Annihilation mechanism of V-shaped pits in c-GaN grown by hydride vapor-phase epitaxy

Kenji Iso, Hirotaka Ikeda, Riki Gouda, Tae Mochizuki, and Satoru Izumisawa

Gallium Nitride Technology Center, Tsukuba Plant, Mitsubishi Chemical Corporation, Ushiku, Ibaraki 300-1295, Japan

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1. Introduction

Electronic devices, such as RF devices and high-power devices using freestanding bulk c-GaN substrates, attract great attention due to their threading dislocation densities being lower than those of devices fabricated on foreign substrates.1–4 The only commercially available growth method that is suitable for the manufacture of bulk c-GaN substrates is the use of hydride vapor-phase epitaxy (HVPE), because of its relatively high growth rate, which can reach as high as 100 μm h−1.5–10 One evident issue in performing GaN growth along the c-direction is the generation of V-shaped pits on its surface.11–14 On its surface, which might be caused by dust particles, irregularly generated polycrystalline and macro defects on the substrates.15,16 The effective thickness of an as-grown GaN boule is decreased by V-shaped pits, reducing the number of sliced wafers without penetrated pits (holes) and increasing the cost for GaN wafers. Reference 11 demonstrated that pits on c-GaN are composed of {1011} facets. Furthermore, Ref. 17 reported that {1012} facets were formed at the bottom of the V-shaped pits and annihilated due to fast growth rate. However, to date, the study on accurate growth rates for the c-plane, (1011) and (1012) planes has been rarely reported.

In this paper, we investigated the transition for the angle of facets forming a V-shaped pit when the growth was instituted using three-photon excitation photoluminescence (3PPL).18 In this method, the excitation light can be focused inside the sample and the photoluminescence (PL) process occurs near the focal point.19 Thus, the cross-section at the center of a V-shaped pit is allowed to be observed, while precise angles of the facets forming a V-shaped pit can be determined. Here, the intermittent doping of Ge was introduced to GaN growth to observe the growth front. Furthermore, to determine growth rates of each plane and to evaluate the V-shaped pit size scaling, planar growths on c-plane and semipolar planes for facets forming a V-shaped pit were performed by changing the carrier gas (H2 and N2 were used). The computational fluid dynamics (CFD) calculation was used to evaluate partial pressures of the reactant gas. In conclusion, the annihilation mechanism for the V-shaped pit was discussed.

2. Experimental section

2.1. Growth

The GaN sample for the V-shaped pit measurement using 3PPL was grown on the GaN template by HVPE, which had a stripe mask composed of SiN4. The GaN template was grown on the 3 in. sapphire substrate using conventional metal–organic CVD. The stripe mask was used to perform spontaneous separation of the sapphire substrate and grown GaN film, which was prepared as follows: an 80 nm SiN4 mask (mask area/window area = 60/40) was deposited by plasma-enhanced CVD, followed by reactive ion etching using conventional lithography. GaN films were grown in an originally designed vertical flow reactor made of quartz at atmospheric pressure, using the generated GaCl and NH3 as group-III and -V precursors, respectively. The details for the reactor were reported previously.20 GaCl as the group-III precursor was generated by the reaction between metallic Ga and HCl gas in the source zone at 850 °C. The GaN sample was grown at 1020 °C for 2 h using H2 carrier gas, followed by growth for 6 h using N2 carrier gas. The input partial pressures of NH3 and generated GaCl were 8.1 × 10−2 and 1.2 × 10−2 atm for the H2 carrier gas condition, and 3.0 × 10−2 and 9.1 × 10−3 atm for the N2 carrier gas condition, respectively. NH3 was introduced as an ambient gas flowing throughout the reactor, whereas GaCl was introduced through the gas nozzle. Ge was doped for 1 min with GeCl4, every 1 h, during the growth, using N2 carrier gas. Carrier gas was bubbled through liquid GeCl4, which was held at the temperature of −25 °C and the saturated gas with GeCl4 was transported to the GaN deposition zone using the stainless steel pipe. The doping concentration was controlled to be ~1.0 × 1018 cm−3, which did not affect the characteristics (such as the crystal quality and structure) of the epi-layer.

The GaN sample for the planar growth was grown on freestanding GaN substrates for 1 h, including the polar c-plane and semipolar planes (1011), (1012), (1013) and (1014). Those semipolar planes were sliced from a bulk crystal grown by conventional HVPE along the c-direction. The planar growth was performed by changing the carrier gas...
condition, i.e. \( F = 1, 0.5 \) and 0, respectively. Here, \( F \) is defined as:

\[
F = \frac{P_{\text{H}_2}}{(P_{\text{H}_2} + P_{\text{N}_2})},
\]

where \( P_{\text{H}_2} \) and \( P_{\text{N}_2} \) are partial pressures of \( \text{H}_2 \) and \( \text{N}_2 \) during the growth, respectively.\(^{22}\) Film thicknesses were determined by cross-sectional fluorescent (FL) microscopy.

### 2.2. 3PPL sample preparation and measurement

The GaN sample having a film thickness of \(~1\ \text{mm}~\) was sliced along the \( a \)-plane near the V-shaped pit, while chemical mechanical polishing was implemented. As shown in Fig. 1, excitation light was irradiated from the \( a \)-plane of the sample. A three-photon excitation microscopy system (Nikon A1R MP+) was used for 3PPL measurement. The excitation laser system (Coherent Chameleon Vision II) having a Ti-sapphire mode-locked laser (800 nm) was used for the photon generation of 3PPL. The laser was operated in the pulse mode with a pulse width of 140 fs and a repetition rate of 80 MHz. The laser beam was irradiated through a \( \times 10 \) objective lens. The intensities of near-band-edge (NBE) and yellow luminescence (YL) emissions were measured using optical bandpass filters having a center wavelength of 370 nm and a band width of 36 nm, and a center wavelength of 560 nm and a band width of 94 nm, respectively. Pixels of \( 2048 \times 2048 \) were recorded using an in-plane area of \( 1.2 \times 1.2 \ \mu\text{m}^2 \). The excitation light was focused into the sample to observe the cross-section at the center of a V-shaped pit. The focal depth was determined as the maximum of the diameter for the V-shaped pit [Fig. 1(a)]. In contrast, the excitation light was focused on the surface of the cross-section for FL measurement [Fig. 1(b)].

### 2.3. CFD calculation

The CFD calculation was performed using a fluid dynamics code, STAR-CCM + by CD-adapco.\(^{23,24}\) This code enabled us to predict partial pressures near the V-shaped pit. Before calculation, partial pressures of \( \text{NH}_3 \) and \( \text{GaCl} \) on the \( c \)-GaN surface were determined by considering forward and reverse reactions for GaN formation (\( \text{GaCl} + \text{NH}_3 \rightarrow \text{GaN} + \text{HCl} + \text{H}_2 \)) on the bottom surface of the 3D geometry for both \( c \)-plane and facet planes that formed a V-shaped pit. A temperature of 1020 °C was employed.

### 3. Results

Figure 3 shows cross-sectional FL microscopic and 3PPL images. The 3PPL image is the superposition of NBE and YL. For FL measurement, as shown in Fig. 3(a), it is possible to distinguish the facet growth area from the \( c \)-plane growth area as the contrast.\(^{25}\) The bright part indicates (0001) growth, while the dark part indicates the facet growth, because the absolute YL emission intensity for (0001) growth regions is larger than that for facet growth regions. The growth front in the facet growth region cannot be confirmed due to poor contrast, while the pulse doping of Ge was clearly observed for the (0001) growth region. As far as the 3PPL image was concerned, the contrast between the facet growth region and (0001) growth region was distinguishable, as shown in Fig. 3(b). Moreover, different to FL images, the growth front in the facet growth area was clearly observed for the Ge doping. Random dark lines that showed the growth front among intermittent doping of Ge were also observed, which was reported for the cathode luminescence image.\(^{25}\) This is possibly attributed to the slight accumulation of impurities, such as Si and O, during the growth. The bundle of the threading dislocation was observed at the center of the V-shaped pit as the black line. The degree of the expansion for the V-shaped pit became small when the carrier gas was changed from \( \text{H}_2 \) to \( \text{N}_2 \). The angle of the facet forming the V-shaped pit changed to 42° for the \( a \)-plane of \( 724 \ \mu\text{m} \) thickness reached 763 \( \mu\text{m} \), i.e. the \{011\} plane. However, when the \( c \)-plane film thickness increased from 400 to 724 \( \mu\text{m} \), the angles of the facets were 26°–33° that are close to the angle of 28° for the \{011\} plane. Thus, the \{012\} plane with an angle of 47° appeared. The V-shaped pit was composed of facets having different angles at \( c \)-plane film thicknesses of 724–763 \( \mu\text{m} \), i.e. the \{011\} and \{012\}.
planes at the outer and inner regions of the V-shaped pit, respectively. When the c-plane film thickness was larger than 832 μm, the facet plane was unified to [1012] and the V-shaped pit began to shrink. This result suggested that the difference in the growth rates between the c-plane and facet planes resulted in the annihilation of the V-shaped pit. The center of the V-shaped pit did not contain the inversion domain or nanotubes. This was confirmed using the KOH etching method.

Planar growths on semipolar planes for c-plane and facets were performed by changing F to determine the growth rate of each plane. Figure 5 illustrates cross-sectional FL microscopic images at F = 0 for the planar growth of polar (0001) and semipolar planes (1011), (1012), (1013) and (1014). We can distinguish the epi-layer from the each substrate as the contrast due to the difference of the impurity incorporation. Every film shows relatively uniform thickness. Each film thickness was determined using these figures. Film thicknesses for F = 0.5 and 1 were calculated in the same way (not shown). Figure 6 shows the schematic illustration of the growth for the c-plane and the facet plane to evaluate the V-shaped pit growth. Solid and dashed lines represent crystal surfaces, before and after growth, respectively. The facet growth is divided into an x-y component, i.e. m-direction and c-direction. The evolution of the V-shaped pit can be determined by the difference in the growth rate between the c-plane and c-component of the facet plane forming the V-shaped pit. Film thickness for the c-component of the facet plane (t½) is expressed as follows:

\[ t_{\frac{1}{2}} = \frac{t_f}{\sin \theta'}, \]

where \( t_f \) is film thickness for the facet plane (semipolar plane) and \( \theta' \) is an angle between the facet plane and m-plane. The growth rate for the c-component of the facet plane is expressed as:

\[ GR_{c} = \frac{t_{\frac{1}{2}}}{T}, \]

where \( T \) is growth time. The growth rate for the c-plane is expressed as:

\[ GR_{c} = \frac{t_c}{T}, \]

for (1011) plane that was the facet forming the V-shaped pit at the first stage, \( GR_{c}/GR_{c} \) for F = 1 and 0.5 was 2.2 and 1.6, respectively. Thus, the pit size can expand. However, \( GR_{c}/GR_{c} \) reduced to 0.90 for F = 0, suggesting that the pit size can be reduced slightly. However, the pit size under F = 0 slightly expanded, as shown in Fig. 3(c). The reason is discussed in the following section. The trend on F coincides with the experimental results for epitaxial lateral overgrowth. For the (1012) plane that is the key plane for the annihilation of a V-shaped pit, \( GR_{c}/GR_{c} \) decreased by decreasing F from 1 to 0, as with the (1011) plane. The \( GR_{c}/GR_{c} \) of 0.83 for F = 0 indicates the reduction of the V-shaped pit size, which correlates with the result for 3PPL. Interestingly, \( GR_{c}/GR_{c} \) values for both (1013) and (1014) planes were independent of F. The \( GR_{c}/GR_{c} \) for (1013) was consistently smaller than 1.0. On the other hand, \( GR_{c}/GR_{c} \) for (1014) was consistently larger than 1.0. These results suggest that once these planes appear, the V-shaped pit size, which correlates with the result for...
pit size composed of \( \{10\bar{1}3\} \) might reduce and that of \( \{10\bar{1}4\} \) might expand, irrespective of the carrier gas. It is strongly expected that the growth condition should be studied to change the surface orientation of the facet plane forming the V-shaped pit to \( \{10\bar{1}3\} \) for the realization of the V-shaped pit free even under H\(_2\) carrier condition.

4. Discussion

As mentioned, growth rates for \( c \)-plane and several semipolar planes were determined by changing \( F \). However, it is supposed that partial pressures of the reactant gases on the growth surface of the substrate would be different to that at the bottom of a V-shaped pit, which might affect the evolution of a V-shaped pit. In this section, the influence of the shape of the V-shaped pit on the growth rate was studied by CFD calculation. The annihilation of the V-shaped pit was discussed by considering the result of CFD. Under the growth condition having relatively low V/III ratio such as HVPE, the growth rate of GaN is proportional to a product for partial pressures of NH\(_3\) and GaCl, \( P_{\text{NH}_3} \times P_{\text{GaCl}} \). Therefore, their distribution was calculated just near the V-shaped pit by a CFD code.\(^{29}\) Figure 8 shows the distribution of \( P_{\text{NH}_3} \times P_{\text{GaCl}} \) near V-shaped pits having depths of (a) 100, (b) 300 and (c) 1000 \( \mu m \), respectively. \( P_{\text{NH}_3} \times P_{\text{GaCl}} \) was normalized to 1 at the position of 2 mm away, horizontally from the center of a V-shaped pit. \( P_{\text{NH}_3} \times P_{\text{GaCl}} \) inside a V-shaped pit was smaller than that for the \( c \)-plane. Furthermore, \( P_{\text{NH}_3} \times P_{\text{GaCl}} \) at the bottom of a V-shaped pit decreased in the order of 100 > 300 > 1000 \( \mu m \). By increasing the depth of a V-shaped pit, \( P_{\text{NH}_3} \times P_{\text{GaCl}} \) became smaller, i.e. the growth rate of GaN. These results suggest that the growth rate of the \( \{10\bar{1}1\} \) plane forming the V-shaped pit is much smaller than that of planer growth. Thus, the film thickness for semipolar plane, \( t_f \), in Eq. (2) becomes smaller, leading to smaller \( GR_c/GR_{fc} \) and larger \( GR_c/GR_{fc} \). We suppose that the \( GR_c/GR_{fc} \) for the \( \{10\bar{1}1\} \) plane in Fig. 7(b) become larger than 1.0 at the boundary determining the V-shaped pit size scaling by considering the result of the CFD calculation. On the other hand, the \( GR_c/GR_{fc} \) for the \( \{10\bar{1}2\} \) plane is still smaller than 1.0. Therefore, the V-shaped pit size composed of \( \{10\bar{1}1\} \) expanded and that of \( \{10\bar{1}2\} \) reduced at \( F = 0 \) as a result of 3PPL.

![Fig. 5. (Color online) Cross-sectional FL microscopic images at \( F = 0 \) for the planar growth of polar (0001) and semipolar planes (10\bar{1}1), (10\bar{1}2), (10\bar{1}3) and (10\bar{1}4).](image)

![Fig. 6. Schematic illustration of the growth for the \( c \)-plane and facet plane to evaluate the V-shaped pit. Solid and dashed lines represent crystal surfaces before and after growth, respectively. Facet growth was divided into \( x \)-\( y \) components, i.e. \( m \)-direction and \( c \)-direction.](image)

![Fig. 7. (Color online) (a) Dependence of \( GR_c/GR_{fc} \) ratio for the growth rate of the \( c \)-plane and the \( c \)-component of the facet plane determined by the planar growth on \( F \). The \( GR_c/GR_{fc} \) on the vertical axis smaller than 1.0 indicates a reduction of the V-shaped pit size. The dashed lines are visual guides. (b) Enlarged graph around horizontal axis with \( F = 0 \).](image)
Fig. 8. (Color online) Distribution of the product for partial pressures of NH$_3$ and GaCl near a V-shaped pit in respect of the depth of (a) 100, (b) 300 and (c) 1000 μm.

5. Conclusion
We investigated the transition for the angle of facets forming a V-shaped pit using 3PPL. The surface orientation of facets was changed from {10T1} to {10T2} as the growth proceeded. The size of the V-shaped pit composed of {10T2} decreased along the growth direction, whereas that of {10T1} increased. Such a change of the facet plane, thus, contributed to the annihilation of the V-shaped pit. Planar growths of c-GaN and semipolar GaN having various surface orientations were performed in combination with CFD calculation near the V-shaped pit. The V-shaped pit size composed of {10T1} and {10T2} tended to reduce by changing $F$ from 1.0 to 0. Furthermore, the V-shaped pit composed of {10T2} was likely to annihilate rather than that of {10T1} at $F = 0$, which coincides with the result of 3PPL. Thus, the V-shaped pit annihilation for c-GaN reflects the intrinsic difference in the growth rate among the {10T1}, {10T2} and (0001) planes.

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ORCID iDs
Kenji ISO https://orcid.org/0000-0002-4785-7621

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