

Fabrication of Pores in a Silicon Carbide Wafer by Electrochemical Etching with a Glassy-Carbon Needle Electrode

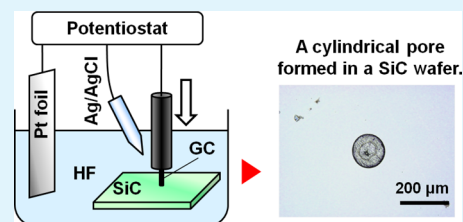
Tomohiko Sugita, Kazuki Hiramatsu, Shigeru Ikeda, and Michio Matsumura*

Research Center for Solar Energy Chemistry, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan

S Supporting Information

ABSTRACT: An electrochemical method for making pores in a silicon carbide (SiC) wafer, in which a glassy-carbon (GC) needle electrode was used for processing, is described. By bringing the GC electrode into contact with SiC at its tip end in 20 mol dm⁻³ HF solution and applying an anodic potential of or higher than 4 V vs Ag/AgCl to it, SiC was etched at the SiC/GC contact area, leading to pore formation in SiC. The diameter of the pore was almost the same as the diameter of the tip of the GC electrode (about 130 μm). By addition of sulfuric acid to the HF solution, the rate of pore formation was increased. As a result, the depth of pores formed after processing for 5 h at 10 V vs Ag/AgCl was increased from 15.3 μm to about 33 μm by addition of sulfuric acid at a concentration of 3.0 mol dm⁻³.

KEYWORDS: silicon carbide, glassy carbon, micromachining, electrochemistry, wet etching



INTRODUCTION

Silicon carbide (SiC) is expected to be an ideal semiconductor for electronic devices working at high power levels and at high temperatures because SiC has a wide band gap and excellent electrical, mechanical and thermal properties. In addition, SiC has many advantages, such as its high chemical stability and physical toughness, which promises development of micro-electro-mechanical systems (MEMS) for working in harsh environment.^{1,2} However, the stability and robustness pose the problem of difficulty in fabricating microstructures. Previously reported processes for making microstructures in SiC are plasma etching processes such as inductively coupled plasma,^{3,4} helicon plasma,⁵ and magnetron plasma,⁶ in which high-intensity plasma is necessary. With wet processes, which are milder than plasma etching, it is usually difficult to etch SiC except for the process in molten alkaline salts at a high temperature.^{7,8} However, it is known that SiC can be etched electrochemically in an electrolyte containing fluoride compounds^{9–11} or alkaline compounds.¹² The electrochemical etching is based on strong oxidation power produced by application of an anodic potential to SiC.

In the case of Si, electrochemical etching can proceed not by applying anodic potential to Si but by bringing anodically biased catalytic electrodes into contact with Si in hydrofluoric acid (HF),^{13–16} a process called electrochemical etching with a catalytic electrode (EECE). As a result of the etching, pores or grooves can be formed in Si using anodically biased needle or wire electrodes. The mechanism of these electrochemical processes is similar to that of metal-assisted chemical etching (MACE), in which metal particles catalyze oxidative dissolution of Si at the Si/solution interface.^{17–26} Metals such as Ag, Au and Pt are effective as catalysts because they have good catalytic activity for the reaction and are stable in the etching solution. Etching of Si by EECE and MACE is induced by oxidation of Si

at the metal/Si interface followed by dissolution as SiF₆²⁻ into HF solution. Being operated under an ambient condition in solution, these processes do not produce debris or cause thermal damage to Si substrates, which are sometimes problematic in vacuum processes. In addition, EECE is controllable through an external power source and does not need resist masks to make microstructures because etching proceeds only at sites where the electrode is brought into contact.

In contrast to Si, SiC is very stable even under electrochemical conditions. Mostly because of the stability of SiC, it has been difficult to apply EECE to pore formation in SiC, as we experienced in our preliminary work. Here, we report that pores can be formed in SiC by EECE using a glassy carbon (GC) electrode instead of a metal electrode with application of potentials of or higher than 4 V vs Ag/AgCl, which could not be applied to metal electrodes because they dissolve in HF solution under such severe conditions. In addition, we report enhancement of the etching rate by addition of sulfuric acid to the HF solution.

EXPERIMENTAL SECTION

N-type 4H-SiC wafers with a thickness of 341 μm, crystallographic orientation of (0001) and resistivity of 0.085 Ω cm were obtained from TanKeBlue Semiconductor Co., Ltd. They were cut into about 0.5 × 0.5 cm² square pieces and their mirror-polished (0001) face was used for electrochemical processing. Prior to the processing, the samples were cleaned by immersing in a mixture of hydrogen peroxide and sulfuric acid (30% H₂O₂: 97% H₂SO₄ = 1:4 in volume) for 10 min, rinsing with ultrapure water (UPW) for 10 min, immersing in diluted HF solution (1%) for 1 min, and rinsing again with UPW for 10 min.

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All of the chemicals used in this study were of reagent grade and used as received.

Electrochemical processing of SiC was carried out with a standard three-electrode system in a solution of 20 mol dm⁻³ HF. The experimental setup is shown in Figure 1a. Since hydrofluoric acid is a

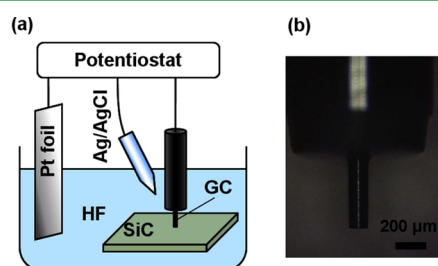


Figure 1. (a) Setup of an electrochemical system for fabrication of a pore in a SiC sample and (b) a micrograph of a tip of a GC electrode.

hazardous reagent, experiments were carried out in a hood equipped with a scrubber. A fine needle of glassy carbon (GC) with a diameter of about 130 μm at its tip, as shown in Figure 1b, was used as an electrode for making pores in SiC. Fine GC needle electrodes were prepared from GC rods (ALS Co., Ltd.) with a diameter of 1 mm. The rods were cut into 5 cm-long pieces, and a tip of each of them was thinned to a diameter of about 130 μm by grinding and finally polishing with emery papers with different degrees of roughness. The GC needle electrode was fixed with a plastic holder to make contact with a SiC sample in HF solution. A Pt foil was used as a counter electrode, and Ag/AgCl was used as a reference electrode, which was linked to the HF solution through a salt bridge filled with a saturated KCl solution. To ensure contact during the process, a weight of 26 g was loaded on the GC needle electrode. After the setup had been completed, the GC needle electrode was anodically polarized using a potentiostat (ALS, 700C). The electrochemical process was carried out in the dark at room temperature in HF solution, which was not stirred. The morphologies and depth profiles of pores formed in SiC were observed with a laser scanning microscope (KEYENCE VK-9700) after the samples had been rinsed with UPW and dried in air.

RESULTS AND DISCUSSION

Making a Pore in a SiC Sample by Applying Anodic Potential to a GC Needle Electrode. Although a Si wafer was easily etched by using a Pt or Ir needle electrode, which was anodically biased at a potential of 2.25 V vs Ag/AgCl, at the site where the electrode was brought into contact,¹⁸ SiC was hardly etched because of its outstanding chemical stability. Only a very shallow concave was formed in SiC when the anodic potential applied to a Pt electrode was increased to 4 V vs Ag/AgCl. In addition, the Pt electrode was harshly corroded under such severe conditions in HF solution. Therefore, in practice it was impossible to make pores in SiC using a metal electrode. Hence, we tried to use GC, which is more stable than metals in HF solution, as the needle electrode for processing SiC. The GC electrodes hardly corroded in HF solution even at a potential of 10 V vs Ag/AgCl, whereas Pt electrodes were severely corroded in about 4 h even at a potential of 4 V vs Ag/AgCl.

To confirm that pores can be formed in SiC using a GC needle electrode, we applied various anodic potentials to a GC needle electrode that was in contact with a SiC sample at its tip end. Figure 2 shows photographs and depth profiles of the pores formed in SiC samples after processing for 5 h at various anodic potentials. When a potential of 2 V vs Ag/AgCl was applied, only a very shallow concave, as shown in Figure 2a, was formed at the site where the tip of the GC electrode was placed.

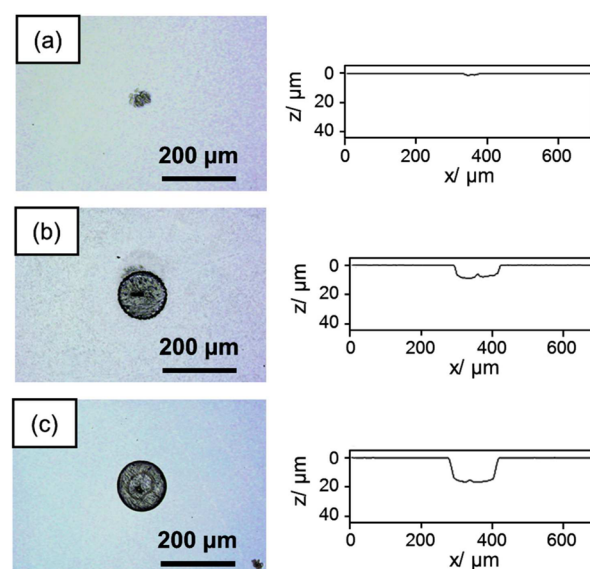


Figure 2. Plan-view micrographs and depth profiles of SiC samples after electrochemical processing with a GC electrode in 20 mol dm⁻³ HF solution. Potentials applied to the GC electrode were (a) 2, (b) 4, and (c) 10 V vs Ag/AgCl. Depth profiles of the pores are shown along lines passing through centers of the pores. Depths of pores formed were about 7.4 μm (4 V) and about 15.3 μm (10 V).

When a potential of 4 V vs Ag/AgCl was applied to the GC electrode, a distinct pore was formed in SiC (Figure 2b). The depth was 7.4 μm and the diameter was 130–133 μm, which was close to the diameter of the tip of the GC electrode. The bottom shape reflected the shape of the contacting end of the GC electrode. When the potential was raised to 10 V vs Ag/AgCl, the depth of the pore formed in SiC was increased to 15.3 μm, but the diameter of the pore was almost unchanged (Figure 2c). The depth of the pore was proportional to the process time, as shown in Figure 3. The etching rate for the

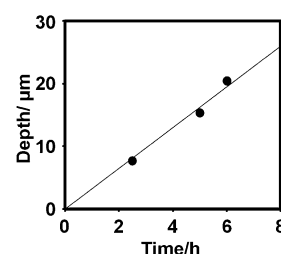


Figure 3. Depth of pores formed in SiC substrates by electrochemical processing in 20 mol dm⁻³ HF solution as a function of the processing time.

pores formed during the process for 5 h is plotted against the potential applied to the GC needle electrode in Figure 4. The tendency for etching rate to level off with increase in the potential above 6 V vs Ag/AgCl might be due to formation of a carbon-rich layer at the SiC/GC interface.^{27,28}

It is important that corrosion of SiC was hardly observed around the pores even at an extremely high electrochemical potential of 10 V vs Ag/AgCl, as shown in Figure 2c. This result is in marked contrast to the behavior of electrochemical pore formation in Si by EEC. In the case of Si, the mouth of the pore formed was corroded and the whole surface of a Si sample was matted due to the formation of a porous Si layer;

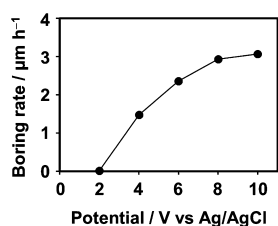
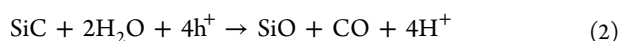
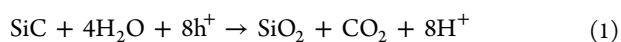


Figure 4. Average rates of pore formation in SiC substrates during electrochemical processing for 5 h in 20 mol dm⁻³ HF solution as a function of potential applied to the GC electrode.

the degree depended on the conductive type and resistivity of the Si wafers. Such changes in Si are due to injection of too many electron holes (hereafter referred to as holes) into the bulk of Si. The holes then corrode the Si surface and form a porous Si layer, depending on the flux of holes at the Si/solution interface. On the other hand, in the case of SiC, the results suggest that there is little injection of holes into the bulk, possibly due to a deep energy level of the valence band of SiC (1.25 V vs Ag/AgCl).²⁹ In principle, if current does not flow at the electrode, anodic potentials more positive than 5 V vs Ag/AgCl must be more positive than the top of the valence band of SiC. However, in the present case, current flows at high density at the GC electrode due to oxidation of water. Hence, most of the potential applied to the electrode is distributed to so-called transport polarization (or concentration polarization) and polarization of the electrode relative to nearby substrates (or SiC) may be small, which prevents hole injection from the GC electrode into SiC. Alternatively, injection of holes may be prevented by a thin carbon-rich layer containing some functional groups formed at the SiC/GC interface,^{27,28} as described above. In either case, etching of SiC proceeds at the SiC/GC interface, possibly by a chemical reaction caused by nascent oxygen formed on the surface of the GC electrode under the highly anodic condition.

In the case of conventional electrochemical etching of SiC, SiC is connected to an external circuit, in contrast to our method, and holes are supplied to SiC from a connecting wire through a back contact.^{10,11} For processing of n-type SiC, holes photogenerated in the bulk of SiC are often used.⁷ In this case, electrons, which are counterparts of the photogenerated holes, are removed from SiC through the back contact. In both cases, the etching site on SiC must be defined using a resist pattern, which limits exposure of the SiC surface to HF solution at the place to be etched. In our system, a resist pattern is unnecessary, because the etching site of SiC is defined by the site where a GC electrode is brought into contact with SiC.

Concerning anodic oxidation of SiC, the following electrochemical reactions are proposed:^{9,10}



SiO₂ and SiO produced by the reactions dissolve into the HF solution as SiF₆²⁻. Hence, SiC is etched with formation of SiF₆²⁻, CO₂, and CO. In the case of EECE, although injection of holes into the bulk of SiC is scarce, similar reactions are expected for the etching processes. Reaction 1 becomes more dominant over reaction 2 with increase in oxidation power used for etching, which can be determined from the ratio of CO₂/CO produced from SiC. However, in the present study, we did

not analyze CO₂ or CO included in the gaseous products of the electrochemical etching.

Increase in the Rate of Pore Formation in SiC by Addition of Sulfuric Acid to HF Solution. The process rate is one of the most important issues for applying the EECE method to practical processes for structuring SiC. To increase the rate of pore formation in SiC by EECE, we examined the effect of addition of sulfuric acid (H₂SO₄) to HF solution. This approach was based on the idea that oxidative dissolution of SiC and the reaction intermediates is enhanced by a chemical oxidant, leading to an increase in the etching rate of SiC.

Figure 5 shows micrographs and depth profiles of pores formed in SiC samples after processing for 5 h at a potential of

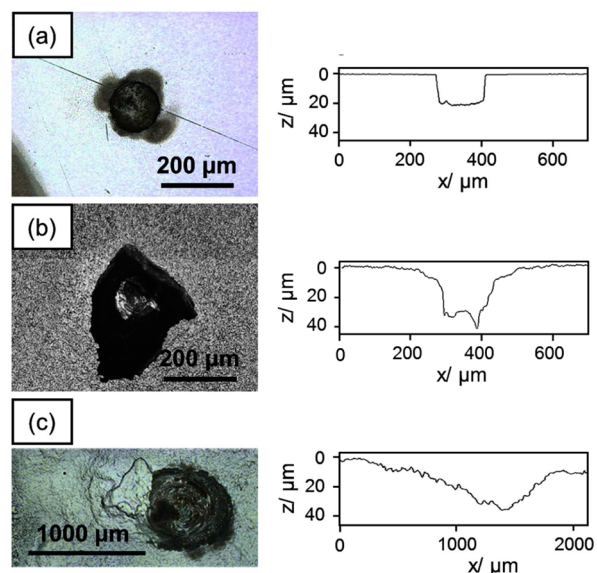


Figure 5. Plan-view micrographs and depth profiles of pores formed in SiC by electrochemical processing for 5 h with a GC electrode in 20 mol dm⁻³ HF solution containing H₂SO₄ at concentrations of (a) 1.5, (b) 3, and (c) 12 mol dm⁻³. The potential applied to the GC electrode was 10 V vs Ag/AgCl. Depth profiles of the pores are shown along lines passing through centers of the pores.

10 V vs Ag/AgCl in 20 mol dm⁻³ HF solutions containing sulfuric acid at various concentrations. In all cases, addition of sulfuric acid was effective to increase the rate of pore formation. However, the wall and bottom of the pore became rough as the concentration of sulfuric acid increased. The depth of the pore formed in a solution containing 1.5 mol dm⁻³ sulfuric acid reached 20.5 μm , as shown in Figure 5a, whereas the depth was 15.3 μm without sulfuric acid. The depth increased further with increase in the concentration of sulfuric acid. The depth was about 33 μm , when the concentration was 3 mol dm⁻³, as shown in Figure 5b. When the concentration was 12 mol dm⁻³, the depth reached about 37 μm , as shown in Figure 5c. The results indicate that addition of sulfuric acid is effective for increasing the rate of pore formation. However, addition of sulfuric acid deteriorated SiC in the area around the pore. When the concentration was 1.5 mol dm⁻³, the surface near the pore was slightly matted, but the edge of the pore was sharp, as shown in Figure 5a. When the concentration of sulfuric acid was 3 mol dm⁻³, corrosion of SiC was observed around the pore and the mouth of the pore was expanded to about 240 μm and the diameter of the pore was slightly expanded to about 140 μm , as shown in Figure 5b. When the concentration was 12

mol dm⁻³, no sharp pore was formed anymore; the diameter of the pore became larger than 1 mm, as shown in Figure 5c. In addition, the GC electrode was thinned after the processing, as shown in Figure 6. Hence, the maximum concentration of

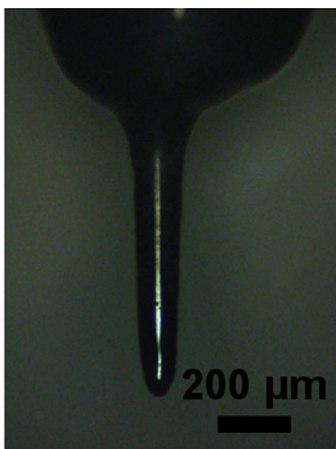
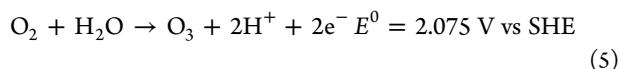
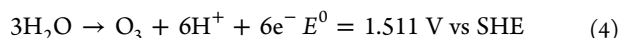
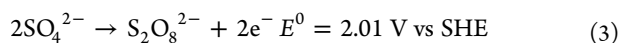


Figure 6. Micrograph of a tip of a GC electrode observed after electrochemical processing for 5 h at 10 V vs Ag/AgCl in 20 mol dm⁻³ HF solution containing 12 mol dm⁻³ sulfuric acid. Compare the morphology of the tip with that shown in Figure 1b.

sulfuric acid to be added to the solution should be below 3 mol dm⁻³ from the viewpoint of micromachining, which requires precise machining. Although further study is necessary to determine the mechanisms of these phenomena, we speculate that species having very high oxidation power such as peroxydisulfuric acid and ozone may be electrochemically produced at the GC electrode and that SiC and some intermediates are etched by them or sulfuric acid itself. Diffusion of these strongly reactive species in the solution leads to corrosion of SiC near the electrode, i.e., the area around a pore. Three possible reactions for production of these species and their standard electrode potentials are as follows^{30,31}



When K₂SO₄ (3 mol dm⁻³) was added to the HF solution, SiC surface was corroded more harshly than SiC surface processed in a solution containing H₂SO₄ (3 mol dm⁻³) (see Figure S1 in the Supporting Information). This result suggests that S₂O₈²⁻ generated from SO₄²⁻ (K₂SO₄ or H₂SO₄) plays the role of a strong oxidant, as expected. The milder etching of SiC in solution containing H₂SO₄ may be attributed to rapid hydrolysis of S₂O₈²⁻ in low-pH solutions.³²

CONCLUSION

Pores can be formed in SiC by applying an anodic potential to a GC needle electrode that is in contact with a SiC sample at its tip in HF solution. During the process, etching of SiC occurs at the contact area between the SiC sample and the tip of the GC electrode, which leads to fabrication of a pore. Addition of sulfuric acid to the HF solution is effective for increasing the rate of pore formation. The diameter of the pore was almost the

same as the diameter of the tip of the GC needle electrode if the concentration of sulfuric acid is 1.5 mol dm⁻³. Because etching occurs at the interface of SiC/GC electrode, desired patterns or plural pores can be formed by designing the structure of the GC electrode or by using plural electrodes. Although further studies are necessary to increase the process rate, the method may be applicable to advanced micromachining of SiC for a wide range of applications.

ASSOCIATED CONTENT

Supporting Information

Plan-view micrograph and the depth profile of a pore formed in SiC by electrochemical processing for 5 h with a GC electrode in 20 mol dm⁻³ HF solution containing K₂SO₄ at a concentration of 3 mol dm⁻³. The potential applied to the GC electrode was 10 V vs Ag/AgCl. Depth profile of the pore is shown along a line passing through the center of the pore. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: matsu@chem.es.osaka-u.ac.jp

Notes

The authors declare no competing financial interest.

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