A novel approach for bulk micromachining of 4H-SiC by tool-based electrolytic plasma etching in HF-free aqueous solution

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ABSTRACT

Bulk micromachining of single-crystal SiC has been challenging due to its extreme stability both mechanically and chemically. To address this issue, a novel tool-based electrolytic plasma etching method is proposed, with which micropatterns and micro-holes are fabricated in SiC in a hydrofluoric acid-free aqueous solution with no need for masks. The material removal is the result of the combined effects of electrolytic plasma chemistry and physics. The chemistry refers to the reaction of Si with hydroxyl radical to form various SiOx and with H to form silanes, and the reactions of C to form volatile carbon oxides or hydrocarbons, all of which are accomplished and enhanced under the electrolytic plasma atmosphere. Besides, the local high temperature of plasma thermally promotes the evaporation or dissolution of SiO2 in NaOH solution. The tool-based electrolytic plasma etching method provides alternative approaches for the fabrication of SiC-based MEMS and devices.

1. Introduction

Single-crystal silicon carbide (SiC) semiconductor has experienced tremendous growth in the past decade towards their applications in the fabrication of electronic devices, precision MEMS and sensors, energy storage devices, and for chemical and biomedical technology [1–3] owing to its outstanding mechanical properties, such as high mechanical hardness, high thermal conductivity, wide bandgap, and high electric breakdown strength, etc. Machining of micro/ nanoscale structures in SiC is essential to fabricate these devices. For example, SiC nanosturcture like nanowires is reported to exhibit a remarkable ability for photocatalytic water splitting and become a suitable candidate for hydrogen generation application due to the large surface area ratio of nanomaterials and high chemical/mechanical stability [4,5]. Porous SiC with high-temperature stability is finding applications in the fields of biomedical engineering and protein dialysis etc. [6]. On the other hand, SiC microstructures like micro-hole and micro-groove, etc., are frequently used in micro electrochemical systems and sensors as functional structure or sensing components, which can work under harsh conditions like extreme high temperature or corrosive environment [7]. To maximize the device performance, both the surface quality and geometric uniformity of micro/nanostructures should be ensured in the machining process. However, SiC exhibits extreme stability and robustness both chemically and mechanically due to its short Si-C interatomic distance (0.189 nm) and high binding energy (about 4.5 eV), which make it significantly difficult to fabricate micro-/nanostructures. For example, SiC is resistant to almost all chemicals except for molten KOH above 600 °C [8].

So far, only a few fabrication technologies, primarily non-traditional approaches, are applied to the micromachining of SiC. Conventional cutting approaches using diamond tools are used for drilling [9] or surface finishing of SiC such as diamond turning [10]. However, they are not applicable for micromachining of SiC due to the serious problem of tool failure, the presence of cutting forces and microstructure fracture, and the high cost of microtools, etc. Featuring non-contact characteristics, non-traditional machining approaches including melting, ablation, and etching have drawn significant attention. For example, laser micromachining [11] and electrical discharge machining [12], as thermal processes, have been developed for micro-drilling or micro-milling of SiC. However, both of them cause subsurface damage and leave a heat-affected zone on the resulted surface. Dry etching based on reaction ion or plasma has been primarily applied for micro- or nano-structuring of SiC [7,13,14]. For example, Luna et al. used the deep reactive ion etching method to etch 4H-SiC, and a vertical trench with an aspect ratio of 8.5 for 5.5 μm opening was fabricated using SF6/O2 plasma [15]. Nevertheless, the ion bombardment causes surface damage. Besides, the...
processes are of the high cost. On the other hand, wet chemical etching is an attractive approach owing to the low process cost and low process-induced damage [16, 17]. However, the large bandgap and low-lying valence band edge cause direct chemical etching of SiC nearly impossible except for the molten KOH etching [8]. Recently, various hybrid approaches, mainly including electrochemical etching [18, 19], photochemical etching [20, 21], and metal-assisted hybrid etching methods [22, 23] have been explored. For example, Van Dorp et al. described comprehensively the electrochemical etching of 4H-SiC in HF solution of pH 3 considering the surface reactions, kinetics, and mass transport [18]. Chen et al. successfully fabricated gourd-shaped nanowires on 4H-SiC by anodic oxidation with pulsed voltage in a solution of HF: C\textsubscript{4}H\textsubscript{10}OH: H\textsubscript{2}O = 3:6:1 [19]. Zhao et al. fabricated a suspended SiC MEMS microstructure by photochemical etching based on the selective etching of p-SiC and n-SiC taking advantage of their different flat-band potentials [20]. Leitgeb et al. investigated the metal-assisted photochemical etching of the 4H-SiC method to form a porous 4H-SiC layer and concluded the importance of UV light irradiation and oxidizing agent in the formation of the porous layer [22]. To reduce the required high voltage and high current density that are required to create holes in an anodic etching of SiC, Chen et al. proposed a hybrid anodic and metal-assisted chemical etching technique to fabricate SiC nanowires at a low voltage below 10 V, as the Pt metal can catalyze the reaction of hole production and induce the band bending for hole concentration at the surface for etching [23]. Despite their effectiveness for surface micro/nanostructuring, the active substance of fluorine is indispensable in either case, which poses a serious threat to both humans and the environment. It is therefore in urgent need to develop a simple and efficient method for bulk micromachining of 4H-SiC substrates with an eco-friendly aqueous electrolyte solution.

Spark-assisted chemical engraving (SACE) has been widely studied and applied for micromachining of non-conductive materials [24, 25], such as pyrex glass, quartz glass, and zirconia ceramics materials [26]. Based on the principle of heat-promoted chemical etching, SACE can result in burr- and crack-free machining of glass while maintaining transparency. Therefore, SACE is finding applications in the fabrication of lab-on-a-chip, biomedical sensors, and microreactors [27]. Further, micro-drilling of holes of 30 μm in diameter [28] and deep micromachining with an aspect ratio of 11 is achievable by SACE [29]. By reducing the gas film thickness [30] and stabilizing the spark ignition [31], the processing accuracy and stability are being further improved. On the other hand, there has been no research focusing on the processing of semiconductor material.

Inspired by SACE, in this study, a novel microtool-based HF-free wet etching method, namely, the electrolytic plasma etching (EPE) method, was proposed to fabricate SiC microstructures in an eco-friendly electrolyte solution. The etching mechanism of 4H-SiC (0001) is elucidated through comparative experiments and process simulation considering the electric fields, mass transfer, and surface reactions and kinetics. Based on the results, the importance of electrolytic plasma in the machining of SiC is discussed. Meanwhile, several examples of machining experiments for the fabrication of SiC micro-/nano-structures are shown to demonstrate the feasibility of EPE for bulk micromachining of SiC.

2. Experimental section

2.1. Materials

A chemical mechanical planarization (CMP) finished n-type 4H-SiC substrate (TanseBlue Semiconductor Co. Ltd) with a thickness of 350 μm and a specific resistance 0.015–0.028 Ω·cm was used as the specimen. Before the experiments, the SiC specimens were ultrasonically cleaned with acetone and alcohol for 2 min respectively and then rinsed with deionized water for 1 min to remove contaminants. Fig. 1 shows schematically the experimental method of electrolytic plasma etching. An electrolytic cell composed of an anode of graphite with a size of 50*30*5 mm³, a cathode of tungsten microrod with a diameter of 300 μm, and NaOH aqueous solution was prepared. The SiC specimen, with the (0001) plane as the working surface, was placed right under the tungsten microrod but with no feed of electricity. In this configuration, the cathodic tungsten microrod was employed as the microtool to perform localized etching and micromachining. The electrolyte concentration and electric conductivity of NaOH were 6 mol/L and 41.2 S/cm, respectively. Electric bias is applied between the microtool electrode and graphite counter electrode, which are distanced by a few centimeters, to induce electrolytic plasma. A power amplifier (HSA4014, NF) was used to supply the voltage bias, of which the output could be arbitrarily controlled by a function generator (33612A, Keysight). A numerically-controlled motion platform (V-731, Physik Instrumente) was employed to accurately position the microtool electrode.

2.2. Concept and principle of tool-based electrolytic plasma etching method

The concept of the newly proposed tool-based electrolytic plasma etching (EPE) method is schematically depicted in Fig. 1. The electrode reactions occurring in the electrolytic cell includes:

\[
\text{Cathode reaction: } 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \tag{1}
\]

\[
\text{Anode reaction: } 4\text{OH}^- - 4e^- 
\rightarrow 2\text{H}_2\text{O} + \text{O}_2 \tag{2}
\]

Cathodic hydrogen gas evolution can be enhanced by concentrating a high current density on the microtool surface, which can be realized by adjusting the applied voltage and electrode surface area. The accumulation of the evolved gas bubbles can eventually form a gas layer around
the microtool electrode and insulate, or partially, the microtool surface. At a critical voltage, breakdown occurs and electrolytic plasma is generated around the microtool electrode [24]. The machining target is placed right below the plasma, facing the microtool tip with a gap distance of several micrometers. The energetic particles within the plasma including neutral molecules, ions, and free radicals can oxidize and etch the SiC surface locally, thus realizing micromachining or surface modification.

The electrolytic plasma etching process of SiC is considered a two-step process. First, electrochemical and/or chemical oxidation of SiC occurs under the external electric potential and plasma, as expressed by Eq. (3) and Eq. (4) [32,33]. To be noted is that the semiconductor 4H-SiC is electrically powered because of the contact with the electrolyte, although it is not directly wired. As a result, as shown in Fig. 2, SiC possesses a relatively positive potential than the microtool electrode. Under the electric field, holes (h⁺) are transported to the SiC surface, and the electrochemical oxidation reaction of SiC which requires holes (h⁺) takes place when it is exposed to NaOH electrolyte [34–36]. Further, more holes are promptly generated by the plasma irradiation, resulting in promoted oxidation of SiC. The transportation of holes to the surface can be promoted with the external voltage bias owing to enhanced band bending. On the other hand, the resulted oxide layer is either chemically dissolved into the electrolyte solution, as described by Eq. (5) and Eq. (6) [37], or thermally removed or evaporated by high-temperature plasma to progress the machining. Meanwhile, the plasma may also directly remove the oxide layer by plasma-induced physical/chemical reactions such as the local breakdown of oxide film and dissociation. By feeding the microtool electrode along a programmed path, arbitrary microstructure patterns can be generated on the SiC specimen.

\[
\text{SiC} + 4\text{OH}^- + 4h^+ \rightarrow \text{SiO}_2 + 2\text{H}_2\text{O} + \text{CO}_2 \uparrow \tag{3}
\]

\[
\text{SiC} + 8\text{OH}^- + 8h^+ \rightarrow 2\text{SiO}_2 + 4\text{H}_2\text{O} + \text{CO}_2 \uparrow \tag{4}
\]

2.3. Characterization

The surface morphology of SiC specimens after machining was studied by a field emission scanning electron microscope (Merlin, Zeiss). The surface element composition was analyzed with an energy dispersive spectrometer (EDS, Octane Pro). The change in surface profile was measured using a confocal laser scanning microscope (VK-X1000, Keyence). The confocal laser Raman spectrometer (LabRAM HR Evolution, Horiba) with a wavelength of 532 nm and laser spot size smaller than 5 μm were used to investigate the mechanism of surface formation and the structural change of the material.

2.4. Simulation model

Modeling of the EPE process is carried out to analyze and describe the electric field distribution. The following assumptions are made to simplify the model: (1) no bubbles generation, and (2) no temperature
change during the process. Also, the dissolution of material is not considered.

Fig. 3 shows the established 3D model of EPE in a finite element-based analysis software COMSOL, which consists of an electrolyte solution, a counter electrode, a tool electrode, and a workpiece. Table 1 shows the simulation conditions. Based on the electric field theory of charge conversation, the distribution of electrical potential $\phi$ in the machining area can be obtained by solving Laplace’s equation, Eq. (7) [38,39].

$$\nabla^2 \phi = \frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} + \frac{\partial^2 \phi}{\partial z^2} = 0$$  

(7)

The corresponding boundary conditions are as follows, where $n$ is the unit normal vector of surface:

$$\phi |_{\Gamma_{\text{cathode surface}}} = 0 \quad \text{(Cathode boundary)}$$  

(8)

$$\phi |_{\Gamma_{\text{anode surface}}} = 55 \quad \text{(Anode boundary)}$$  

(9)

$$\frac{\partial \phi}{\partial n} |_{\Gamma_{\text{remaining surface}}} = 0 \quad \text{(Insulating boundaries)}$$  

(10)

3. Results and discussion

3.1. Electric field distribution

Fig. 4 shows the simulation result of electric field distribution in EPE.

As can be seen in Fig. 4(b), SiC possesses high electric potentials due to its conductivity as a semiconductor, although it is not wired. According to the electrical potential distribution shown in Fig. 4(c) and (d), the potential decreases slightly in the electrolyte due to the electrolyte resistance (ii~iii region), and drops significantly in the SiC substrate owing to its resistance (iii~iv region) along the measurement line $l_1$. In
Fig. 6. Calculated current density distribution in EPE, arrows represent the electric current density.

Fig. 7. Experimental setup for tool-based electrolytic plasma etching of 4H-SiC.
the peripheral region far away from the microtool electrode, the surface of SiC is at high potentials of about 20–46 V, while the local potential near the microtool gets close to 0 V. This potential difference creates a bias between the grounded microtool electrode and SiC substrate. The equivalent circuit of EPE can be drawn as in Fig. 5. In the electrochemical system for EPE of SiC, the main current ($i_1$) flows from the graphite counter electrode to the cathodic microtool electrode, inducing a plasma. Meanwhile, a minute current ($i_2$) with a very small current amplitude is flowing through the SiC, which causes SiC to be slightly charged and have a weak anodic environment.

Fig. 6(a) shows the current density distribution along the cross-sectional surface of the microtool. Fig. 6(b) shows an enlarged view of the machining area between the microtool and the SiC specimen, where the concentration of current density at the microtool edge can be observed. By contrast, the current density in the machining gap is very small. Fig. 6(c) shows the current density distribution on the specimen surface, where a ring area of concentrated current density near the microtool edge is confirmed. In comparison with the current density (280 A/cm²) in the electrolyte region, as shown in Fig. 6(d), the current density flowing through the SiC is as low as 10 A/cm². If we plot the current density distribution along the measurement line $l_2$ (Fig. 6(e)), a sharp rise at the SiC-electrolyte interface can be found. The locally concentrated high current density near the edge of the microtool at the machining gap can cause the preferential oxidation and dissolution of SiC (Fig. 6(f)), which are verified in the later experimental sections.

### Table 2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulse voltage (V), $U$</td>
<td>30 (ECE), 55 (EPE)</td>
</tr>
<tr>
<td>Pulse frequency (kHz), $f$</td>
<td>100</td>
</tr>
<tr>
<td>Pulse duty ratio (%), $D$</td>
<td>50</td>
</tr>
<tr>
<td>Processing time (s), $t$</td>
<td>10</td>
</tr>
<tr>
<td>Gap distance ($\mu$m), $G$</td>
<td>30</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>6 mol/L NaOH aqueous solution</td>
</tr>
<tr>
<td>Tool electrode</td>
<td>Tungsten rod, diameter 300 $\mu$m</td>
</tr>
<tr>
<td>Counter electrode</td>
<td>Graphite plate, 50<em>30</em>5 mm³</td>
</tr>
</tbody>
</table>

3.2. Electrolytic plasma etching of 4H-SiC (0001)

Fig. 7 shows photos of the home-made experimental setup. The microtool is grounded relative to the positive counter electrode during experiments. The SiC specimen is positioned below the microtool and kept unwired. Electrolytic plasma is induced at the microtool by application of voltage bias, and the typical current-voltage curve during the process is shown in Fig. 7(c). The transient current rapidly decreases to 0.6 A after the voltage is applied due to the formation of a gaseous film of high resistance around the microtool. Plasma ignition occurs when the electric field intensity across the gaseous film reaches a critical breakdown value (about $10^8$ V·cm⁻¹) [24]. For comparative study, the material response to the process with and without plasma was investigated by controlling the applied voltage. Unless otherwise specified, all experiments were carried out under the conditions shown in Table 2.

First, point-processing experiments of electrochemical etching (ECE) with no plasma were conducted by keeping the microtool stationary. A low voltage of 30 V was applied to avoid plasma generation. However, it is surprisingly found that, as shown in Fig. 8, 4H-SiC can be etched even without plasma. In Fig. 8(a), a halo-like circular etching mark can be observed on the SiC surface near the microtool edge. According to the profile measurement, this etching mark is a shallow micro-hole with depth $< 500$ nm. Fig. 8(b) and (d) show the enlarged view of the boundary area of the etching mark where porous nanostructures composed of hexagonal or rounded nanopores appear. In comparison, the surface area right below the microtool exhibits a relatively smooth surface with uniform, dense, and much smaller nanoporous structure (Fig. 8(c)). The distribution of nanopores in aspects of size is in accord with the current density distribution calculated above, implying that the etching is related to the electrode reactions at the microtool. As hydrogen formation and alkalization occur at the cathodic microtool, the nanopores probably result from hydrogen etching under high temperature caused by ohmic heating and the resulted alkaline environment. Referring to the literature [40-42], we infer that the hydrogen etching here involves the reaction of surface Si with H to form silanes, and the reactions of C to form carbon oxides or hydrocarbons. Further, the implosion impact of hydrogen bubbles as they collapse may also
contribute to the nanopore formation.

On the other hand, the resulted surface morphology of 4H-SiC (0001) differs considerably when plasma is induced. As shown in Fig. 9(a), a circular etching region with two distinctive colors can be confirmed. The inset shows the cross-section profile of the produced feature. A larger material removal depth of 700 nm is found around the tool edge as compared to that of 400 nm in the tool center area, indicating preferential removal of material around the tool edge. This is considered due to the concentration of electric field at the tool edge, as suggested by the simulation results, which intensify the plasma ionization degree and the current flow locally. In the central etching area right beneath the microtool, as shown in Fig. 9(c), the SiC surface is slightly roughed by the plasma compared to the initial polished SiC surface. In the peripheral region of the microtool (Fig. 9(d)), however, parallelly arranged nano-stripes appear on the SiC surface which is similar to the periodic arrays of atomically flat terraces obtained from CMP. We infer that the nano-stripes are caused by the effect of the plasma oxidation along the terraces surrounding the microtool. Notably, nanoparticles are found at the boundary between the central etching area and the peripheral area, as shown in Fig. 9(b), and the nanoparticles become sparse towards the center of the etching region. As this boundary coincides with the microtool diameter, we consider that the nanoparticles result from the

![Fig. 9. SEM observation of surface response of 4H-SiC to EPE point-processing with plasma (U = 55 V, t = 10 s, G = 30 μm). (a) The etching area resulted from point-processing. (b) Nanoparticles appear at the boundary and gradually become sparse towards the central etching area. (c) The resulted surface morphology at the microtool center. (d) Parallel nano-stripes appear at the peripheral etching region.](image)

![Fig. 10. EDS spectra of the resulted surface by ECE and EPE.](image)
concentrated high electric field at the microtool edge. The high electric field strength probably causes a local breakdown of the oxide layer and further enhance localized chemical etching. In comparison to the etching results of ECE with no plasma (Fig. 8), EPE results in a more significant etching influence area while exhibiting a different surface morphology, of which the reason is discussed in the following sections. On the other hand, in EPE, a uniform material removal will happen if a smaller electrode is used.

3.3. Etching mechanism

To explore the machining mechanism in ECE and EPE, the EDS analysis of the resulted surface was carried out. As shown in Fig. 10 (a) and (b), no oxygen can be detected on the ECE surface, either at the flat surface area or the etched nano-hole area, proving our previous inference that hydrogen etching probably occurs on the SiC surface. Further, the abundant hydrogen gas absorbed on the surface probably protects SiC from oxidizing. On the other hand, the weight content of carbon in the nano-hole area is 29.5 %, slightly lower than that in the flat surface area, implying the possibility of dissociation of carbon from SiC by hydrogen. On the other hand, in EPE, as shown in Fig. 10 (c) and (d), the oxygen content of nanoparticles is 3.8 %, considerably higher than that of the nano-hole area, 0.06 %. This result suggests that oxidation reaction occurs in electrolytic plasma etching, and the SiC is partially oxidized into SiO$_x$.

To detect the possible structural changes of material in the subsurface layer of SiC after EPE, Raman spectroscopy was conducted on the machined surface. In Fig. 11, three typical Raman peaks of SiC can be identified on the pristine SiC surface. In comparison, no new peak, peak shift, or change in peak intensity can be observed in the Raman spectra of the machined surface areas, indicating that EPE exerts little influence on the material properties of SiC after machining.

While EPE exhibits a similar system configuration, this method differs from SACE by the inclusion of electrochemical reactions, as the semiconductor 4H-SiC exhibits a high conductivity of 0.015–0.028 $\Omega \cdot$ cm. Furthermore, EPE features a no-contact characteristic. The experiments of EPE have confirmed that, once the microtool contacts the conductive 4H-SiC workpiece, the electrolytic plasma will rapidly disappear due to sharply decreased current density. Therefore, a constant gap distance is required in the EPE of a semiconductor. The possible etching mechanisms involved in the tool-based EPE process include (1) plasma-enhanced electrochemical oxidation, (2) plasma-enhanced thermochemical etching, (3) electric breakdown of oxide film, and (4) plasma etching, which are depicted in Fig. 12. With the electric bias, holes can be transported to the SiC surface and bring about the electrochemical oxidation of SiC. Further, in EPE, holes can be promptly generated by the plasma heating and irradiation, leading to an enhanced oxidation reaction with hydroxyl radical, that is, the reaction of surface Si with OH radicals to form various SiO$_x$ [20]. Meanwhile, as discussed above, cathodic hydrogen formation and alkalization occur at the microtool, which can lead to hydrogen etching of SiC [40]. On the other hand, the resulted nano-scale thin oxide film SiO$_x$, together with SiC, can be thermochemically etched or dissolved by the NaOH electrolyte, as illustrated in Fig. 12(b) taking advantage of the local high temperature of the energetic plasma [37]. Furthermore, the oxide film can be electrically broken down and thus removed by the voltage drop across it (Fig. 12(c)). At last, the plasma can result in plasma reactions such as vapor ionization and hydrothermal reactions which can cause material dissolution (Fig. 12(d)) [40]. The hydrodynamic force caused by the implosion of the plasma bubble can further promote material removal. Eventually, an etching surface morphology with a nanoporous structure is formed.

Fig. 12 shows a schematic diagram of the material removal process at the atomic level. First, the SiC is oxidized by hydroxide ions or hydroxyl radicals by breaking the Si-C bond to form a Si-O oxide layer and CO$_2$ [34–36], as shown in Fig. 13(a). On the other hand, in Fig. 13(b), the oxide layer is rapidly dissolved and etched by the plasma-enhanced...
active electrolyte, leaving an exposed new Si-C surface [37]. The etching progresses by repeating an alternating process of oxidation and dissolution or disassociation under the combined effect of the electric field and electrolytic plasma.

3.4. Effects of key machining parameters on EPE

To clarify the machining characteristics of EPE, the key process parameters including machining time and machining gap are experimentally studied. Fig. 14 shows the influence of machining time on resulted surface morphology. The SiC surface is evenly modified in a very short
machining period of 6 s. Specifically, the specimen surface near the microtool is roughed. However, no evident etching morphology can be observed. With increasing the machining time, the etching trace on the specimen surface gradually becomes clearer. Eventually, a double-circle etching region can be observed on the workpiece surface, as shown in Fig. 14 (b) and (c). According to Fig. 14 (g), the etching area gets stable after \( t = 8 \) s, and the size of the etching circle stabilizes at 240 \( \mu \)m for the inner-circle and 500 \( \mu \)m for the outer-circle.

The influences of the gap distance, \( G \), are shown in Fig. 15. At a large gap distance \( G = 100 \) \( \mu \)m, the workpiece surface exhibits a circular and uniform modified area with no identifiable etching trace, indicating an even and mild impact of plasma on the material. The double-circle etching area gradually appears when the machining gap is narrow down below 80 \( \mu \)m. The main reason is considered that at a small machining gap, both the current density flowing through SiC and the plasma energy distributed to the SiC surface is increased. Furthermore, the current density distribution tends to concentrate at the microtool edge at a smaller gap distance. As a result, etching becomes more significant and uneven at smaller gap distances. Notably, at \( G = 0 \) \( \mu \)m when the microtool gets short-circuited with the specimen, electrolytic plasma disappears due to reduced current density on the microtool surface and spark/arc discharge occurs instead, leaving an arc discharge crater with microcracks in it. Fig. 16 shows an example of the typical current waveform during EPE. When keeping a normal gap distance, the typical current waveform is oscillating and varying during machining due to the dynamic behavior of gaseous bubbles and plasma surrounding the microtool. When the gap is shorted at \( G = 0 \) \( \mu \)m, the machining current in the main circuit considerably increases due to the vanishing of plasma and gaseous bubbles at the cathodic microtool. This can be effectively used as a criterion to distinguish the gap conditions and realize servo control of the gap distance during the machining.

3.5. Micropatterning by EPE

Micropatterning of SiC by scanning EPE was carried out by transversing the microtool electrode over the SiC surface at a speed of 5 \( \mu \)m/s. The machining gap was set at 10 \( \mu \)m, and the microtool was not fed during machining. All the other machining conditions were the same as in Table 2.

Fig. 17(a) shows the schematic diagram of the scanning EPE. Fig. 17 (b) and (c) show the experimental results. Microstructures of micro-triangle and micro-circle which show a clear profile were successfully fabricated by the scanning EPE method. Furthermore, no micro-cracks or discharge craters were generated on the machined surface, indicating that EPE is an electrochemical or chemical removal process. In Fig. 17(b), the micro-groove width is 308 \( \mu \)m, and the overcut is only 4 \( \mu \)m, demonstrating the feasibility of EPE for microstructure fabrication with micro-scale precision. On the other hand, the process is not immediately functioning and not so stable at the beginning stage, as shown in Fig. 17(c). Two possible reasons are considered for this. First, the generation of plasma takes time. However, the tool scanning motion

Fig. 16. The typical current waveform in EPE.

Fig. 17. Micropatterning of 4H-SiC by EPE. (\( U = 55 \) V, \( f = 100 \) kHz, \( D = 50 \% \)).
and the application of voltage were not accurately synchronized in the experiments. Therefore, the functioning of plasma is delayed relative to the tool electrode movement. Secondly, the positioning error of the workpiece may cause variation of machining gap, while the EPE process is sensitive to the machining gap. Both the reasons can result in a delayed and unstable process at the initial machining stage. However, once the process gets stable, the feature depth along the scanning route becomes even and consistent, as evidenced in Fig. 17(d).

3.6. Application of EPE in micro-hole drilling

Micro-hole drilling by EPE can be expected by feeding the microtool

Table 3
Experimental conditions for micro-hole drilling by EPE.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC substrate thickness (μm)</td>
<td>350</td>
</tr>
<tr>
<td>Spiral microtool diameter (μm)</td>
<td>100</td>
</tr>
<tr>
<td>Spiral microtool material</td>
<td>Tungsten steel</td>
</tr>
<tr>
<td>Immersion depth (mm)</td>
<td>2</td>
</tr>
<tr>
<td>Rotate speed (r/min)</td>
<td>3000</td>
</tr>
<tr>
<td>Feed rate (μm/s)</td>
<td>0.5</td>
</tr>
<tr>
<td>Machining time (minute)</td>
<td>20</td>
</tr>
</tbody>
</table>

Fig. 18. Schematic diagram of machining gap in EPE micro-drilling: (a) using a rod microtool. (b) using a spiral microtool.

Fig. 19. SEM study of obtained micro-hole by EPE drilling using a spiral microtool electrode. \((U = 55 \text{ V}, f = 100 \text{ kHz}, D = 50 \%)\).
axially towards the workpiece. However, as illustrated in Fig. 18(a), in deep hole drilling by EPE using a rod microtool, it is difficult for the electrolyte to flow into the machining area and recycle, which easily causes the lack of electrolyte at the machining gap, and thus affecting the machining stability [43]. Besides, the current density is preferentially concentrated at the microtool edge, which is no suitable for deep-hole drilling. Therefore, a spiral microtool as shown in Fig. 18(b) is used in this study, which can enhance the electrolyte replenishment by the spiral grooves of the microtool. This can lead to a stable electrolytic plasma on the microtool surface. Furthermore, the current density is concentrated at the tip of the microtool, which is beneficial to improve the process efficiency of drilling. During drilling, a low feed rate of 0.5 μm/s is applied to ensure that there is no short-circuiting. The specific experimental conditions are shown in Table 2 and Table 3.

Fig. 19 shows SEM observation of the machined holes by the proposed method using Φ100 μm spiral microtool. A through-hole on the 350 μm thick SiC substrate is obtained, of which the entrance and exit diameters are 220 μm and 176 μm, respectively. The tape angle of the micro-hole is 3.6°. According to the observation, the non-processed area surrounding the micro-hole presents an unaffected smooth surface with no stray corrosion and oxidation, just the same as the initial surface. On the other hand, the side-wall of the micro-hole exhibits a rough surface morphology with microcracks observed, as shown in Fig. 19(c), which are probably caused by violent etching. We infer that a large temperature gradient is produced inside the SiC specimen due to the high-temperature plasma, and the insufficient supply of the cooling electrolyte to the machining gap further enhances the heat accumulation. The hydrodynamic force resulted from the kinetic energy of plasma due to the implosion of the plasma bubble may also contribute to the violent etching of SiC [44]. According to the enlarged views of the surface micromorphology at the edge of the hole entrance shown in Fig. 19(d) and (e), an etching morphology with a multi-layered nanoscale porous structure can be confirmed. To be noted is that, in Fig. 19(e), an oxide film-like layer is observed, which is dissolved and etched into nanoporous structure probably under the combined action of plasma-chemical-electrochemical etching. The layer thickness is measured to be about 800 nm, and part of the layer is broken and probably peeled off, leaving an evident breaking edge. Furthermore, the exposed SiC surface beneath the layer also presents numerous nanoscales etching holes. Fig. 19(f) shows a typical microscopic morphology of the side-wall of the micro-hole. A dense nanoporous structured surface can be confirmed, indicating that the etching is the principal material removal mechanism in EPE. The above results demonstrate the feasibility of EPE for micromachining SiC with an HF-free aqueous solution. On the other hand, tool wear occurred during the drilling process, as shown in Fig. 20. The micro-bit tool is shorted for 0.12 mm after the machining, and the tip is deformed probably due to collision with the workpiece during the tool feed. Previous research has demonstrated that the occurrence of plasma phenomena around the tool electrode causes no tool wear [45]. It is therefore considered that the heat derived from the plasma probably accumulates at the narrow and lack-of-fluid machining gap and burns the microtool, which gives rise to the melt-and-resolidification of the tool tip.

4. Conclusion

A novel bulk micromachining method of semiconductor 4H-SiC (0001) by electrolytic plasma etching (EPE) in an HF-free aqueous solution is studied in this paper. A surface modification and material removal mechanism were developed based on process modeling and experiments. From the results obtained, the SiC specimen shows a sensitive response to the microtool-induced electrolytic plasma. Either etching, oxidizing, or bulk removal can be achieved by situating the plasma-specimen gap conditions, enabling the surface modification and micromachining of SiC. This approach is a derivative technique inspired by the SACE process and differs from SACE by the inclusion of electrochemical reactions to machine semiconductor materials. Furthermore, EPE features non-contact machining characteristics. By contrast experiments with pure electrochemical etching, an initial understanding of the electrolytic plasma etching process is discussed. It is hoped that this method described here provides alternative approaches for the fabrication of SiC-based MEMS and devices.

The main findings of this study are summarized as the following:

(a) Both electrochemical hydrogen etching and plasma-assisted etching occur on the surface of the 4H-SiC (0001) with
situating the gap conditions, of which the extent is determined by the current density.

(b) The inert 4H-SiC (0001) can be easily etched/machined under the combined effect of electrochemical reaction and plasma reactions. SiC oxidation is enhanced due to a bent band and promoted hole generation under the combined action of cathodic plasma and electric field. The etching mechanism involves (1) plasma-enhanced electrochemical oxidation, (2) plasma-enhanced thermochemical etching, (3) electric breakdown of oxide film, and (4) plasma etching.

(c) Arbitrary bulk micromachining of SiC, including micro-circles and micro-triangles, is successfully demonstrated with translating the plasma. The micromachining performance can be optimized by using a spiral microtool electrode owing to improved stability of plasma and enhanced replenishment of the electrolyte to the machining gap. As an example, a 350 μm deep micro-hole is successfully drilled using a Φ100 μm microtool, proving the feasibility of high-aspect-ratio micromachining of 4H-SiC (0001) with HF-free solution by electrolytic plasma etching.

Declaration of Competing 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.

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