Effect of methane additive on GaN growth using the OVPE method

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The oxide vapor phase epitaxy (OVPE) method is expected to be a useful technique for bulk GaN growth, because it allows long-term growth without producing a solid byproduct. However, thick GaN crystals have not been realized due to the growth inhibition caused by polycrystal formation resulting from high H\textsubscript{2}O partial pressure. In this study, we formed GaN crystals with CH\textsubscript{4} gas to decrease the H\textsubscript{2}O partial pressure in a growth zone by the reaction of CH\textsubscript{4} with H\textsubscript{2}O to produce CO and H\textsubscript{2}. As a result, H\textsubscript{2}O partial pressure decreased with increasing CH\textsubscript{4} flow rate, and GaN layers could be grown without decrease of growth rate or degradation of the crystalline qualities at a flow rate of 50–100 sccm of CH\textsubscript{4} gas. Furthermore, we obtained high crystalline 400-μm thick GaN crystals after a growth period of 10 h. © 2019 The Japan Society of Applied Physics

1. Introduction

Gallium nitride (GaN) is an attractive material for optoelectronic devices and high power electronic devices, because of physical properties such as a large direct band gap (\( \sim 3.4 \text{ eV} \)), high breakdown field (\( \sim 3 \times 10^6 \text{ V cm}^{-1} \)), and high saturated electron velocity (\( 1 \times 10^7 \text{ cm s}^{-1} \)).\textsuperscript{1,2}) However, the performance characteristics of these devices are reduced, owing to high dislocation density.\textsuperscript{3–5}) These dislocations are caused by the mismatch between GaN and substrates such as sapphire or silicon carbide (SiC).\textsuperscript{6,7)} To solve this problem, high-quality bulk GaN crystals are needed.

Recently, several useful techniques have been developed for the growth of GaN bulk single crystals, including hydride vapor phase epitaxy (HVPE),\textsuperscript{8–10)} ammonothermal growth,\textsuperscript{11–13)} and the Na flux method.\textsuperscript{14–16)} Of these, HVPE is the most advanced technology for bulk GaN growth because it provides a high growth rate of 1870 μm h\textsuperscript{−1}.\textsuperscript{1,17)} However, the process deposits a solid NH\textsubscript{4}Cl byproduct in the exhaust pipe, which impedes prolonged growth.

We have been developing an oxide vapor phase epitaxy (OVPE) method for the growth of GaN crystals.\textsuperscript{18–23)} In this method, GaN crystals are grown by the reaction between Ga\textsubscript{2}O vapor and NH\textsubscript{3} gas, as shown in the following reaction formula:

\[
\text{GaN}(g) + 2\text{NH}_3(g) \rightarrow 2\text{GaN}(s) + \text{H}_2\text{O}(g) + 2\text{H}_2(g). \quad (1)
\]

This method is expected to be a useful technique for bulk growth, because it allows long-term growth without producing a solid byproduct. In a previous study, we reported two methods for generating Ga\textsubscript{2}O vapor. The first generates Ga\textsubscript{2}O vapor by the reduction of Ga\textsubscript{2}O\textsubscript{3} powder with H\textsubscript{2} gas in a source zone (Ga\textsubscript{2}O\textsubscript{3}–H\textsubscript{2} system), as shown in the following equation.\textsuperscript{18)}

\[
\text{Ga}_2\text{O}_3(s) + 2\text{H}_2(g) \rightarrow \text{Ga}_2\text{O}(g) + 2\text{H}_2\text{O}(g). \quad (2)
\]

The conversion efficiency of H\textsubscript{2} gas into H\textsubscript{2}O vapor is 5%–10% under general experimental conditions, and its value agrees with that of thermodynamic calculation.\textsuperscript{24)} The number of moles of H\textsubscript{2}O formed in this reaction process is twice that of Ga\textsubscript{2}O. Thus, H\textsubscript{2}O partial pressure in the growth zone increased with Ga\textsubscript{2}O partial pressure for high growth rates. The other method generates Ga\textsubscript{2}O vapor by the oxidation of liquid Ga with H\textsubscript{2}O vapor in a source zone (Ga–H\textsubscript{2}O system).\textsuperscript{19,20)} This reaction can be described as follows:

\[
2\text{Ga}(l) + \text{H}_2\text{O}(g) \rightarrow \text{Ga}_2\text{O}(g) + \text{H}_2(g). \quad (3)
\]

In this process, the partial pressure of H\textsubscript{2}O vapor introduced into the growth zone decreases by increasing the conversion efficiency of the H\textsubscript{2}O vapor into Ga\textsubscript{2}O vapor.

In our recent study, we compared the polycrystal density of GaN layers grown using the Ga\textsubscript{2}O\textsubscript{3}–H\textsubscript{2} system with those grown using the Ga–H\textsubscript{2}O system.\textsuperscript{20)) In the Ga–H\textsubscript{2}O system, the polycrystal density of GaN layers was reduced at a high growth rate compared to the Ga\textsubscript{2}O\textsubscript{3}–H\textsubscript{2} system. We considered that this was due to a lower H\textsubscript{2}O partial pressure in a growth zone. In this experiment, the conversion efficiency of H\textsubscript{2}O vapor into Ga\textsubscript{2}O vapor was approximately 45%, resulting in lower H\textsubscript{2}O partial pressure in the growth zone, which was about 60% compared to the Ga\textsubscript{2}O\textsubscript{3}–H\textsubscript{2} system. These results suggest that in this method, the reduction of H\textsubscript{2}O partial pressure in the growth zone is important for the suppression of polycrystal formation.

We recently reduced the H\textsubscript{2}O partial pressure in a growth zone by improving the efficiency of conversion from H\textsubscript{2}O vapor to Ga\textsubscript{2}O vapor to about 70%, and then attempted thick-GaN growth.\textsuperscript{25)} However, we have not been able to realize GaN crystals of 300 μm or more in thickness due to the inhibition of growth caused by polycrystal formation. This indicates that to grow thick GaN crystals, it will be necessary to further reduce the H\textsubscript{2}O partial pressure in the growth zone. The results of a thermodynamic analysis showed that there is a limit to the conversion efficiency of H\textsubscript{2}O vapor into Ga\textsubscript{2}O vapor, and as shown in Eq. (1), H\textsubscript{2}O vapor is generated as a

\[ G_{a2O} + 2H_{2} \rightarrow G_{a2O} + 2H_{2}O. \]
hybrid product in a growth zone. Therefore, another approach will be necessary to further reduce the H\textsubscript{2}O partial pressure.

In this study, we grew GaN layers by the OVPE method with CH\textsubscript{4} gas to decrease the H\textsubscript{2}O partial pressure in a growth zone by the reaction of CH\textsubscript{4} with H\textsubscript{2}O to produce CO and H\textsubscript{2} as shown in the following equation.

$$\text{CH}_4(g) + \text{H}_2\text{O}(g) \rightarrow \text{CO}(g) + 3\text{H}_2(g).$$  \hspace{1cm} (4)

First, we investigated the flow conditions of CH\textsubscript{4} gas, in which we grow GaN crystals without decreasing the growth rate or degrading crystalline qualities resulting in the flow condition being optimized. Next, we attempted to grow thick GaN crystal under the optimized CH\textsubscript{4} flow-rate condition, and 400-μm thick GaN crystal was obtained by substantial suppression of polycrystal formation.

2. Experimental methods

Commercially available free-standing GaN substrates [full width at half maximum (FWHM) values of X-ray rocking curve (XRC) for the 0002 and 10\text{2} diffraction were 50–70 arcsec and 60–90 arcsec, respectively] fabricated by HVPE was used as seed substrates. Seed substrates were subjected to chemical mechanical polishing. Commercially available Ga\textsubscript{2}O\textsubscript{3} [4N, Si (≤30 ppm), Cu, Fe, Ca and In (≤10ppm) contained as main impurities] were used as a starting material. H\textsubscript{2} gas (6N) was used to reduce the Ga3O\textsubscript{3}, and NH\textsubscript{3} (6N) and CH\textsubscript{4} (6N) gas were used as the nitrogen source and additives, respectively. H\textsubscript{2} and N\textsubscript{2} (5N) gases were used as the carrier gas. GaN epitaxial growth was performed in a horizontal quartz tube surrounded by two resistive heaters at atmospheric pressure, as shown in Fig. 1. The thermocouples located outside the quartz tube.

Epitaxial growth was accomplished as follows. The quartz tube was first purged with N\textsubscript{2} gas, and the source and growth zones were heated to 1100 °C and 1200 °C, respectively. These temperatures were maintained for the growth period of 60–600 min. During the growth period, H\textsubscript{2} gas diluted with N\textsubscript{2} gas (total flow rate: 3000–4000 sccm) was introduced into the reactor as a carrier gas. GaN epitaxial growth was performed in a horizontal quartz tube surrounded by two resistive heaters at atmospheric pressure, as shown in Fig. 1. The thermocouples located outside the quartz tube.

The growth rate and surface morphology of the epitaxial layer was measured by scanning electron microscopy (SEM; JEOL JSM-7610F). The FWHM of XRC for the GaN 0002 and 10\text{2} diffraction was measured by X-ray diffraction (XRD; Bruker D8 DISCOVER). Impurity concentrations in the epitaxial layer were detected by secondary ion mass spectrometry (SIMS; Cameca IMS-7f). The partial pressure of CO and H\textsubscript{2}O vapor were determined from the analysis of the gas in the exhaust line using gas chromatography (GC; GL-Science GC-4000Plus C DDTF and GC-3200G).

3. Results and discussion

3.1. Investigation of CH\textsubscript{4} flow condition

Prior to the growth process, we investigated the effect of decreasing the H\textsubscript{2}O partial pressure in the reactor by the addition of CH\textsubscript{4} gas. Figure 2 shows the dependence of H\textsubscript{2}O and CO partial pressures in the reactor on CH\textsubscript{4} flow rate. As can be seen from the figure, H\textsubscript{2}O partial pressure decreased with an increase in CH\textsubscript{4} flow rate, and decreased to 38 Pa at the minimum, which was 22% of the case without the addition of CH\textsubscript{4}. On the other hand, the CO partial pressure in the reactor increased with the increase of CH\textsubscript{4} flow rate. This result indicates that H\textsubscript{2}O partial pressure is reduced by the reaction in Eq. (4).

We then investigated the influence of the addition of CH\textsubscript{4} on the growth rate and surface morphology. Figure 3(a) shows the relationship between CH\textsubscript{4} flow rate and growth rate. The growth rate tended to decrease slightly as CH\textsubscript{4} flow rate increased. The reason why is unclear, but probably has to do with the fact that the driving force of GaN growth decreased due to the decrease in source gas partial pressure by unexpected reactions caused by the addition of CH\textsubscript{4} gas. Details of “unexpected reactions” are currently under investigation. Figure 3(b) shows SEM images of epitaxial layers grown at CH\textsubscript{4} flow rates of 0, 100, 200 and 300 sccm. Epitaxial layers grown at a CH\textsubscript{4} flow rate of 0, 200, 300 sccm had some pits, which were remarkable in a high-CH\textsubscript{4} flow rate condition. We discuss possible reasons for this below. On the other hand, pits were not observed at the CH\textsubscript{4} flow rate of 100 sccm.

Figure 4(a) shows the dependence of the FWHM of XRC for the GaN 0002 and 10\text{2} diffraction on CH\textsubscript{4} flow rate. The FWHM values of the epitaxial layers in the case of a CH\textsubscript{4} flow rate of up to 200 sccm were almost the same as that of the seed substrate, while the FWHM values grown at a flow rate of 300 sccm increased. The dependence of impurity concentrations on CH\textsubscript{4} flow rate is shown Fig. 4(b). Oxygen concentrations in the epitaxial layers were almost the same at any CH\textsubscript{4} flow rate. On the other hand, carbon concentrations in GaN layers increased with increasing CH\textsubscript{4} flow rate.

We now consider the reasons for the increase in pit density and degradation of crystalline quality of the epitaxial layer growing at a flow rate of 300 sccm. We focus on the carbon precipitates generated by the decomposition of CH\textsubscript{4} gas and the high concentration of carbon impurities in the GaN layers. Reference 26 reported that carbon precipitates were observed at the bottom of pits on carbon-doped GaN layers. It is thought that the formation of pits were caused by carbon

![Fig. 1. Schematic drawing of the reactor used in this study. The reactor is composed of source and growth zones, and heated by resistive heating.](Image)
precipitates, which increase as the flow rate of CH$_4$ gas increases. Reference 27 reported that the crystalline qualities of the GaN layers grown by molecular beam epitaxy deteriorated with increasing carbon concentration. Also, in this method, it was suggested that excessive incorporation of carbon impurities leads to degradation of the crystallinity of the GaN layers. As a result, we concluded that the optimum flow rate of CH$_4$ gas was 50–100 sccm.

3.2. Growth of thick-GaN crystal with CH$_4$ gas in the OVPE method

Next, we performed long-term growth of GaN crystals at the optimized CH$_4$ flow rate with a growth rate of about 40 $\mu$m h$^{-1}$. Figure 5(a) shows the thickness of GaN crystals grown with and without CH$_4$ gas as function of the growth period. In the case of crystals grown without-CH$_4$ gas, growth rate gradually decreased, resulting in a 272-$\mu$m thick GaN crystal after a growth period of 8 h. On the other hand, growth thickness increased linearly with the growth period in the case crystals grown with CH$_4$ gas, and a 400-$\mu$m thick GaN crystal was obtained after a growth period of 10 h. Figures 5(b) and 5(c) contain photographs of the 272-$\mu$m thick GaN crystal grown without CH$_4$ gas, and the 400-$\mu$m thick GaN crystal grown with CH$_4$ gas, respectively. As may be seen in Fig. 5(b), many polycrystals were formed on the surface of the GaN crystal grown without CH$_4$ gas. The decrease in the growth rate of the crystal grown without CH$_4$ gas, shown in Fig. 5(a), was likely due to the interruption of the supply of source materials by consumption for the development of polycrystals. In contrast, as shown in Fig. 5(c), while some pits were observed on the surface of the GaN crystal with CH$_4$ gas, polycrystals were hardly observed, which led to the maintenance of the growth rate.

Figure 6(a) shows the dependence of FWHM of XRC for the GaN 0002 diffraction on the growth thickness. We can see that FWHM values increased as the growth thickness exceeded 200 $\mu$m in the crystal grown without CH$_4$ gas, while they stayed almost the same as that of a seed substrate for crystals grown with CH$_4$ gas. The dependence of polycrystal density on growth thickness is shown in Fig. 6(b). As can be seen from the figure, polycrystal density increased rapidly over 200 $\mu$m without CH$_4$ gas. In contrast, there was little increase with CH$_4$ gas. This series of results suggested that worsening of crystallinity was correlated with the formation of polycrystals.

Finally, we consider why the increase in FWHM values and polycrystal density was suppressed in crystals grown with CH$_4$ gas. It has been reported that the formation of oxides such as Ga$_2$O$_3$ or GaN$_x$O$_{1-x}$ at a high partial pressure of oxygen is predicted from thermodynamic calculations. Reference 28) Reference 29 reported that the formation of Ga$_2$O$_3$-related precipitates may lead to structural defects. Therefore, we assume that the formation of gallium oxide species, as described above, was suppressed by the addition of CH$_4$ gas. However, the results in Fig. 2 clarified that H$_2$O vapor was converted to CO vapor by the addition of CH$_4$ gas, which means the number of oxygen atoms in the reactor did not change. These facts can be explained by the binding energy of the oxygen source; those of H$_2$O and CO are 463 and 615 kJ mol$^{-1}$, respectively. With decreasing binding energy of the oxygen source, oxides containing gallium are likely to be generated. Consequently, the conversion of H$_2$O vapor to more stable CO gas by the addition of CH$_4$ gas led to the suppression of polycrystals and the degradation of crystalline quality.

4. Conclusions

In this study, the growth of GaN crystals by the OVPE method with CH$_4$ gas was performed. First, we investigated the dependence of properties of grown GaN layers on the flow rate of CH$_4$ gas. Results showed that H$_2$O partial pressure in a growth zone decreased with an increase in CH$_4$ flow rate, while pit density and FWHM values of grown layers
increased at a CH₄ flow rate of 300 sccm. It is considered that the formation of pits and degradation of crystalline quality were caused by carbon precipitates and high concentrations of carbon, respectively. Further, as a result of long-term growth after the optimization of CH₄ gas flow rate, we obtained a high-crystalline 400-μm thick GaN crystal. From these results, we concluded that the addition of CH₄ gas in the OVPE method led to the suppression of polycrystals and degradation of crystalline quality, which allowed thick GaN growth.

Acknowledgments

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