

## Optimization of the plasma oxidation and abrasive polishing processes in plasma-assisted polishing for highly effective planarization of 4H-SiC

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For the finishing of difficult-to-machine materials, plasma-assisted polishing (PAP), which combines modification by water vapor plasma and polishing by a soft abrasive, was proposed. Optimization of plasma oxidation and abrasive polishing was conducted to increase the material removal rate of PAP, which was applied to 4H-SiC (0001). It was found that with a low concentration of water vapor in helium gas, the plasma oxidation rate was greatly increased. Also, because of the different oxidation rates of the four types of terrace that appear alternately in 4H-SiC, a high removal rate of the oxide was necessary to obtain a uniform step-terrace structure with atomic order.

Polishing, Single crystal, Surface integrity

### 1. Introduction

Compared with the traditional semiconductor material of silicon (Si), single-crystal silicon carbide (SiC) has many excellent properties, such as a wide band gap, high breakdown electric field, and high thermal conductivity. There are thousands of poly-types of single-crystal SiC, among which 4H-SiC is widely used in the field of high-power and high-temperature electronic devices. An atomically flat and defect-free substrate surface is crucial to realize a high-quality epitaxial layer and excellent electronic device performance. However, owing to the high hardness and chemical inertness of 4H-SiC, flattening of the substrate is very difficult, which greatly limits its application.

The conventional method of flattening 4H-SiC is mechanical polishing using diamond as an abrasive. Although the material removal rate (MRR) of this method is very high, micrometer order per hour, many scratches and considerable subsurface damage are introduced, making 4H-SiC substrates unacceptable for applications. Since mechanical polishing is not an ideal method for the flattening of 4H-SiC, some other flattening methods, in which chemical reactions are involved, have been proposed. Mechanochemical polishing (MCP) has been proposed for the damage-free polishing of 4H-SiC [1]. In this process,  $\text{Cr}_2\text{O}_3$  is used as a catalyst material for surface oxidation as well as an abrasive material for removal of the oxide. Chemical mechanical polishing (CMP) is now the most widely used finishing process for 4H-SiC substrates [2]. As a wet process, 4H-SiC can be polished by concentrated colloidal silica slurry in alkaline solution. The flattening ability of CMP is acceptable and little subsurface damage is introduced. This is the reason why CMP has been industrially used. However, the cost of CMP is very high owing to the use of slurry and other chemicals. Other flattening techniques, such as catalyst-referred etching (CARE), photochemical polishing, and electrical CMP, are under development [3, 4].

We previously proposed a polishing technique named plasma-assisted polishing (PAP), which combines atmospheric-pressure water vapor plasma irradiation and soft abrasive polishing [5, 6]. In our previous research, PAP using  $\text{CeO}_2$  abrasive was proved to be very effective for removing surface scratches and subsurface

damage on SiC substrates. Also, atomically flat SiC surfaces with a well-ordered one-bilayer step-terrace structure were obtained [5].

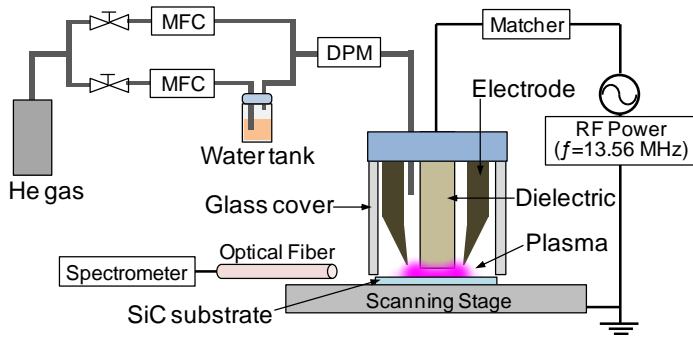
To increase the MRR of PAP and ensure the formation of the step-terrace structure, the optimization of PAP, which was applied to 4H-SiC (0001), was conducted by the following two processes: oxidation by water vapor plasma irradiation and polishing using a soft abrasive.

### 2. Concept of Plasma-Assisted Polishing

Because of the strong modification property of plasma, PAP, which combines surface modification by plasma irradiation and polishing by a soft abrasive, has been used for the flattening of difficult-to-machine materials such as SiC, GaN,  $\text{Al}_2\text{O}_3$ , diamond, and so forth. The experimental setup of PAP is shown in [5]. When PAP was used to flatten the Si faces of 4H-SiC substrates, water vapor plasma containing a high concentration of hydroxyl (OH) radicals was used for surface modification. When a SiC substrate surface is irradiated by water vapor plasma, SiC is oxidized by OH radicals generated by the water vapor plasma owing to its strong oxidation potential. It was confirmed that the main oxidation product was  $\text{SiO}_2$ , and a thin transition layer (silicon oxycarbide) was found to be located between  $\text{SiO}_2$  and SiC [6]. The hardness of the substrate surface was greatly decreased from 37.4 GPa to 4.5 GPa after plasma irradiation. This made it possible to polish the modified surfaces using a soft abrasive.

A soft oxide layer is generated by plasma irradiation, which can then be polished using a soft abrasive. The selection of the abrasive material is an important factor in the PAP process. The hardness of the abrasive material must be lower than that of the base material (SiC) so that no scratches or subsurface damage is introduced. Also, the selected abrasive material must be able to remove the oxide layer efficiently. Thus, we used  $\text{CeO}_2$  to polish the oxidized surface because of its excellent polishing characteristics for silica glasses.

In the PAP process using  $\text{CeO}_2$  as an abrasive, plasma irradiation softens the surface of the SiC substrate, and  $\text{CeO}_2$  particles preferentially remove the oxide layer. Since plasma



**Fig. 1.** Schematic image of the experimental setup used for plasma irradiation.

irradiation and abrasive polishing are simultaneously conducted, a scratch-free and damage-free SiC surface is obtained.

### 3. Experimental setup

Commercially available single-crystalline 4H-SiC wafers (on axis, n-type) were used in this study. All of the experiments were conducted on the Si face (0001), which is more commonly applied for epitaxial growth or power devices.

Fig. 1 shows the experimental setup used for plasma irradiation. He gas, which was used as the carrier gas for plasma generation, was made to flow along two paths. One path passes through a water tank to induce the flow of water molecules. The water vapor content in He was obtained from the dew point temperature measured by a dew point meter (DPM). The process gas (He containing water vapor) was introduced into the space between the electrode and the stage. The flow rate of He gas was measured using a mass flow controller (MFC). A 4H-SiC specimen was set on the stage. The gap between the electrode and the SiC substrate was 1 mm. The diameter of the powered electrode was 4 mm, and it was made of aluminium alloy. An impedance matcher was used to realize a maximum power transfer from the power source to the load. Atmospheric-pressure He-based water vapor plasma was generated by applying a 13.56 MHz radio frequency (RF) power between the electrode and the stage. The experimental parameters of plasma irradiation are shown in Table 1.

### 4. Optimization of plasma oxidation process

To realize the practical use of PAP, a higher MRR than that in commercial CMP processes is crucial. In the PAP process, when the SiC surface is irradiated by water vapor plasma, it is oxidized and a soft oxide layer is generated. Since plasma irradiation and abrasive polishing are simultaneously conducted, the oxide layer can be immediately removed by polishing. Thus, it is necessary to increase the oxidation rate of plasma ( $R_{oxi}$ ) to increase the MRR of the PAP process.

Although the oxidation mechanism of SiC by water vapor plasma has not yet been completely clarified, it is considered that this process may be affected by several factors such as the temperature of the substrate, the density of OH radicals, the pressure of the ambient, the flow rate of the process gas, and so

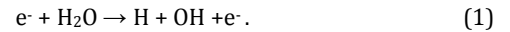
**Table 1**

Experimental parameters of plasma irradiation.

Parameters	Conditions
Specimen	n-type 4H-SiC (0001), on axis
Carrier gas	He
Flow rate	2.0 slm
RF power	25 W
Time for plasma irradiation	10 min
Time for measurement of OES	10 s

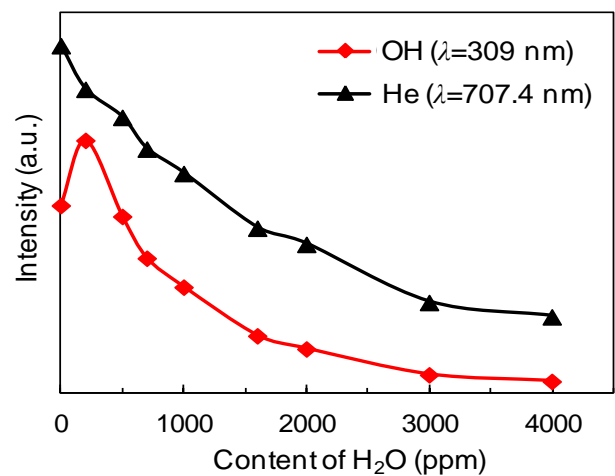
forth. Since SiC is oxidized by OH radicals, the density of OH radicals appears to be the most important factor. Therefore, in this article, we focus on the optical emission intensity from OH radicals in He-based water vapor plasma.

As previously reported, the water vapor content in the carrier gas (He or Ar) can greatly affect the density of OH radicals in the plasma [7]. Therefore, optimization of the plasma oxidation process was conducted to find the optimum water vapor content resulting in the highest  $R_{oxi}$ . Plasma irradiation was conducted with different concentrations of water vapor in the process gas. During plasma irradiation, optical emission spectra (OES) were continuously measured. Fig. 2 shows the relationship between the intensity of OH and He radicals and the water vapor content in He. In this figure, a water vapor content of 0 ppm corresponds to the lower limit of detection (LLD) of the DPM. It was found that the intensity of the head of the OH band ( $\lambda=309$  nm) was greatest when the water vapor content was approximately 200 ppm. Although there are several possible reactions for the generation of OH radicals in plasma, the most likely reaction in water vapor plasma is considered to be as follows:



OH radicals were generated by the dissociation of water due to electron impact. When the water vapor content was lower than 200 ppm, the intensity of OH radicals increased with increasing water vapor content, because the increase in water vapor content promoted the dissociation due to electron impact. On the other hand, when the water vapor content exceeded 200 ppm, the excessive supply of water vapor decreased the electron temperature ( $T_e$ ), inhibiting the reaction shown in equation (1). Also, the effective quenching of excited states of OH radicals at a high water vapor content greatly decreased their density. These factors could explain why there was an optimal water vapor content for obtaining the strongest optical emission intensity from OH radicals.

Fig. 3 shows the Si2p spectra of SiC surfaces processed by the irradiation of plasma with water vapor contents of 200 ppm and 4000 ppm. In these experiments, the stage with the SiC specimen was heated to 200 °C to increase the oxidation rate. As shown in Fig. 2, when the water vapor content was 200 ppm, the intensity of OH radicals was much higher than that for a water vapor content of 4000 ppm. Therefore, as revealed in Fig. 3, the thickness of the oxide on the surface processed by plasma oxidation with a water vapor content of 4000 ppm was very small, while the surface irradiated by plasma with a water vapor content of 200 ppm was completely oxidized within the measuring depth of X-ray photoelectron spectroscopy (XPS).



**Fig. 2.** Dependence of the OH and He optical emission intensity from water vapor plasma on the content of water vapor in He.

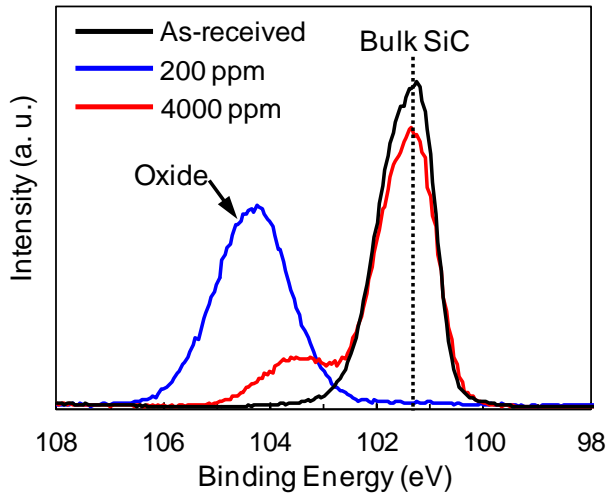


Fig. 3. Si2p spectra of SiC surfaces with different processes.

### 5. Optimization of abrasive polishing process

As mentioned in the introduction, an atomically flat 4H-SiC surface with a uniform step-terrace structure is indispensable to realize high-performance applications. For a “uniform” step-terrace structure of 4H-SiC, a one-bilayer step height, a uniform terrace width, and no residual material at the step edge are essential. However, in most of the polishing techniques applied to 4H-SiC substrates, the simultaneous realization of the above three characteristics has seldom been reported, particularly the uniform terrace width. Even in the application of PAP to 4H-SiC (0001), although a well-ordered step-terrace structure was obtained, the terrace width was not uniform. Usually, a step-terrace structure with four types of terrace that appear alternately is generated (two narrow terraces and two wide terraces). This type of step-terrace structure is called the a-b-a\*-b\* type. In the case of CMP or another flattening process [3], step-terrace structures with alternating narrow and wide terrace pairs (a-b type) can be found. In this study, optimization of the polishing process of SiC was conducted to clarify the removal mechanism of Si-C bilayers in oxidation-assisted abrasive polishing.

Consistent with its name, there are four Si-C bilayers in one unit cell of 4H-SiC crystal as shown in Fig. 4. In all the above-mentioned techniques, chemical reactions occur during the removal of the SiC surface. We consider that these periodic step-terrace structures with different terrace widths result from the different reaction rates of the four Si-C bilayers in a unit cell of 4H-SiC. It has been reported that there are two types of terrace (4H1 and 4H2) existing in 4H-SiC depending on the physical relationship with the bilayers below [8, 9]. Also, taking the number of dangling bonds (DBs) of C atoms at the step edge into consideration, it has been found that there are two step pairs in one unit of 4H-SiC. In one step pair, there are two dangling bonds for each C atom at the terrace edge (4H1 and 4H2), while in the neighbouring step pair there is only one dangling bond for each C atom at the terrace edge (4H1\* and 4H2\*) as shown in Fig. 4. In 4H1-4H2 and 4H1\*-4H2\*, the extra amounts of energy required for the deposition of one new Si-C bilayer are different according to the results of first-principles calculations [8, 9]. Correspondingly, these two terraces in a step pair should have different oxidation rates in the oxidation process. Also, the number of dangling bonds at the step edge of neighboring step pairs is different. Therefore, the oxidation rates of neighboring step pairs are also different. We conclude that the oxidation rates of these four types of Si-C bilayer in a unit cell of 4H-SiC (4H1, 4H2, 4H1\*, and 4H2\*) are different.

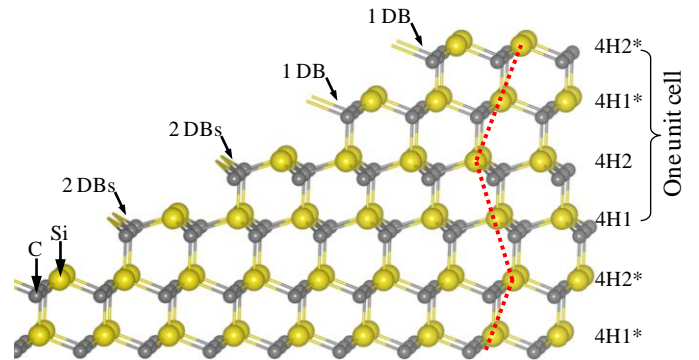


Fig. 4. Schematic image of terraces on 4H-SiC (0001) surfaces viewed from the [11-20] direction.

In the oxidation-assisted polishing of 4H-SiC substrates such as by CMP and PAP, not only the oxidation process but also the polishing process should be taken into consideration. Since the oxidation rates of the four Si-C bilayers in a unit cell were different, the oxidation process preferentially generates different step widths in a unit cell. On the other hand, the mechanical polishing process preferentially generates a uniform step width. On the basis of the above analysis, we considered that the three types of step-terrace structure, a-a, a-b, and a-b-a\*-b\*, result from the interaction between the oxidation process and the mechanical removal process.

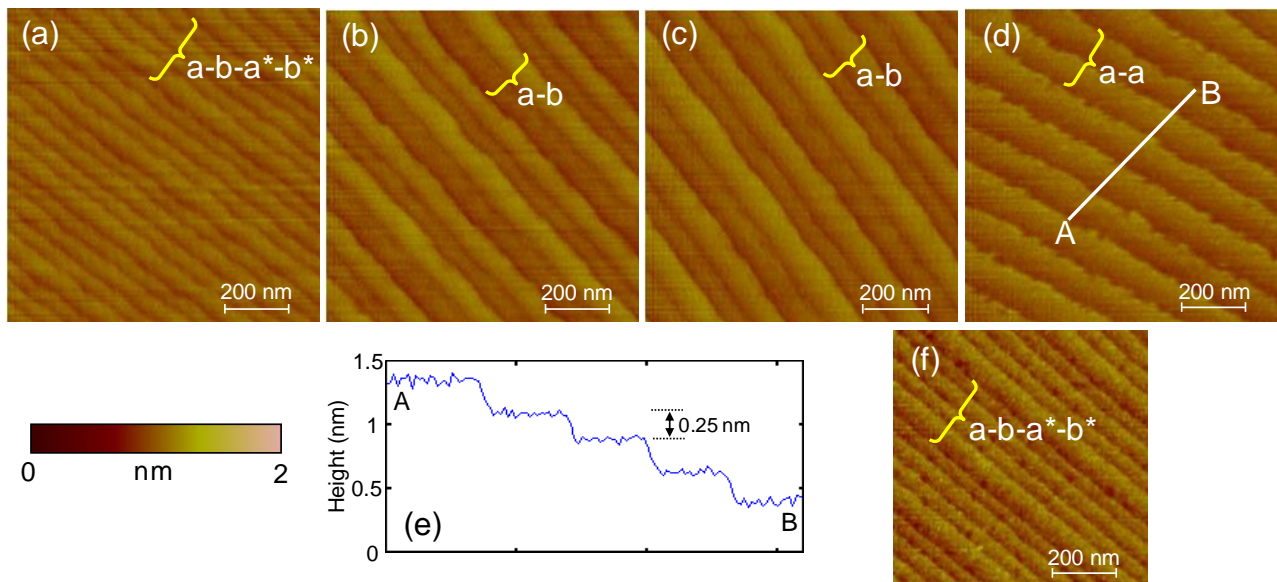
To prove the above mechanism, we polished SiC (0001) using CeO<sub>2</sub> slurry with different rotation speeds of the polishing pad. In this study, we did not perform a preliminary oxidation process. This was because it has been experimentally confirmed that SiC can be polished by CeO<sub>2</sub> slurry through its reaction with SiC. This means that a chemical reaction and mechanical polishing were both employed in this polishing process using CeO<sub>2</sub> slurry. Table 2 shows the experimental parameters for the polishing of SiC substrates using CeO<sub>2</sub> slurry. To ensure that each SiC surface in CeO<sub>2</sub> slurry was oxidized under the same conditions, the pressure and slurry concentration were fixed in these experiments. According to Preston’s law, the material removal rate of polishing can be linearly increased by increasing the rotation speed of the polishing pad. Therefore, polishing experiments with the rotation speed of the polishing pad increased from 500 rpm to 2000 rpm were conducted.

In Fig. 5, atomic force microscopy (AFM) images of SiC substrate surfaces processed by CeO<sub>2</sub> slurry polishing with different rotation speeds of the polishing pad are presented. When the rotation speed was 500 rpm, the removal rate by polishing ( $R_{pol}$ ) was very low. In this case, the mechanical removal of Si-C bilayers was very limited and only the oxide layer was removed by slurry polishing. The four types of Si-C bilayers have different oxidation rates, so after the oxide layer was removed by polishing, the terrace widths in each unit cell were different. This was why the a-b-a\*-b\* type step-terrace structure was generated as shown in Fig. 5 (a). When the rotation speed of the polishing pad was increased to 1000 rpm and 1500 rpm,  $R_{pol}$  was also increased and became comparable with  $R_{oxi}$ . In such cases, after the oxide layer was removed, because of the preferential mechanical removal of the wide terraces, the a-b-a\*-b\* type step-

Table 2

Experimental parameters of polishing using CeO<sub>2</sub> slurry.

Parameters	Conditions
Specimen	n-type 4H-SiC (0001), on axis
Load	50 g
Abrasive material	CeO <sub>2</sub> ( $\phi$ 190 nm)
Size of the polishing pad	$\phi$ 10 mm
Slurry concentration	1.0 wt%
Polishing time	3 h
Rotation speed	500, 1000, 1500, 2000 rpm



**Fig. 5.** (a-d): AFM images of the SiC surfaces processed by CeO<sub>2</sub> abrasive polishing for 3 h with different rotation speed of the polishing pad. (a) 500 rpm, (b) 1000 rpm, (c) 1500 rpm, (d) 2000 rpm. (e): Cross-sectional cut along the line between A and B in (d). (f): AFM image of a SiC surface processed by CeO<sub>2</sub> abrasive polishing for 12 h with 500 rpm of the rotation speed of the polishing pad.

terrace structure was changed to the a-b type as shown in Figs. 5 (b) and (c). When the rotation speed was increased to 2000 rpm, it is considered that the  $R_{pol}$  was higher than  $R_{oxi}$ . In such a case, the mechanical removal of the oxide layer and Si-C bilayers in the polishing process was faster than that due to the oxidation process. Since the mechanical removal of the Si-C bilayers was uniform, a step-terrace structure with a uniform terrace width was generated. Fig. 5 (d) shows the surface polished by CeO<sub>2</sub> slurry with a rotation speed of 2000 rpm, for which the generation of a uniform step-terrace structure (a-a type) was confirmed.

The step height of the step-terrace structure generated by CeO<sub>2</sub> slurry polishing was also measured. Fig. 5 (e) shows a cross section taken along the line between A and B in Fig. 5 (d) with the slope corrected. A very uniform step height of 0.25 nm was obtained, which corresponds to a single 4H-SiC bilayer.

The dependence of the periodicity of the step terrace of 4H-SiC on the rotation speed of the polishing pad has been experimentally confirmed and replicated. However, the removal volume in each of the above experiments was different. Thus, an experiment in which the effect of the removal volume was excluded was conducted. Fig. 5 (f) shows a surface processed by CeO<sub>2</sub> slurry polishing for 12 h with a rotation speed of the polishing pad of 500 rpm. The removal volume of this surface was three times larger than that of the surface shown in Fig. 5 (a) while the rotation speed of the polishing pad was the same. Despite the difference in the removal volume, the step-terrace structure was almost the same. This result also proved that the different periodic step-terrace structures were generated as a consequence of the interaction between the oxidation process and the polishing process rather than the removal volume.

In the PAP process, plasma oxidation and abrasive polishing were also simultaneously conducted. The oxidation rate of SiC by water vapor plasma was much higher than that in CeO<sub>2</sub> slurry. In another words,  $R_{oxi}$  for PAP was much higher than  $R_{pol}$ . Therefore, the surfaces processed by PAP have a step-terrace structure of the a-b-a\*-b\* type. To obtain a uniform step width, it is essential to increase  $R_{pol}$  in the PAP process, such by increasing the rotation speed, polishing pressure, or abrasive particle size. Also, abrasive polishing without plasma irradiation after the PAP process is also considered to be very effective for changing the step-terrace structure from the a-b-a\*-b\* type to the uniform a-a type.

## 6. Conclusions

In this study, optimization of the plasma oxidation and abrasive polishing of 4H-SiC (0001) was conducted.

(1) In the plasma oxidation process, the density of OH radicals, which are the dominant oxide species, was greatly affected by the content of water vapor in the carrier gas. The strongest optical emission intensity from OH radicals was obtained when the water vapor content in He was approximately 200 ppm.

(2) Different periodic step-terrace structures of 4H-SiC were generated as a result of the interaction between the oxidation process and the polishing process. A one-bilayer step-terrace structure with a uniform terrace width was obtained when the polishing rate was higher than the oxidation rate.

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