

Anomalous Electrochemical Behavior of N-Type GaN Films on α -Al₂O₃ Substrates

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1. Introduction

Gallium nitride (GaN) and related materials have been extensively studied owing to their optical and electronic device applications. For the development of those applications, characterization and understanding of these materials from a variety of viewpoints are required.

Recently, some results of the electrochemical etching of n-type GaN (1,2) as a method for selective removal have been reported. In those reports, it is shown that an n-type GaN sample of "high quality" can anodically dissolve in the dark (1) and shows a small effect of illumination as a method of extra hole supply in the anodic reaction (2). They can not be understood from the viewpoint of electrochemistry of semiconductors. As a results of huge amount of works on electrochemical behavior of semiconductors including IV, III-V and II-VI, it has been concluded that the anodic dissolution process of a semiconductor needs holes and contribution rate of holes to anodic dissolution reaction is higher for a semiconductor with a wider bandgap (3).

This study has been made to clarify and discuss the uncertain or confusion described above and find an answer to the questions presented.

2. Experimental

Single crystalline GaN films were grown on α -Al₂O₃(0001) substrates using metal-organic vapor phase epitaxy (MOVPE) with triethylegallium and ammonia as source materials. The 2-step growth method (the 1-st layer at 550°C and the 2-nd layer at 1000 °C) was employed. Carrier concentration of a grown film measured with Van der Pauw method is about $1 \times 10^{18} \text{ cm}^{-3}$ and FWHM of X-ray rocking curve is about 800 arcsec. As electrolytes for electrochemical measurements of n-GaN, a 0.1 mol/l NaOH and a 1 mol/l H₂SO₄ solutions were used. Anodic current-electrode potential characteristics of n-type GaN were measured galvanostatically at 20°C. As a source of UV irradiation for the GaN electrode, a "Black Light" of 10W was used.

3. Results and Discussion

Figure 1 shows a trace of electrode potential as a function of time for a constant anodic current of $5 \times 10^{-5} \text{ A/cm}^2$. As seen in Fig. 1, electrode potential is low at the initial stage and then suddenly becomes very high. It should be noted that UV-irradiation effect becomes

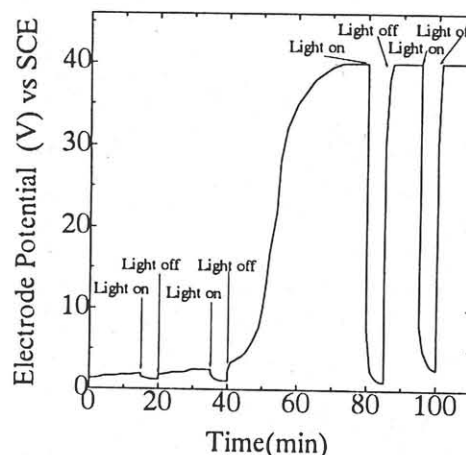


Fig. 1 Time dependence of electrode potential for a constant anodic current of $5 \times 10^{-5} \text{ A/cm}^2$.

large as the potential becomes high. It should be pointed out that the UV-light response of potential is very swift. Although the phenomenon of such a steep potential increase was explained by Ohkubo (1) to show a surface passivation with Ga(OH)₃, such a interpretation is not reasonable since the UV-irradiation can not remove the Ga(OH)₃ layer. Figure 2 shows current density-electrode potential curves for n-type GaN film in the dark and under UV irradiation in a NaOH and a H₂SO₄ solutions. The measurement was made after the samples showed the steep increase in electrode potential (see Fig. 1). The results in Fig. 2 are similar to those for n-type GaAs (4) or n-type InP (5), showing a marked effect of illumination. These results should be said to be "normal". It is noted that there is no difference between the curves for both solutions. The interpretation of passivation is also denied because

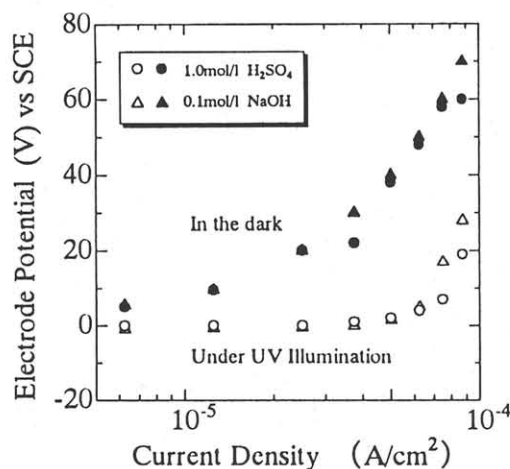


Fig. 2. Current density-electrode potential curves for n-type GaN films in the dark and under UV irradiation in a NaOH and a H_2SO_4 solutions. The measurements were made after the samples showed the steep increase in electrode potential (see Fig. 1).

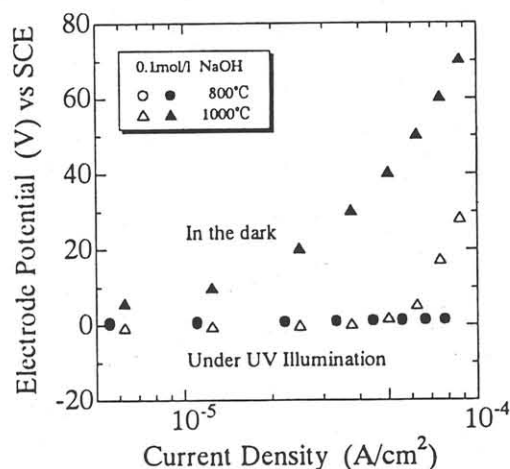


Fig. 3. Current density-electrode potential curves for an n-type GaN film grown at 800°C in comparison with those for the GaN grown at 1000°C .

$\text{Ga}(\text{OH})_3$ can easily dissolve in an acidic solution like H_2SO_4 solution. The remarkable decrease of electrode potential by illumination shows a diminution of depletion layer at the n-GaN/electrolyte interface. Inversely, the high electrode potential in the dark shows the formation of a depletion layer at the interface because of no holes in n-type GaN. The question is that why do not the GaN samples used here show such a "normal" behavior at the initial stage of the anodization. It is known that n-type semiconductors containing a high density of defects can chemically dissolve (4) and those having a high carrier density ($\sim 10^{17} \text{ cm}^{-3}$) can electrochemically dissolve without extra hole supply (5). Figure 3 shows current density-electrode potential curves for an n-type GaN film grown at 800°C in the dark and under UV irradiation, in comparison with those for the GaN grown at 1000°C . The "low quality" sample prepared at 800°C shows no effects of illumination and dissolve easily even in the dark. Therefore, it is reasonable to understand that the change in electrode potential with time, seen in Fig. 1, results from inhomogeneity in defect density and/or carrier density in the GaN film. In other words, low quality portion in the sample can selectively dissolve at the initial stage, where electrode potential is very low and, after that, voltage is applied to the high quality portions which show a high electrode potential.

It should be noted that the area of a GaN film, contacted with the NaOH electrolyte, is peeled off after the long time (~ 1 h) anodization. This means

that the part of GaN layer near the substrate surface is selectively dissolved. It is possible to consider that through pits (nano-pipes) the part of GaN layer near the substrate is selectively dissolved, because such a part has a high density of defects.

4. Summary

Anodic behavior of n-type GaN films grown on $\alpha\text{-Al}_2\text{O}_3(0001)$ substrates has been studied in the dark and under UV irradiation. Electrode potential of a GaN sample becomes very high as the anodization proceeds. This is not due to the passivation effect with $\text{Ga}(\text{OH})_3$ but to the selective dissolution of low-quality and/or high carrier-density part in the GaN film. The GaN sample shows a "normal" anodic behavior, that is, a marked illumination effect, after electrode potential becomes high.

Thus, the anomalous electrochemical behavior is believed to be due to inhomogeneity in defect density and/or carrier concentration in GaN films. Measurement of anodic behavior will become a useful method for inhomogeneity evaluation for GaN films.

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