Growth of GaN on a three-dimensional SCAATM bulk seed by tri-halide vapor phase epitaxy using GaCl3

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GaN with a film thickness of 200–600 μm was grown on the as-grown three-dimensional supercritical acidic ammonia technology (SCAATM) bulk seed that comprised only semipolar {1011} planes at a temperature as high as 1390 °C by tri-halide vapor phase epitaxy; further, the GaN film was also characterized. The FWHM value of the X-ray rocking curves was ~40°, which was almost similar to the value of the used seed. The curvature radii were as large as 40–64 m. Further, the carrier concentrations were observed to be as small as 5.1 × 1017–9.1 × 1017 cm−2. However, the basal plane stacking fault densities were observed to be 3.4 × 105–5.4 × 105 cm−1 and were observed to increase during the growth process because of the as-grown SCAATM seed surface condition.

1. Introduction

Recently, electronic devices have been extensively investigated using free-standing bulk c-GaN substrates because of their lower threading dislocation densities (TDDs) as compared to those of the devices that are fabricated using foreign substrates.1–4 The potential of GaN semiconductors for both radio frequency devices and power electronics exceeds that of SiC, which has been used for several applications in power electronics, including air conditioners, power conditioners of solar cell systems, and railway vehicle systems. Generally, bulk c-GaN substrates that are fabricated using hydride vapor phase epitaxy (HVPE) are used in electronic devices, which exhibit a TDD of approximately 1 × 1010 cm−2.5–8 However, several groups have observed that an increase in TDD caused various device performance issues such as decreased electron mobility, deterioration of transconductance gm, and increased current leakage.9–11 Reference 12 reported that the screw component of threading dislocation would cause leakage current and that the edge and mixed components would not cause leakage current by using conductive atomic force microscopy. Therefore, HVPE-GaN materials that are grown on true bulk GaN crystals are fabricated using solution growth methods, including the ammonothermal method and the Na-flux method. These methods could potentially balance low TDD values of 1 × 1010 cm−2 or lower because HVPE enables high growth temperatures of ~1400 °C.18–20 High growth temperatures can lead to high-quality GaN and suppress the growth of polycrystalline GaN. Our group previously reported that GaN could be grown on the (10T0), (30T1), (20Z1), (10H1), and (0001) planes using THVPE at temperatures as high as 1280 °C but not on the (0001), (10T1), (20Z1), and (30Z1) planes.21 These results show that THVPE growth denotes surface orientation selectivity for the growth of GaN. Furthermore, planar growth with a film thickness of ~1.0 mm by THVPE on GaN substrates, which were sliced from a bulk crystal grown by SCAATM, revealed that crystal characteristics, such as the FWHM and the basal plane stacking fault (BSF) density of the GaN film on the semipolar (10T1) plane, were superior to those of the nonpolar m-plane (10T0).22 Hence, we propose the growth process in which the GaN crystal diameter could increase during the growth. Figure 1 illustrates a flowchart for the production of GaN wafers with a high crystal quality by combining THVPE with the SCAATM bulk seed. It was expected that the crystal size would increase during the growth because the SCAATM bulk seed comprised only of the {1011} planes. After growth, the crystal boule was sliced. Further, GaN wafers with TDDs of 1 × 104 cm−2 or lower could be obtained. The top-part of the crystal boule could be recycled for performing the forthcoming growths.

In this study, we conducted GaN growth on the as-grown three-dimensional SCAATM bulk seed comprising semipolar {1011} planes with six-fold symmetry at a temperature as high as 1390 °C. Two samples with different growth times were grown using THVPE. Further, the growth rate, FWHM of the X-ray rocking curve (XRC), curvature radius, carrier concentration, impurity concentration, cathodoluminescence (CL), and photoluminescence (PL) of the GaN films were evaluated.

2. Experimental section

A three-dimensional SCAATM bulk seed that comprised semipolar {1011} planes with six-fold symmetry was employed as depicted in Fig. 2(a). This seed exhibited a shape...
that extended laterally because it was sliced from the GaN boule grown by SCAATTM, mainly toward the $m$-direction. The seed was dipped in a 1 M HCl aqueous solution for a few seconds and was followed by washing with water and drying. The XRC-FWHM and TDD were approximately 40 arcsec and $1 \times 10^3$ to $1 \times 10^4$ cm$^{-3}$, respectively.

For the THVPE of GaN, GaCl$_3$ was used as a group-III precursor, which was generated by the two-step reaction between Cl$_2$ gas and Ga metal, as denoted in Eqs. (1) and (2). In the deposition zone, NH$_3$ was introduced to contact the substrate, and GaN was grown using the reaction between GaCl$_3$ gas and NH$_3$ gas, as depicted in Eq. (3). Further, the details of THVPE used in this experiment have been reported in a previous study.  

\begin{align}
\text{Ga(l)} + 0.5\text{Cl}_2(g) & \rightarrow \text{GaCl}_3(g), \\
\text{GaCl}_3(g) + \text{Cl}_2(g) & \rightarrow \text{GaCl}_4(g), \\
\text{GaCl}_4(g) + \text{NH}_3(g) & \rightarrow \text{GaN(s)} + 3\text{HCl(g)}.
\end{align}

The schematic of the reactor was depicted in Fig. 3. Optimized THVPE growth conditions were used in this study. The growth was conducted by employing N$_2$ as the carrier gas at 1390 °C using a residence heating susceptor. Two growth conditions (named sample #1 and sample #2) with different growth times of 3 and 10 h, respectively, were used to observe the influence of film thickness on the number of properties of GaN. The partial input pressures of NH$_3$ and the generated GaCl$_3$ were 1.2 $\times$ 10$^{-1}$ and 2.3 $\times$ 10$^{-3}$ atm, respectively. The film thickness was determined using cross-sectional fluorescence (FL) microscopy. Further, the crystal quality was evaluated by XRC-FWHM using double crystal X-ray diffraction (XRD). The curvature radius toward $\langle 11\overline{2}0 \rangle$ was evaluated by o-scan peak dependence on the crystal position using XRD.  

Figures 2(a) and 2(b) depict the photographs of the SCAATTM bulk crystal seed before and after the growth process. (c) The corresponding schematic of the SCAATTM bulk crystal.

Additionally, impurity concentrations of oxygen and silicon that were incorporated into GaN were investigated using secondary-ion mass spectrometry (SIMS). The BSF was characterized using a scanning electron microscope (SEM) equipped with CL and a liquid nitrogen cooling stage at low temperatures (82–83 K). Further, PL measurements were conducted to evaluate the optical properties of the materials.

3. Results and discussion

Figures 2(a) and 2(b) depict the photographs of the SCAATTM bulk crystal seed before and after growth. Prior to growth, the seed displayed a yellow color because impurities were incorporated during acidic ammonothermal growth. After growth, the color of the seed became almost transparent, and it could be observed that the surface morphology displayed some undulations along $\langle 11\overline{2}0 \rangle$. Further, the differential interference contrast microscopy images of the sample surfaces are depicted in Fig. 4.
is the plasmon frequency and $\omega_p$ is the LO phonon frequency in the uncoupled limit for SIMS measurement. Furthermore, the impurity concentrations of oxygen (O) for samples #1 and #2 were measured using SIMS and were observed to be $8 \times 10^{17}$ and $3 \times 10^{17}$ cm$^{-3}$, respectively, while the impurity concentration of silicon (Si) for both samples was $1 \times 10^{17}$ cm$^{-3}$. Thus, the difference between carrier concentrations could be attributed to the incorporation of oxygen in GaN based on the amount of H$_2$O degasification in the reactor during growth. Note that hydrogen concentrations were below the detection limit for SIMS measurement. Furthermore, SIMS measurement for SCAAT$^\text{TM}$ bulk seed exhibited that the impurity concentrations of oxygen, silicon, and hydrogen were $2 \times 10^{18}$ cm$^{-3}$, below the detection limit, and $5 \times 10^{19}$ cm$^{-3}$, respectively, which shows that THVPE growth on SCAAT$^\text{TM}$ bulk seed could lead to a significant reduction of impurities in GaN except for silicon.

BSFs appear considerably often during the GaN growth of nonpolar and semipolar planes. The BSFs in wurtzite GaN can be categorized into three types, I$_1$ (…ABABCABCABA…), I$_2$ (…ABABCACA…), and E (…ABABCABA…), with each exhibiting different atomic sequences of c-plane stacking.\(^{(27)}\) The BSF for type I$_1$, which has the lowest formation energy, is the most dominant in wurtzite GaN. BSFs exhibit a local deviation from the hexagonal wurtzite to the cubic zinc-blende crystal structure.\(^{(28)}\) This wurtzite/zinc-blende heterostructure results in a zinc-blende quantum well in the wurtzite nanosheets grown on the SCAAT$^\text{TM}$ bulk seed.
CL (LT-CL) measurements at a wavelength of 364 nm for type I$_1$ BSFs. Further, typical images of each sample are depicted in Fig. 7. The bright lines in the LT-CL image indicate the BSFs that were generated during homoepitaxial growth by THVPE. The CL images were obtained at five different points over a sample wafer for evaluating the BSF density. The average BSF densities are presented in Table I. Further, the average BSF densities for samples #1 and #2 were $3.4 \times 10^{17}$ and $5.4 \times 10^{17}$ cm$^{-1}$, respectively. Samples with longer growth times resulted in larger BSF densities, indicating that the BSF densities increased during the growth process.

Figure 8 depicts the PL spectra of samples #1 and #2, which are measured at 4 K. The PL spectra comprised a dominant donor-bound exciton (D$^0$X) at 3.478 eV. BSFs in the GaN layer manifest in the PL spectra in the form of an emission band at $\sim$3.42 eV, which corresponds to type I$_1$ BSF. An emission band was observed at 3.425 eV for sample #2, whereas a weak emission band (shoulder peak) resulting from BSFs was observed for sample #1, which was in agreement with the results of CL measurements. The emission arising from the donor–acceptor pair recombination (D$^0$A$^0$) at 3.3 eV has also been identified for sample #2. Yellow luminescence (YL) was not observed from 2.0 to 2.5 eV in either of the samples, which was a typical feature of carrier recombination via native point defects and impurities in GaN. SCAAT$^{TM}$ bulk seed itself showed a strong YL peak intensity due to a vacancy–impurity complex such as Ga vacancy coupled with impurities such as oxygen or hydrogen, which was identified using a positron annihilation measurement.

We previously performed planar growth with a thickness of $\sim$0.5 mm on the SCAAT$^{TM}$ (10I) substrate, and the BSF density was observed to be as small as 3.0 cm$^{-1}$, which was an order of magnitude smaller than that observed in this study. We assume that there are two possibilities to explain this difference in BSF density. One is that BSF densities could be attributed to the difference between the substrate surface conditions prior to the growth process. Thus, chemically and mechanically polished treated substrates that were used in our previous study resulted in a relatively small BSF density. The other is that BSF could be generated due to the difference in a substrate shape between the planar and the three-dimensional bulk seed comprising semipolar {1101} planes. Reference 32 reported that BSFs for types I$_1$ and I$_2$ were generated during the semipolar {1101} side facets of the triangle shape growth by using SiO$_2$ stripe mask on c-plane sapphire. Furthermore, Ref. 33 reported that stacking faults with high density were observed during GaN nano-rod growth along the c-direction. Reference 34 reported that the exposed c-plane facets presenting during growth accounts for

![Fig. 6.](image1) (Color online) Raman spectra of the GaN film grown on the SCAAT$^{TM}$ bulk seed using THVPE for (a) 3 h and (b) 10 h. The inset depicts an enlarged spectra around the A$_1$(LO) peak.

![Fig. 7.](image2) Monochromatic (364 nm) low-temperature cathodoluminescence images of GaN grown using THVPE for (a) 3 h and (b) 10 h.

### Table I. Range of characteristics for samples #1 and #2. $R_c$ and $n$ refer to the curvature radius and carrier concentration, respectively.

| #  | Growth time (h) | Growth rate ($\mu$m h$^{-1}$) | Thickness ($\mu$m) | FWHM (arcsec) | $R_c$ (m) | $n$ (cm$^{-3}$) | O-conc. (cm$^{-3}$) | Si-conc. (cm$^{-3}$) | BSF density (cm$^{-1}$) |
|----|----------------|-------------------------------|-------------------|---------------|----------|------------|----------------|----------------|------------------|
| 1  | 3              | 56–69                         | 167–208           | 42"           | 64       | $9.1 \times 10^{17}$ | $8 \times 10^{17}$ | $1 \times 10^{17}$ | $3.4 \times 10^{4}$ |
| 2  | 10             | 52–62                         | 519–615           | 41"           | 36       | $5.1 \times 10^{17}$ | $3 \times 10^{17}$ | $1 \times 10^{17}$ | $5.4 \times 10^{4}$ |
the consequent coalescence behavior of these facets and the formation of high-density BSFs. Thus, the emergence and consequent coalescence of facets along with some undulations toward ($\{11\overline{2}0\}$) in Fig. 2(b) would result in BSF generation. In future studies, we intend to achieve a reduced BSF density for the (1011) plane to optimize the treatment of the SCAATTM seed surface and to elucidate the cause of occurrence of BSF.

4. Conclusions

To summarize, GaN with a film thickness of 200–600 $\mu$m was grown on the as-grown three-dimensional SCAATTM bulk seed that comprised only semipolar {$\{10\overline{1}1\}$} planes at temperatures as high as 1390 °C using THVPE; further, GaN films were evaluated using various characterization methods. XRC-FWHM values were as small as $\sim$40°, which was almost similar to the XRC-FWHM value of the seed that was used. The curvature radii were as large as 40–64 μm. Additionally, carrier concentrations were as small as 5.1 × 10$^{17}$–9.1 × 10$^{17}$ cm$^{-3}$, which can be attributed to the oxygen impurities in GaN. The BSF densities ranged from 3.4 × 10$^4$ and 5.4 × 10$^4$ cm$^{-1}$ and increased during growth probably because of the as-grown SCAATTM seed surface condition. Further investigation of the treatment of the SCAATTM seed surface is required to suppress the occurrence of BSFs. In future, we intend to achieve a low BSF density for the (10\overline{1}1) plane to optimize the treatment of the SCAATTM seed surface.

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Fig. 8. (Color online) The photoluminescence spectra with logarithmic scales for the GaN film grown on the SCAATTM bulk seed using THVPE for (a) 3 h and (b) 10 h. The PL measurements were performed at 4 K.