Gallium nitride (GaN) is a semiconductor material used in ultraviolet light-emitting diodes and laser diodes owing to its wide-band gap (3.38 eV) and thermal and chemical stability.\(^1\) GaN powder sintered into mechanically robust and machinable ceramics is an economical alternative to GaN single-crystal substrates in optoelectronics.\(^2\) GaN powder is synthesized typically by thermal annealing of gallium sulﬁde, was not retained after calcination under a ﬂow of ammonia (NH\(_3\)) and hydrogen (H\(_2\)) at elevated temperatures. The morphology of the microsized \(\beta\)-Ga\(_2\)O\(_3\) single crystals grown on the \(c\)-plane sapphire by the thermal annealing of gallium sulﬁde, was not retained after calcination under a ﬂow of NH\(_3\) and H\(_2\). These microstructural observations strongly support that the ammonolysis of \(\beta\)-Ga\(_2\)O\(_3\) to GaN proceeds through gaseous Ga\(_2\)O, and that the rate of the reduction of \(\beta\)-Ga\(_2\)O\(_3\) to Ga\(_2\)O is slower than that of the nitridation of Ga\(_2\)O to GaN.

Another way to clarify the reaction mechanism is to examine the change in morphology during the ammonolysis of Ga\(_2\)O to GaN because the formation of the gaseous and solid-state intermediates will cause a change and retention of the original morphology, respectively. The examination was applied to elucidate the nitridation mechanism for other Group 13 oxides such as Al\(_2\)O\(_3\) and In\(_2\)O\(_3\). For example, the original morphology of the starting Al\(_2\)O\(_3\) particles was maintained during their nitridation to AlN under a mixed gas ﬂow of NH\(_3\) and C\(_3\)H\(_8\) because the nitridation proceeded via aluminum oxynitride species (Al\(_x\)O\(_y\)N\(_z\)) as the reaction intermediate.\(^12\) On the other hand, the morphology of In\(_2\)O\(_3\) powder, which was obtained from the reaction of In\(_2\)O\(_3\) powder with NH\(_3\) at temperatures above 630°C, was completely different from that of the initial In\(_2\)O\(_3\) powder because the reaction proceeded through gaseous intermediates such as In\(_2\)O\(_y\).\(^13\) The occurrence of Ga\(_x\)O\(_y\)N\(_z\) intermediates was suggested based on the morphology retention during the ammonolysis of \(\alpha\)-Ga\(_2\)O\(_3\) powder to GaN.\(^14\),\(^15\) Nevertheless, an assessment of the retention may be ambiguous when Ga\(_2\)O\(_3\) powder, which is an agglomerate of polycrystalline Ga\(_2\)O\(_3\) particles, is used as the precursor. The ambiguity will be reduced considerably, if Ga\(_2\)O\(_3\) single crystals with a distinct shape are used.

In this note, to elucidate the reaction mechanism of reaction (1), microsized \(\beta\)-Ga\(_2\)O\(_3\) single crystals on the sapphire were prepared by thermal annealing of gallium sulﬁde (Ga\(_2\)S\(_3\)) powder under a ﬂow of nitrogen (N\(_2\)) and then nitridated under a ﬂow of NH\(_3\). The morphology of \(\beta\)-Ga\(_2\)O\(_3\) single crystals with a distinct shape was compared with that after the nitridation. In addition, \(\beta\)-Ga\(_2\)O\(_3\) single crystals were calcined under a ﬂow of hydrogen (H\(_2\)) and the morphology of the product was compared with that of the nitridated \(\beta\)-Ga\(_2\)O\(_3\) single crystals.

The \(c\)-plane sapphire was placed on \(\alpha\)-Ga\(_2\)S\(_3\) powder (99.99%, Kojundo Chemical Laboratory Co.) and put in an alumina crucible. The sapphires used in this work were cleaned through sonication in organic solvents (trichloroethylene, acetone, and methanol) and rinsed with deionized water. The alumina crucible was transferred to the center of an alumina tube with an inner diameter of 33 mm and heated to 1000°C at a rate of 5°C/min.
under a flow of N\textsubscript{2}. The duration time was 3 h. The alumina crucible was taken from the furnace after it had cooled to the room temperature. The $\beta$-Ga\textsubscript{2}O\textsubscript{3} single crystals and their nitridated products were characterized by XRD (PANalytical X'Pert PRO MPD X-ray diffractometer) using glancing incident Cu-K\textalpha radiation ($2^\circ$).

Figure 1(a) shows the XRD pattern of the layer grown on the c-plane sapphire. A comparison in XRD patterns between the layer and $\beta$-Ga\textsubscript{2}O\textsubscript{3} powder (ICDD-PDF #98-003-8338) indicated that the layer was mainly composed of (510)-, (511)-, and (710)-oriented $\beta$-Ga\textsubscript{2}O\textsubscript{3} single crystals. This result is compared to $\beta$-Ga\textsubscript{2}O\textsubscript{3} thin films grown on the c-plane sapphire by plasma-assisted molecular beam epitaxy technique, the film being (201)-oriented.\textsuperscript{16,17)  

Figure 2 shows the evolution process of $\beta$-Ga\textsubscript{2}O\textsubscript{3} layer on the c-plane sapphire. At the initial growth stage [Fig. 2(a)] the nucleated islands were scattered randomly and grew radially on the sapphire surface, producing asterisk-like $\beta$-Ga\textsubscript{2}O\textsubscript{3} hillocks. The radial growth of the hillocks was hindered by impingement with nearby hillocks. This hindrance induced lateral growth, resulting in the formation of a $\beta$-Ga\textsubscript{2}O\textsubscript{3} layer, as shown in Fig. 2(b). Further growth yielded a scale-like surface [Figs. 2(c) and 2(d)] with each scale being a single crystal. The nucleated $\beta$-Ga\textsubscript{2}O\textsubscript{3} islands may be formed by the oxidation of Ga vapor formed from decomposition of Ga\textsubscript{2}S\textsubscript{3}. The Ga vapor is deposited on oxygen sites of the sapphire surface. Therefore, the array of oxygen sites of the sapphire determines the surface morphology of the Ga\textsubscript{2}O\textsubscript{3} layers, as shown in Fig. 3. Oxygen was not added intentionally to the furnace, suggesting that the residual oxygen in the N\textsubscript{2} flow may be the source of oxygen for the oxidation of Ga.

In order to elucidate the reaction mechanism of reaction (1), microsized $\beta$-Ga\textsubscript{2}O\textsubscript{3} single crystals grown on the c-plane sapphire were nitridated under a flow of NH\textsubscript{3} (Showadenko, 99.999\%) at 1000°C for 3 h. The flow rate of NH\textsubscript{3} was 100 ml/min. The nitridated layer was characterized by XRD, photoluminescence (PL), and scanning electron microscopy (SEM, Hitachi S-4200). Positions and relative intensities of diffraction peaks [Fig. 1(b)] of the nitridated $\beta$-Ga\textsubscript{2}O\textsubscript{3} single crystals were almost the same as those of hexagonal GaN powder (ICDD-PDF #98-000-9127). The room-temperature PL spectrum (Fig. 4) of the nitridated $\beta$-Ga\textsubscript{2}O\textsubscript{3} single crystals was measured by using a He-Cd laser (excitation wavelength = 325 nm). The intense emission peak at 363 nm in the spectrum is the band edge of GaN with the wurtzite structure. The yellow band at about 580 nm was very weak, indicating that the nitridated $\beta$-Ga\textsubscript{2}O\textsubscript{3} single crystals are almost defect-free GaN powder.
At 700°C. When calcined at 1000°C, crystals grown on the H2 single crystals before and after ammonolysis showed that the morphology of β-Ga2O3 single crystals was almost retained. Such contour retention had been observed in the ammonolysis of α-Ga2O3 powders. A close observation [Fig. 5(c)], however, revealed triangular pyramids protruding from the upper surface along with striated pillars, leaving a space among them at the lateral side.

To examine the origin of the change in morphology by ammonolysis, the β-Ga2O3 single crystals were calcined under a flow of H2. Butt et al. showed that Ga2O3 vaporizes as Ga2O under a mixed gas flow of H2 and argon (Ar) at temperatures above 720°C. Kiyono et al. measured the weight loss of Ga2O3 powder under a mixed gas flow of H2 and Ar, and suggested that the weight loss is caused by the generation of gaseous Ga2O. Therefore, the reduction of Ga2O3 to gaseous Ga2O by H2 is expected to affect the morphology of β-Ga2O3 single crystals due to the evolution of gaseous Ga2O. Microsized β-Ga2O3 single crystals grown on the c-plane sapphire were calcined under a mixed gas flow of Ar and H2 (10 vol %) (hereafter, 10 vol % H2/Ar) at 700 and 1000°C for 3 h. The surface of β-Ga2O3 single crystals [Fig. 6(a)] was damaged (decomposed) by calcination at 700°C. When calcined at 1000°C, β-Ga2O3 single crystals transformed into a bundle of fibers without retaining the original morphology, as shown in Fig. 6(b). The fibers were quite aligned, indicating that the decomposition rate of β-Ga2O3 single crystals by H2 depends on the crystal plane. The decomposition mechanism of β-Ga2O3 single crystals by H2 is not clear, but the change in the morphology could be tentatively explained in terms of the difference in adsorption of hydrogen on Ga sites in β-Ga2O3. Hydrogen adsorption on Ga2O3 surfaces has been extensively studied for understanding the mechanism of H2 detection and catalytic activities in various reactions such as alkane dehydrogenation and/or aromatization. The hydrogen adsorption occurs on Ga sites close to oxygen vacancies and the bonding between hydrogen and coordinatively unsaturated gallium cations is stronger for GaO3 sites than for GaO6 sites. Therefore, the reduction of β-Ga2O3 to gaseous Ga2O by H2 at elevated temperatures is expected to be more facile for Ga3O4 sites than for GaO6 sites and thereby the crystal plane abundant in GaO4 sites will be more easily decomposed than that abundant in GaO6 sites.

The difference in the morphology of β-Ga2O3 single crystals under a flow of NH3 and H2 indicated that as suggested by Balka and Davis, reaction (1) consists of two successive reactions as follows:

\[
\begin{align*}
\text{Ga}_3\text{O}_4(s) + 2\text{H}_2(g) & \rightarrow \text{Ga}_2\text{O}(g) + 2\text{H}_2\text{O}(g) \quad (2) \\
\text{Ga}_2\text{O}(g) + 2\text{NH}_3(g) & \rightarrow 2\text{GaN}(s) + \text{H}_2\text{O}(g) + \text{H}_2(g) \quad (3)
\end{align*}
\]

The successive reactions have been employed for the growth of GaN films or single crystals, in which Ga2O vapor was formed by the reaction of Ga3O4 powder with H2 or carbon. If the rate of reaction (2) is faster than that of reaction (3), the morphology of Ga2O3 single crystals will show remarkable changes after ammonolysis. The contour retention by the ammonolysis in this study indicates that the rate of reaction (3) is faster than that of reaction (2). Under that condition, a small part of Ga2O vapor formed by reaction (2) is escaped from β-Ga2O3 single crystals without nitridation to GaN, but most Ga2O vapor is nitridated to GaN without escaping, resulting in contour retention. The nitridation of Ga2O vapor to GaN might result in the formation of pyramidal protrusions from the upper surface. Martín et al. obtained a foam-shaped GaN powder by the ammonolysis of block-shaped β-Ga2O3 powder and explained the change in morphology in terms of the stress in the Ga2O3 bulk by the formation of an inner GaN phase due to different molar volumes of Ga2O3 and GaN. The striated pillars at the lateral side of the nitridated β-Ga2O3 single crystals [Fig. 5(c)] might be formed by the nitridation of bundle of Ga2O3 fibers shown in Fig. 6(b). In summary, the change in the morphology of microsized β-Ga2O3 single crystals under an flow of NH3 and H2 provided a useful clue for elucidating the reaction mechanism for the ammonolysis of β-Ga2O3 to GaN. The lack of the morphology retention of β-Ga2O3 single crystals after ammonolysis supported the mechanism in which the ammonolysis consists of two successive reactions, i.e., the reduction of β-Ga2O3 to gaseous Ga2O and nitridation of Ga2O to GaN. And the contour retention indicated that the rate of the reduction of β-Ga2O3 to Ga2O is slower than that of the nitridation of Ga2O to GaN.

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