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The exploration of DLVO theory and adsorption principles during the polishing process of 6H-SiC wafers with SiO_2 and CeO_2 abrasives

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Abstract: *This manuscript provides an introduction to third-generation semiconductor material, single-crystal silicon carbide (SiC), offering a concise overview of its fabrication process. It delves into the chemical mechanical polishing of SiC wafers employing silica (SiO_2) and ceria (CeO_2) abrasives; it examines the variations in the wettability of SiC surfaces with pH changes, noting reduced contact angles and increased spreading coefficients in highly acidic and alkaline conditions. The study further analyzes the impact of SiO_2 abrasive concentration, revealing that an increase to 8wt% leads to a peak material removal rate of 185 nm/h. Predictive forces based on DLVO theory suggest that SiO_2 particles are prone to adhesion on the wafer surface within the pH range of 2-5, primarily due to DLVO-induced electrostatic attraction, which can result in surface contamination. In contrast, adsorption theories predict that CeO_2 particles are likely to adhere to the wafer surface in both acidic and alkaline solutions, predominantly through the chemical chelating actions of CeO_2 particles, without contaminating the surface.*

Keywords: *Single-crystal SiC; Chemomechanical polishing; SiO_2 abrasives; CeO_2 abrasives; DLVO theory; Adsorption phenomena; Zeta potential*

1. Introduction

In recent years, semiconductor materials have risen to prominence as a burgeoning industry, playing an increasingly pivotal role in cutting-edge technologies and the national economy. Exemplified by gallium nitride (GaN) and silicon carbide (SiC), third-generation semiconductors exhibit superior characteristics such as high-temperature resistance, high-voltage tolerance, high-frequency operation, high power capabilities, and radiation hardness[1]. Despite these attributes, their application has been historically constrained to a limited scope due to factors such as manufacturing processes and costs. However, with continuous breakthroughs in material growth and device fabrication techniques, the cost-performance ratio of third-generation semiconductors is gradually becoming apparent, thereby catalyzing their penetration into the market. SiC components have been employed in automotive inverters, while GaN-based fast chargers have been widely commercialized. Over the next five years, electronic devices founded upon third-generation semiconductor materials are anticipated to find extensive applications across various domains, including 5G base stations, renewable energy vehicles, ultra-high voltage systems, and data centers.

Silicon carbide (SiC), as the quintessential representative of third-generation wide-bandgap semiconductor materials, significantly outperforms first-generation elemental semiconductors (Si) and second-generation compound semiconductors (GaAs, InP, etc.) in both performance and reliability. This is particularly true in extreme conditions and harsh environments, making it an asset with vast potential for deployment in the realm of high-performance power semiconductor technology. Nonetheless, the inherent hardness, brittleness, and chemical inertness of SiC present substantial challenges in achieving wafer thinning and ensuring damage-free, smooth surfaces. On one hand lies the material's intrinsic processing difficulty; on the other, the stringent substrate specifications for epitaxial layers in integrated circuit fabrication demand flawlessly flat and ultrasmooth surfaces, virtually free from defects or damage. In concert with the advances propelled by smart technologies and the Internet of Things, the functionality and applications of integrated circuit chips have expanded, necessitating that substrate wafers evolve towards diminished thickness and enhanced, ultra-smooth, undamaged surfaces to accommodate the sophisticated requirements of high-end chips[2].

The quality and precision of SiC surface preparation critically influence the quality of epitaxial films and, by extension, the performance of corresponding devices. Thus, in their applications, an ultrasmooth,

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defect-free, and damage-less chip surface is imperative, with surface roughness values reaching sub-nanometer scales. The ultra-precision machining process for SiC wafers primarily entails a series of steps: orientation cutting, grinding (coarse and fine), mechanical polishing, and final chemical mechanical polishing (CMP). Traditional mechanical polishing and CMP are the primary methodologies employed, given the high hardness and chemical inertness of SiC crystals which resist chemical interactions at room temperature. Mechanical polishing is required to eliminate minuscule pits, reduce the surface damage layer, and remove scratches, pits, and orange peel-like defects induced during the grinding process, thus further smoothing the wafer surface and enhancing its planarity and overall quality. To achieve a polished surface of superior quality, it necessitates altering the abrasive type, reducing particle size, adjusting relevant processing parameters, and selecting polishing materials and cloths of sufficient hardness. However, traditional mechanical polishing can induce issues such as surface damage, alteration, subsurface destruction, and residual stresses.

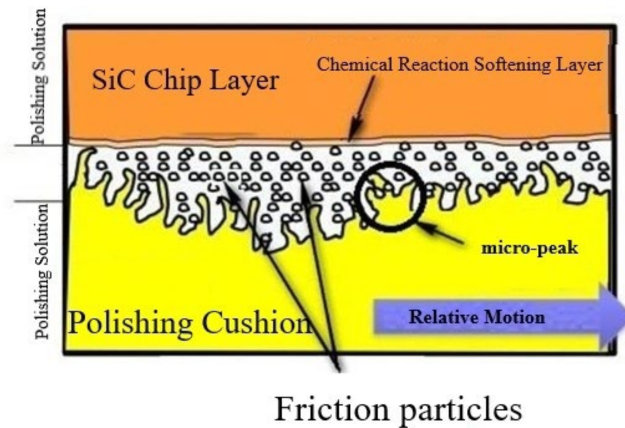

Figure 1: Chemical mechanical polishing mechanism illustration

In contrast to conventional mechanical polishing, the Chemical Mechanical Polishing (CMP) process of SiC wafer introduces a chemical effect. The chemically induced oxidation by oxidizers within the polishing slurry leads to the formation of a softened SiO_2 layer on the surface of the SiC wafer through the transformation of SiC into SiO_2. This enhances the machinability of the SiC wafer's surface. Subsequent mechanical abrasion by the abrasive particles removes this softened layer, thereby facilitating the elimination of material from the SiC wafer's surface and yielding a superior polished finish, as depicted in Figure 1. Consequently, the generation of the surface oxidized softening layer is central to the CMP process of SiC wafers, representing a pivotal step that determines the material removal rate. Chemical Mechanical Polishing (CMP) stands as one of the most efficacious methodologies to attain an ultra-smooth and damage-free SiC wafer surface.

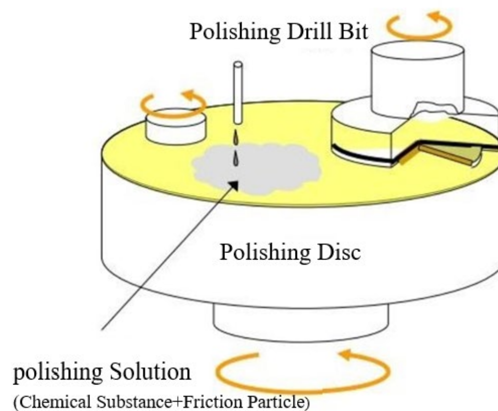

Figure 2: Chemical mechanical planarization apparatus diagram

To address the limitations of traditional mechanical polishing, contemporary advancements have led to the development of Chemical Mechanical Polishing (CMP). This process synergistically combines

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chemical etching and mechanical abrasion to remove and flatten surface materials on workpieces. During polishing, the wafers undergo chemical oxidation in the presence of the polishing slurry, leading to the formation of a chemically reactive layer. Subsequently, this softened reactive layer is removed under the mechanical action of the abrasives. The Chemical Mechanical Polishing apparatus is illustrated in Figure 2. This report primarily investigates the DLVO theory and adsorption mechanisms during the Chemical Mechanical Polishing of SiC wafers using SiO_2 and CeO2 abrasives.

2. The wettability analysis of polishing slurries on 6H-SiC wafers

Figure 3 presents a schematic representation of the interfacial free energy when an aqueous solution is placed upon the surface of a 6H-SiC crystal sample, where θ denotes the contact angle at the three-phase boundary.

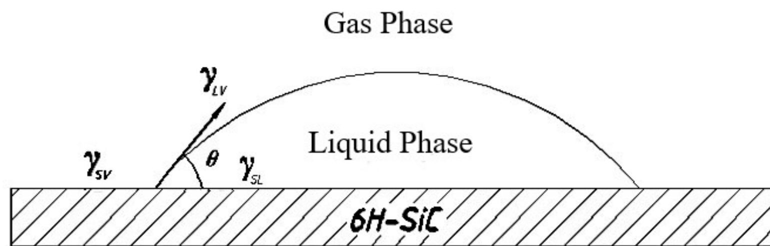

Figure 3: Diagram illustrating the surface interfacial free energy of 6H-SiC wafers[3]

Investigators ascertained the profile of the contact angle θ as a function of pH in aqueous solutions as delineated in Figure 4. It is evident from the figure that the contact angle initially escalates with an increase in pH, attaining a zenith between pH 5 and 6[3], before subsequently diminishing. A diminished contact angle characterizes both the low and high pH extremities on the chip surface. A quintic polynomial regression applied to the data in Figure 4 yielded a correlation coefficient, R^2, of 0.99. The regression revealed a maximum contact angle of 58.0°, corresponding to a solution pH of approximately 5.5. The apex of the three-phase contact angle indicates the minimization of electrostatic interactions at the solid-liquid interface, designating this particular pH as the point of zero charge for the interface.

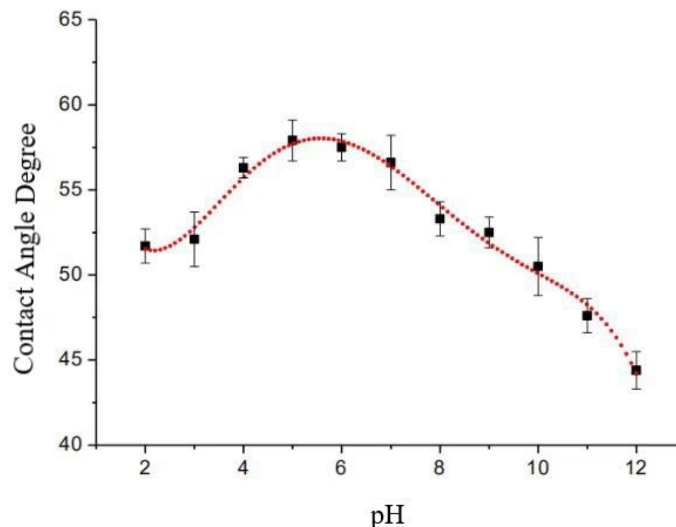

Figure 4: The variation curve of the contact angle as a function of pH[3]

The wettability coefficient at the 6H-SiC chip-water interface diminishes with rising pH levels, reaching a nadir within the pH range of 5-6. Beyond this threshold, as pH exceeds 6, there is a gradual enhancement in the wettability coefficient, as illustrated in the figure. In essence, under conditions of low (pH 2-3) and high (pH > 9) pH values, the surface of the chip exhibits elevated wettability coefficients, indicative of enhanced hydrophilicity. This promotes the spread of solutions across the chip's surface, thereby increasing the effective contact area between the solution and the chip—a phenomenon

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conducive to surface chemical reactions.

3. The role of SiO_2 abrasives in the polishing process of 6H-SiC wafers

Abrasive particles play a pivotal role in the mechanical removal during the CMP polishing process, representing a critical component within the polishing slurry. Their hardness, size, concentration, morphology, and properties considerably influence the efficiency of polishing. Researchers have investigated the impact of slurry pH and abrasive concentration on the CMP outcomes of 6H-SiC wafers using colloidal SiO_2 as the abrasive medium through experimental studies.

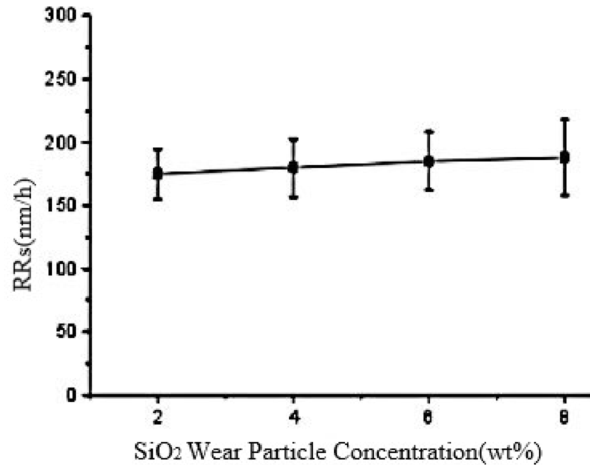

Figure 5: The concentration of SiO_2 abrasives significantly influences the polishing outcome[3]

As the concentration of SiO_2 abrasives increased from 2wt% to 6wt%, the material removal rate escalated from 175 nm/h to 185 nm/h. However, further augmentation of the SiO_2 concentration to 8wt% did not alter the removal rate significantly, as illustrated in Figure 5. The primary function of SiO_2 particles during the CMP polishing of 6H-SiC wafers is mechanical abrasion. With the increment in silica concentration, the mechanical action intensifies during polishing, thereby increasing the material removal rate. Nevertheless, as the concentration of SiO_2 particles continues to rise from 6wt% to 8wt%, the contact area between SiO_2 abrasives and the surface of the 6H-SiC wafer reaches its maximum, resulting in a saturation of mechanical effects and thus, the material removal rate remains essentially unchanged[3].

4. Adsorption mechanisms of SiO_2 and CeO_2 abrasives during the polishing process of 6H-SiC wafers

The colloidal stability of abrasive particles in a polishing fluid is commonly characterized by their zeta potential (ζ, mV), which is influenced by the pH of the solution and the presence of chemical additives. According to the DLVO theory, the zeta potential represents the electrokinetic potential at the slipping plane, distinct from the particle surface potential or Stern potential. Ions within the Stern layer are constrained, and the slipping plane moves with the particle, rendering the zeta potential a measure of the effective charge on the surface. A higher absolute value of zeta potential indicates a reduced propensity for particle aggregation. It is generally accepted that polishing fluid particles exhibit good stability when their zeta potential's absolute value exceeds 30mV. Electrostatic interactions between the abrasives and the wafer surface primarily cause particle adhesion, leading to wafer surface contamination, reduced contact between the wafer surface and oxidizers in the polishing fluid, impeded chemical oxidation, and consequently, a diminished material removal rate. Measuring the zeta potential of abrasives not only allows investigation into their interaction with the wafer surface based on the principle of like-charges repelling and opposite charges attracting but also serves as an indicator of suspension stability; larger absolute values of zeta potential correlate with greater inter-particle repulsive forces, dispersion, and stability, whereas smaller magnitudes indicate lesser repulsion, a propensity for flocculation, and poor stability.

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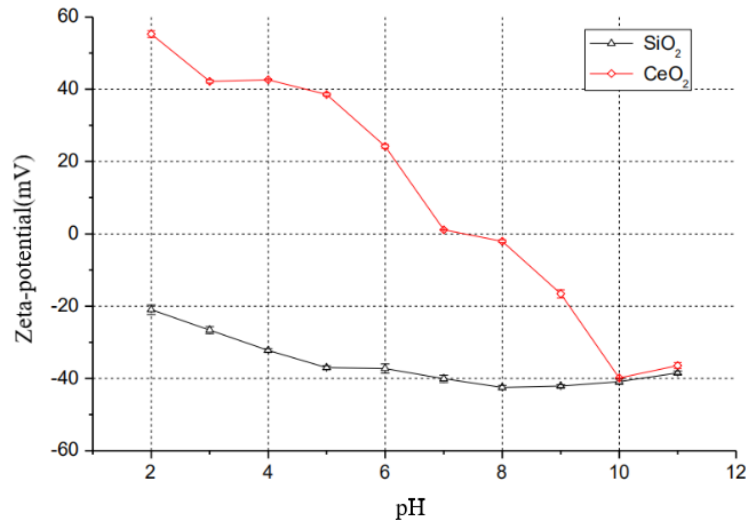

Figure 6: The zeta potential of SiO_2 and CeO_2 abrasives[4]

Figure 6 illustrates the relationship curves of zeta potential for nanoscale cerium dioxide abrasives and colloidal silica particles in deionized water as a function of pH. To predict the electrostatic attraction or repulsion between charged CeO_2 abrasives and charged 6H-SiC wafer surfaces, researchers[4] have employed the DLVO theory for computational optimization. The net DLVO interaction force F_{DLVO} is solely the sum of the double-layer electrostatic force F_{ELE} and the Van der Waals force F_{VdW}, excluding non-electrostatic double-layer interactions. Assuming the interplay between the particles and wafer is analogous to the interaction between spherical particles and a plane, the total DLVO energy (W_{TOT}) between the abrasive particles and the wafer surface is the aggregate of the double-layer electrostatic energy and the Van der Waals energy W_{VdW}. The correlation between the net DLVO interaction force F_{DLVO} and the total DLVO energy W_{TOT} is presented in Equation (1):

$$F_{DLVO} = -\frac{dW_{TOT}}{dD} \tag{1}$$

Utilizing the aforementioned equations, we have been able to simulate the relationship between the theoretical normalized force F_{DLVO}/R acting on SiC wafer surfaces and abrasive particles as a function of their proximity, denoted by distance D, under varying environmental conditions. This simulation has yielded the corresponding variations in interactions between SiO_2 and CeO_2 abrasives with 6H-SiC wafer surfaces across a range of pH levels, as illustrated in Figures 7 and 8. It is posited that the abrasives are spherical particles sharing an identical surface potential with their zeta potential.

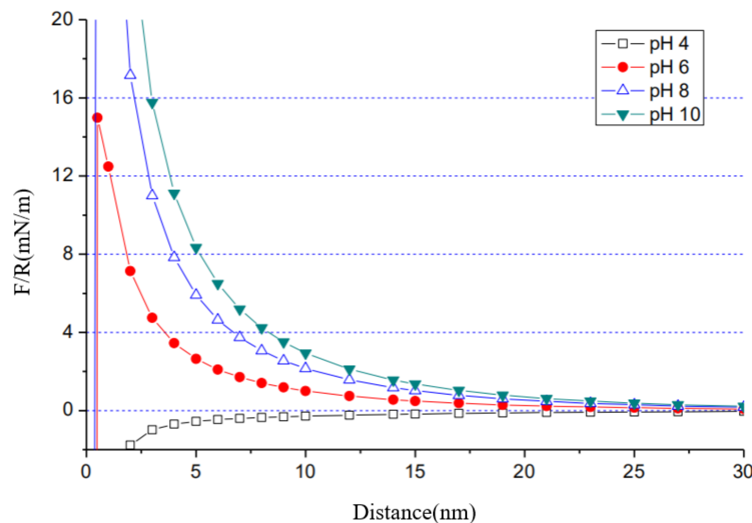

Figure 7: The relationship between SiO_2 abrasives and the surface of 6H-SiC wafers varies with distance D under different pH conditions[5].

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The adsorption of SiO_2 abrasive particles on the surface of 6H-SiC wafers is predominantly driven by electrostatic attraction. Examination of the chemical mechanical polishing (CMP) effects of SiO_2 particles on 6H-SiC wafers reveals that the slurry containing the oxidizer KMnO4 achieves its maximum material removal rate at a pH of 6, approximately 185 nm/h, whereas the minimum rate, about 88 nm/h, is observed at a pH of 4[6]. Theoretically, the oxidative potential of KMnO4 is higher at pH 4 than at pH 6; nonetheless, the lower material removal rate at pH 4 suggests an alternative mechanism. At this acidity, the electronegative SiO_2 particles are strongly attracted and adhere to the electropositive 6H-SiC wafer surface due to electrostatic forces, thereby hindering their removal and leading to the formation of a SiO_2 particle isolation layer that suppresses the oxidation of the wafer surface. In contrast, at pH 6, these electronegative SiO_2 particles are repelled by electrostatic forces and do not adhere to the 6H-SiC wafer surface, thus not impeding the oxidation process[7]. This electrostatic adhesion of particles presents a significant challenge in post-polishing cleaning, making it difficult to remove these contaminants and potentially compromising the polished surface quality.

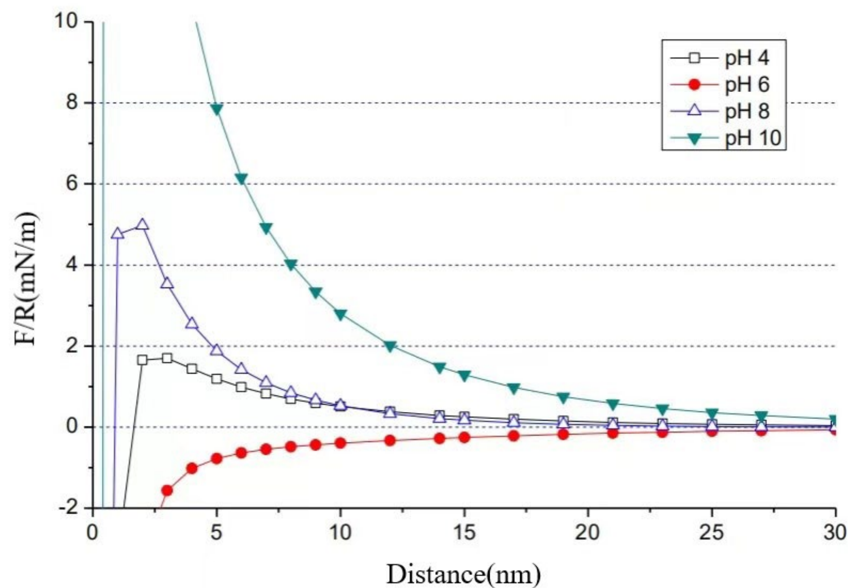

Figure 8: The relationship between CeO_2 abrasives and the surface of 6H-SiC wafers varies with distance D under different pH conditions[5].

The adherence of CeO_2 abrasives on the surface of 6H-SiC wafers is primarily attributed to the chemical mechanical interlocking. Observations of the material removal rate (MRR) during the Chemical Mechanical Polishing (CMP) of 6H-SiC wafers with CeO_2 reveal that the MRR correlates with the oxidizing potency of the polishing slurry; a more robust oxidative environment enhances the MRR, with rates at pH 2 and pH 4 measured at 1089 nm/h and 678 nm/h, respectively[7]. This indicates that particle adhesion induced by chemical mechanical interlocking not only fails to suppress the oxidation of the wafer surface but indeed facilitates the removal of material, resulting in elevated MRRs in highly oxidative polishing slurries[8]. At pH 2, the adhesion of CeO_2 particles via chemical mechanical interlocking onto the wafer surface is transient, readily disrupted during the tribological interactions. Surface hydrolytic oxidation catalyzed by $KMnO_4$, coupled with relative motion against the polishing pad, allows chemically-adhered CeO_2 particles to exert a tearing action on the oxidized layer of the wafer, thereby promoting material removal. The CeO_2 particles anchored through chemical mechanical interlocking are easily eliminated during the cleaning process, thus preventing the contamination of the polished surface with residual particles.

5. Conclusions

In summary, the DLVO theory-based predictions of adhesive forces indicate that SiO_2 particles are prone to adhere to wafer surfaces within the pH range of 2 to 5. This adhesion, primarily driven by DLVO electrostatic attraction, results in the SiO_2 particles being adsorbed onto the wafer surfaces through electrostatic interactions, inhibiting the oxidative hydrolysis of the surface, reducing the material removal rate, and contributing to particulate contamination of polished surfaces. Conversely, predictive forces

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based on adsorption theories suggest that CeO_2 particles readily adhere to wafer surfaces in both acidic and alkaline solutions, predominantly due to the chemisorptive interactions of the CeO_2 particles. The adherence of CeO_2 particles, facilitated by chemical bonding, not only does not obstruct the oxidative hydrolysis of wafer surfaces but also promotes the removal of oxidized material without causing particulate contamination of the polished surfaces.

References

[1] He, Chao; Wang, Yingmin; Li, Bin, et al. Current Status and Trends in SiC Chip Processing Technology[J]. Special Equipment for the Electronics Industry, 2016, 45(06): 1-6+54.
[2] Wuchang Hao, Bing Guo, Guang Yao. Study on the Chemical Mechanical Polishing Mechanism of Brittle Materials [J]. Machinery Design & Manufacture, 2014, 2: 37-39.
[3] Matovu J B, Ong P, Teugels L G, et al. Chemical mechanical planarization of patterned InP in shallow trench isolation (STI) template structures using hydrogen peroxide–based silica slurries containing oxalic acid or citric acid[J]. Microelectronic Engineering, 2014, 116(3): 17-21.
[4] Chen Guomei. Study on the Ultra-Precision Polishing Process and Mechanism of Silicon Carbide Wafers [D]. Jiangnan University, 2017.
[5] Wang Haibo, Yu Qincong, Liu Weili, et al. The influence of process conditions on the chemical mechanical polishing of sapphire [J]. Journal of Functional Materials and Devices, 2010, 16(3): 206-210.
[6] Zhang Zesheng. Study on the growth and physical properties of silicon carbide crystals by liquid phase epitaxy [D]. University of Chinese Academy of Sciences (Institute of Physics, Chinese Academy of Sciences), 2020.
[7] Deng H, Hosoya K, Imanishi Y, et al. Electro-chemical mechanical polishing of single-crystal SiC using CeO_2 slurry [J]. Electrochemistry Communications, 2015, 52: 5-8.
[8] Zhang Zhuqing. Design of a Chemical Mechanical Polishing Slurry for the Consolidation of SiC Single Crystals [D]. Henan University of Technology, 2014.