



Full Length Article

Atomic-scale finishing of carbon face of single crystal SiC by combination of thermal oxidation pretreatment and slurry polishing

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ABSTRACT

Single-crystal silicon carbide (4H-SiC) has a range of useful physical, mechanical and electronic properties that make it a promising material for fabrication of next-generation semiconductor devices. In this work, we report a hybrid polishing process combining thermal oxidation pretreatment and soft abrasive polishing to realize the damage-free and atomic-scale smooth finishing of the carbon face of 4H-SiC. By thermal oxidation pretreatment, the hardness of the carbon face has been reduced from 4.6 GPa to 1.7 GPa, which enables highly efficient polishing using CeO₂ slurry. For conventional CeO₂ slurry polishing without pretreatment, scratches still existed after a long polishing duration for 16 h. The probable scratch removal mechanism in CeO₂ slurry polishing has been proposed based on surface morphology changes during polishing. Whereas a scratch-free surface with well-ordered SiC atomic steps was obtained within a short polishing duration of only 3 h when polishing was conducted on a thermally oxidized surface. Our results demonstrate that hybrid polishing combining surface pretreatment and soft abrasive polishing is a promising approach to realize the damage-free and atomic-scale smooth finishing of the carbon face of 4H-SiC.

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1. Background

Single-crystal silicon carbide (SiC) has a wide bandgap, a high hardness and strong chemical inertness, thus, it has been widely considered to be one of the most promising next-generation semiconductor materials for fabrication of power devices working with a high voltage, a high frequency and under high temperature conditions [1,2]. Among the thousand polytypes of single-crystal SiC, 4H-SiC is the most widely utilized. 4H-SiC wafers are usually sliced from a SiC ingot. Prior device fabrication, grinding, rough polishing and fine finishing are required to correct the wafer thickness, minimize the subsurface damage (SSD) layer and decrease the surface roughness. Final finishing, which determines the surface quality of the wafer, is a critical step in the semiconductor device manufacturing process. As devices will be fabricated on the wafer, the surface quality including the integrity, the flatness, the SSD layer and the roughness will greatly affect the device performance. However, finishing of 4H-SiC with good surface quality is challenging

owing to its high hardness and chemical inertness. 4H-SiC has a very high hardness which is only lower than that of diamond and cubic boron nitride (cBN), meanwhile, it rarely reacts with common acid or alkaline solutions, making it difficult to obtain a damage-free 4H-SiC surface using existed finishing techniques.

Hybrid polishing combining surface modification and soft abrasive polishing is a promising approach to polish 4H-SiC without forming scratch or SSD. Surface modification softens the substrate surface and enables polishing using soft abrasives. As the modified layer can be removed by polishing using soft abrasive, smaller surface roughness can be achieved. Meanwhile, as the abrasives are softer than SiC, only the modified layer is removed and SSD is not formed. Based on the efficient combination of surface modification and soft abrasive polishing, damage-free and highly efficient finishing of 4H-SiC is expected to be realized. In recent years, several hybrid polishing processes utilizing different modification methods have been developed for damage-free finishing of 4H-SiC [3–6]. Chemical mechanical polishing (CMP) is widely used in semiconductor industry as the final finishing process for semiconductor substrates [7]. For CMP of 4H-SiC, alkaline colloidal silica slurry is used. SiC is modified by the chemicals in slurry and then the modified layer is removed by abrasion with the silica abrasives. As the material removal rate (MRR) of CMP is limited by the surface

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modification process, a lot of effort have been made to improve the MRR [8,9]. Kurokawa et al. reported that the addition of H_2O_2 and KMnO_4 into slurry had the effect for increase in MRR [8]. Pan et al. developed some catalyst-added slurries to strengthen the surface modification in CMP [9]. Even though a damage-free and ultrasmooth surface can be obtained by CMP, the low MRR of CMP and the high polishing costs become challenges. Electro-chemical mechanical polishing (ECMP), which is combined of anodizing and CMP, has been applied to SiC to realize the highly efficient surface finishing [6,10]. It has been reported that a high oxidation rate of $7 \mu\text{m}/\text{h}$, which is much faster than the modification rate in conventional CMP, has been obtained by anodic oxidation [10]. A hybrid dry polishing process combining modification by irradiation of atmospheric pressure water vapor plasma and polishing using soft abrasives has been developed for finishing of some hard and brittle materials [11]. This polishing process has been successfully applied to 4H-SiC, chemical vapor deposition SiC and GaN [12–14]. It has been reported that an atomically flat silicon face of 4H-SiC with a well-ordered step-terrace structure was obtained using the plasma-assisted hybrid polishing process [12]. In addition, some novel polishing processes like catalyst referred etching [15], UV-irradiation assisted polishing [16], and laser-assisted CMP [17] and so forth have also been proposed and are still under development.

Although there are several alternative polishing techniques for 4H-SiC, all of these techniques are targeting on the silicon face (Si-face). The Si-face of 4H-SiC is generally used for device applications, however, more and more interest has been focused on the carbon face (C-face). In recent years, devices fabricated on C-face have been widely reported [18–21]. C-face has several advantages over Si-face. First, C-face can be used for bulk growth of 4H-SiC crystals to effectively avoid the switching of polytypes to 6H-SiC which usually takes place in bulk growth on Si-face; second, the inversion channel mobility on a C-face has been proved higher than that on a Si-face; third, the dislocations in SiC has been found not correlated with the reliability of the metal-oxide-semiconductor field-effect transistors fabricated on the C-face. Owing to the hexagonal crystal structure of 4H-SiC, the Si-face and the C-face have different electronic properties. Even though the previously introduced polishing techniques have demonstrated their excellent polishing performance for the Si-face of 4H-SiC, the applicable finishing process for the C-face with an epi-ready level has not been established yet.

In this work, a hybrid polishing process combining thermal oxidation pretreatment and soft abrasive polishing is developed for atomic-scale smooth finishing of the C-face of 4H-SiC. Thermal oxidation pretreatment softens the C-face and enables highly efficient polishing using soft abrasives. Then, soft abrasive polishing removes the oxide layer and realizes obtaining of a smooth surface. Abrasive material selection is first conducted among diamond, Al_2O_3 , SiO_2 and CeO_2 . Then, results and mechanisms on slurry polishing without and with thermal oxidation pretreatment are presented respectively, demonstrating the effectiveness of the proposed hybrid polishing process.

2. Experimental details

2.1. 4H-SiC substrate

4H-SiC substrates (On-axis, n-type) supplied by TanKeBlue Co. Ltd. were used in this research. On the basis of dimensional analysis of SiC, it has been understood that if the step-terrace structure of an on-axis 4H-SiC substrate can be generated by polishing, it can be observed using atomic force microscopy (AFM). The as-received Si-face was processed by CMP while the C-face was processed by polishing using diamond slurry. Fig. 1 shows the scanning white light interferometer (SWLI; ZYGO NewView 200) and AFM (Dig-

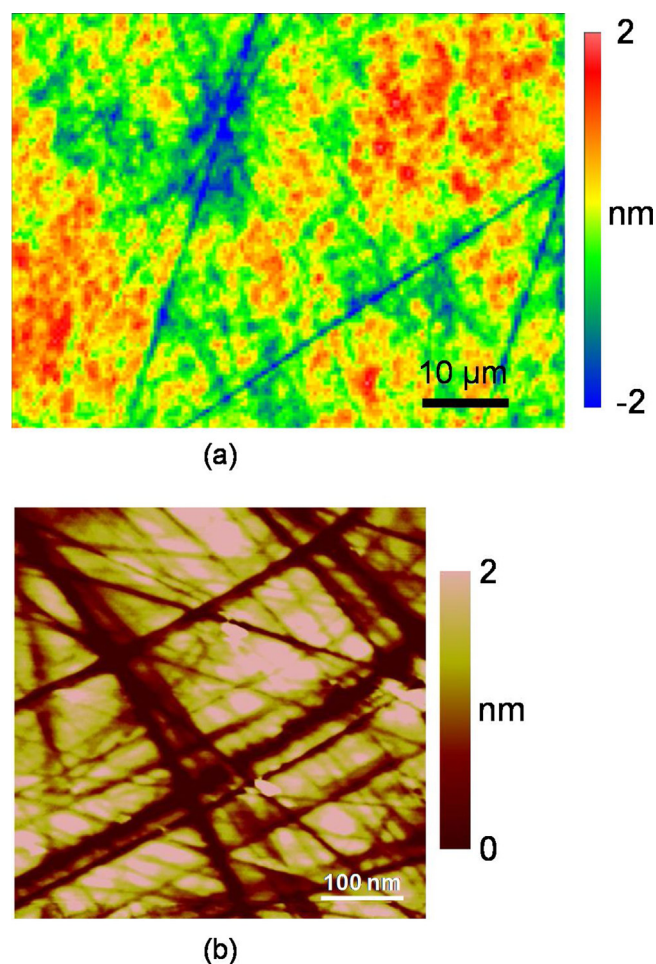


Fig. 1. SWLI and AFM images of as-received C-face of 4H-SiC. (a) SWLI image (S_z : 4.89 nm, S_q : 0.64 nm). (b) AFM image (S_z : 8.34 nm, S_q : 0.83 nm).

ital Instruments D3100) images of the as-received C-face. Many scratches were formed on the surface. Even though the surface has been observed using AFM in a small area as shown in Fig. 1(b), the atomic steps of SiC can't be observed as the surface is fully covered by scratches introduced by diamond abrasives. As diamond is much harder than 4H-SiC, it is assumed that a subsurface damage (SSD) layer was also formed beneath the scratched surface. In this research, soft abrasive polishing experiments without and with thermal oxidation pretreatment were both conducted on the C-face with scratches as shown in Fig. 1.

2.2. Slurry polishing

Polishing of 4H-SiC by commercially available slurries was conducted using the experimental setup shown in Fig. 2. Polishing was carried out in a plastic container with slurry inside. A suede type polishing pad (NP178, FILWEL Co. Ltd.), which has been widely used for final finishing of optical components, was pasted beneath the rotary spindle. In each polishing experiment, a new polishing pad was used and the slurry was replaced.

In order to select the suitable abrasive material for 4H-SiC, slurry polishing experiments using different abrasive materials: diamond, Al_2O_3 , SiO_2 and CeO_2 were conducted. To evaluate their polishing characteristics, a scratch-free surface is required to be used as the reference. Currently, 4H-SiC substrates with scratch-free C-faces are not commercially available, whereas the commercially CMP-processed Si-faces are smooth and free of scratch. Thus, the Si-face was used as the reference surface for abrasive material selection,

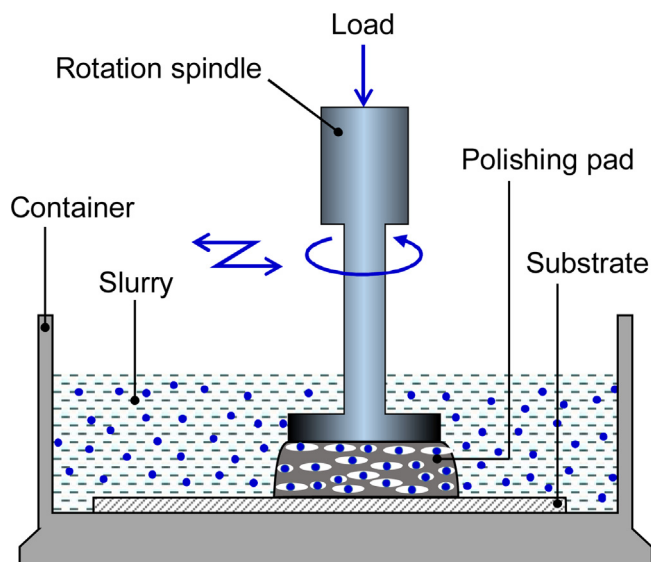


Fig. 2. Schematic of experimental setup used for slurry polishing.

even though it is more convincing to compare their polishing performances on the C-face which is the target face of this research.

With the appropriate abrasive material selected, slurry polishing experiments of C-face were conducted. Along with the increasing of the polishing duration, the change of surface morphology was investigated using AFM to study the scratch removal mechanism in the conventional slurry polishing process.

2.3. Thermal oxidation-combined slurry polishing

Slurry polishing of a thermally oxidized C-face was conducted using the same experimental setup shown in Fig. 2. Thermal oxidation pretreatment was performed using a miniature lamp annealer (MILA5000, ULVAC Technologies, Inc.). Dry oxygen with a flow rate of 22.4 sccm was used as the reactive gas for thermal oxidation and the oxidation temperature was 1100 °C. The thickness of the oxide layer was measured using a spectroscopic ellipsometer (SOPRA GES-5 M) with an operation wavelength range of 300–900 nm. The surface hardness before and after thermal oxidation was measured using a nanoindentation tester (ENT-2100, ELIONIX Inc.). The maximum load in nanoindentation tests was set to 0.1 mN to only measure the hardness of the top surface layer and 9 points located on the substrate surface were measured to calculate the average hardness.

The change of surface roughness and the generation of atomic steps of SiC were confirmed by observation using SWLI and AFM. Before surface characterization, to remove the organic contaminants on the substrate, cleaning in a sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) mixture (SPM) was conducted for 10 min followed by cleaning in pure water for 10 min. The concentration of the SPM solution was H_2SO_4 (97 wt%): H_2O_2 (30 wt%) = 4:1.

3. Results and discussion

3.1. Abrasive material selection for 4H-SiC

To initiate a damage-free and scratch-free polishing process for 4H-SiC, one critical parameter is the abrasive material. In order to select the appropriate abrasive material, slurry polishing experiments using different abrasive materials including diamond, Al_2O_3 , SiO_2 and CeO_2 were conducted for comparison. A CMP-processed Si-face was used as the reference. Table 1 shows the polishing

Table 1
Polishing conditions.

Substrate	4H-SiC (On axis, 0001)
Load	50 g
Polishing pad	Swede type (ϕ 10 mm)
Pad rotation speed	2000 rpm
Slurry concentration	Diamond: 0.4 wt%, Al_2O_3 : 10 wt% SiO_2 : 1 wt%, CeO_2 : 1 wt%
Grain size	Diamond: 100 nm, Al_2O_3 : 100 nm SiO_2 : 72 nm, CeO_2 : 190 nm
Duration	3 h

conditions. Shown in Fig. 3(a) is AFM image of the as-received CMP-processed Si-face. It is free of scratch and the step-terrace structure of SiC can be observed. Polishing experiments were carried out on CMP-processed Si-faces using diamond, Al_2O_3 , SiO_2 and CeO_2 slurries and the polished surfaces were observed using an AFM.

Diamond slurry has been widely used for rough polishing of SiC substrates as well as many other hard and brittle materials. Compared with the original surface, it has been found that many scratches were formed owing to the high hardness of diamond as shown in Fig. 3(b). When Al_2O_3 was used, the polished surface was also very rough as shown in Fig. 3(c). Scratches were also formed and it was found that the formed scratches were discontinuous. The hardness of Al_2O_3 is comparable with that of 4H-SiC. Therefore, it is assumed that scratches were formed only in some over-stressed sites during polishing making the scratches discontinuous. Very similar results have been observed in plasma-assisted polishing of 4H-SiC using an Al_2O_3 -coated polishing film [22], which also supports the assumption. On the basis of these results, it is concluded that both diamond and Al_2O_3 slurry are not suitable for final finishing of 4H-SiC.

SiO_2 slurry has been commercially used in CMP of 4H-SiC based on the following mechanism: the substrate surface is modified by the chemicals in SiO_2 slurry and the modified layer is mechanically removed by abrasion. The hardness of SiO_2 is much lower than that of SiC, thus, no scratches will be formed and an ultra-smooth surface can be obtained as widely reported [9]. Fig. 3(d) shows the SiC surface polished by SiO_2 slurry. A scratch-free and ultra-smooth surface with a S_q roughness of 0.15 nm has been obtained. Different with the step-terrace structure on the as-received Si-face, a step-terrace structure with four types of terrace that appear alternately is formed in our previous experiments even though the step edges are very rough. Consistent with its name, there are four Si-C bilayers in one unit cell of 4H-SiC single crystal. Based on the analysis of the physical relationship between these four bilayers and the different number of dangling bonds at the bilayer step edge, it has been found that these four types of Si-C terrace in a unit cell of 4H-SiC have different stability, meaning that they have different modification rates in slurry polishing [23–25]. Thus, the periodicity of the step-terrace structure of 4H-SiC generated by slurry polishing varies according to the change of the balance between surface modification and mechanical abrasion [26]. The step-terrace structure shown in Fig. 3(d) indicates that surface modification was dominant in the polishing experiment using SiO_2 slurry [26].

The polishing performance of CeO_2 slurry, which is also a soft abrasive material, was also investigated. CeO_2 slurry is widely used to polish glass substrates [27,28]. CMP of glass substrates with high polishing efficiency and good surface quality has been achieved. The removal mechanism of CMP of glass using CeO_2 has been widely studied. Different with SiO_2 -CMP in which the substrate is modified by the chemicals in slurry, CeO_2 itself can be used as a tribo-catalyst which could directly react with the substrate [29–31]. CeO_2 was tried in this study because excellent polishing characteristics have been demonstrated in plasma-assisted polishing of 4H-SiC using CeO_2 abrasives [12]. Fig. 3(e) shows the AFM image of the surface

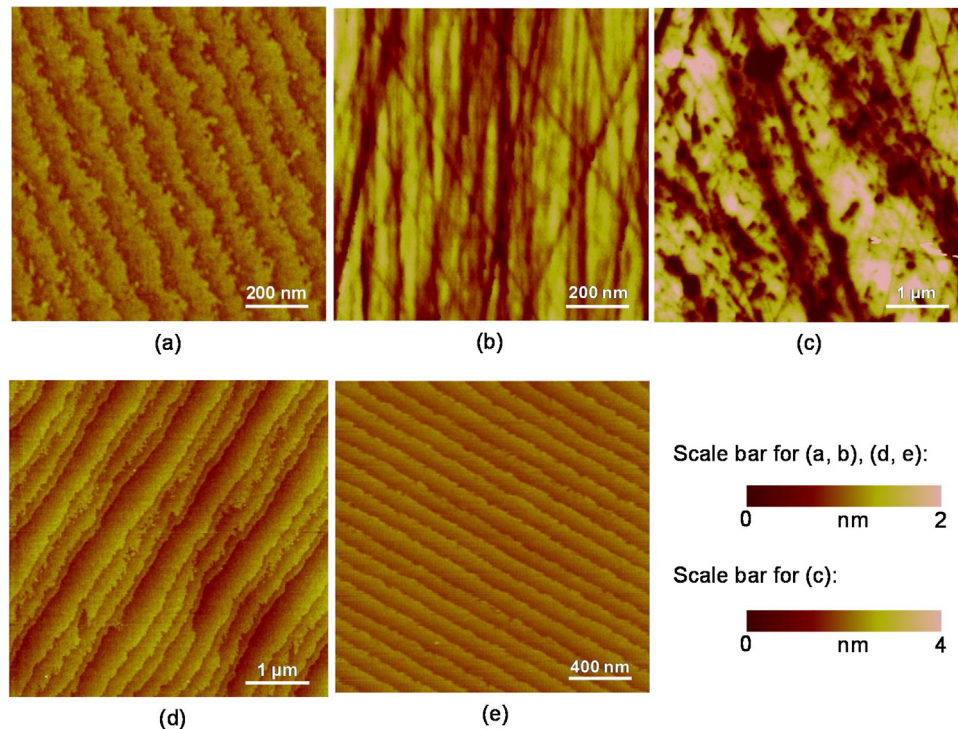


Fig. 3. AFM images of slurry-processed SiC (Si-face). (a) As-received (S_z : 0.82 nm, S_q : 0.12 nm). (b) Diamond slurry (S_z : 2.46 nm, S_q : 0.30 nm). (c) Al_2O_3 slurry (S_z : 30.63 nm, S_q : 1.28 nm). (d) SiO_2 (S_z : 2.01 nm, S_q : 0.15 nm). (e) CeO_2 (S_z : 0.68 nm, S_q : 0.08 nm).

polished by CeO_2 slurry. An atomically smooth surface with well-ordered step-terrace structure was obtained. While the atomic step edges obtained by SiO_2 slurry polishing was very rough, the atomic steps obtained by CeO_2 slurry polishing have very smooth and straight edges. The step-terrace structure has a uniform terrace width, indicating that mechanical factors were dominant in the polishing process [26].

Although SiO_2 is the most widely used slurry for polishing of SiC, our results demonstrate that CeO_2 slurry has the superior polishing performance compared with SiO_2 slurry. Meanwhile, in the proposed hybrid polishing process combining thermal oxidation pretreatment and slurry polishing, the major removal material is the oxide layer (SiO_2) for which CeO_2 is the most suitable abrasive material. Hence, in the following polishing experiments, CeO_2 slurry was used.

3.2. CeO_2 slurry polishing of C-face

For comparison with the proposed thermal oxidation-combined slurry polishing process, conventional CeO_2 slurry polishing without thermal oxidation pretreatment was conducted on the C-face. The polishing conditions were the same with those shown in Table 1. In order to study the scratch removal mechanism in CeO_2 slurry polishing, the polished surface was observed using AFM after different polishing durations and the results were shown in Fig. 4. On the as-received surface, there are many small scratches introduced by diamond slurry polishing as shown in Fig. 4(a). However, these scratches are shallow with a depth less than 5 nm as can be observed from the surface cross-sectional profile.

Fig. 4(b–f) shows the AFM images and diagonal cross sectional profiles of the polished C-face with different polishing durations. With the increase of the polishing duration, morphology of the scratches significantly changed. Overall, most of the scratches on the original surface have been gradually removed and only few discontinuous scratches remained on the polished surface after a long polishing duration for 15 h as shown in Fig. 4(e). However,

it has been revealed that the removal mechanisms for the shallow scratches and the deep scratches are different. As shown in Fig. 4(b), after polishing for 3 h, the amount of scratch has been significantly reduced due to the removal of some shallow scratches on the original surface. Some scratches became discontinuous and were transformed to micro pits located along the scratch directions. Meanwhile, it is worth noting that the deep scratches on the original surface became wider and deeper during polishing as can be observed from the profile. Owing to the formation of micro pits and the broadened scratches, the surface roughness also greatly deteriorated. After an additional 3 h of polishing, the above mentioned phenomenon also occurred as shown in Fig. 4(c). Some scratches were further broadened while the number of micro pit reduced as some micro pits were removed. The surface roughness was deteriorated owing to the broadened scratches. After polishing for 9 h, only some scratch-transformed grooves and very limited micro pits can be observed as shown in Fig. 4(d). With a total polishing duration of 15 h, the grooves shown in Fig. 4(e) were further transformed to discontinuous scratches and some micro pits. AFM observation of a small area of $500 \text{ nm} \times 500 \text{ nm}$ was conducted on the scratch-free and pit-free area, and disordered atomic steps of SiC on the C-face were observed as shown in Fig. 4(f). Based on these results, the removal process for shallow and deep scratches has been clarified. For shallow scratches, they were first transformed to discontinuous scratches which were further transformed to micro pits and finally removed. As for deep scratches, they were first broadened and then transformed to wide and deep grooves. These grooves were further transformed to discontinuous scratches which were further transformed to micro pits and finally removed.

A probably scratch removal mechanism of the C-face in CeO_2 slurry polishing was proposed as shown in Fig. 5. It has been reported that CeO_2 , as a tribo-catalyst, could react with 4H-SiC, especially the C-face [30]. Kido et al. used CeO_2 containing grinding wheels to grind the C-face of 4H-SiC, and a very high MRR was obtained owing to the tribo-catalytic reaction [30]. Thus, in

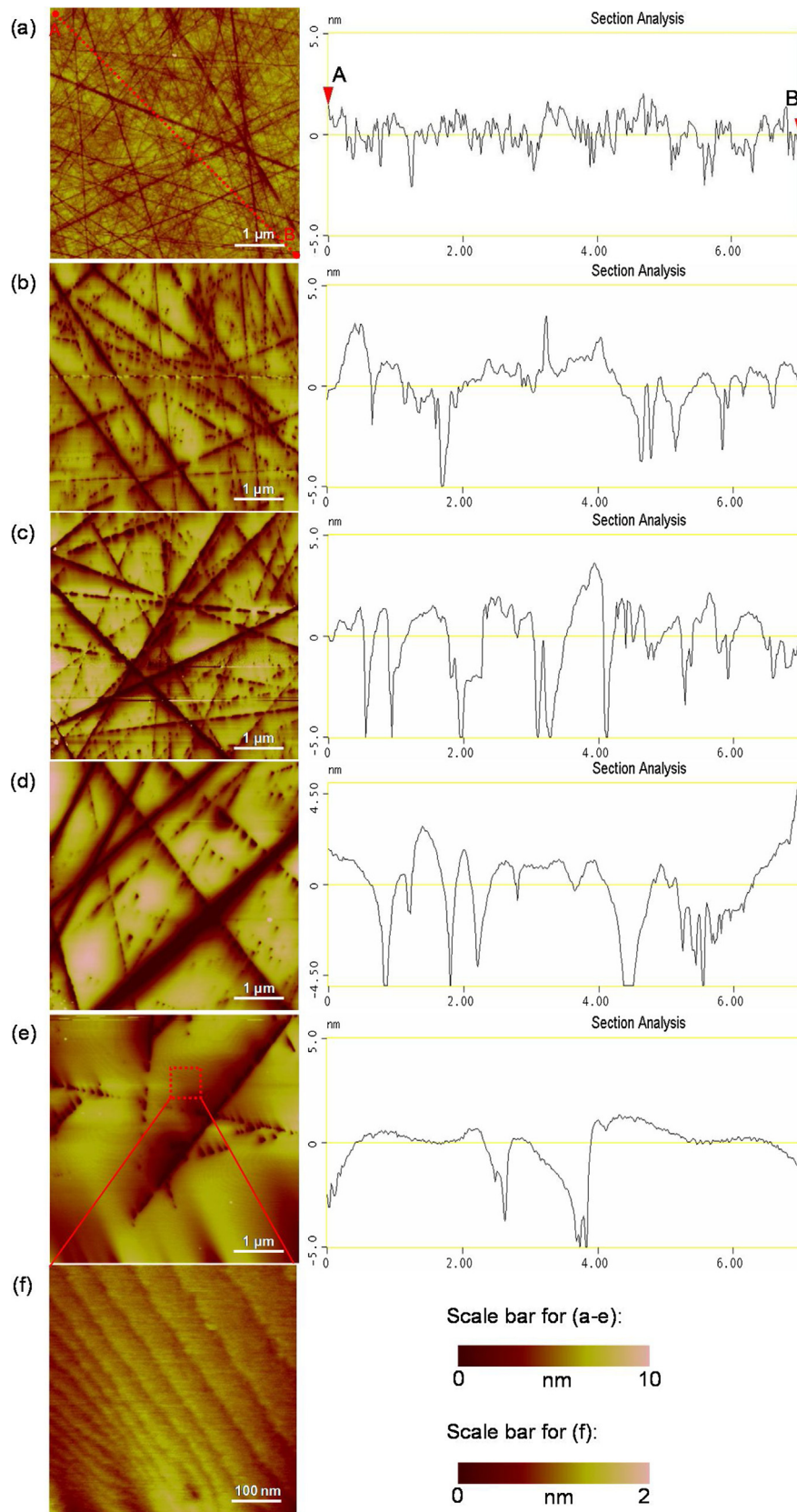


Fig. 4. AFM images and diagonal cross sectional profiles of the C-face polished by CeO₂ slurry with different polishing durations. (a) As-received surface (S_z : 21.15 nm, S_q : 1.08 nm). (b) 3 h (S_z : 29.25 nm, S_q : 1.67 nm). (c) 6 h (S_z : 59.21 nm, S_q : 2.77 nm). (d) 9 h (S_z : 35.49 nm, S_q : 3.10 nm). (e) 15 h (S_z : 17.03 nm, S_q : 1.63 nm). (f) The step-terrace structure on surface (e).

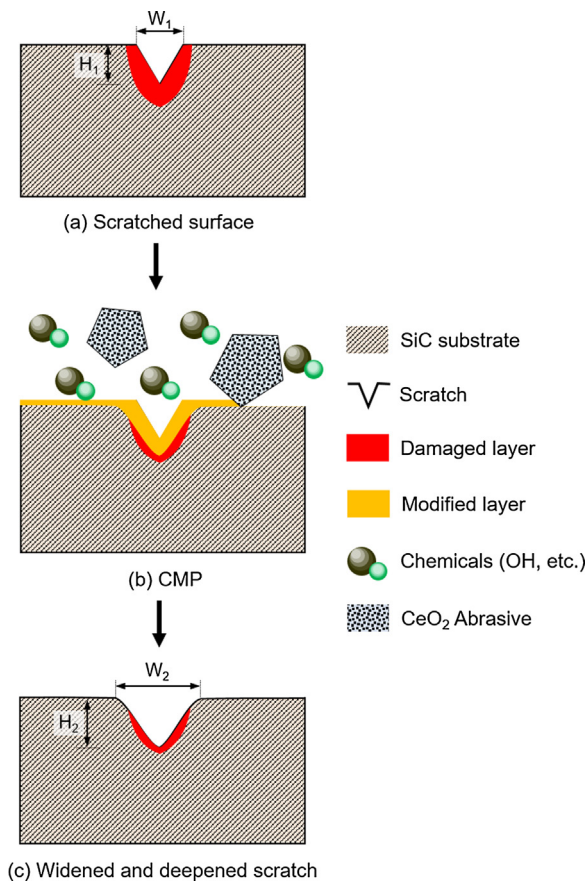


Fig. 5. Probable scratch removal mechanism in conventional CeO_2 slurry polishing without pretreatment.

CeO_2 slurry polishing of C-face, two types of surface modification can be expected: the surface modification by chemicals in the slurry and the tribo-catalytic reaction between CeO_2 and SiC. As the original surface was polished using diamond slurry, a SSD layer existed beneath the polished surface and more damage were introduced along the deep scratches as shown in Fig. 5(a). Meanwhile, these damaged areas are more easily to be modified as there are residual stress and dislocations. Thus, as shown in Fig. 5(b), the scratched areas were preferentially modified (oxidized) by CeO_2 slurry and the modified layer was removed by mechanical abrasion, resulting in the formation of grooves. This could explain why the deep scratches became wider and deeper in the early polishing stage shown in Fig. 4. As the depth of the damaged areas along scratches was not uniform, the damaged sites with large depth were transformed to micro pits during polishing. Thus, a long polishing duration was required to completely remove the surface scratches.

Based on the above results and analysis, it is concluded that conventional slurry process is not an efficient approach to achieve a scratch-free and atomically smooth C-face as a long polishing duration is required for complete scratch removal. To solve the problem of preferential removal of scratched areas in CeO_2 slurry polishing, the thermal oxidation-combined slurry polishing process was developed.

3.3. CeO_2 slurry polishing of thermally oxidized C-face

As shown in Fig. 5, the preferential removal of the scratched areas makes it a time-consuming process to completely remove the scratches by CeO_2 slurry polishing. A two-step polishing process combining thermal oxidation pretreatment and slurry polishing was developed as a promising approach to solve this problem. Fig. 6

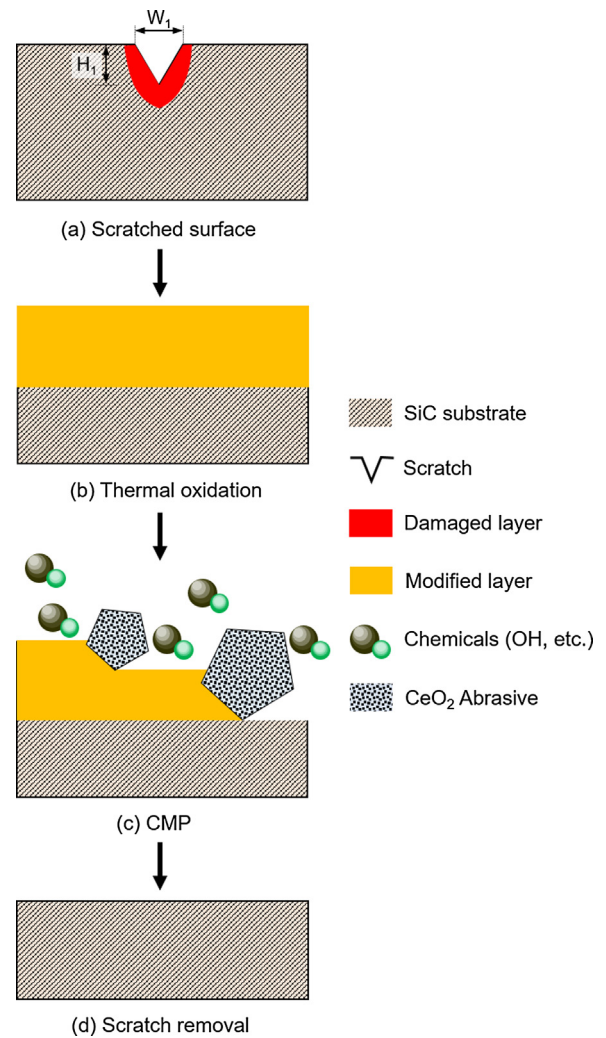


Fig. 6. Schematic of hybrid polishing combining thermal oxidation pretreatment and soft abrasive polishing.

shows the schematic of the proposed hybrid polishing process. As shown in Fig. 4(a), the scratches on the original as-ground surface are shallow and their depths are less than 5 nm. In thermal oxidation pretreatment, these scratches as well as the SSD layer will be completely oxidized as shown in Fig. 6(b). Then, in the following slurry polishing step, the oxide layer, which is softer than the bulk substrate, will be removed by abrasion with the abrasives. As the scratched areas have been completely oxidized, preferential removal of scratched areas, which is the bottleneck of the slurry polishing process limiting the reduction of polishing duration, will not occur in this hybrid polishing process. Thus, it is expected that the required polishing time can be greatly shortened compared with conventional polishing without pretreatment. After the oxide layer is completely removed by slurry polishing as shown in Fig. 6(c), a scratch-free surface is expected to be obtained as shown in Fig. 6(d). Even though there are several modification methods which can be applied to 4H-SiC, thermal oxidation is tried in this work because it has been reported that thermal oxidation is a more uniform oxidation process during which a smooth oxide-SiC interface can be formed [32].

Thermal oxidation for 4 h was conducted on a C-face of 4H-SiC. According to measurement results using an ellipsometer, an oxide layer with a thickness of about 33 nm was formed, which was considered enough to oxidize the scratched areas. Before polishing of the oxidized surface, the surface hardness before and after thermal

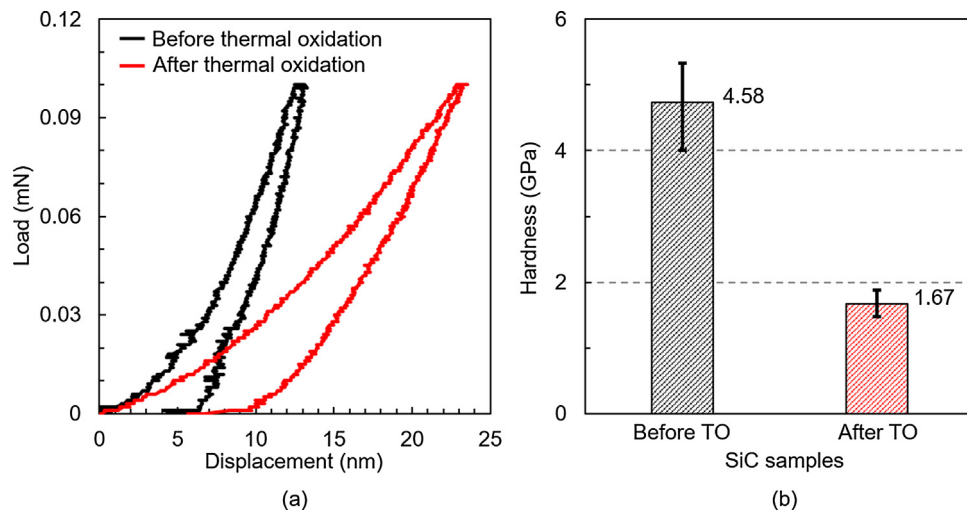


Fig. 7. Nanoindentation tests on the as-received C-face and thermally oxidized C-face. (a) Load-displacement curves. (b) Hardness calculated from the load-displacement curves.

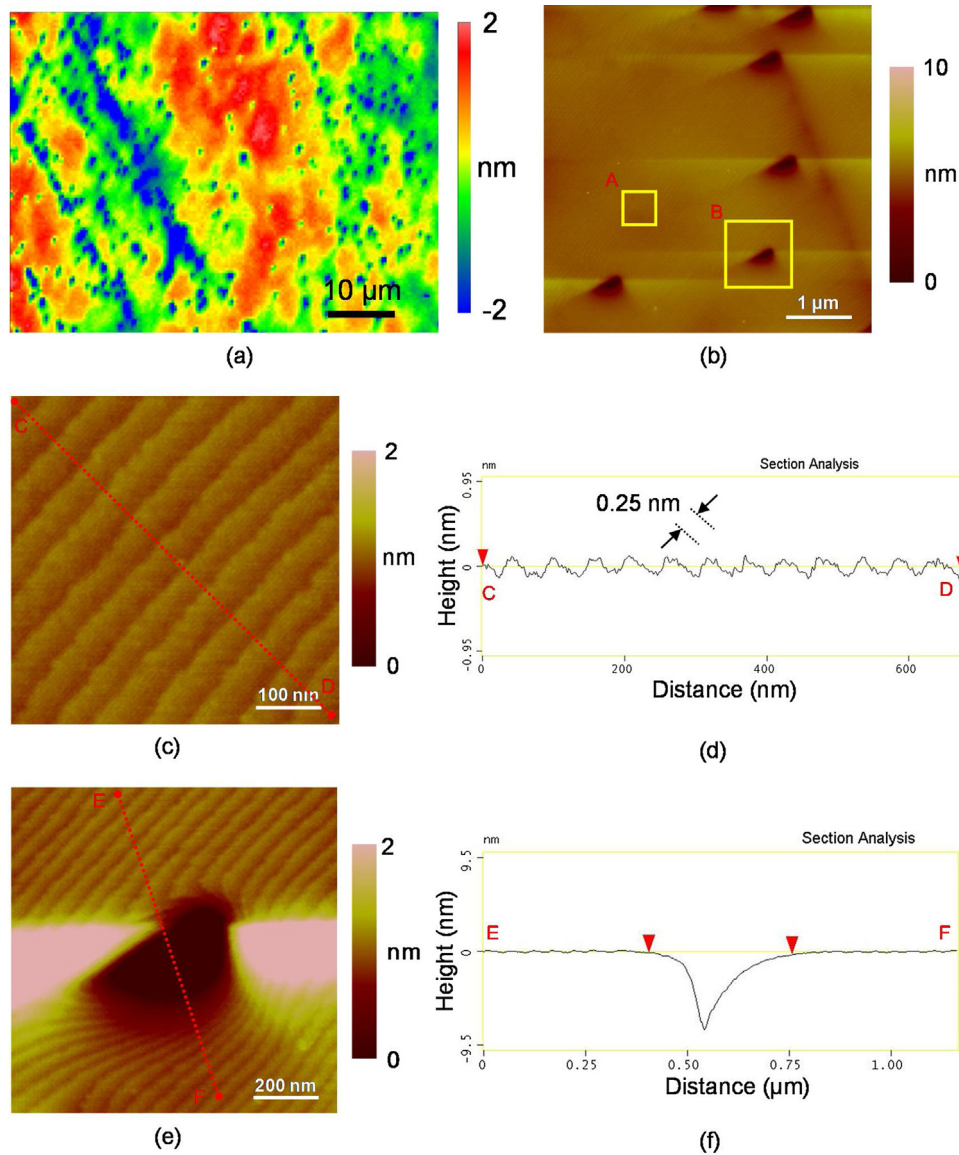


Fig. 8. SWLI and AFM images of C-face processed by thermal oxidation pretreatment (3 h) followed by polishing using CeO₂. (a) SWLI image (S_z : 16.60 nm, S_q : 0.94 nm). (b) AFM image (S_z : 25.13 nm, S_q : 0.75 nm). (c) AFM image of a pit-free area (S_z : 0.41 nm, S_q : 0.07 nm). (d) Cross-sectional profile of surface (c). (e) AFM image of a pit-contained area (S_z : 18.43 nm, S_q : 0.98 nm). (f) Cross-sectional profile of a pit.

oxidation was measured using a nanoindentation tester. Fig. 7(a) shows the load-displacement curves obtained in nanoindentation tests. It was found that the maximum displacement for the initial SiC surface was only 12 nm while it was greatly increased to 24 nm for the oxidized surface. Fig. 7(b) shows the results of the hardnesses calculated from the load-displacement curves using the Oliver-Pharr method [33]. The oxidized surface was much softer than the original SiC surface, meaning that the oxidized surface was much easier to remove. Meanwhile, the main oxidation product for thermal oxidation of SiC is SiO₂ as has been widely reported [34], for which CeO₂ slurry is an appropriate polishing media [31]. Hence, it is expected that the oxide layer can be efficiently removed by polishing using CeO₂ slurry and a smooth surface, which is free of scratch, can be obtained.

The thermally oxidized C-face was polished using CeO₂ slurry under the same conditions as shown in Table 1 and the polishing duration was 3 h. Fig. 8 shows SWLI and AFM images of the surface after polishing. As shown in Fig. 8(a) and (b), all the scratches on the original surface, which can be observed in Fig. 1, have been completely removed. However, many micro pits were formed on the polished surface. Enlarged observations were conducted on a pit-free area (location A) as well as a pit-contained area (location B). Fig. 8(c) shows the AFM image of area (A), it was found that a well-ordered step-terrace structure has been formed on the polished surface. These atomic steps are uniform and straight just like the polished Si-face shown in Fig. 3(e). Shown in Fig. 8(d) is the cross-sectional profile of the atomic steps. The step height was measured to be 0.25 nm, corresponding to one bilayer of 4H-SiC, indicating that an *epi*-ready C-face, which is smooth in atomic scale, has been obtained without any step bunching. To clarify the origin of the micro pits, enlarged observation of a micro pit was conducted and shown in Fig. 8(e). From a detailed observation of the micro pit, it was found that these micro pits generated after the hybrid polishing process were originated from the screw dislocations in 4H-SiC. As it was reported, the preferential oxidation of the defects in SiC occurred in thermal oxidation owing to the high oxidation temperature [35]. Thus, micro pits were formed after the oxide layer was removed by polishing. Although the depth of these micro pits was small as shown in Fig. 8(f), the surface integrity was deteriorated.

To further confirm the proposed pit generation mechanism, thermal oxidation-combined slurry polishing with a longer oxidation pretreatment duration for 6 h was conducted under the same polishing conditions. Fig. 9 shows the SWLI and AFM images of the polished surface. The same with the surface shown in Fig. 8, scratches were completely removed while many micro pits were formed. Meanwhile, it was found that the pits shown in Fig. 9 were larger than these shown in Fig. 8. As the polishing conditions were constant, it was considered that the micro pits became larger owing to the prolonged thermal oxidation duration. This result also supports the proposed mechanism regarding micro pit generation in thermal oxidation-combined slurry polishing.

The experimental results have demonstrated that the combination of thermal oxidation pretreatment and CeO₂ slurry polishing is effective to reduce the total polishing time to achieve a scratch-free and atomically flat C-face. For conventional slurry polishing without pretreatment, scratch cannot be completely removed even after a long polishing duration for 15 h while a scratch-free C-face with well-ordered SiC atomic steps has been achieved by polishing for only 3 h on a thermally oxidized surface. For finishing of 4H-SiC, not only the surface roughness but also the surface integrity is considered important. Thus, the formation of micro pits, which deteriorates the surface integrity, becomes a problem, meaning that thermal oxidation is not the best pretreatment method for hybrid finishing of the C-face of 4H-SiC. To modify SiC, there are several approaches besides thermal oxidation such as anodic oxidation, plasma irradiation, laser irradiation and so forth. It is expected

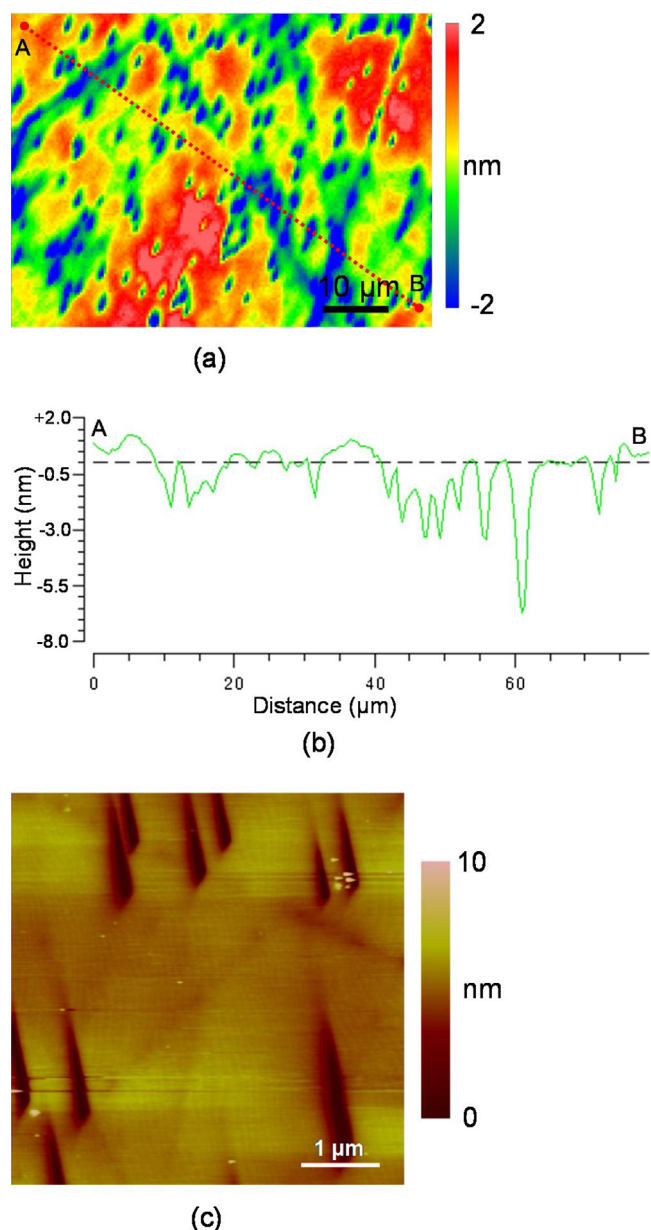


Fig. 9. SWLI and AFM images of C-face processed by thermal oxidation (6 h) followed by polishing using CeO₂. (a) SWLI image (S_2 : 9.57 nm, S_q : 1.09 nm). (b) Cross-sectional profile on surface (a). (c) AFM image (S_2 : 25.22 nm, S_q : 1.49 nm).

that micro pits will not be formed in hybrid polishing using a low temperature pretreatment method, which will need to be validated in future studies.

4. Conclusions

In this paper, finishing of the C-face of 4H-SiC using a hybrid polishing process combining thermal oxidation pretreatment and slurry polishing has been presented. To summarize, the following conclusions can be drawn from this study:

- (1) CeO₂ slurry demonstrates more excellent polishing performance of 4H-SiC from the view of the surface roughness, integrity and the uniformity of the obtained atomic steps compared with diamond, Al₂O₃ and SiO₂ slurries.
- (2) Conventional slurry polishing of the C-face using CeO₂ slurry is a time consuming process owing to the preferential removal of

the scratched areas on the original surface. Even after a long polishing duration for 15 h, scratch cannot be completely removed and the polished C-face is still rough.

- (3) The proposed hybrid polishing process, in which thermal oxidation pretreatment and slurry polishing are combined, has been proved to be effective for finishing of C-face of 4H-SiC. Thermal pretreatment reduces the surface hardness of the C-face and enables highly efficient polishing using CeO₂ abrasives. The scratch can be completely removed within a short polishing duration for only 3 h and a well-ordered atomic steps of SiC can be formed on the polished surface. However, micro pits are introduced after polishing due to the high oxidation temperature.
- (4) The surface modification method need to be further optimized. It is expected that a pretreatment method conducted under a low temperature will be able to solve the problem of micro pit generation in hybrid finishing of the C-face of 4H-SiC.

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References

- [1] D. Nakamura, I. Gunjishima, S. Yamaguchi, T. Ito, A. Okamoto, H. Kondo, S. Onda, K. Takatori, Ultrahigh-quality silicon carbide single crystals, *Nature* 430 (2004) 1009–1012.
- [2] X. She, A.Q. Huang, O. Lucia, B. Ozpineci, Review of silicon carbide power devices and their applications, *IEEE Trans. Ind. Electron.* (2017) 1.
- [3] M. Kikuchi, Y. Takahashi, T. Suga, S. Suzuki, Y. Bando, Mechanochemical polishing of silicon carbide single crystal with chromium (III) oxide abrasive, *J. Am. Ceram. Soc.* 75 (1992) 189–194.
- [4] L. Zhou, V. Audurier, P. Pirouz, J.A. Powell, Chemomechanical polishing of silicon carbide, *J. Electrochem. Soc.* 144 (1997) L161–L163.
- [5] H. Deng, K. Endo, K. Yamamura, Atomic-scale planarization of 4H-SiC (0001) by combination of thermal oxidation and abrasive polishing, *Appl. Phys. Lett.* 103 (2013) 111603.
- [6] Lucia, B. Ozpineci, Review of silicon carbide power devices and their applications, *IEEE Trans. Ind. Electron.* (2017) 1.
- [7] M. Kikuchi, Y. Takahashi, T. Suga, S. Suzuki, Y. Bando, Mechanochemical polishing of silicon carbide single crystal with chromium (III) oxide abrasive, *J. Am. Ceram. Soc.* 75 (1992) 189–194.
- [8] L. Zhou, V. Audurier, P. Pirouz, J.A. Powell, Chemomechanical polishing of silicon carbide, *J. Electrochem. Soc.* 144 (1997) L161–L163.
- [9] H. Deng, K. Endo, K. Yamamura, Atomic-scale planarization of 4H-SiC (0001) by combination of thermal oxidation and abrasive polishing, *Appl. Phys. Lett.* 103 (2013) 111603.
- [10] C. Li, I.B. Bhat, R. Wang, J. Seiler, Electro-chemical mechanical polishing of silicon carbide, *J. Electron. Mater.* 33 (2004) 481–486.
- [11] H. Aida, T. Doi, H. Takeda, H. Katakura, S.-W. Kim, K. Koyama, T. Yamazaki, M. Ueda, Ultra-precision CMP for sapphire, GaN, and SiC for advanced optoelectronics materials, *Curr. Appl. Phys.* 12 (2012) S41–S46.
- [12] S. Kurokawa, T. Doi, O. Ohnishi, T. Yamazaki, Z. Tan, T. Yin, Characteristics in Sic-cmp Using Mno 2 Slurry with Strong Oxidant under Different Atmospheric Conditions, in: *Mrs Proceedings*, Cambridge Univ. Press, 2013, pp. mrss13-1560-bb1503-1501.
- [13] Y. Zhou, G. Pan, X. Shi, H. Gong, G. Luo, Z. Gu, Chemical mechanical planarization (CMP) of on-axis Si-face SiC wafer using catalyst nanoparticles in slurry, *Surf. Coat. Technol.* 251 (2014) 48–55.
- [14] H. Deng, K. Hosoya, Y. Imanishi, K. Endo, K. Yamamura, Electro-chemical mechanical polishing of single-crystal SiC using CeO₂ slurry, *Electrochem. Commun.* 52 (2015) 5–8.
- [15] H. Deng, T. Takiguchi, M. Ueda, A.N. Hattori, N. Zettsu, K. Yamamura, Damage-free dry polishing of 4H-SiC combined with atmospheric-pressure water vapor plasma oxidation, *Jpn. J. Appl. Phys.* 50 (2011) 08JG05.
- [16] K. Yamamura, T. Takiguchi, M. Ueda, H. Deng, A.N. Hattori, N. Zettsu, Plasma assisted polishing of single crystal SiC for obtaining atomically flat strain-free surface, *CIRP Ann. Manuf. Technol.* 60 (2011) 571–574.
- [17] H. Deng, K. Endo, K. Yamamura, Damage-free finishing of CVD-SiC by a combination of dry plasma etching and plasma-assisted polishing, *Int. J. Mach. Tools Manuf.* 115 (2017) 38–46.
- [18] H. Deng, K. Endo, K. Yamamura, Plasma-assisted polishing of gallium nitride to obtain a pit-free and atomically flat surface, *CIRP Ann. Manuf. Technol.* 64 (2015) 531–534.
- [19] H. Hara, Y. Sano, H. Mimura, K. Arima, A. Kubota, K. Yagi, J. Murata, K. Yamauchi, Novel abrasive-free planarization of 4H-SiC (0001) using catalyst, *J. Electron. Mater.* 35 (2006) L11–L14.
- [20] J. Watanabe, M. Touge, T. Sakamoto, Ultraviolet-irradiated precision polishing of diamond and its related materials, *Diamond Relat. Mater.* 39 (2013) 14–19.
- [21] C. Wang, S. Kurokawa, T. Doi, J. Yuan, Y. Sano, H. Aida, K. Zhang, Q. Deng, The polishing effect of SiC substrates in femtosecond laser irradiation assisted chemical mechanical polishing (CMP), *ECS J. Solid State Sci. Technol.* 6 (2017) P105–P112.
- [22] C. Bouhafs, A.A. Zakharov, I.G. Ivanov, F. Giannazzo, J. Eriksson, V. Stanishev, P. Kühne, T. Iakimov, T. Hofmann, M. Schubert, F. Roccaforte, R. Yakimova, V. Darakchieva, Multi-scale investigation of interface properties, stacking order and decoupling of few layer graphene on C-face 4H-SiC, *Carbon* 116 (2017) 722–732.
- [23] Y. Saitoh, H. Itoh, K. Wada, M. Sakai, T. Horii, K. Hiratsuka, S. Tanaka, Y. Mikamura, 150A SiC V-groove trench gate MOSFET with 6 × 6 mm² chip size on a 150 mm C-face in-house epitaxial wafer, *Jpn. J. Appl. Phys.* 55 (2016) 04ER05.
- [24] T. Yamashita, H. Matsuhata, T. Sekiguchi, K. Momose, H. Osawa, M. Kitabatake, Characterization of comet-shaped defects on C-face 4H-SiC epitaxial wafers by electron microscopy, *J. Cryst. Growth* 416 (2015) 142–147.
- [25] H. Lee, H. Kim, H.S. Seo, D. Lee, C. Kim, S. Lee, H. Kang, J. Heo, H.J. Kim, Comparative study of 4H-SiC epitaxial layers grown on 4 off-axis Si- and C-face substrates using bistrimethylsilylmethane precursor, *ECS J. Solid State Sci. Technol.* 4 (2015) N89–N95.
- [26] H. Deng, M. Ueda, K. Yamamura, Characterization of 4H-SiC (0001) surface processed by plasma-assisted polishing, *Int. J. Adv. Manuf. Technol.* 72 (2012) 1–7.
- [27] T. Kimoto, A. Itoh, H. Matsunami, T. Okano, Step bunching mechanism in chemical vapor deposition of 6H- and 4H-SiC{0001}, *J. Appl. Phys.* 81 (1997) 3494–3500.
- [28] F. Chien, S. Nutt, W. Yoo, T. Kimoto, H. Matsunami, Terrace growth and polytype development in epitaxial β-SiC films on α-SiC (6H and 15R) substrates, *J. Mater. Res.* 9 (1994) 940–954.
- [29] J. Shaw, V. Heine, The nature of interplanar interactions in SiC polytypes, *J. Phys. Condens. Matter* 2 (1990) 4351.
- [30] H. Deng, K. Endo, K. Yamamura, Competition between surface modification and abrasive polishing: a method of controlling the surface atomic structure of 4H-SiC (0001), *Sci. Rep.* 5 (2015).
- [31] L.M. Cook, Chemical processes in glass polishing, *J. Non-Cryst. Solids* 120 (1990) 152–171.
- [32] A. Rajendran, Y. Takahashi, M. Koyama, M. Kubo, A. Miyamoto, Tight-binding quantum chemical molecular dynamics simulation of mechano-chemical reactions during chemical-mechanical polishing process of SiO₂ surface by CeO₂ particle, *Appl. Surf. Sci.* 244 (2005) 34–38.
- [33] L. Zhou, H. Eda, J. Shimizu, S. Kamiya, H. Iwase, H. Kimura, H. Sato, Defect-free fabrication for single crystal silicon substrate by chemo-Mechanical grinding, *CIRP Ann. Manuf. Technol.* 55 (2006) 313–316.
- [34] T. Kido, M. Nagaya, K. Kawata, T. Kato, A novel grinding technique for 4H-SiC single-crystal wafers using tribo-catalytic abrasives, *Mater. Sci. Forum* 778–780 (2014) 754–758.
- [35] T. Suratwala, M. Feit, W. Steele, L. Wong, N. Shen, R. Dylla-Spears, R. Desjardin, D. Mason, P. Geraghty, P. Miller, S. Baxamusa, G. Pharr, Microscopic removal function and the relationship between slurry particle size distribution and workpiece roughness during pad polishing, *J. Am. Ceram. Soc.* 97 (2014) 81–91.
- [36] H. Deng, K. Endo, K. Yamamura, Comparison of thermal oxidation and plasma oxidation of 4H-SiC (0001) for surface flattening, *Appl. Phys. Lett.* 104 (2014) 101608.
- [37] W.C. Oliver, G.M. Pharr, An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments, *J. Mater. Res.* 7 (1992) 1564–1583.
- [38] Y. Song, S. Dhar, L.C. Feldman, G. Chung, J. Williams, Modified deal groove model for the thermal oxidation of silicon carbide, *J. Appl. Phys.* 95 (2004) 4953–4957.
- [39] S. Saddow, T. Schattner, J. Brown, L. Grazulis, Effects of substrate surface preparation on chemical vapor deposition growth of 4H-SiC epitaxial layers, *J. Electron. Mater.* 30 (2001) 228.