Reuse of ScAlMgO$_4$ substrates utilized for halide vapor phase epitaxy of GaN

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ScAlMgO$_4$ (SCAM) substrates with a small lattice-mismatch to GaN and c-plane cleavability are promising for fabricating high-quality free-standing GaN wafers. To reduce the cost in the fabrication of free-standing GaN wafers, the reuse of a SCAM substrate is demonstrated. By cleaving a SCAM substrate which has been already utilized for the growth of a thick GaN film by halide vapor phase epitaxy, the atomically flat surface can be obtained. The threading dislocation density of a 320 $\mu$m thick GaN film grown on this cleaved SCAM substrate is 2.4 $\times$ 10$^7$ cm$^{-2}$, which is almost the same as that on a new SCAM substrate. This result indicates that a SCAM substrate can be reused for GaN growth.

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1. Introduction

GaN-based optical devices such as visible LEDs$^1$ and high-power and high-frequency transistors$^2$ have been expected to be key products for energy-saving societies. These devices have been fabricated on the foreign substrates such as sapphire, Si, and SiC substrates because the growth of bulk GaN with high equilibrium vapor pressure of nitrogen is very difficult. The lattice mismatch between GaN and the foreign materials generates a threading dislocation density (TDD) as high as 10$^8$−10$^{10}$ cm$^{-2}$ in GaN epitaxial layers. To realize high-performance devices, the fabrication of GaN wafers with high-quality and low TDD is urgently needed. There has been many attempts to fabricate GaN epitaxial layers such as a halide vapor phase epitaxy (MOVPE) method,$^{3,17,18}$ a high-pressure method,$^9,10$ a Na flux method,$^9,10$ and an ammonothermal method.$^{11,12}$ Commercially available free-standing GaN wafers have been fabricated with the HVPE method because of their high growth rate and lower impurity concentrations. Substrates used in HVPE are sapphire and GaAs.$^3,6$ After the growth, these foreign substrates are removed with a laser lift-off process,$^4$ a void-assisted separation method,$^5$ and a chemical etching technique.$^6$ Unfortunately, free-standing GaN wafers have included high TDD of 10$^5$−10$^6$ cm$^{-2}$ owing to the lattice mismatch between GaN and foreign substrates.$^5,6$

The novel ScAlMgO$_4$ (SCAM) has been understood to be attractive for fabricating high-quality GaN wafers with low costs. The lattice mismatch of SCAM to GaN is 1.7%, which is approximately one order magnitude smaller than that of sapphire to GaN. The synthesis of SCAM was first reported in 1989. The growth of a GaN film on an SCAM substrate by molecular beam epitaxy was demonstrated in 1996. Then, a SCAM substrate with a lattice-mismatch as small as 0.09% to ZnO was used for the growth of the ZnO film and the ZnO-based LED.$^{15,16}$ Recently, a GaN film and an In$_{0.17}$Ga$_{0.83}$N film, which is lattice-match to SCAM, were grown on an SCAM substrate by metalorganic vapor phase epitaxy (MOVPE),$^{17,18}$ and an InGaN-based LED was subsequently fabricated on an SCAM substrate.$^{19}$ The difference in thermal-expansion coefficients between SCAM and GaN is also approximately 60% smaller than that between sapphire and GaN.$^{18,20,21}$ This small difference can reduce the thermal stress in the GaN wafer and the bow of the GaN wafer. In addition, in the fabrication of free-standing GaN wafers, SCAM has the cleavability which is useful for naturally separating a thick GaN film from a substrate during the cooling down process in the GaN growth.$^{22}$ The cleavage occurs along the c-plane between Al/MgO layers.$^{14,15,23}$ This natural separation makes it possible to fabricate low-cost “free-standing GaN substrates”.

To further reduce the fabrication cost of free-standing GaN wafers, the reuse of separated SCAM substrates can be considered to be favorable. In order to reuse SCAM substrates, it is important to recover the surface morphology of the separated SCAM substrate to be smooth. In this paper, the reuse of a SCAM substrate for the multiple growth of GaN films is demonstrated.

2. Experimental methods

Schematics of the reuse process are shown in Fig. 1. A “new” SCAM substrate was prepared by cleaving a SCAM boule grown by the Czochralski method.$^{18}$ Firstly, an approximately 2 $\mu$m thick GaN film as a template by MOVPE on the new SCAM substrate.$^{18,22}$ A 320 $\mu$m thick GaN film was subsequently grown on the GaN/SCAM template by HVPE. The GaN film was naturally separated from the SCAM substrate during the cooling down process in the HVPE growth as shown in Fig. 1(a). For obtaining an atomically flat SCAM surface, the as-separated SCAM substrate was cleaved at the position of about 160 $\mu$m from the surface with a razor blade as shown in Fig. 1(b). Here, this SCAM substrate is named “reused” SCAM substrate. After the cleaving process, a 320 $\mu$m thick GaN film was grown through the growth process shown in Fig. 1(c). The surface morphologies of the reused SCAM substrates and MOVPE-grown GaN films were measured with the Nomarski-type optical microscope (Olympus DP22) and atomic force microscopes (AFM; Shimadzu SPM-9600, and SII Nanocube).
A high-resolution X-ray diffraction and an X-ray rocking curve (XRC) were measured with the X-ray diffractometer (XRD; Bruker AXS D8 Discover) to evaluate the properties of the crystal structure. TDD in the HVPE-grown GaN films was measured with a multi-photon excitation photoluminescence (MPPL) system (Nikon A1MP series) whose excitation source was a femtosecond laser with an emission wavelength of 1030 nm. The near-band edge emission from GaN was detected with a photomultiplier tube. The details of the MPPL measurement are shown in Ref. 24.

### 3. Results and discussion

Overviews and Nomarski microscope images of an as-separated and a reused SCAM substrates are shown in Fig. 2. Although the band-gap energy of SCAM is as high as 6.2 eV, the as-separated SCAM substrate was brown-colored as shown in Fig. 2(a). This color change can be considered to be caused with the formation of an ScN layer at the SCAM surface during annealing a SCAM substrate in an ammonia atmosphere. This reddish or rusty color comes from ScN with the band-gap energies of 0.9 eV and 2.2–2.7 eV for the indirectly and the direct optical transitions, respectively. In the Nomarski microscope image of the as-separated SCAM substrate shown in Fig. 2(c), several steps are observed. It can be considered that many cracks appeared at the side wall of SCAM close to the interface between GaN and SCAM, and that the cleavage occurred along the c-plane of a SCAM substrate with different cleaving planes near the heterointerface. These steps are as high as a several micrometers measured by a stylus profilometer. These steps are higher than the atomic step height of SCAM, which is approximately 0.8 nm. The formation of nitrided layers is also not favorable. From these results, it is considered that the use of an as-separated SCAM substrate is difficult for GaN growth.

The reused SCAM surface with steps as high as atomic steps was formed by cleaving the as-separated SCAM substrate. Figure 2(b) shows that the reused SCAM substrate is colorless and Fig. 2(d) shows its surface is atomically flat. To precisely investigate the surface roughness of this reused SCAM substrate, the surface morphology was observed with AFM. Figure 3 shows an AFM image of the reused SCAM surface. The calculated average roughness ($R_a$) of the reused SCAM substrate in the $20 \times 20 \mu m^2$ area was 0.08 nm, which was smaller than the minimum resolution of 0.1 nm for the AFM system used in this study. This small value shows that the atomically flat surface can be formed on the reused SCAM substrate by cleaving the as-separated SCAM surface. XRCs of a reused SCAM substrate, an as-separated one, and a new one are shown in Fig. 4. Their full widths at half maximum (FWHMs) are approximately 20 arcsec, however, there is the hem of the spectrum for an as-separated SCAM substrate. This hem can be considered to come from large steps and nitrided layers as mentioned above. By cleaving an as-separated SCAM substrate, this hem was removed as shown in the XRC of a reused SCAM substrate.

To investigate the surface morphology and the crystalline quality of the MOVPE-grown GaN film on the reused SCAM substrate, the surface morphology and the structural properties were characterized with an AFM and an XRD measurements, respectively. AFM images of the MOVPE-grown GaN films on the new SCAM substrate and the reused one are shown in Fig. 5. Atomic steps were clearly observed at both GaN surfaces. The $R_a$ values of the GaN film on the reused SCAM substrate and that on the new SCAM substrate in the $5 \times 5 \mu m^2$ area were 0.10 nm and 0.33 nm, respectively. The surfaces of MOVPE-grown GaN films on the reused SCAM substrate and the new SCAM substrate were flat, and the surface roughness was almost the same. To investigate the TDDs of MOVPE-grown GaN films on a new SCAM substrate and a reused one, the XRC profiles were measured. Symmetric and asymmetric XRC profiles of both MOVPE-grown GaN films are shown in Fig. 6. The TDDs calculated from the FWHMs of XRC profiles are shown in Table I. The FWHMs of the XRCs for the symmetric 0002 and the asymmetric 1011 reflections were 352 and 382 arcsec, respectively. The screw and edge TDDs of the MOVPE-grown GaN film on the reused SCAM
substrates were estimated as $2.5 \times 10^8$ and $8.1 \times 10^8$ cm$^{-2}$, respectively. These values were almost the same as those of the MOVPE-grown GaN film on the new SCAM substrate.

The MPPL measurement was performed to investigate the crystalline quality of the HVPE-grown GaN film on the reused SCAM substrate. MPPL images of GaN surfaces on the new and the reused SCAM substrates are shown in Fig. 7. Dark spots correspond to TDs. Dark spot densities of the GaN films on the new and the reused SCAM substrates were $2.2 \times 10^7$ and $2.4 \times 10^7$ cm$^{-2}$, respectively. TDD of the GaN film on the reused SCAM substrate was almost the same as that on the new one. These results show that a reused SCAM substrate can be used for the MOVPE and HVPE growth processes of GaN films in the same way as a new SCAM substrate.

Moreover, the height of steps on an as-separated SCAM surface are four orders of magnitude larger than the lattice constant of 0.5185 nm along the c-axis for of GaN. This large roughness makes the crystalline quality of a GaN film grown on this surface poor. From these results, for the reuse of an SCAM substrate, it is necessary to remove the nitrided

| Substrate | As-separated SCAM | Reused SCAM |
|-----------|-------------------|-------------|
| Overview  | ![Image](image1.png) | ![Image](image2.png) |
| Nomarski microscope image | ![Image](image3.png) | ![Image](image4.png) |

Table I. FWHMs of XRC and calculated TDDs of MOVPE-grown GaN films on (a) a new SCAM substrate and (b) a reused one.

|                      | GaN/new SCAM | GaN/reused SCAM |
|----------------------|--------------|-----------------|
| FWHM of 0002 reflection (arcsec) | 336          | 352             |
| FWHM of 1011 reflection (arcsec)  | 402          | 382             |
| Screw dislocation density ($\times 10^8$ cm$^{-2}$) | 2.3          | 2.5             |
| Edge dislocation density ($\times 10^8$ cm$^{-2}$)  | 9.4          | 8.1             |

Fig. 2. (Color online) Overviews and Nomarski images of both an as-separated and a reused SCAM substrates.

Fig. 3. (Color online) AFM image of a reused SCAM surface.

Fig. 4. (Color online) XRC profiles of symmetric 0009 reflections for a reused SCAM substrate, as-separated one, and a new one.

Fig. 5. (Color online) AFM images of MOVPE-grown GaN films grown on (a) a new SCAM substrate and (b) a reused one.
layer by cleavage. By cleaving along the $c$-plane, the atomically flat surface was successfully obtained. The crystalline quality of the GaN film grown on the reused SCAM substrate was comparable with that of the new one.

For the reuse of a SCAM substrate, it is necessary to know the thickness removed from a SCAM substrate after the natural separation of a GaN film from an SCAM substrate. In this natural separation, a several-micrometer-thick SCAM layer has been reported to be removed. For the reuse, about a 160-μm thick SCAM layer was removed by the cleavage of an as-separated SCAM substrate. The reason why this large thickness was removed is that the cleavage has not yet been controlled in this demonstration. For the effectively repeatable usage, the thickness of a nitrided SCAM layer has to be made clear. To evaluate the depth of a nitrided layer, confocal Raman spectroscopy was performed for a SCAM substrate annealed with ammonia in the MOVPE reactor. The excitation source was an Ar$^+$ ion laser with an emission wavelength of 514.5 nm. Figure 8 shows the Raman spectra of an annealed SCAM substrate and a new one. For a nitrided SCAM substrate, a Raman peak was observed near 680 cm$^{-1}$, which was not observed in a new SCAM substrate. This Raman peak is considered to originate from ScN. This Raman peak was observed to be about 30 μm from the surface. This result means the surface of an as-separated SCAM substrate has to be removed by several tens of micrometers for the reuse of a SCAM substrate.

4. Conclusions

It has been reported that a thick GaN epitaxial film grown on an SCAM substrate naturally separated from a SCAM substrate during the cooling down process in HVPE growth. The SCAM substrate reuse necessary for cost reduction in the fabrication of free-standing GaN wafers was attempted. On the surface of an as-separated SCAM substrate, a nitrided layer was formed and there are many high steps at the surface. It was removed by cleaving a substrate with a razor blade and the fresh surface was formed. On this substrate, a GaN film was grown and its crystalline quality was almost same as a GaN film grown on a new SCAM substrate. This result means that a SCAM substrate can be reused many times by controlling the cleaving layer.

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