V-shaped pits in HVPE-grown GaN associated with columnar inversion domains originating from foreign particles of α -Si₃N₄ and graphitic carbon

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The v-shaped pits (so-called V-pits) observed in hydride-vapor-phase-epitaxy-grown GaN and associated with the columnar inversion domains originating from foreign particles were investigated. The inversion domains on the front and back surfaces of the test sample were recognized after chemical mechanical polishing. It was found that the V-pits originate from the columnar inversion domains. The inversion domains, in turn, arise from the particles that exist on a low-temperature GaN buffer layer on sapphire substrate. Using transmission electron microscopy, these particles were found to be of α -Si₃N₄ and graphitic carbon. Such particles are attributable to the components of the reactor and adhere to the low-temperature GaN buffer layer, which has a surface roughness of the order of several nanometers. Thus, an effective way of obtaining HVPE-grown thick GaN layers without the V-pits associated with columnar IDs is maintain the parts of the HVPE chamber to prevent generating foreign particles.

Keywords: GaN, V-shaped pits, inversion domain, foreign particle, TEM, STEM

I. INTRODUCTION

Hydride vapor phase epitaxy (HVPE) is known to be a suitable growth technique for producing thick GaN substrates, owing to its high growth rate. Thick HVPE-grown GaN layers usually require GaN template layers grown on substrates by metalorganic vapor phase epitaxy (MOVPE).^{1,2} Even though HVPE-grown GaN layers with smooth surfaces have been achieved,^{3,4} the formation of V-shaped pits (so-called V-pits) on the surfaces on these GaN layers under extreme conditions is a significant problem.^{5,6} The formation of V-pits is often associated with the presence of inversion domains (IDs).⁷⁻¹² In this case, the appearance of V-pits is believed to result from the difference in the growth rates for different polarities. It was shown that the growth rate of the N-polar IDs is lower than that of the surrounding GaN.⁷ Further, it has been suggested that the IDs originate at the interface between the GaN layer and the substrate.⁷⁻¹² Therefore, researchers have concluded that IDs are probably formed because of imperfect substrate preparation^{10,11} or owing to the formation of polycrystalline particles at the interface.¹³ However, the relationship between the formation of V-pits, IDs, and foreign particles has not yet been investigated in detail. In this work, we tried to elucidate the origin of V-pits and IDs using a HVPE-grown GaN layer with often generated V-pits. The obtained results indicated that the surfaces of GaN layers with or without V-pits are appeared when they are grown by HVPE directly on an as-deposited low-temperature GaN (LT-GaN) buffer layer, notwithstanding in identical growth condition. The LT-GaN buffer layer was grown on *c*-plane sapphire substrates by MOVPE. The HVPE-grown GaN layer was subjected to optimized grinding and chemical mechanical polishing (CMP), which were investigated using optical microscopy (OM), scanning electron microscopy (SEM) in combination with energy-dispersive X-ray spectrometry (EDS), transmission electron microscopy (TEM), convergence beam electron diffraction (CBED) pattern analysis, high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM), and annular bright-field (ABF)-STEM.

II. EXPERIMENTAL METHODS

As mentioned above, the GaN layers were grown by HVPE on LT-GaN buffer layers deposited by MOVPE on *c*-plane sapphire substrates. During the MOVPE procedure, after the substrates had been subjected to thermal annealing, a LT-GaN buffer layer (thickness of approximately 30 nm) was deposited on them at 460 °C using trimethylgallium and ammonia (NH₃) as the precursors for Ga and N, respectively. Subsequently, the primary growth process was performed by HVPE. The substrate temperature was raised to 1040 °C under an 8-slm NH₃

supply. The GaN layer was grown under a V/III ratio of 10 for 8 h. GaCl and NH₃ mixed with H₂ as the carrier gas were used as the Ga and N sources, respectively.

Front- and back-surface-polished specimens were prepared for OM and SEM by grinding and CMP. CMP was performed using a felt pad and a colloidal silica suspension (Musashino Denshi, COMPOL80). The SEM observations were carried out on a JEOL JSM-7800F system, which was operated at 5 keV for the SEM observations and 30 keV for the EDS analysis. Cross-sectional TEM specimens were prepared by mechanical polishing and Ar ion milling or focused ion beam (FIB) milling. The TEM and STEM observations were made using a JEOL JEM-2100F system equipped with an aberration corrector for STEM (operated at 120 keV). The HAADF and ABF-STEM images were obtained at collection angles of 49–130 and 11–21 mrad, respectively. The high-resolution STEM images were filtered slightly using a two-dimensional fast Fourier transform low-pass filter. Finally, simulated STEM images and CBED patterns were obtained through simulations performed using the HREM Research xHREM STEM software package.

III. RESULTS AND DISCUSSION

A. Origin of V-pits

An SEM image of the V-pits formed on the surface of a HVPE-grown GaN layer is shown in Fig. 1(a). A dark region can be seen at the bottom of an individual V-pit in Fig. 1(b). Similar dark regions were observed in most of the V-pits in this sample. To investigate the origin of the V-pits, we polished the front and back surfaces of the sample and subjected it to SEM analysis. Figure 2(a) shows a magnified surface SEM image of the bottom of a V-pit before polishing while Fig. 2(b) shows an SEM image of the front-polished surface just below the V-pit. The dark region in the image of the bottom of the V-pit is concave. On the other hand, in the back-polished surface, the dark region has a convex, flipped horizontal shape (see Fig. 2(c)). The difference in the polarities of Ga and N resulted in the concave and convex regions, which allowed the IDs to be visualized, because of the difference in the polishing rates. It is known that N-polar GaN exhibits a higher polishing rate than does Ga-polar GaN.¹⁴ Therefore, the N-polar IDs in Ga-polar GaN have concave surfaces and vice versa. Figure 3(a) shows a cross-sectional TEM image of the GaN layer, including the bottom of a V-pit. Two nearly parallel lines can be observed along <0001> below the V-pit. The CBED patterns of the area outside the lines (points 1 and 3) and those of the area within the lines (point 2) are shown in Figs. 3(b)–3(d). A comparison of these CBED patterns and the simulated ones¹⁵ is shown in Fig. 3(e); it can be concluded that an ID exists below the V-pit and that the two nearly parallel lines are ID boundaries

(IDBs). The fact that the growth rate of the N-polar ID was lower than that of the surrounding GaN resulted in the formation of the V-pit.⁷ Therefore, columnar IDs extending from approximately the LT-GaN buffer layer on the sapphire substrate to the bottom were present, resulting in V-pits.

FIG. 1. Surface SEM images of (a) a HVPE-grown GaN layer and (a) the V-pit indicated by the white arrow in (a).

FIG. 2. Magnified surface SEM image (a) of the bottom of the V-pit shown in Fig. 1(b). SEM images of the areas of the (b) front- and (c) back-polished surfaces below the V-pit shown in (a). (d) Cross-sectional schematic model of a GaN layer with V-pits and the underlying sapphire substrate.

FIG. 3. Cross-sectional TEM [10-10] image of a GaN layer, including the bottom of a V-pit. Two nearly parallel lines are observed along $\langle 0001 \rangle$ below the V-pit (the white dot lines are visual guides). (b) and (d) CBED pattern of the area outside the lines indicated by points 1 and 3, (c) that of the area inside the lines indicated as point 2, and (e) simulated CBED pattern for a thickness of 119 nm.

B. Origin of inversion domains

To elucidate the origin of the columnar IDs, we polished the front surface of the GaN layer such that its thickness was reduced to several micrometers. The reflection and transmission plan-view OM images in Fig. 4 show the IDs as concave regions (indicated by arrows). In the transmission plan-view OM image, dark particles can be observed below the IDs. The composition of these particles was determined using SEM-EDS. Figure 5(a) shows a transmission plan-view OM image of a GaN layer front-polished until such particles were exposed. These particles are the dark points indicated by the arrows. The EDS maps of the area in Fig. 5(a) are shown in Figs. 5(b)–5(d). Of all the elements detected, only C and Si exhibited the same distributions in the particles. Thus, it is likely that two types of particles, namely, those containing C and Si, were present.

FIG. 4. (a) Reflection and (b) transmission plan-view OM images of the front-polished surface of a GaN layer close to the sapphire substrate.

FIG. 5. (a) Transmission plan-view OM images of a front-polished surface of GaN layer close to the sapphire substrate. EDS maps of (b) Ga, (c) C, and (d) Si.

Figure 6(a) shows a cross-sectional TEM image of the GaN layer; a particle containing Si is present near the LT-GaN buffer layer. This particle was confirmed to be of α - Si_3N_4 based on the electron diffraction pattern shown in Fig. 6(b). On the other hand, a cross-sectional TEM image of the GaN layer containing a particle composed of C near the interfacial region is shown in Fig. 7(a). The electron diffraction pattern of the particle contained spots related to the graphitic (10-10) and (0002) planes, as seen in Figs. 7(b) and 7(c). That an ID was present above the particle was determined on the basis of the results of the CBED analysis shown in Figs. 8(b)–8(d). Further, the top of the polished surface was concave, in keeping with the ID (see Fig. 8(a)). Such particles are attributable to the components of the HVPE reactor. It is estimated that the Si_3N_4 is formed on the LT-GaN buffer layer as a result of come-flying particle from the deteriorated quartz chamber surface and nitriding reaction by NH_3 . Similarly, the graphitic carbon particle is carried from the deteriorated carbon nozzle by the gas flow. The deterioration mechanism of the components of the HVPE reactor is not clear and has not yet been reported in detail. Additionally, micron-scale foreign particles can readily adhere to the as-deposited LT-GaN buffer layer having a surface roughness of the order to several nanometers.¹⁶⁻¹⁸ Although this particular graphitic carbon particle was isolated from the LT-GaN buffer layer in the observed cross-section, it is highly likely that it was in contact with the LT-GaN buffer layer elsewhere.

FIG. 6. (a) Cross-sectional TEM image of a GaN layer, including a foreign particle present near the interfacial region, and (b) electron diffraction pattern of the foreign particle indicated by the circle in the TEM image in (a).

FIG. 7. (a) Cross-sectional TEM image of a GaN layer, including a foreign particle present near the interfacial region, and (b) and (c) electron diffraction patterns of the foreign particle corresponding to the area indicated by circles 1 and 2 in the TEM image in (a).

FIG. 8. Cross-sectional BF-TEM [10-10] image of the GaN layer of the area above the foreign particle. (b)-(c) CBED patterns of the areas labeled 1 and 2 in the TEM image in (a) and (d) simulated CBED pattern for a thickness 57 nm.

The effects of polarity inversion on Ga-polar surfaces owing to Si adsorption have been investigated previously.¹⁹ The formation of an N-adlayer on a Si-terminated surface is energetically favorable, as shown in Fig. 9(a). As a result, the Si impurities form Si_3N_4 particles, which induce the formation of IDs on themselves. On the other hand, an N-polar GaN has been grown epitaxially on graphene (see Fig. 9(b)).²⁰ In the present study, the carbon particles below the IDs were polycrystalline, and the IDs were generated not from the basal plane but the edge plane of graphitic carbon. The atomic arrangements of the edge plane of polycrystalline graphitic carbon are different from those of the basal plane of graphene. The N incorporated into the edge plane of graphitic carbon after exposure to NH_3 ²¹ probably acts in a manner similar to that of N bonded to the basal plane. The interfaces between the particles

and the IDs were not parallel to the zone axis of GaN. Therefore, high-resolution imaging of the interfaces was not possible.

FIG. 9. (a) Schematic model of formation of N-polar GaN because of Si adsorption and (b) N-polar GaN grown on graphene. The large and small circles denote Ga and N, respectively, while the mid-sized circles denote Si in (a) and C in (b).

FIG. 10. (a) High-resolution cross-sectional HAADF and (b) ABF STEM [11-20] images of a GaN layer including IDB of the region indicated by the circle in Fig. 8(a). (c) Composite image formed by overlaying the HAADF- and contrast- inverted ABF-STEM images. (d) Magnified composite STEM image of the IDB and (e) the simulated composite STEM image and the corresponding atomic structure model. (f) The atomic structure model is assumed to be composed of two shifted overlying structures aligned along the STEM observation direction. The large and small circles denote Ga and N, respectively.

The presence of an IDB in the region indicated by the circle in Fig. 8(a) was confirmed using high-resolution STEM. Figure 10 shows (a) HAADF and (b) ABF-STEM images. HAADF-STEM images can be directly inverted into the object function, which represents the atomic positions and species.^{22,23} The bright spots in the HAADF-STEM images correspond to the positions of the heavier Ga atomic columns along the observation direction.²⁴ ABF-STEM has been used to observe both light and heavy atoms.^{25,26} The dark spots in the ABF-STEM images

correspond to the positions of the heavier Ga and lighter N atomic columns.²⁷ Figure 10(c) shows an overlaid HAADF-STEM (red) and a contrast-inversed ABF-STEM image (green). In this composite image, the Ga atomic columns and N atomic columns are expected to exhibit the colors yellow (red + green) and green, respectively. One can identify Ga-polar GaN on the right side and N-polar Ga-N on the left side of the IDB in this composite image. A magnified version of the composite image is shown in Fig. 10(d). The atomic arrangements of the IDB are more complex than the ones proposed.²⁸⁻³¹ We could construe the two overlaid and shifted IDB*-type structures²⁸ in the observation direction. The IDB* structure contains fourfold and eightfold rings of bonds, but there are no Ga-Ga or N-N bonds. The estimated atomic arrangements in the IDB and the simulated composite image are shown in Fig. 10(e). The simulated image was similar to the experimentally obtained one. This suggested that the proposed low-energy and electrically nonactive IDB*-type structures were inclined or jagged along the observation direction. Thus, it was concluded that V-pits originate in columnar IDs because the growth rate of the N-polar IDs is lower than that of the surrounding Ga-polar GaN. The IDs, in turn, arise from the particles that exist on the LT-GaN buffer layer formed on the sapphire substrate.

IV. CONCLUSIONS

We investigated the origin of the V-pits observed in HVPE-grown GaN and associated with columnar IDs, which originate from the foreign particles present on the LT-GaN buffer layer. This was done using the CMP method, OM, SEM, TEM, and STEM. It was found that the V-pits originate from the columnar inversion domains. The origin of the IDs, in turn, was determined to be the presence of foreign particles containing C or Si. We were able to observe particles of α -Si₃N₄ and graphitic carbon below the IDs. Such particles are attributable to the components of the HVPE reactor and adhere to the as-deposited LT-GaN buffer layer, which has a surface roughness of the order of several nanometers. The Si impurities form Si₃N₄ particles, while the N incorporated into the surface of the graphitic carbon induce IDs to form on themselves. Thus, an effective way of obtaining HVPE-grown thick GaN layers without the V-pits associated with columnar IDs is maintain the parts of the HVPE chamber to prevent generating foreign particles.

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