Floral design GaN crystals: low-resistive and low-dislocation-density growth by oxide vapor phase epitaxy

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GaN crystal growth mode in the oxide vapor phase epitaxy (OVPE) method, which simultaneously provides low electrical resistance and low threading dislocation density (TDD), has been investigated in detail. The results clarified that these qualities can be achieved by the expression of numerous inverted pyramidal pits, called three-dimensional (3D) growth mode. This mode reduced TDD from 3.8 × 10⁶ cm⁻² to 2.0 × 10⁴ cm⁻² for 1 mm thick growth because the threading dislocations (TDs) converged to the center of each pit. Moreover, when the crystal surface after polishing was observed by photoluminescence measurement, peculiar floral designs reflecting the distribution of oxygen concentration were observed over the entire surface. In addition, the etch pits exhibited TDs in the center of each floral design. On the basis of our results, we proposed that the 3D-OVPE-GaN will serve as a key material for improving the performance of vertical GaN devices. © 2021 The Author(s). Published on behalf of The Japan Society of Applied Physics by IOP Publishing Ltd

1. Introduction

Electronic devices using gallium nitride (GaN)1,2) are a key technology for improving energy efficiency toward the achievement of sustainable development goals.3–5) Vertical GaN power devices are promising for high-power applications because they offer higher breakdown voltages and higher current operation on smaller chip sizes than horizontal structures. Despite such high potential, the development speed of GaN devices has been slower than that of silicon carbide devices. One reason for this is the lack of high-quality and low-cost freestanding GaN wafers.6) To fully draw out the potential of vertical GaN power devices and to implement them in society, it will be necessary to establish a manufacturing technology for GaN wafers featuring low dislocation density, low electrical resistance, large diameter, and low cost.7,8) To reduce threading dislocation density (TDD), the hydride vapor phase epitaxy (HVPE) method using a technique called dislocation elimination by epitaxial-growth with inverse-pyramidal pits,9) the epitaxial lateral overgrowth (ELO)10) or maskless-3D technique,11) the Na-flux method with multipoint seed technique,12,13) and the ammonothermal method14,15) have been proposed. To reduce resistance, Ge and Si doping techniques in the HVPE method have been reported.16–19) Further, to increase the diameter, 6–7 inch GaN wafers have been achieved by the HVPE and Na-flux methods.13,20–22) We have been developing the oxide vapor phase epitaxy (OVPE) method to manufacture high-performance, low-cost GaN wafers.23) This method can be used to manufacture large bulk GaN crystals with a simple apparatus for long-term growth, since no NH₄Cl is generated as a solid by-product, unlike the case with the HVPE method, which is the mainstream GaN manufacturing technology. Therefore, we expect the OVPE method to be able to produce low-cost GaN wafers. We have also reported the fabrication of low-TDD (TDD: the order of 10⁶ cm⁻²) and low-resistance (resistivity: the order of 10⁻⁴ Ω cm) 2 inch GaN wafers. Moreover, the characteristics of the p-n diodes fabricated on the OVPE-GaN wafers include a high breakdown voltage of 1.8 kV, and extremely low on-resistance of 0.08 mΩ cm² was demonstrated by conductivity modulation with highly efficient photon recycling.24) However, the origins of the reduction of TDs and of the low resistivity have not yet been presented. This paper discusses for the first time the characteristics of OVPE-GaN crystals, with a focus on the growth mode. 3D-OVPE growth was the key technique for achieving simultaneously low TDD and low resistance. Furthermore, distinctive floral design patterns were observed in the overall polished surfaces of the OVPE-GaN crystals grown by the 3D growth mode.

2. Experimental methods

2.1. Crystal growth conditions

We constructed the vertical reactor shown in Fig. 1 for use in this experiment. The reactor consisted of a source zone and a growth zone, each with electric resistance heaters. The reactor materials were quartz and ceramic. The temperature of each zone was controlled by the respective heaters. The source zone had four gas lines (lines 1–4) and a Ga boat. The growth zone had a seed substrate set on the seed holder, which had a rotation system. In the OVPE method in this experiment, Ga₂O₃ gas as a Ga source and GaN crystals were generated using the following Eqs. (1) and (2).

\[ 2\text{Ga}(l) + \text{H}_2\text{O}(g) = \text{Ga}_2\text{O}(g) + \text{H}_2(g), \]  

(1)

\[ \text{Ga}_2\text{O}(g) + 2\text{NH}_3(g) = 2\text{GaN}(s) + 2\text{H}_2(g) + \text{H}_2\text{O}(g). \]  

(2)

The following materials were used in this crystal growth. Metallic Ga (6N) was used as a starting gallium source, and NH₃ gas (5N) was used as a nitrogen source. H₂ gas (7N) and N₂ gas (6N) were supplied as carrier gases, and O₂ gas (6N) was supplied to generate H₂O gas. H₂O gas was generated upstream of the metallic Ga in Fig. 1. As seed substrates, commercially available GaN substrates manufactured by the HVPE method (+c-plane with 0.3 ± 0.2° off-angle toward the
3. Results and discussion

3.1. Comparison of 2D and 3D growth modes

3.1.1. Appearance and surface morphology

Figures 2(a) and 2(b) show photographs of cutout chips from the 2 inch OVPE-GaN crystals grown for 3 h under conditions A and B on HVPE-GaN seed substrates. Top-view SEM images of the layers grown under conditions A and B are shown in Figs. 2(c) and 2(d). The GaN crystal grown under condition A was transparent enough that the GaN under condition A was shown in Figs. 2(a) and 2(b). In Fig. 2(a), normal points at the surface are indicated by the arrows in the dashed frame. These polycrystals were likely created by a high supersaturation ratio under the growth condition. The relationship between the supersaturation ratio and the occurrence of polycrystals was reported in Ref. 23; under these growth conditions, the supersaturation ratios of conditions A and B were 605 and 2.6, respectively. As can be seen from Fig. 2(c), the grown crystal surface under condition A had a 2D morphology featuring step bunching. On the other hand, as shown in Fig. 2(d), the surface under condition B had a 3D morphology with numerous inverted pyramidal pits. We named the GaN crystals prepared in 2D and 3D modes as 2D- and 3D-OVPE-GaN, respectively. In this experiment, the growth rates of the 2D- and 3D-OVPE-GaN were 26 and 2.5 \text{ l min}^{-1}.

2.2. Crystal evaluation methods

To evaluate the quality of the grown crystal, the following were analyzed: surface morphology, growth rate, growth mode, emission spectrum, impurity concentration, lattice constant, radius of lattice curvature, electrical properties, TDD, and TD behavior. Surface morphology was observed by scanning electron microscopy (SEM) (JEOL JSM-7610F). Growth rates were evaluated by measuring weight change. Growth modes of grown crystals were confirmed by the cross-sectional SEM and the depth observation of two-photon excitation photoluminescence (2PPL) (Bruker D8 DISCOVER). The electrical properties were examined by Hall-effect measurement (TOYO ResiTest 8300) at room temperature. TDD was evaluated by measuring etch pit density. Etching was carried out with a mixed melt of NaOH-KOH (NaOH: KOH = 1: 1) at 450 °C for 10 min. The TDD of the grown crystal was evaluated after surface mechanical polishing (MP) and chemical mechanical polishing (CMP). The behavior of dislocation propagation was observed by transmission X-ray topography (XRT) of a cross section of a thinning sample. The XRT experiments were performed at the Hyogo beamline (BL24XU) of Spring-8.

| Table I. | Gas flow rates and zone temperatures of growth conditions A and B. |
|----------|------------------------------------------------------------------|
| Condition | Line 1 (l min$^{-1}$) | Line 2 (l min$^{-1}$) | Line 3 (l min$^{-1}$) | Line 4 (l min$^{-1}$) | Source zone | Growth zone |
| A        | H$_2$ + N$_2$ + H$_2$O | H$_2$ + N$_2$ | H$_2$ + N$_2$ + NH$_3$ | H$_2$ + N$_2$ | 1130 | 1200 |
| B        | 7.2 + 1.8 + 0.014 | 0 + 10 | 10 + 0 + 20 | 0 + 24 | 1130 | 1200 |
|          | 4 + 1 + 0.04 | 2.5 + 2.5 | 0 + 13-14 + 1-2 | 12.5 + 12.5 | 1130 | 1200 |

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Fig. 1. (Color online) Schematic image of OVPE-GaN crystal growth reactor.

α-axis direction; 0.4 mm thick, φ 2 inch) were used. The TDD of the HVPE-GaN substrates was 1−5 \text{×}\ 10^8 \text{ cm}^2.

OVPE-GaN crystals with different growth modes were prepared by changing the V/III (nitrogen source flow rate/gallium source flow rate) ratio during growth and were used as analytical samples for investigating the structural and electrical properties. According to previous research, 2D growth was promoted in the case of a high V/III ratio by the OVPE method on the +c-plane, and 3D growth was advanced in the low V/III ratio. In this experiment, the temperatures of the source and growth zones were set to 1130 °C and 1200 °C, respectively. The input conditions of the gas flows were fixed as 10 and 20 l min$^{-1}$ for H$_2$ and N$_2$, respectively, from line 3. The total flow rate of N$_2$ and NH$_3$ was 101 \text{min}^{-1} from line 2. From line 3, H$_2$ and NH$_3$ were introduced at 10 and 20 l min$^{-1}$, respectively. Under condition A, H$_2$, N$_2$, and H$_2$O were flowed at rates of 7.2, 1.8, and 0.014 l min$^{-1}$ from gas line 1. N$_2$ was flowed at 101 \text{min}^{-1} from line 2. From line 3, H$_2$ and NH$_3$ were introduced at 10 and 20 l min$^{-1}$, respectively, when the V/III ratio was replaced by the ratio of the nitrogen source to the oxygen source. According to previous research, the growth was promoted in the case of a high V/III ratio by the OVPE method on the +c-plane, and 3D growth was advanced in the low V/III ratio. In this experiment, the temperatures of the source and growth zones were set to 1130 °C and 1200 °C, respectively. The input conditions of the gas flows were fixed as 10 and 20 l min$^{-1}$ for H$_2$ and N$_2$, respectively, from line 3. The total flow rate of N$_2$ and NH$_3$ was 101 \text{min}^{-1} from line 2. From line 3, H$_2$ and NH$_3$ were introduced at 10 and 20 l min$^{-1}$, respectively, when the V/III ratio was replaced by the ratio of the nitrogen source to the oxygen source.
60 μm h⁻¹, and the growth rates were controlled by the partial pressure of Ga₂O supplied to the substrate surface within these experimental conditions.

3.1.2. Impurity concentration. The impurity concentration of each crystal grown for 3 h after surface smoothing was evaluated by SIMS at 2–10 μm depth from the surface in the 75 μm × 75 μm range. The SIMS results appear in Table II. The average concentrations of oxygen and silicon in the 2D-OVPE-GaN were 3.8 × 10¹⁷ and 1.4 × 10¹⁹ atoms cm⁻³, respectively, and carbon was below the detection limits. In the 3D-OVPE-GaN, the concentrations of oxygen and silicon were 4.8 × 10²⁰ and 2.0 × 10¹⁹ atoms cm⁻³, respectively, and carbon was below the detection limit. The oxygen concentration in the 3D-OVPE-GaN was extremely high relative to that in the 2D-OVPE-GaN because the main growth plane in the latter is a (0001) polar plane, whereas that in the 3D-OVPE-GaN is semipolar. Compared with the (0001) polar plane and the semipolar plane of the ideal surfaces, the (0001) polar plane is a Ga-rich surface while the semipolar plane is often an N-rich surface. It was reported that oxygen atoms are more easily incorporated into the N site than the Ga site.²⁸) Consistent with this, oxygen incorporation was much higher in the 3D-OVPE-GaN than in the 2D-OVPE-GaN. Moreover, the silicon concentration was almost equally high in both growth modes because quartz was used as the reactor material. In this experiment, the reactor was heated to over 1130 °C, so the quartz evaporated and a large amount of silicon was mixed in the OVPE-GaN crystals.

3.1.3. Lattice constant and lattice curvature radius. In Fig. 3(a), the lattice constants of the 2D- and 3D-OVPE-GaN grown for 3 h are depicted with the values of the HVPE-GaN seeds. The average a-axis and c-axis lattice constants of the 2D-OVPE-GaN were 3.1895 and 5.1857 Å, respectively. These values were almost the same as those with the HVPE-GaN seed. In contrast, the values of the 3D-OVPE-GaN were 3.1898 and 5.1873 Å. The c-axis expanded remarkably compared with the seed. This is attributable to the fact that the a-axis lattice constant of OVPE-GaN is close to the value of the seed substrate because it grows under the restraint of the lattice spacing of the seed substrate a-axis, while the expansion of the c-axis lattice constant is due to volume change by a high concentration of oxygen. Additionally, the radii of the lattice curvatures were measured by 0002 GaN XRC mapping as shown in Fig. 3(b). The radius of the lattice curvature calculated from the following Eq. (3), here, Δx is the distance between the measurement positions, and Δω is the difference between the ω values.

\[ R = \frac{\Delta x}{\Delta \omega}. \]  

The R values of the 2D- and 3D-OVPE-GaN were concave 6.01 m and convex 7.82 m, respectively. The seed lattice curvature radii were 8.27 and 5.74 m concave. In the 3D-OVPE, the radius of the lattice curvature changed from

Table II. Impurity concentrations of the 2D- and 3D-OVPE-GaN crystals.

| Growth mode | Impurity (cm⁻³) |  |
|-------------|-----------------|---|
|             | O    | Si   | C   |
| 2D          | 3.8 × 10¹⁷ | 1.4 × 10¹⁹ | N.D. |
| 3D          | 4.8 × 10²⁰ | 2.0 × 10¹⁹ | N.D. |
| Detection limit | 5.0 × 10¹⁶ | 1.0 × 10¹⁶ | 2.6 × 10¹⁵ |
concave to convex, which we attribute to the volume increase due to the high oxygen concentration incorporated in the crystal. In addition, in other 3D-OVPE-GaN, the lattice constant of the c-axis sometimes varied to as low as the result of Ref. 23. The cause of this is currently under investigation.

3.1.4. Electrical properties. Table III shows the Hall-effect measurement results of the 2D- and 3D-OVPE-GaN grown for 3 h. The carrier concentration, electron mobility, and resistivity of the 2D-OVPE-GaN were $1.19 \times 10^{19}$ cm$^{-3}$, $2.96 \times 10^{2}$ cm$^2$ V$^{-1}$ s$^{-1}$, and $3.14 \times 10^{-3}$ Ω cm, respectively. On the other hand, the values for the 3D-OVPE-GaN were $7.51 \times 10^{19}$ cm$^{-3}$, $1.28 \times 10^{2}$ cm$^2$ V$^{-1}$ s$^{-1}$, and $9.77 \times 10^{-4}$ Ω cm. The dopant activation rates ($N_c/(N_d-N_a)$; $N_d$: donor concentration (oxygen and silicon concentrations evaluated by SIMS), $N_a$: acceptor concentration (carbon concentration evaluated by SIMS), $N_c$: carrier concentration measured by Hall-effect measurement) of the 2D- and 3D-OVPE-GaN were 80% and 15%, respectively. This was because 3D-OVPE-GaN was a very high concentration n-type GaN as a result of the oxygen incorporation. That is, Ga vacancies, which are cation vacancies, are likely to be formed by the high concentration of free electrons.$^{29,30}$ These results suggested that Ga vacancies in the 3D-OVPE-GaN would promote the self-compensation effect of the free carrier. Figure 4 shows the relationships between the impurity concentrations and the carrier concentrations of each dopant in each growth method, including the results of 2D- and 3D-OVPE-GaN. For the plural plots of Si in HVPE and Ge in MOCVD, we referred to the results in Ref. 29. The decrease in the activation ratio was confirmed to be similar to that in the case of high-concentration Ge doping, and the results obtained with the OVPE-GaN crystals are shown to be consistent with the tendencies in previous reports. The electron mobility result in each growth-mode crystal also matches the trends in Si- and Ge-doped HVPE-GaN reported by H. Fujikura et al.$^{31}$ as shown in Fig. 5. As the figure

![Fig. 3. (Color online) (a) Lattice constants of 2D-OVPE GaN, 3D-OVPE GaN, and the GaN seeds. (b) The measurement positions and the peak top $\omega$ angles of 0002 GaN XRC of the 2D- and 3D-OVPE-GaN.](image)

![Fig. 4. (Color online) Relationship between the impurity concentrations and carrier concentrations of Si-doped HVPE-GaN, Ge-doped MOCVD-GaN, and OVPE-GaN.](image)

![Fig. 5. (Color online) Relationship between the carrier concentrations and the electron mobilities of Si-doped HVPE-GaN, Ge-doped HVPE-GaN, and OVPE-GaN.](image)

| Growth mode | Carrier concentration (cm$^{-3}$) | Mobility (cm$^2$ V$^{-1}$ s$^{-1}$) | Resistivity (Ω cm) |
|-------------|---------------------------------|------------------------------------|-------------------|
| 2D          | $1.19 \times 10^{19}$          | $2.96 \times 10^{2}$              | $3.14 \times 10^{-3}$ |
| 3D          | $7.51 \times 10^{19}$          | $1.28 \times 10^{2}$              | $9.77 \times 10^{-4}$ |

Table III. Carrier concentrations, electron mobilities, and resistivities of the 2D- and 3D-OVPE-GaN by Hall-effect measurement.
shows, the dashed line is the ideal curve showing the relationship between carrier concentration and electron mobility when the compensation ratio $\theta$ (Na/Nd) is 0; as the compensation ratio increases, the mobility value with respect to the carrier concentration decreases.\textsuperscript{32} As these results show, the compensation ratio in the relationship between the carrier concentration and the mobility did not increase significantly in 3D-OVPE-GaN. This might be due to the crystallographic feature of the 3D-OVPE-GaN. Research into this result is ongoing.

3.1.5. Threading dislocation density. Figures 6(a)–6(c) contain surface SEM images after NaOH-KOH etching of the HVPE-GaN seed substrate and of OVPE-GaN crystals grown for 3 h in each growth mode after polishing to a thickness of 50 $\mu$m. When the threading dislocations (TDs) were estimated from the etch pit densities of the SEM images, the TDDs of the HVPE-GaN seed substrate, the 2D-OVPE-GaN, and the 3D-OVPE-GaN were $3.8 \times 10^6$ cm$^{-2}$, $3.5 \times 10^6$ cm$^{-2}$, and $7.7 \times 10^5$ cm$^{-2}$, respectively, as shown in Fig. 6(d). According to these results, while the TDD of the 2D-OVPE-GaN was almost equivalent to that of the HVPE-GaN seed substrate, the TDD of the 3D-OVPE-GaN was reduced to about 20% of that of the HVPE-GaN with only 50 $\mu$m thick growth.

3.1.6. Photoluminescence spectrum. Figure 7 presents the measurement results of the PL spectra of the 2D- and 3D-OVPE-GaN at room temperature. The measured samples are the same as the 50 $\mu$m thick OVPE-GaN described in the previous section. The integration times were 3 and 100 ms in each 2D- and 3D-OVPE-GaN measurement, respectively, and the vertical axis in Fig. 7 represents values normalized by the integration times. The peak top, the peak intensity, and the full width at half maximum (FWHM) of the 2D- and 3D-OVPE-GaN were 3.418 and 3.492 eV, 17328 and 198, and 93 and 236 meV, respectively. The PL peak top in each crystal was shifted from a pure GaN band-gap energy of 3.39 eV to the higher-energy side. This is mainly the Burstein–Moss effect, which is more pronounced at high carrier concentrations.\textsuperscript{29} Therefore, the peak top of the 3D-OVPE-GaN shifted to a value larger than that of the
2D-OVPE-GaN. The PL intensity of the 3D-OVPE-GaN was much lower than that of the 2D-OVPE-GaN, and the FWHM of 3D-OVPE-GaN was larger than that of the 2D-OVPE-GaN. It can be inferred that these results were caused by the 3D-OVPE-GaN having more Ga vacancies and composite defects with Ga vacancies than 2D-OVPE-GaN, as explained in part of Fig. 4.

3.2. Origin of 3D growth mode and the growth facet

3.2.1. Origin of 3D-OVPE-GaN. The change in the OVPE-GaN growth mode revealed that the 3D growth mode can realize ultralow-resistance GaN crystals with extremely high carrier concentrations and can dramatically reduce the TDD with only 50 μm thick growth. Additionally, 3D-OVPE-GaN is grown under the condition of a low V/III ratio, which is favorable for a high rate of growth. The origin and the forming planes of the pits were then identified in order to elucidate the 3D growth mode in detail. The interface between the seed substrate and the 3D-OVPE-GaN grown layer was observed to confirm the starting point of the pits with 2PPL. Figures 8(a)–8(d) show 2D PL images from the seed substrate side to the grown layer side. The nearest position of the interface is shown in Fig. 8(b). If we consider the Fig. 8(b) position as the origin point (z = 0), assuming that the seed substrate side is minus and the grown layer side is plus, then the positions of Figs. 8(a)–8(d) are z = −3 μm, 0 μm, 1 μm, and 4 μm, respectively. The dark spots are TDs in Figs. 8(a) and 8(b), which originally existed in the seed substrate. In Figs. 8(b) and 8(c), the dark lines are basal plane dislocations (BPDs), which may have been generated by the stress occurring from the lattice constant difference between the substrate and the grown layer, because BPDs were prominently observed near the interface. The occurrence of the pits was captured on the PL images in Figs. 8(c) and 8(d), and one of the pits is indicated by a white arrow. Luminescence was significantly reduced when the pits were formed in the 3D growth mode, as explained by the PL spectrum results in Fig. 7. Additionally, the pits grew as the thickness increased, as exhibited in Figs. 8(c) to 8(d). Here, the densities of the dark spots and pits in Fig. 8 were 5 × 10⁶ cm⁻² at each depth, showing equivalent values. It is therefore assumed that the pits are generated starting from TDs. In an attempt to directly confirm the connection between TDs and pits, the TDs of the seed substrates were determined as shown by the red and yellow arrows in Fig. 8(a), and the 2D PL images were confirmed from the cross-sectional direction on the red line and yellow line containing the TDs illustrated by red and yellow arrows, respectively. The cross-sectional PL images appear in Figs. 8(e) and 8(f). These cross-sectional images were created by integrating 150 images of 2D-PL taken at equally spaced distances from z = −7 to 6 μm. Therefore, the plurality of horizontal lines are from the noise due to the integrated image. Also, the yellow, blue, and red lines and frames in Figs. 8(e) and 8(f) correspond to the observation positions in Fig. 8(a). As the images show, the pits were generated on the TDs as indicated by the red and yellow arrows, which are the same TDs as in Fig. 8(a). Additionally, a 3D image, with inverted light and dark, is shown in Fig. 8(g). The image confirmed that the pits were opened mainly on the TDs like flowers blooming on stems. These results suggested that the TDs of the seed substrate were the origin of the formation of the 3D-OVPE-GaN.

3.2.2. Growth facet of 3D-OVPE-GaN. Next, the surface morphology of the 3D-OVPE-GaN grown for 6 h in condition B was observed in order to identify the surface crystal planes. Figure 9(a) exhibits a bird’s-eye view SEM image of the 3D-OVPE-GaN.
one of the numerous inverted pyramidal pits. The pits were composed mainly of three types of planes \([\alpha, \beta, \text{ and } \gamma]\) in Fig. 9(a): \(\alpha\) having an \(a\)-plane component, \(\beta\) having an \(m\)-plane component, and \(\gamma\) connecting \(\alpha\) and \(\beta\). To identify \(\alpha\) and \(\beta\) with \(a\)- and \(m\)-plane components, the pits were cut so as to include the center of the bottom as shown in Figs. 9(b) and 9(c), and the pit angles were observed. The pit angles formed of \(\alpha\) and \(\beta\) were approximately 64° and 70° from the results of the cross-sectional observation shown in Figs. 9(d) and 9(e). That is, \(\alpha\) and \(\beta\) were tilted 58° and 55° from (0001), suggesting that \(\alpha\) and \(\beta\) were \{11\(\bar{2}\)2\} and \{30\(\bar{3}\)4\}. In addition, the difference in oxygen incorporation at each plane was evaluated. Figure 10(a) shows an optical microscope image of the position where SIMS was performed on the crystal surface after OVPE-GaN was surface polished to a thickness of 300 \(\mu\)m. The in-plane distribution image of oxygen concentration in the area inside the green frame in Fig. 10(a) is shown in Fig. 10(b). The growth history of the pits formed in 3D-OVPE was observed even on the surface after polishing as shown in Fig. 10(a). Figure 10(b) shows that the oxygen concentration of \(\beta\{30\bar{3}4\}\) was higher than that of \(\alpha\{11\bar{2}2\}\). The average oxygen concentration at \(\beta\{30\bar{3}4\}\) in Fig. 10(b) was \(5.1 \times 10^{20}\) atoms cm\(^{-3}\), and that at \(\alpha\{11\bar{2}2\}\) was \(3.2 \times 10^{20}\) atoms cm\(^{-3}\). Each average value was calculated for a 2 \(\mu\)m\(^2\) area.

It is possible to consider the nitrogen density of each grown surface in order to discuss this oxygen concentration difference. At the ideal surfaces, the nitrogen densities of the \{11\(\bar{2}\)2\} and \{30\(\bar{3}\)4\} were \(1.22 \times 10^{15}\) cm\(^{-2}\) and \(1.01 \times 10^{15}\) cm\(^{-2}\) considering the surface area in Ref. 33. However, in the case of the semipolar planes of GaN crystal, the ideal surfaces are not stable in a growth atmosphere,
Therefore, when comparing semipolar planes such as \{11\overline{2}2\} and \{30\overline{3}4\}, it is necessary to consider surface reconstruction in the growth atmosphere on each plane. In addition, the step-and-terrace structures of the different facets during growth are not the same. Hence, it is expected that more detail on these semipolar planes will be reported in the near future, making it possible to discuss this oxygen concentration difference.

### 3.2.3. Features of 3D-OVPE-GaN on +c-plane.

The 3D-OVPE-GaN grown for 6 h was polished to a thickness of 300 μm. The polished surface after NaOH-KOH etching was observed by SEM and CL as shown in Figs. 11(a) and 11(b). The etch pits in Fig. 11(a), indicated by yellow arrows, correspond to the center of the pit history in Fig. 11(b). The TDD was \(7.7 \times 10^4\) cm\(^{-2}\) for the 300 μm thick OVPE-GaN calculated by etch pit density; the seed TDD was 1–5 \(10^6\) cm\(^{-2}\). In 3D growth mode, since the surfaces exposed during growth were mainly \{11\overline{2}2\} and \{30\overline{3}4\}, TDs tended to propagate in the direction toward these inclined facets from the +c-plane. Consequently, the TDs converged at the bottom of each pit, thus facilitating dislocation coalescence and annihilation. In other words, it is possible to estimate the TDD by counting the numbers of pit histories of polished crystals or the growth pits of as-grown crystals. Moreover, Fig. 12 shows a surface PL image of the 3D-OVPE-GaN over a wide range. The image confirms that the etch pit density is the TDD, the dislocation reaction cross section, and \(h\) is the growth thickness. The parameter \(\hat{h}\) corresponds to the initial TDD \(\rho_0\) at some thickness \(h_0\).

\[
\rho = \frac{1}{K} \left( h + \hat{h} \right),
\]

\[
\hat{h} = (K \rho_0)^{-1} - h_0.
\]

The solid line in Fig. 13 is the fitting curve derived from the experimental results. The values of the parameters optimized by fitting and the coefficient of determination \(R^2\) are shown in the inset. Both fitting curves had a sufficiently high \(R^2\). It is noteworthy that the \(K\) of the OVPE-GaN was about 100 times that of the HVPE-GaN. The OVPE-GaN grown in 3D mode constantly exposed a large number of pits formed by the planes inclined from the c-plane. These pits coalesced with each other as the OVPE-GaN growing, resulting in the convergence of the TDs. Therefore, the \(K\) of 3D-OVPE growth reached a dramatically large value compared to that of the HVPE-GaN by the r-FIELO technique.

Moreover, a cross-sectional thinning sample of the 3D-OVPE-GaN was produced so as to observe TD propagation. The sample was extracted as shown in Fig. 14(a). First, a 5 × 5.3 mm tip was taken from the 2 inch, 400 μm thick 3D-OVPE-GaN grown on the HVPE-GaN substrate, which was also 400 μm thick, after which the thinning sample was sliced from the tip. The sample size (length × width × thickness) was 0.8 mm × 5.3 mm × 0.1 mm. Both the front and back surfaces of the sample were treated by MP and CMP to remove the damaged layer. Figure 14(b) is a photograph of the cross-sectional thinning sample of the 3D-OVPE-GaN crystal on the HVPE-GaN substrate. The black region shows the OVPE-GaN and the transparent region the HVPE-GaN.

Figures 15(a) and 15(b) show the transmission XRT in 0002 and 2\(\overline{1}\)10 diffractions taken with the same view as the thinned sample overall. It was confirmed that the black lines estimated to be TDs decreased in the OVPE-GaN region in both images. It can be seen that the black line is lighter in the OVPE-GaN than in the HVPE-GaN. The XRT image in the 0002 diffraction reflects c-type and (a+c)-type dislocations,
and the image in the 2T100 diffraction reflects a-type and (a+c)-type dislocations, suggesting that 3D-OVPE growth decreased all types of TDs.

Also, the interface between the HVPE-GaN substrate and the 3D-OVPE-GaN crystal in the 0002 diffraction is significantly darker than in the image of 2110 diffraction. This is because of the lattice distortion of the substrate and the grown layer. As shown in Fig. 3(a), the lattice constants of the 3D-OVPE-GaN crystal in the a-axis and c-axis directions were 3.1898 and 5.1873 Å, respectively. On the other hand, the lattice constants of the HVPE-GaN substrate were 3.1895 and 5.1858 Å. The lattice constants of the c-axis and a-axis of 3D-OVPE-GaN increased by 0.0290% and 0.0099%, respectively, compared to HVPE-GaN. Because the c-axis showed a larger change, it is considered that the strain at the interface is more prominent in the c-axis direction.

3.4. Challenges for large-diameter 3D-OVPE-GaN

We previously reported on 2 inch OVPE-GaN wafers. Fabrication of larger-diameter wafers is needed to meet the needs of the GaN power device industry. By optimizing growth temperature, gas flow rate, and growth reactor design, we succeeded in fabricating—wafers of up to 6 inches with 3D-OVPE growth. Figure 16 displays 2, 4, and 6 inch OVPE-GaN as grown. The 2 and 4 inch OVPE-GaN were grown on freestanding GaN wafers, whereas the 6 inch OVPE-GaN was grown on a GaN template (GaN on silicon). Hence, thick (>400 μm) 2 and 4 inch OVPE-GaN were grown, while the 6 inch OVPE-GaN was grown as a thin film of 100 μm or less. 3D-OVPE-GaN will be a key technology that will greatly accelerate the development of next-generation GaN power devices, because it enables larger-diameter wafers with low resistance and low TDD.

4. Conclusions

In this study, we discussed GaN crystal growth technology by the OVPE method, which simultaneously realizes low electrical resistance and low TDD and which had not been reported in detail until now, with a focus on the growth mode. In growth using this method, the uptake of high-concentration oxygen into the crystal was promoted and the carrier concentration became high with the 3D growth mode, which
mainly exposed semipolar planes such as \{11\overline{2}2\} and \{3034\}. GaN crystals having extremely low resistivity were obtained as a result. Also in the 3D growth mode, since the growth surface was formed by a large number of inverted pyramidal pits, we clarified that the TDD was reduced from $3.8 \times 10^6 \text{ cm}^{-2}$ to $2.0 \times 10^5 \text{ cm}^{-2}$ with 1 mm thick growth, and the dislocation reaction cross-section $K$ was a large value of 2.663 $\mu$m. To investigate the starting point of the pits for 3D growth, the seed substrate and the grown layer interface were observed using 2PPL, enabling us to confirm that the pits of the OVPE-GaN layer began to open starting from the TDs of the seed substrate. Moreover, PL observation of the grown crystal surface after polishing revealed a uniform floral pattern on the entire surface. This was attributed to the difference in oxygen incorporation between \{11\overline{2}2\} and \{3034\}. In addition, etch pit and CL observation in the same region of the crystal surface confirmed the presence of the threading dislocation in the center of each floral pattern. In other words, 3D-OVPE-GaN has a uniform TDD distribution over the entire surface. These results revealed that utilizing the 3D mode in OVPE-GaN growth is important for preparing crystals with low resistance and low TDD. We believe that this technology will be important for accelerating the development of next-generation GaN power devices because it enables large-diameter growth with low resistance and low dislocation density in 3D mode.

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**Fig. 15.** (Color online) Transmission XRT images of (a) 0002 and (b) 2\overline{1}10 diffractions taken on the thinned sample overall. Enlargements of the (c) 0002 and (d) 2\overline{1}10 diffraction images.

**Fig. 16.** (Color online) Photograph of 2, 4, and 6 inch 3D-OVPE-GaN crystals.
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