Review



Recent Advances in Chemical Mechanical Polishing Technologies of Silicon Carbide



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Abstract: Silicon Carbide (SiC) as the third generation semiconductor material has a very high surface quality requirement, which is the core index in the engineering application. Chemical Mechanical Polishing (CMP) is the only technology that can realize global flattening and non-damage surfaces at present. In this paper the recent advances in traditional CMP, the effects of slurry, and hybrid CMP of SiC were reviewed. The principles and recent developments of CMP were introduced. Then the influence of various factors of slurry on polishing performance was discussed. In addition, recent advances in hybrid CMP technologies, such as Electrochemical Mechanical Polishing (ECMP), Photocatalytic Chemical Mechanical Polishing (PCMP), Plasma Assisted Polishing (PAP), Catalyst-Referred Etching (CARE) were reported, especially some efforts to make these technologies environmentally friendly. Finally, some shortcomings of CMP technology in the application of SiC are summarized and prospect its future development trends.

Keywords: silicon carbide (SiC), chemical mechanical polishing (CMP), slurry, hybrid CMP

Abbreviations

CARE	Catalyst-Referred Etching
CMP	Chemical Mechanical Polishing
CoF	Coefficient of Friction
ECMP	Electrochemical Mechanical Polishing
MRR	Material Removal Rate
MAS	Mixed Abrasive Slurry
PCMP	Photocatalytic Chemical Mechanical Polishing
PAP	Plasma Assisted Polishing
PCVM	Plasma Chemical Vaporization Machining
PECO	Plasma Electrochemical Oxidation
PEP-MP	Plasma Electrolytic Processing and Mechanical Polishing
RMS	Root Mean Square
SWLI	Scanning White Light Interferometer
UV	Ultraviolet

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SSD	Subsurface Damage
C_{60}/β -CD	β-Cyclodextrin
PS	Polystyrene
PEC	Photoelectrical

Notations

Al_2O_3	Aluminium oxide
С	Carbon
CeO ₂	Ceric dioxide
Fe ₃ O ₄	Ferroferric oxide
GaAs	Gallium arsenide
HCl	Hydrochloric acid
HF	Hydrogen fluoride
H_2O_2	Hydrogen peroxide
·ОН	Hydroxyl radicals
Mn	Manganese
MnO_2	Manganese dioxide
Mn_2O_3	Manganese(III) oxide
HNO ₃	Nitric acid
N ₂	Nitrogen
O_2	Oxygen
H ₅ IO ₆	Periodic acid
Pt	Platinum
KClO ₃	Potassium Chlorate
КОН	Potassium hydroxide
KIO ₃	Potassium iodate
KMnO ₄	Potassium Permanganate
SiC	Silicon carbide
Si	Silicon
SiO ₂	Silicon dioxide
Na ₂ CO ₃	Sodium Carbonate
NaCl	Sodium chloride
NaOH	Sodium hydroxide
NaNO ₃	Sodium nitrate
Na ₂ SiO ₃	Sodium silicate
TiO ₂	Titanium dioxide
ZrO_2	Zirconium dioxide

1. Introduction

Silicon Carbide (SiC) is the third generation of semiconductor ideal material after the first generation of semiconductor Silicon (Si) and the second generation of semiconductor Gallium Arsenide (GaAs). It has the advantages of the wide band gap, high electron breakdown rate, good thermal conductivity, high saturated electron drift rate, and is very suitable for the requirements of high frequency and high power electronic device materials.¹⁻³ At the same time, the Mohs hardness of silicon carbide is as high as 9.5, second only to diamond, with high brittleness and stable chemical properties.⁴ These characteristics also lead to the difficulty of its processing. At present, more than 250 types of silicon carbide crystals have been found, of which 3C-SiC, 4H-SiC and 6H-SiC silicon carbide are the most widely used, and

4H-SiC and 6H-SiC wafers with a diameter of 8 inches have been successfully commercialized.²

As the integrated circuit industry continues to advance and structure size is continuously reduced, the requirements for the surface quality of silicon carbide wafers continue to improve.⁵ In the semiconductor industry, the surface quality of the SiC wafer has a significant effect on the quality of the final product.⁶ For application, the roughness (Ra) of the substrate is usually required to be below 0.3 nm.⁷ The surface flattening technology of silicon carbide materials must be continuously improved to meet the needs of industry development. Typical wafer processing processes include ingot processing, slicing, edging, laser marking, rough grinding, fine grinding, CMP, post-CMP cleaning, inspection, packaging, and other process steps.² Chemical-Mechanical Polishing (CMP) is the sole method to obtain global flattening polishing with almost no damage and is the main processing method to obtain high surface quality silicon carbide wafers in industry at present.⁶

Although CMP technology has been widely used in the industrial production of SiC wafers, it still has problems such as low processing efficiency and unclear material removal mechanism.^{2,3,8} This paper summarizes the principle and classification of chemical-mechanical polishing technology, focusing on the factors that affect the efficiency and precision of CMP and the auxiliary efficiency enhancement technology of chemical-mechanical polishing.

2. Traditional CMP technology

The typical working principle of chemical-mechanical polishing is shown in Figure 1. The polishing head moves relative to the worktable. At the same time, the wafer fixed on the polishing head is pressured with a certain value, which generates a certain relative movement with the polishing pad in the polishing fluid. The material removal process in CMP is a process of chemical reaction and mechanical grinding. First of all, the polishing slurry composed of abrasive particles and a chemical solution is uniformly distributed onto the surface of the polishing pad by the centrifugal force when the workbench rotates at high speed, and a soft SiO₂ oxidation layer is formed under the action of the oxidant in the polishing fluid.³ During the process of corrosion and oxidation, oxygen atoms in the medium will be adsorbed on the surface of the substrate, generating oxidation products.^{9,10} Subsequently, the oxidation layer is removed by friction under relative motion between abrasive particles and the wafer to obtain a high-quality wafer surface.



Figure 1. Typical setup of chemical mechanical polishing

In 2021, Zhang et al.¹¹ conducted a comparative study on the mechanical, chemical, and chemical mechanical effects of the CMP process. When there is only mechanical effect, obvious scratches and larger CoF value were observed. And when there is only chemical effect, the SiC surface generated a loose and porous oxidant layer, causing lager Ra and fluctuating CoF curve. However, when they worked together, more stable and higher MRR were obtained.¹¹

In the CMP process, the balance between chemical reactions and mechanical grinding is very important. If the

chemical action is too strong, corrosion pits will be produced on the wafer surface; if the mechanical action is too strong, many scratches will be left on the wafer surface, resulting in a high damage layer. At the same time, the difference between the chemical and mechanical properties of the C-face and the Si-face will also affect the establishment of this balance.¹² In 2019, Lu et al.¹² conducted a comparative experiment on the Material Removal Rate (MRR) and surface quality of 4H-SiC and 6H-SiC wafers on the C and Si surfaces, and the phenomenon that the C-face is easier to be removed than the Si-face was observed, and the surface quality is better. With consistent polishing conditions, the roughness Ra of the C surface was below 2 nm, while the roughness of the Si surface was more than 10 nm. Moreover, for N-type 4H-SiC, N-type 6H-SiC, and V-type 6H-SiC, the MRR of the C-face was 45.9%, 127.4%, and 61.7% higher than that of the Si side, respectively. In addition, at the scratch speed of 1 μ m/s the nano-scratching test was carried out at a certain load of 4 mN, and the Coefficient of Friction (CoF) of the Si surface and C surface were 0.1778 and 0.2176, respectively. It can be seen that removing materials from the Si surface was more difficult than that from the C surface.¹²

3. Influencing factors of CMP slurry

The input variables of the CMP system are numerous, and the state variables are also changing with the continuous processing, and various factors interact with each other, which makes it very difficult to study and control the MRR, the uniformity of surface material removal, and defects. At present, there is no clear and unified theory on the impact of diverse factors on MRR and polishing quality, which needs further study. This chapter will summarize the existing research results in this field.

3.1 Abrasive

In the CMP process of SiC, after the wafer surface is oxidized to form a soft oxidation layer, the surface material is mechanically removed through the interaction between abrasive particles and the machined surface. The diameter of abrasive particles is generally tens of nanometers. Commonly used abrasive particles include SiO_2 , CeO_2 , Al_2O_3 , nanodiamond, etc. In addition, polymers and composite materials also have the potential to be used for abrasive particles.^{13,14}

Colloidal silica is one of the most widely used abrasives. Its hardness is low, and it can obtain a high-quality, lowdamage polished surface. In 2014, Pan et al.¹⁵ studied the effect of SiO₂ abrasive particles with different particle sizes on the performance of 4H-SiC chemical-mechanical polishing. It can be observed that the MRR of abrasive material with large particle size was high, yet the polishing quality was not good. The MRR was found to be lower for abrasive materials with smaller particle sizes, but the polishing quality was better, and the adhesion of abrasive particles was stronger.¹⁵ Wang et al.¹⁶ conducted the CMP tests on 4H-SiC and 6H-SiC using Al₂O₃ abrasive particles with different particle sizes. It was found that the MRR also increased as the particle size raised. But when the particle size increases to 0.75 µm at about, the MRR no longer increased, but the surface roughness continues to increase.¹⁶

Single abrasive particles have their limitations in performance, such as the low hardness of SiO₂ abrasive, the difficulty in breaking through the bottleneck of material removal rate, and the fact that Al₂O₃ abrasive particles had a tendency to agglomerate into larger particle micelles because of the electrostatic force in aqueous solution, resulting in flocculation delamination and other phenomena, resulting in poor stability of the polishing solution. To solve these problems, some researchers have studied mixed abrasive polishing fluid. Jindal et al. prepared the polishing solution with SiO₂ (average particle size 50 nm) and Al₂O₃ (average particle size 220 nm) mixed abrasive particles according to the appropriate mass ratio, effectively improving the polishing efficiency.¹⁷ Tsai et al.¹⁸ used β -Cyclodextrin (C₆₀/ β -CD) as the adhesive abrasive of SiC-CMP, and found that the MRR of only C₆₀/ β -CD of abrasive polishing slurry is 49.9% higher compared to only colloidal SiO₂ polishing slurry, and the polishing quality is only slightly drop, revealing application potential of C₆₀/ β -CD abrasive in SiC-CMP.

In practice, the abrasive particle size also has a considerable effect on MRR and surface roughness. In 2022, Wang et al.¹⁹ studied the impact of different alumina abrasive particle size distribution D50 on 4H-SiC (0001) MRR and surface roughness. The pH adjustment that was applied to regulate the pH value to 9.20 in the test is KOH, and the oxidant was 3 wt% KMnO₄. As shown in Figure 2, the MRR increased from 0.61 μ m/h to 0.70 μ m/h as the particle size D50 increases from 0.1 μ m to 0.75 μ m. In particular, when the particle size D50 outnumber 0.75 μ m, the MRR of

SiC was not changing anymore. From Figure 2, it can be seen that the surface roughness increased as the particle size D50 increased from 0.1 μ m to 2 μ m can be obtained.¹⁹ Similarly, in 2022, Zhao et al.²⁰ studied the MRR variation in Mn-based polishing slurry abrasive size with three different abrasive sizes of 0.4 μ m, 1 μ m and 3 μ m. As the polishing abrasive size became larger, the mechanical removal ability was improved. However, the improvement of the MRR of the Mn-based slurry with the abrasive size increases was limited.²⁰

From the above research, it can be obtained that the mechanical removal ability of diverse abrasive particles is very distinct, and the removal mechanism of SiC by abrasive particles is not well understood. The abrasive particles with better comprehensive performance are also the current research direction, which needs further research.



Figure 2. 4H-SiC(0001) removal rate and surface roughness as a function of alumina particle size¹⁹

3.2 Oxidant

The oxidant can accelerate the fracture of the Si-C bond, forming a lower hardness oxide layer on the wafer surface, enhancing the MRR, and obtaining better surface quality. Using diverse oxidants and concentrations affects how well and fast wafers are polished.

In 2011, Hiroshi et al.²¹ examined the impact of three distinct polishing fluids, colloidal silica with 5 wt% H_2O_2 and colloidal silica with 5 wt% H_5IO_{62} on 4H-SiC polishing in an alkaline environment with pH = 10. It can be obtained that the MRR of only silica colloid in the polishing solution was the lowest, only 12 nm/h. The MRR of the polishing solution with H_2O_2 and H_5IO_6 was prominently higher than that of the polishing solution with only silica colloid, which was 62 nm/h and 34 nm/h respectively. Besides, form the phenomenon that the removal rate of H_3IO_6 material with stronger oxidizability was lower than that of H₂O₂, Hiroshi et al. believed that the difference was caused by the difference of free radical reaction between the two in the polishing solution, and its effect on material removal cannot be discussed only from the oxidizability of the oxidizer.²¹ In 2021, Wang et al.¹⁶ studied the effect of polishing solution with KMnO₄ as oxidant on polishing rate. In this study, 6.5 wt% polishing solution was used to carry out comparative experiments at pH 2, 4, 6, 8, 10 and 12. As shown in Figure 3, the pH values had an important effect on the oxidation of KMnO₄, and the MRR reached the peak at pH = 2. As the pH value increases, the MRR gradually decreased.¹⁶ In 2021, Qi et al.²² investigated the impact of solid-phase oxidants in CMP. In this study, five solid phase oxidizers, Na2CO3-1.5H2O2, NaOH, KIO3, KClO3 and KMnO4, were compared and studied. It can be obtained that the solid phase oxidizer reacted with SiC during polishing and oxidized on the contact surface. The reaction product was silicon oxide, mainly SiO₂. In addition, due to the polishing interface having a high flash point temperature, when SiC reacted with H₂O, it underwent a chemical reaction and resulted in the forming of a SiO₂ oxide layer on the surface. In the meantime, comparing the MRR of five solid phase oxidizers, it can be observed that the MRR of NaOH dry polishing was the highest, while the KClO₃ dry polishing MRR was the lowest, but the use of NaOH polishing will produce soluble Na_2SiO_3 , the polished surface exhibited enhanced visibility of scratches and pits, and the roughness was greatly improved, while the surface quality of the other four solid phase oxidizers remained relatively unchanged.²²



Figure 3. Effect of pH on the 4H-SiC (0001) material removal rate¹⁶

It can be seen that different kinds of oxidants have an important impact on the MRR and surface quality of silicon carbide wafers, and different oxidants behave differently in different polishing fluid environments. It is necessary to select the appropriate oxidant type and polishing solution acid-base environment according to different material properties and processing parameters for the comprehensive performance of CMP. The oxidation rate needs to be adapted to the mechanical removal rate in order to obtain the best surface quality.^{23,24}

3.3 PH value of polishing slurry

In the polishing process, the pH value will affect the generation of oxide layer on the surface of SiC and indirectly influence the MRR. At the moment, most of the CMP of SiC is carried out in alkaline environments.^{19,25,26} Numerous researchers have explored the impact of different pH values on the effect of SiC in the CMP process.

In 2012, Su et al.²⁷ investigated the change in MRR as the pH value increases between 9 and 13. From the result, the MRR improved as the pH value increased until the pH reached a certain value, and then began to decrease. In particular, the optimum pH values of the C surface and Si surface were different, and the MRR of Si-face was more sensitive to changes in pH value.²⁷ In 2021, Wang et al.²⁸ developed a kind of Fe₃O₄ catalyst, and compared the removal rate in acidic and alkaline environments, which pH values are 2.5 and 9.0 respectively. The result determined that the removal rate in alkaline environment exceeded that in acidic environment by a significant margin.²⁸ Similar result were obtained in experiments on acidic- and alkaline-based colloidal silica slurries in CMP by Aida et al.²⁶ Likewise, in 2022, Zhao et al.²⁰ varied the pH values of the MnO₂ and Mn₂O₃ slurries to determine how pH value influences the polishing efficiency of SiC wafer. From Figure 4, the MRR showed an increasing trend when the pH value changed from <7 (acidic) to >7 (alkaline).²⁰ This trend aligns with the findings reported by Yin et al. in 2018.²⁹

However, some researchers have obtained distinct results in different slurry environments. In 2020, Chen et al.³⁰ performed CMP on 6H-SiC using a slurry containing a 2 wt% KMnO₄ oxidant and alumina nanoparticles abrasive. The pH values of the slurry were controlled by nitric acid or potassium hydroxide to explore their effect. Based on the data presented in Figure 5, it is evident that the MRR of two different surfaces exhibited a significant drop from pH 2 to 6,

subsequently, appearing a gradual decline from pH 6 to 10. The highest MRR (1,554 and 6,412 nm/h) was observed on the Si surface and C surface, respectively. The significantly higher MRR observed on the C surface suggests that the MRR was strongly influenced by the surface polarity of the SiC wafer.³⁰ Similar result was gained in 4H-SiC CMP using different pH value slurries composed of 6.5 wt% KMnO₄ oxidant and Al₂O₃ abrasive by Wang et al.³¹ In 2021, Wang et al.³² proposed a novel ultraviolet-TiO₂ (UV-TiO₂) activation of persulfate and examined the synergistic catalytic effect in enhancing the removal rate in different pH values environments. The results demonstrated that the MRR exhibited an upward trend with increasing pH values within the range of 2 to 6. However, beyond this range, as the pH value continued to rise, the MRR showed a subsequent decrease.³²



Figure 4. Effect of the slurry pH on the MRR of the SiC substrate²⁰



Figure 5. The effect of pH value on the MRR of 6H-SiC substrates: (a) Si-face; (b) C-face³⁰

It can be seen that different compositions of slurries have distinct reactions to pH changes from many studies above. This is mainly because the performance of different oxidants is different in environments with the same pH value. However, further research is still needed on the mechanism of pH value in the SiC CMP process.

4. Variants of CMP technology

The ultra-high hardness and chemical inertness of SiC contribute to low MRR during the CMP process. Therefore, researchers have developed many auxiliary efficiency technologies based on traditional CMP to achieve higher MRR and improved surface quality. Integrating other forms of energy such as electric energy and light energy into the CMP system can effectively promote oxidation efficiency and MRR. The design of these auxiliary efficiency technologies is also based on this principle, such as Electrochemical Polishing (ECMP), Photocatalytic Chemical Mechanical Polishing (PCMP), Plasma-Assisted Polishing (PAP), Catalyst-Referred Etching (CARE) and other technologies. The principle of these technologies and their latest progress are focused on as follows.

4.1 Electrochemical Mechanical Polishing (ECMP)

Figure 6 illustrates representative equipment of ECMP. Different from traditional CMP, ECMP uses electrolytes as the polishing slurry. In the polishing process, the SiC surface serves as the anode, leading to the formation of an oxide layer with lower hardness because of the applied charge. Subsequently, this softer surface is mechanically eliminated through the use of soft abrasives. Because of the lower hardness of the soft abrasives, the Subsurface Damage (SSD) is not introduced when the surface oxide is removed, making a damage-free surface possible.^{8,33}



Figure 6. Typical equipment for SiC ECMP²

In 2018, Liu et al.³³ found that surface oxidation of SiC is related to scratches during the anodic process, which means that areas with scratches oxidized before areas without scratches. Besides, anodic oxidation occurred randomly in the non-damaged areas because of the stochastic distribution of doping sites.³³ In 2019, Chen et al.⁸ experimentally investigated the oxidation characteristics of 4H-SiC ECMP in terms of electrolyte types, ionic concentration and crystalline anisotropy. Under the same conditions, the highest current density was found in NaOH solution, while the acidic solutions exhibited the lowest current densities among the five electrolytes of HCl, HNO₃, NaCl, NaNO₃ and NaOH. On the other hand, the oxidation rate of the C surface was found to be 5-15 times higher than that of the Si surface, as shown in Figure 7, particularly when the anodization potential was increased.⁸



Figure 7. Variation of surface oxidation film at different potentiostatic potentials. (a) Oxidation film thickness; (b) oxygen content⁸

In 2020, Deng et al.³⁴ found that the Fenton reaction, which produced more hydroxyl radicals, can effectively enhance the oxidation effect. The top-flight catalyst concentration of Fe_3O_4 was identified before the experiment. Besides, in 2021, Deng et al.³⁵ conducted further research to investigate the role of the Fenton reaction in ECMP. The coumarin capture hydroxyl radicals (·OH) method was used to make a quantitative comparison. As shown in Figure 8, the concentration of ·OH exhibited a gradual increase over time in all five different reactions. In particular, it achieved a maximum point and distinctly declined. The maximum ·OH concentrations recorded were 181.137, 288.947, 414.283, 576.622, and 649.025 µmol/L within the time range of 80-120 mins. The higher peak of the ·OH concentration and total ·OH concentration was observed under the action of an external field voltage. It can be also obtained that the Fenton reaction made a considerable contribution to the production of ·OH, but it is not as significant as the effect of the external field voltage.³⁵

Driven by the growing awareness of environmental concerns, numerous scholars have made efforts to make ECMP more environmentally friendly. In 2021, Yang et al.³⁶ introduced a three-step slurryless ECMP process that can obtain significantly high surface quality while improving removal efficiency. In 2022, Yang et al.³⁷ put forward a slurry-less ultrasonic vibration assisted ECMP with the assistance of a vibrator. By eliminating the use of slurry, these methods not only significantly reduced polishing costs but also improved environmental sustainability. In 2022, Yang et al.³⁸ conducted a comparison of energy utilization efficiency at different current densities to reduce energy consumption. The findings revealed that the charge utilization efficiency remained unchanged when the current density was below 20. However, when the current density exceeded 30, both the charge utilization efficiency and material removal rate exhibited an obvious decrease.³⁸ Studying the relationship between current density and machining efficiency is of great significance for selecting the optimal polishing conditions and reducing energy consumption. In 2023, Murata et al.³⁹ proposed an environmentally friendly and highly efficient ECMP approach that eliminated the need for harsh liquids. The MRR exhibited a considerably higher about 10 times than that observed by traditional CMP.

Although ECMP has been gradually used in production, the mechanism of ECMP is still unclear. With the continuous exploration of researchers, many new ECMP methods are also emerging.



Figure 8. Change in: (a) concentration of \cdot OH with time; (b) total concentration of \cdot OH under different reaction conditions³⁵

4.2 Photocatalytic Chemical Mechanical Polishing (PCMP)

PCMP requires additional catalyst differencing form ECMP. As shown in Figure 9, photogenerated electrons and holes form on the surface of highly photocatalytic particles, such as TiO_2 .³² The hydroxyl group produced in this process has a strong oxidizing property and can oxidize SiC to SiO₂, which is softer and can be removed easily.

In 2018, Yuan et al.⁴⁰ presented a practical and high efficient polishing method of photocatalysis-assisted chemical mechanical polishing together with mechanical lapping. The final surface quality can be improved to about Ra 0.528 nm in the area of 0.14 mm \times 0.11 mm. The MRR of rough polishing and fine polishing were 1.8 µm/h and 0.96 µm/h,

respectively.⁴⁰ In 2012, Ohnishi et al.⁴¹ researched the impact of the atmosphere on the polishing rate of PCMP. And the MRR increased was the O_2 pressure was raised was found in this paper.⁴¹ Similarly, in 2021, Yin et al.⁴² carried out some experiments to investigate the impact of different gas atmospheres. By pressurizing the air pressure from atmospheric pressure to 300 kPa, a significant enhancement in the removal rate was observed, approximately doubling the rate. In comparison, under a pure $O_2 + 300$ kPa atmosphere, the MRR increased by about 2.3 times, indicating a slightly higher improvement in performance. However, if O_2 was replaced with N_2 , the removal rate was not even as good as under the open-air atmosphere.⁴²



Figure 9. Typical setup for the SiC PCMP³²

In 2019, Gao et al.⁴³ developed a novel polystyrene (PS)/CeO₂-TiO₂ multi-component core/shell abrasives, which is used for PCMP in the hope of improving polishing efficiency and quality. From Figure 10, it was found that the PS/CeO₂-TiO₂ abrasives, which exhibited a distinctive yielding effect and considerable improvement in photocatalytic activity, had the best polishing performance under UV irradiation. The PS/CeO₂-TiO₂ abrasives, when subjected to UV irradiation, behaved with highest MRR (1.223 µm/h) and the minimal surface roughness (Ra: 0.497 nm) among the tested conditions.⁴³ In 2022, Wang et al.⁴⁴ combined Mixed Abrasive Slurry (MAS) with a photocatalytic effect to improve performance and reduce the costs of SiC-CMP. Experiments were conducted on alumina and zirconia powders mixed in different proportions. From the results, it can be found that the MAS composed of 1.25 wt% Al₂O₃ and 0.75 ZrO₂ possessed the best polishing performance (MRR: 694 nm/h and Ra: 0.587 nm) under UV irradiation.⁴⁴

4.3 Plasma-Assisted Polishing (PAP)

In 2010, PAP technology was first proposed by Yamamura of Osaka University in Japan.^{45,46} As shown in Figure 11, the combination of atmospheric plasma irradiation and soft abrasive polishing technology is a significant feature of PAP technology. Therefore, PAP technology has good flattening ability at the atomic scale and can obtain high surface quality.



Figure 10. Cross-sectional roughness values and MRRs of (1) CeO₂ under UV irradiation, (2) CeO₂ without UV, (3) PS/CeO₂ under UV irradiation, (4) PS/CeO₂ without UV, (5) CeO₂-TiO₂ under UV irradiation, (6) CeO₂-TiO₂ without UV, (7) PS/CeO₂-TiO₂ under UV irradiation, (8) PS/CeO₂-TiO₂ without UV⁴³

In 2011, Yamamura et al.⁴⁶ conducted in-depth research on this technology. A significant decrease from 37.4 ± 0.5 GPa to 4.5 ± 0.8 GPa of SiC surface hardness was observed in the nanoindentation test. By plasma-assisted polishing using a CeO₂ abrasive, a surface devoid of scratches and possessing an atomic-level flatness was achieved, exhibiting an Root Mean Square (RMS) roughness level of 0.1 nm.⁴⁶ In 2014, Deng et al.⁴⁷ fused the water vapour plasma into PAP. After plasma irradiation, it has been proven through X-ray photoelectron spectroscopy that the oxide produced was predominantly SiO₂, and the surface has been effectively oxidized. From the results of many Characterization tests, an atomic-level flatness was achieved and the surface quality improved from an initial value of 4.410 nm p-v, 0.621 nm rms to 1.889 nm p-v, 0.280 nm rms after PAP. In addition, no introduction of crystallographical defects was observed.⁴⁷



Figure 11. Typical setup of the SiC PAP⁴⁸

In 2017, Deng et al.⁴⁹ combined Plasma Chemical Vaporization Machining (PCVM) and Plasma-Assisted Polishing (PAP). A considerably flat surface without scratches, whose rms roughness was 0.6 nm, was achieved through 5 min of PCVM and subsequent PAP using a resin-bonded CeO₂ grindstone.⁴⁹ In 2021, Yin et al.⁵⁰ introduced a sustainable and potentially powerful oxidation method called Plasma Electrochemical Oxidation (PECO), and integrate it with CMP. The analysis results of the oxide surface composition and Si 2p spectra indicated that the formation of SiO_xC_y and SiO₂ took place during the oxidation process.⁵⁰ Similarly, in 2021, Ma et al.⁵¹ combined Plasma-Electrolytic Processing and Mechanical Polishing (PEP-MP). It can be observed that the hardness of the single-crystal 4H-SiC surface underwent a significant reduction from 2,891.03 to 72.61 HV after PEP. From the images of Scanning White Light Interferometer (SWLI), it can be obtained that the surface quality improved from Sz 607 nm, Ra 64.5 nm to Sz 60.1 nm, Ra 8.1 nm and the MRR of PEP-MP was approximately 21.8 μ m/h.⁵¹

4.4 Catalyst-Referred Etching (CARE)

A chemical etching technique that involves the use of a catalyst to facilitate the etching process, and the catalyst selected promotes the etching of specific materials or regions, resulting in controlled and precise material removal, is a polishing technique called Catalyst-Referred Etching (CARE). Figure 12 presents a representative diagram illustrating the configuration of a CARE system designed for single-crystal SiC. In CARE, the etching reaction exclusively takes place at the surface of the catalyst.⁵² The most prominent feature of CARE is the use of catalyst etching to remove SiC.



Figure 12. Schematic drawing of CARE apparatus⁵³

In 2006, Hara et al.⁵⁴ first introduced the CARE method for reducing the surface roughness of SiC wafer. The polishing pad of the CARE was made of Pt which has a catalytic effect compared with the traditional CMP. The wafers were loaded onto the pad and subjected to a precisely controlled pressure of 0.02 MPa and attached to the sample stage. In the CARE process, a Pt polishing pad was employed as a catalyst, which facilitated the activation of HF into reactive species and enabled the chemical removal of material. CARE resulted in minimal scratching on the polished SiC surface, primarily because of the application of lower pressure compared to the traditional CMP method. A flat surface of 0.1 nm level roughness can be obtained by CARE, and the MRR can achieve 0.1-0.2 μ m/h.⁵⁴

Okamoto et al.⁵³ carried out some tests to investigate the correlation between rotation speed and processing pressure in relation to the MRR to improve the polishing efficiency of CARE in 2012. As the rotation speed and load increased, the MRR increase was observed. Within 15 min, a flat surface with an RMS roughness below 0.1 nm was successfully produced. This was achieved under specific conditions that resulted in the highest MRR of about 500 nm/h.⁵³

However, due to its highly toxic and corrosive nature, hydrofluoric acid poses a significant threat to humans and the environment. Therefore, some scholars have attempted to conduct CARE in more environmentally friendly solution environments. In 2017, Isohashi et al.⁵⁵ found that the chemical etching of SiC can occur in pure water under the effect of the Pt catalyst. A thin Pt film, less than 100 nm in thickness, was coated onto a polishing pad, where the substrate was

positioned and slid. But the MRR was distinctly low compared to that of the HF solution.⁵⁵ In 2019, Kida et al.⁵⁶ come up with an approach of combining CARE and photoelectrical (PEC) oxidation to obtain atomically flat SiC wafer and promote the MRR of CARE in pure water. As shown in Figure 13, by application a bias voltage of 2.0 V and utilizing shorter wavelength UV, the MRR of PEC-assisted water-CARE had increased from 2 to 113 nm/h compared to water-CARE without PEC oxidation.⁵⁶ In these studies, the use of pure water instead of hydrofluoric acid greatly improved the environmental friendliness of CARE.



Figure 13. Removal rate of different CARE condition⁵⁶

CARE has broad application prospects, especially in this method where non-toxic pure water can be used as raw material and has good environmental protection.

Polishing technologies	Characteristics	MRR (µm/h)	Roughness (nm)	Ref.
СМР	• Chemical • Mechanical	6.33	Ra = 1.86	Lu et al. ¹²
ECMP	• Electrical • Chemical • Mechanical	3.62	RMS = 0.23	Deng et al. ⁵⁷
РСМР	· UV · Chemical · Mechanical	1.223	Ra = 0.497	Gao et al. ⁴³
PAP	• Plasma • Chemical • Mechanical	21.8	Ra = 8.1	Ma et al. ⁵¹
CARE	· Catalyst · Etching	0.043	RMS = 0.06	Isohashi et al. ⁵⁸

Table 1. Comparison of different CMP technologies of SiC

5. Conclusions and prospect

The research status of the CMP of SiC is summarized in this paper. Firstly, the principle and developments of the traditional CMP technology are summarized. Then the influence of the abrasive particles and oxidants of polishing slurry on machining is discussed. High-quality and efficient polishing fluid is the goal pursued by researchers. The influence of different kinds of abrasives and oxidants on the MRR and surface quality of silicon carbide CMP material is also the main research direction at present. The balance between the polishing quality, the polishing efficiency and polishing cost is the core issue in the research process. After that, the advantages and disadvantages of various CMP variants developed from the traditional CMP technology and their respective development were discussed. The characteristics and performance parameters of different CMP technologies are compared in Table 1. These technologies play a significant role in solving the problem of low efficiency of SiC processing, and more in-depth research on them is also a hot spot, especially some more environmentally friendly improvement methods. Surface quality and processing speed are two most important requirements in SiC processing. Although SiC has been widely used, the processing technology still needs to be developed.

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Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- [1] Liu, L.; Zhang, Z.; Wu, B.; Hu, W.; Meng, F.; Li, Y. A review: Green chemical mechanical polishing for metals and brittle wafers. *J. Phys. D: Appl. Phys.* **2021**, *54*, 373001.
- [2] Hsieh, C.-H.; Chang, C.-Y.; Hsiao, Y.-K.; Chen, C.-C. A.; Tu, C.-C.; Kuo, H.-C. Recent advances in silicon carbide chemical mechanical polishing technologies. *Micromachines*. 2022, 13, 1752.
- [3] Ma, G.; Li, S.; Liu, F.; Zhang, C.; Jia, Z.; Yin, X. A review on precision polishing technology of single-crystal SiC. *Crystals.* 2022, 12, 101.
- [4] Wang, X.; Chen, J.; Bu, Z.; Wang, H.; Wang, W.; Li, W.; Sun, T. Accelerated C-face polishing of silicon carbide by alkaline polishing slurries with Fe₃O₄ catalysts. J. Environ. Chem. Eng. 2021, 9, 106863.
- [5] Matsunami, H. Fundamental research on semiconductor SiC and its applications to power electronics. *Proc. Jpn. Acad., Ser. B.* **2020**, *96*, 235-254.
- [6] Wang, W.; Lu, X.; Wu, X.; Zhang, Y.; Wang, R.; Yang, D.; Pi, X. Chemical-mechanical polishing of 4H silicon carbide wafers. *Adv. Mater. Interfaces.* **2023**, *10*, 2202369.
- [7] Pan, J.; Yan, Q.; Li, W.; Zhang, X. A nanomechanical analysis of deformation characteristics of 6H-SiC using an indenter and abrasives in different fixed methods. *Micromachines*. **2019**, *10*, 332.
- [8] Chen, Z.; Zhao, Y. Investigation into electrochemical oxidation behavior of 4H-SiC with varying anodizing conditions. *Electrochem. Commun.* **2019**, *109*, 106608.
- [9] He, W.; Zeng, Q.; Cheng, L.; Zhu, J.; Wang, Z.; Zhuang, J.; Wei, X. Droplet size dependent localized corrosion evolution of M50 bearing steel in salt water contaminated lubricant oil. *Corros. Sci.* 2022, 208, 110620.
- [10] Yan, C.; Zeng, Q.; He, W.; Zhu, J. First-principles investigation on the adsorption and dissociation of O₂ and H₂O molecules on the Ni-rich TiNi alloy surface. *Appl. Surf. Sci.* 2020, 534, 147570.
- [11] Zhang, Q.; Pan, J.; Zhang, X.; Lu, J.; Yan, Q. Tribological behavior of 6H-SiC wafers in different chemical

mechanical polishing slurries. Wear. 2021, 472-473, 203649.

- [12] Lu, J.; Luo, Q.; Xu, X.; Huang, H.; Jiang, F. Removal mechanism of 4H- and 6H-SiC substrates (0001 and 0001⁻) in mechanical planarization machining. *Proc. Inst. Mech. Eng.*, *Part B.* 2019, 233, 69-76.
- [13] Sodeifian, G.; Nikooamal, H. R.; Yousefi, A. A. Molecular dynamics study of epoxy/clay nanocomposites: Rheology and molecular confinement. J. Polym. Res. 2012, 19, 9897.
- [14] Sodeifian, G. Non-Linear Rheology of Polymer Melts: Constitutive Equations, Rheological Properties of Polymer Blends, Shear Flow, Sliding Plate Rheometers; LAP LAMBERT Academic Publishing, 2011.
- [15] Shi, X.; Pan, G.; Zhou, Y.; Gu, Z.; Gong, H.; Zou, C. Characterization of colloidal silica abrasives with different sizes and their chemical-mechanical polishing performance on 4H-SiC (0001). *Appl. Surf. Sci.* 2014, 307, 414-427.
- [16] Wang, W.; Liu, W.; Song, Z. Two-step chemical mechanical polishing of 4H-SiC (0001) wafer. Ecs J. Solid State Sci. Technol. 2021, 10, 074004.
- [17] Jindal, A.; Hegde, S.; Babu, S. V. Chemical mechanical polishing using mixed abrasive slurries. *Electrochem. Solid-State Lett.* 2002, 5, G48.
- [18] Tsai, Y.-H.; Chen, C.-C. A.; Suzuki, K.; Khajornrungruang, P.; Chiu, S.-F.; Hua, C.-T. Advanced chemicalmechanical planarization for 4H-SiC substrate by water-soluble inclusion complexes of fullerene. *Jpn. J. Appl. Phys.* 2020, 59, SLLA01.
- [19] Wang, W.; Xu, Q.; Liu, W.; Song, Z. Effect of particle size distribution, PH, and Na+ concentration on the chemical mechanical polishing of sapphire and 4H-SiC (0001). *Ecs J. Solid State Sci. Technol.* 2022, *11*, 044004.
- [20] Zhao, P.; Yin, T.; Doi, T.; Kurokawa, S.; Seshimo, K.; Ye, D.; Cai, J. Effect of Mn-based slurries on chemical mechanical polishing of SiC substrates. *Ecs J. Solid State Sci. Technol.* 2022, 11, 074002.
- [21] Nitta, H.; Isobe, A.; Hong, P.; Hirao, T. Research on reaction method of high removal rate chemical mechanical polishing slurry for 4H-SiC substrate. *Jpn. J. Appl. Phys.* 2011, 50, 046501.
- [22] Qi, W.; Cao, X.; Xiao, W.; Wang, Z.; Su, J. Study on the mechanism of solid-phase oxidant action in tribochemical mechanical polishing of SiC single crystal substrate. *Micromachines*. 2021, 12, 1547.
- [23] Rabie, A. M.; Tantawy, A. S.; Badr, S. M. I. Design, synthesis, and biological evaluation of novel 5-substituted-2-(3,4,5-trihydroxyphenyl)-1,3,4-oxadiazoles as potent antioxidants. Am. J. Org. Chem. 2016, 6, 54-80.
- [24] Rabie, A.; Tantawy, A.; Badr, S. Design, synthesis, and biological evaluation of new 5-substituted-1,3,4-thiadiazole-2-thiols as potent antioxidants. *Researcher*. **2018**, *10*, 21-43.
- [25] Su, J. X.; Du, J. X.; Liu, X. L.; Liu, H. N. Study on material removal rate of CMP 6H-SiC crystal substrate (0001) C surface based on abrasive alumina (Al₂O₃). AMR. 2012, 497, 250-255.
- [26] Aida, H.; Doi, T.; Takeda, H.; Katakura, H.; Kim, S.-W.; Koyama, K.; Yamazaki, T.; Uneda, M. Ultraprecision CMP for sapphire, GaN, and SiC for advanced optoelectronics materials. *Curr. Appl Phys.* 2012, *12*, S41-S46.
- [27] Su, J.; Du, J.; Ma, L.; Zhang, Z.; Kang, R. Material removal rate of 6H-SiC crystal substrate CMP using an alumina (Al₂O₃) abrasive. J. Semicond. 2012, 33, 106003.
- [28] Wang, X.; Chen, J.; Bu, Z.; Wang, H.; Wang, W.; Li, W.; Sun, T. Accelerated C-face polishing of silicon carbide by alkaline polishing slurries with Fe₃O₄ catalysts. *J. Environ. Chem. Eng.* **2021**, *9*, 106863.
- [29] Yin, T.; Doi, T.; Kurokawa, S.; Zhou, Z. Z.; Feng, K. P. Polishing characteristics of MnO₂ polishing slurry on the Si-face of SiC wafer. *Int. J. Precis. Eng. Manuf.* 2018, 19, 1773-1780.
- [30] Chen, G.; Du, C.; Ni, Z.; Liu, Y.; Zhao, Y. The effect of surface polarity on the CMP behavior of 6H-SiC substrates. *Russ. J. Appl. Chem.* 2020, 93, 832-837.
- [31] Wang, W.; Liu, W.; Song, Z. Two-step chemical mechanical polishing of 4H-SiC (0001) wafer. *Ecs J. Solid State Sci. Technol.* 2021, *10*, 074004.
- [32] Wang, W.; Zhang, B.; Shi, Y.; Ma, T.; Zhou, J.; Wang, R.; Wang, H.; Zeng, N. Improvement in chemical mechanical polishing of 4H-SiC wafer by activating persulfate through the synergistic effect of UV and TiO₂. J. Mater. Process. Technol. 2021, 295, 117150.
- [33] Liu, N.; Yi, R.; Deng, H. Study of initiation and development of local oxidation phenomena during anodizing of SiC. *Electrochem. Commun.* 2018, 89, 27-31.
- [34] Deng, J.; Pan, J.; Zhang, Q.; Yan, Q.; Lu, J. The mechanism of fenton reaction of hydrogen peroxide with single crystal 6H-SiC substrate. Surf. Interfaces. 2020, 21, 100730.
- [35] Deng, J.; Lu, J.; Yan, Q.; Pan, J. Enhancement mechanism of chemical mechanical polishing for single-crystal 6H-SiC based on electro-fenton reaction. *Diamond Relat. Mater.* **2021**, *111*, 108147.
- [36] Yang, X.; Yang, X.; Kawai, K.; Arima, K.; Yamamura, K. Novel SiC wafer manufacturing process employing three-step slurryless electrochemical mechanical polishing. J. Manuf. Processes. 2021, 70, 350-360.
- [37] Yang, X.; Yang, X.; Gu, H.; Kawai, K.; Arima, K.; Yamamura, K. Efficient and slurryless ultrasonic vibration

assisted electrochemical mechanical polishing for 4H-SiC wafers. Ceram. Int. 2022, 48, 7570-7583.

- [38] Yang, X.; Yang, X.; Gu, H.; Kawai, K.; Arima, K.; Yamamura, K. Charge utilization efficiency and side reactions in the rlectrochemical mechanical polishing of 4H-SiC (0001). J. Electrochem. Soc. 2022, 169, 023501.
- [39] Murata, J.; Hayama, K.; Takizawa, M. Environment-friendly electrochemical mechanical polishing using solid polymer electrolyte/CeO₂ composite pad for highly efficient finishing of 4H-SiC (0001) surface. *Appl. Surf. Sci.* 2023, 625, 157190.
- [40] Yuan, Z.; Cheng, K.; He, Y.; Zhang, M. Investigation on Smoothing Silicon Carbide Wafer With a Combined Method of Mechanical Lapping and Photocatalysis Assisted Chemical Mechanical Polishing; American Society of Mechanical Engineers Digital Collection, 2018.
- [41] Ohnishi, O.; Doi, T.; Kurokawa, S.; Yamazaki, T.; Uneda, M.; Yin, T.; Koshiyama, I.; Ichikawa, K.; Aida, H. Effects of atmosphere and ultraviolet light irradiation on chemical mechanical polishing characteristics of SiC *Wafers. Jpn. J. Appl. Phys.* 2012, *51*, 05EF05.
- [42] Yin, T.; Zhao, P.; Doi, T.; Kurokawa, S.; Jiang, J. Effect of using high-pressure gas atmosphere with UV photocatalysis on the CMP characteristics of a 4H-SiC substrate. *Ecs J. Solid State Sci. Technol.* **2021**, *10*, 024010.
- [43] Gao, B.; Zhai, W.; Zhai, Q.; Zhang, M. Novel polystyrene/CeO₂-TiO₂ multicomponent core/shell abrasives for high-efficiency and high-quality photocatalytic-assisted chemical mechanical polishing of reaction-bonded silicon carbide. *Appl. Surf. Sci.* 2019, 484, 534-541.
- [44] Wang, W.; Zhang, B.; Shi, Y.; Zhou, J.; Wang, R.; Zeng, N. Improved chemical mechanical polishing performance in 4H-SiC substrate by combining novel mixed abrasive slurry and photocatalytic effect. *Appl. Surf. Sci.* 2022, 575, 151676.
- [45] Yamamura, K.; Takiguchi, T.; Ueda, M.; Hattori, A. N.; Zettsu, N. High-integrity finishing of 4H-SiC (0001) by plasma-assisted polishing. Adv. Mat. Res. 2010, 126-128, 423-428.
- [46] Yamamura, K.; Takiguchi, T.; Ueda, M.; Deng, H.; Hattori, A. N.; Zettsu, N. Plasma assisted polishing of single crystal SiC for obtaining atomically flat strain-free surface. *Cirp Ann.* 2011, 60, 571-574.
- [47] Deng, H.; Ueda, M.; Yamamura, K. Characterization of 4H-SiC (0001) surface processed by plasma-assisted polishing. *Int. J. Adv. Manuf. Technol.* 2014, 72, 1-7.
- [48] Deng, H.; Takiguchi, T.; Ueda, M.; Hattori, A. N.; Zettsu, N.; Yamamura, K. Damage-free dry polishing of 4H-SiC combined with atmospheric-pressure water vapor plasma oxidation. *Jpn. J. Appl. Phys.* 2011, 50, 08JG05.
- [49] Deng, H.; Endo, K.; Yamamura, K. Damage-free finishing of CVD-SiC by a combination of dry plasma etching and plasma-assisted polishing. *Int. J. Mach. Tools Manuf.* 2017, 115, 38-46.
- [50] Yin, X.; Li, S.; Ma, G.; Jia, Z.; Liu, X. Investigation of oxidation mechanism of SiC single crystal for plasma electrochemical oxidation. *RSC Adv.* **2021**, *11*, 27338-27345.
- [51] Ma, G.; Li, S.; Liu, X.; Yin, X.; Jia, Z.; Liu, F. Combination of plasma electrolytic processing and mechanical polishing for single-crystal 4H-SiC. *Micromachines*. 2021, 12, 606.
- [52] Bui, P. V.; Sano, Y.; Morikawa, Y.; Yamauchi, K. Characteristics and mechanism of catalyst-referred etching method: Application to 4H-SiC. Int. J. Autom. Tech. 2018, 12, 154-159.
- [53] Okamoto, T.; Sano, Y.; Tachibana, K.; Pho, B. V.; Arima, K.; Inagaki, K.; Yagi, K.; Murata, J.; Sadakuni, S.; Asano, H.; Isohashi, A.; Yamauchi, K. Improvement of removal rate in abrasive-free planarization of 4H-SiC substrates using catalytic platinum and hydrofluoric acid. *Jpn. J. Appl. Phys.* 2012, *51*, 046501.
- [54] Hara, H.; Sano, Y.; Mimura, H.; Arima, K.; Kubota, A.; Yagi, K.; Murata, J.; Yamauch, K. Novel abrasive-free planarization of 4H-SiC (0001) using catalyst. J. Electron. Mater. 2006, 35, L11-L14.
- [55] Isohashi, A.; Bui, P. V.; Toh, D.; Matsuyama, S.; Sano, Y.; Inagaki, K.; Morikawa, Y.; Yamauchi, K. Chemical etching of silicon carbide in pure water by using platinum catalyst. *Appl. Phys. Lett.* 2017, *110*, 201601.
- [56] Kida, H.; Toh, D.; Bui, P. V.; Isohashi, A.; Ohnishi, R.; Matsuyama, S.; Yamauchi, K.; Sano, Y. High-efficiency planarization of SiC wafers by water-CARE (Catalyst-Referred Etching) employing photoelectrochemical oxidation. *Mater. Sci. Forum.* 2019, 963, 525-529.
- [57] Deng, H.; Hosoya, K.; Imanishi, Y.; Endo, K.; Yamamura, K. Electro-chemical mechanical polishing of singlecrystal SiC using CeO₂ slurry. *Electrochem. Commun.* 2015, 52, 5-8.
- [58] Isohashi, A.; Sano, Y.; Kato, T.; Yamauchi, K. Planarization of 6-Inch 4H-SiC wafer using catalyst-referred etching. *Mater. Sci. Forum.* 2015, 821-823, 537-540.