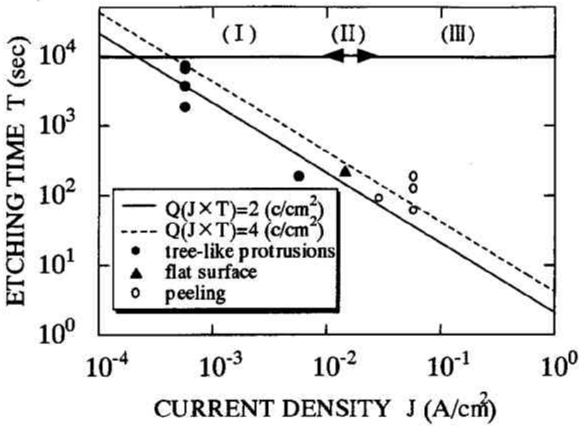


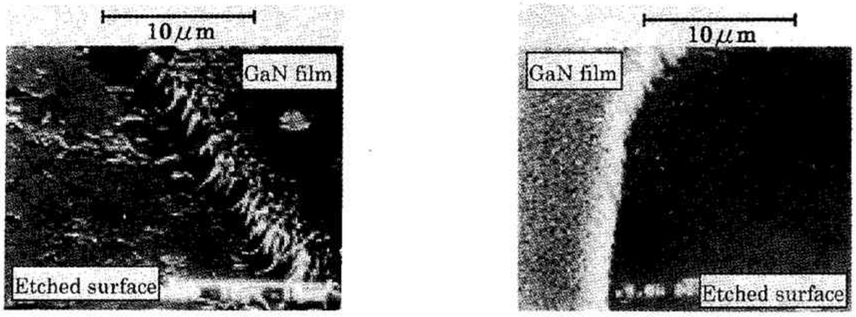
Fig. 2. Current density dependence of etched GaN surface character.

surface is obtained after the etching (Region II). In this region, photoelectrochemical etching can be used as a device process. Under the condition, where consumption rate of holes (current density) is much higher than generation rate of holes by illumination (Region III), illumination effects are not observed in the anodic dissolution effects and deep etch pits were produced on an etched surface of GaAs [1]. The deep etch-pit formation is due to the local breakdown at defect sites because defects act as generation centers of holes in a high electric field in the depletion layer at the semiconductor surface. Although deep etch pits are not formed on an etched GaN surface in this case, anodic behavior of the sample is the same as that for a GaN film without UV illumination [5]. As reported previously [6], a GaN film with a carrier density of about 10^{18} cm^{-3} has a high carrier-density layer, which can be dissolved without UV illumination, near the GaN/α-Al_2O_3 (0001) interface. Due to the relatively high electric field at the GaN surface, weak points such as clusters of dislocations or nano-pipes seem to be selectively attacked. This makes penetration paths (i.e. nano-pipes) for electrolyte to reach the GaN/α-Al_2O_3 (0001). Then, the high carrier-density layer near the GaN/α-Al_2O_3(0001) interface is selectively etched, resulting in the peeling of the GaN film.

Figure 3 shows time dependence of etched surface for a current density of 0.5 mA/cm². The etching time for the result shown in Fig. 1(a) is 30 minutes. With increasing etching time, i.e., etching depth, etched surface becomes smooth. Especially, a very smooth surface is obtained when the etching proceeds to dissolve almost all of the film (Fig. 3(b)). How did the trees formed at the early stage of the etching disappear? As seen in Fig. 3(a), the trees are removed by breaking away when the part of GaN layer near the substrate, which is easily dissolved electrochemically without UV irradiation, is dissolved. Some wrecks of "trees" are found on the etched surface shown in Fig. 3 (a).

4. Conclusions

Electrochemical etching of n-type GaN films grown on sapphire has been studied under UV (λ=325 nm) light illumination. As the cases for photoelectrochemical etching of n-type GaAs and InP, three different features appear on etched n-GaN surfaces depending on anodic current density; a high density (10^{10} cm^{-2}) of tree-like protrusions at a lower current density, a relatively flat surface at an intermediate current density, and peeling of the film from the substrate at a higher



(a) 105 min

(b)120min

Fig. 3. SEM images of photoelectrochemically etched n-GaN with a different etching time.

current density. Tree-like protrusions are standing perpendicularly to the film surface. From the shape and the density of tree-like protrusions, in addition to the analogy of these results with those for n-type GaAs and InP, it is reasonable to conclude that tree-like protrusions formed at a low current density are due to threading dislocations involved in n-GaN films. This means that dislocations in n-GaN can act as recombination centers of photogenerated holes. Thus, the photoelectrochemical etching is found to become a convenient method to detect dislocations in n-type III nitride materials.

1) A. Yamamoto et al. J. Electrochem. Soc.122, 260 (1975).
2) A. Yamamoto et al. J. Electrochem. Soc.128, 1095 (1981).
3) I. Adesida et al., MRS Internet J. Nitride semiconductor Res. 4S1, G1.4 (1999).
4) A. Yamamoto et al. J. Electrochem. Soc.138, 2022 (1991).
5) A. Yamamoto et al. Jpn. J. Appl. Phys. 38, 2619 (1999).
6) A. Yamamoto et al., phys. stat. sol. (a) 176, 689 (1999).