Plasma-assisted polishing of gallium nitride to obtain a pit-free and atomically flat surface

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Plasma-assisted polishing (PAP), which combines plasma modification and soft abrasive polishing, was used to flatten GaN. After the irradiation of CF_4 plasma, GaN was modified to GaF_3 , greatly decreasing its surface hardness. The modified layer was removed by polishing using a CeO_2 grindstone for surface flattening. It was revealed that while many pits were generated in conventional CMP using SiO_2 or CeO_2 slurry, which deteriorated the surface integrity and roughness of GaN, a pit-free and atomically flat GaN surface with a Sq roughness of 0.1 nm order was obtained by the application of PAP, which is a dry polishing process.

Polishing, Single crystal, Surface integrity

1. Background

Owing to the excellent properties of gallium nitride (GaN) such as its wide and direct-transition bandgap and high breakdown electric field, GaN is considered to be one of the most promising materials for light-emitting diodes, field-effect transistors and other high-power and high-frequency electronic devices. Usually, GaN epilayers are grown on foreign substrates such as sapphire, SiC and Si. Recently, the epitaxial growth of GaN on sapphire substrates by metal-organic chemical vapor deposition has been frequently performed [1, 2].

When GaN epilayers are used for device applications, atomically flat surfaces without subsurface damaged layers are indispensable. Similar to single-crystal SiC, GaN is chemically and mechanically stable owing to its chemical inertness and high hardness. Chemical mechanical polishing (CMP), which has been widely used as a finishing technique for Si and SiC wafers, has also been applied to GaN [3, 4]. It was reported that GaN can be polished using colloidal silica slurry. However, the material removal rate (MRR) was less than 20 nm/h, making the process very time-consuming. Another problem of CMP is the destruction of the surface integrity of the GaN epilayer. Owing to the large lattice mismatch and the difference in the thermal expansion of the GaN epilayer and sapphire substrate, many crystal defects exist in the GaN epilayer, including screw dislocations, edge dislocations and mixed dislocations. When a GaN epilayer is processed by CMP using silica slurry, many pits originating from the defects are generated. Moreover, the use of slurry is not environmentally friendly and increases the cost of CMP. Recently, it was reported that a pit-free GaN surface was obtained by an abrasive-free flattening technique [5].

For the flattening of some difficult-to-machine materials such as SiC, GaN, sapphire and diamond, we proposed a dry polishing technique named plasma-assisted polishing (PAP), which combines surface modification by atmospheric-pressure plasma irradiation with the removal of the modified layer by soft abrasive polishing [6-8]. In our previous research, PAP using CeO_2 as an abrasive was successfully used to flatten single-crystal SiC and reaction-sintered SiC ceramic. Scratch-free and damage-free surfaces were obtained. In particular in the case of single-crystal SiC, an atomically flat surface with a well-ordered step-terrace structure was generated.

In this work, PAP using a resin-bonded CeO_2 grindstone was applied to a GaN epilayer to obtain a scratch-free, pit-free and atomically flat surface. As a dry polishing process, PAP is considered to be able to resolve the problems of the conventional CMP process using slurry of a low MRR and the generation of pits.

2. Experimental setup

2.1. Plasma irradiation

Commercially available GaN epilayers with a thickness of 8 μm grown on 2 inch sapphire substrates were used in this study. All experiments were conducted on the Ga face (0001), which is the most widely used face.

Fig. 1(a) shows the experimental setup used for plasma irradiation. A mixture of helium gas with O_2 or CF_4 , which was used as the carrier gas for plasma generation, was supplied from the center of the electrode and flowed through the space between the electrode and the ceramic cover. The flow rates of He and CF_4 were measured using mass flow controllers (MFCs). A GaN specimen was set on the stage. The gap between the electrode and the GaN substrate was 1.6 mm. The diameter of the powered electrode, which was made of aluminium alloy, was 3 mm. An impedance matcher was used to maximize the transfer of power from the power source to the load. Atmospheric-pressure He-based O_2 or CF_4 plasma was generated by applying a 13.56 MHz radio frequency (RF) power between the electrode and the stage.

2.2. Soft abrasive polishing

After the substrate was irradiated by CF_4 plasma, the modified substrate surface was polished using a resin-bonded CeO_2 grindstone (ϕ 5.1 mm, thickness: 1 mm). The average particle size of the CeO_2 abrasive was 1.2 μm . Fig. 1(b) shows the experimental setup used for abrasive polishing. The grindstone was fixed below the rotary spindle. With the scanning of the X-Y table, the GaN substrate was polished by the CeO_2 grindstone through the application of a constant load. After polishing, the substrate was cleaned with SPM solution (H_2SO_4 (97 wt%): H_2O_2 (30 wt%) = 4:1, 10 min) to remove organic and metal contaminants and by dipping in HF (50 wt%, 10 min) to remove the adhered abrasive and other oxides.

The roughness and morphology of GaN surfaces were evaluated by atomic force microscopy (AFM) in the tapping mode. A silicon-made cantilever was used with a typical resonant frequency of 300 kHz, spring constant of 26.1 N/m and a tip curvature radius of 7 nm. The force curve bandwidth of the AFM was 0.1 Hz~5 kHz. All measurements were conducted with a scanning frequency of 2 Hz and scanning area of 2 μm ×2 μm with 256 pixel resolution.

3. Results and discussion

3.1. Conventional CMP using SiO_2 and CeO_2 slurry

Fig. 2 shows an AFM image of the epitaxial grown GaN surface used in this work. This surface was not subjected to a flattening process, thus, the step-terrace structure on this surface was very disordered. Many small pits can be observed at the dislocation sites. As shown in the cross-sectional profile, the step height was about 0.5 nm, corresponding to a two-bilayer step-terrace structure of GaN. This means that step bunching occurred in the epitaxial growth process.

The epitaxially grown GaN substrate was polished by conventional CMP using SiO_2 slurry and CeO_2 slurry under the polishing conditions shown in Table 1. SiO_2 slurry has been widely used for the CMP of semiconductor materials such as Si and SiC. Recently, the CMP of GaN using SiO_2 slurry has also been frequently performed. For comparison, GaN was also polished with CeO_2 slurry because it has been reported that CeO_2 slurry has better polishing characteristics for GaN than SiO_2 slurry [9]. Fig. 3 shows AFM images of the slurry-polished surfaces. Many enlarged pits can be observed after slurry polishing, particularly when SiO_2 slurry was used. These pits greatly affect the surface integrity and roughness. As clearly demonstrated in Fig. 3(b), these pits originate from the dislocations in GaN since they are only generated at the dislocation sites. They are also much larger than the pits on the as-grown surface, which proves that the preferential removal of dislocation sites occurred in slurry polishing.

Fig. 4 shows the probable mechanism by which large pits are generated in the slurry polishing of GaN. The SiO_2 and CeO_2 slurries used in this work are both alkaline. There are many chemicals including species such as hydroxide ions (OH^-) existing in the slurry. The dislocation sites in GaN are chemically unstable owing to the existence of stress and dangling bonds. Therefore, reactions such as etching and oxidation by chemicals in the slurry preferentially occur at these dislocation sites. Moreover, the mechanical abrasion of the abrasive promotes the preferential removal at these sites. Thus, the dislocation sites are preferentially polished, resulting in many large pits as shown in Fig. 3.

3.2. Surface modification of GaN by plasma irradiation

In the PAP of GaN, GaN is first modified by plasma irradiation. Both O_2 plasma and CF_4 plasma were examined in this work. Table 2 shows the conditions used for plasma modification. Fig. 5 shows the surface morphologies of GaN irradiated by O_2 plasma and CF_4 plasma under the same conditions. In the case of O_2 plasma irradiation, the step-terrace structure of GaN could still be observed, while that on the CF_4 -plasma-irradiated surface almost disappeared. This means that CF_4 plasma has higher efficiency than O_2 plasma for the modification of GaN. This result also coincides with the calculated Gibbs free energies of GaF_3 and Ga_2O_3 [10]. Thus, CF_4 -plasma-modified specimens were used in the subsequent experiments.

The surface composition of GaN was analyzed by X-ray photoelectron spectroscopy (XPS) before and after CF_4 plasma irradiation. As shown in Fig. 6, no signal from F1s was detected from the as-grown GaN surface, while strong peaks corresponding to GaF_3 was observed after CF_4 plasma irradiation. This means that GaN was modified to GaF_3 after irradiation by CF_4 plasma. Also, it was found that heating of the substrate was very effective to promote the surface modification of GaN. Therefore, in the following experiments, the substrate was heated to 100°C to increase the surface modification rate.

Nanoindentation tests were conducted to examine the surface hardness before and after CF_4 plasma irradiation. The maximum load in the nanoindentation tests was 0.1 mN and 100 points uniformly located on the surface were measured to calculate the average hardness. The maximum load was very small so that only the top surface was examined. A Berkovich-type indenter made of diamond was used. Fig. 7(a) shows typical load-displacement curves measured by the nanoindentation method. It was revealed that the displacements for the as-received surface and plasma-modified surface were about 10 nm and 15 nm, respectively. The surface hardnesses were calculated by the Oliver-Pharr method [11]. Fig. 7(b) shows the results of the nanoindentation tests calculated from the load-displacement curves. The error bars of measured hardnesses were considered owing to the surface non-uniformity such as step-edges and dislocation sites. It was revealed that after CF_4 plasma irradiation for 30 min, the surface hardness of GaN greatly decreased from 22.7 GPa to 13.9 GPa. This means that GaF_3 is much softer than GaN. In other words, the plasma irradiation of GaN made it easier for the surface to be polished using a soft abrasive.

3.3. Dry polishing of modified GaN using CeO_2 grindstone

Unlike conventional CMP using slurry, PAP is a dry polishing method. After GaN was modified by CF_4 plasma irradiation under the condition shown in Table 2, the modified surface was polished using a CeO_2 grindstone under the conditions shown in Table 3. Fig. 8 shows a scanning electron microscope (SEM) image of the surface of the grindstone. Many small CeO_2 grains of micrometer size can be observed. The CeO_2 grains in the grindstone are held together by resin, which is very soft, as the bonding material.

Before polishing the modified GaN surface, the as-grown GaN was polished with CeO_2 grindstone under the same conditions as before (see Table 3). It was found that the as-grown surface could hardly be polished. It was considered that CeO_2 was too soft to polish GaN. In other words, the surface modification of GaN is necessary for polishing using a soft abrasive.

Fig. 9 shows an AFM image of the GaN surface processed by plasma irradiation followed by polishing using a CeO_2 grindstone. No scratches were introduced and the step-terrace structure is very uniform. As shown in the cross-sectional profile, the step height was about 0.26 nm, corresponding to a one-bilayer step-terrace structure of GaN. This means that the step-bunched surface was atomically polished by the grindstone. Dislocations can still be observed on this polished surface, as shown in the inset figure (a) in the AFM image. However, no pits were generated at these dislocation sites. This means that a scratch-free, pit-free and atomically flat surface was obtained by PAP.

Fig. 10 shows the changes in S_q roughness of GaN surfaces processed by different polishing methods with different polishing times. All these polishing experiments were conducted on the as-received substrates. In the case of PAP, the substrate was first irradiated by CF_4 plasma under the conditions shown in Table 2. The as-received surface was rough owing to its disordered and bunched step-terrace structure. When it was polished by SiO_2 slurry, many large pits were generated, which greatly increased the surface roughness. In the case of CMP using CeO_2 slurry, although many pits were still formed on the polished surface, these pits were much smaller than those generated by SiO_2 slurry polishing. Therefore, the surface roughness was not greatly affected. In the case of PAP using a CeO_2 grindstone,

the surface roughness gradually decreased with the removal of the modified layer. After polishing for 3 h, an atomically flat surface with a Sq roughness of less than 0.1 nm was obtained.

3.4. Mechanism of plasma-assisted polishing of GaN

Fig. 11 shows the probable mechanism for the PAP of GaN. GaN is irradiated by CF_4 plasma, which results in the generation of a soft modified layer. When the modified surface is polished by a CeO_2 grindstone, only the modified layer is removed and no scratches are introduced since CeO_2 is very soft compared with GaN. Because it is a dry polishing process, preferential etching or oxidation of the dislocation sites, both of which occur in slurry polishing, does not occur in this process. Thus, no pits are generated. Finally, an atomically flat GaN surface free from scratches and pits is generated.

4. Conclusions

In this study, a comparison between conventional CMP using slurry and newly proposed PAP using a grindstone was conducted. On the basis of the experimental results, the mechanisms for the CMP and PAP of GaN were proposed.

(1) In conventional CMP, regardless of whether SiO_2 or CeO_2 slurry was used, many pits, which deteriorated the surface integrity and roughness, were generated originated from the dislocations in the GaN epilayer. It was considered that these pits were generated by the preferential etching of the dislocations by the chemicals in the slurry.

(2) In PAP, plasma modification and soft abrasive polishing are combined. CF_4 plasma irradiation efficiently softened the surface of GaN, then the modified layer (GaF_3) was removed by polishing using a CeO_2 grindstone. Finally, a scratch-free and pit-free surface with a well-ordered step-terrace structure was obtained.

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Fig. 1. Schematic images of the experimental setups: (a) plasma irradiation, (b) abrasive polishing.

Fig. 2. AFM image and the surface profile of the as-grown GaN surface (Sz: 3.65 nm, Sq: 0.28 nm).

Fig. 3. AFM images of slurry-polished GaN surfaces: (a) SiO_2 slurry (Sz: 4.04 nm, Sq: 0.43 nm), (b) CeO_2 slurry (Sz: 7.28 nm, Sq: 0.21 nm).

Fig. 4. Probable pit generation mechanism in the slurry polishing of GaN.

Fig. 5. AFM images of plasma irradiated GaN surfaces: (a) O_2 plasma, (b) CF_4 plasma.

Fig. 6. F1s spectra of GaN surfaces: (a) the as-received surface, (b) CF₄ plasma irradiated surface.

Fig. 7. Nanoindentation tests of GaN: (a) Load-displacement curves measured by the nanoindentation method, (b) Hardnesses calculated from measured data (a).

Fig. 8. SEM image of the surface of resin-bonded CeO_2 grindstone.

Fig. 9. AFM image and the surface profile of the PAP processed GaN surface (Sz: 0.67 nm, Sq: 0.08 nm). The insets figure (a) shows a typical image of dislocation site.

Fig. 10. Changes in Sq roughness of polished GaN surfaces with different polishing time.

Fig. 11. Probable mechanism of PAP applied to GaN.

Table 1 Experimental conditions of CMP using slurry.

Parameters	Conditions
Specimen	GaN epi-layer grown on sapphire
Abrasive material	SiO ₂ (ϕ 72 nm), CeO ₂ (ϕ 190 nm)
Slurry pH	SiO ₂ : 9.4, CeO ₂ : 8.5
Load	50 g
Concentration	1.0 wt%
Pad rotation speed	2000 rpm
Polishing time	3 h

Table 2 Experimental conditions of plasma irradiation.

Parameters	Conditions
Specimen	GaN epi-layer grown on sapphire
Carrier gas	He (1.0 slm)
Reactive gas	O ₂ (10 sccm) or CF ₄ (25 sccm)
Applied power	7 W
Irradiation time	30 min

Table 3 Experimental conditions of abrasive polishing.

Parameters	Conditions
Specimen	CF ₄ plasma modified GaN
Abrasive material	Resin bonded CeO ₂ (ϕ 1.2 μ m)
Load	50 g
Pad rotation speed	2000 rpm
Polishing time	3 h