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Chemical etching of silicon carbide in pure water by using platinum catalyst

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Chemical etching of SiC was found to proceed in pure water with the assistance of a Pt catalyst. A 4H-SiC (0001) wafer was placed and slid on a polishing pad in pure water, on which a thin Pt film was deposited to give a catalytic nature. Etching of the wafer surface was observed to remove protrusions preferentially by interacting with the Pt film more frequently, thus flattening the surface. In the case of an on-axis wafer, a crystallographically ordered surface was obtained with a straight step-and-terrace structure, the height of which corresponds to that of an atomic bilayer of Si and C. The etching rate depended upon the electrochemical potential of Pt. The vicinal surface was observed at the potential at which the Pt surface was bare. The primary etching mechanism was hydrolysis with the assistance of a Pt catalyst. This method can, therefore, be used as an environmentally friendly and sustainable technology. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4983206]

Silicon carbide (SiC) has become a more important candidate than silicon for fabricating high-power devices because of its superior physical properties, including a wide bandgap, high breakdown voltage, and high thermal conductivity, which enable lower power-loss characteristics.[1] SiC power devices are expected to be used as electric converters or inverter systems in high-temperature or transportation applications (e.g., electric vehicles, hybrid vehicles, and trains).[2–4] The use of SiC in these devices enables reduction in the power consumption, size, and weight. However, the performances of commercially available SiC devices are lower than their theoretical performances, owing to problems such as the non-uniform thickness of the oxide layer and killer defects.[5–11] One of the reasons for such fundamental problems is the flatness of the SiC substrate. To realize performances equal to the theoretical expectation for SiC devices, an atomically smooth surface without defects must be prepared. However, SiC is known to be a hard, brittle, and chemically inert material; hence, it cannot be etched using chemicals at room temperature.

Hara *et al.*[12] have reported that platinum (Pt)-assisted reaction in hydrofluoric acid (HF) solution can etch SiC at room temperature, and this etching method is called catalyst-referred etching (CARE). Their study clarified that CARE proceeds preferentially at protrusions on the wafer surface where the Pt catalyst can come into contact with the surface more often. This method was applied to flatten a 4H-SiC wafer, and a geometrically and crystallographically highly ordered surface was obtained with an atomic step-and-terrace structure.[13] A simulation study based on the density functional theory clarified the mechanism of CARE as follows, as shown in Fig. 1(a).[14] First, an F^- ion from HF dissociatively adsorbs onto the step-edge Si to form a fivefold coordination as an intermediate state, leading to weakening of the backbond. Subsequently, H^+ transfers from OH on Si to the second-layer C to break the backbond. This is a kind of indirect dissociative adsorption of an HF molecule onto a Si–C backbond. The main role of Pt is to dissociate the HF molecule and stabilize the five-fold coordination.[14] In general, Si can form hypervalent silicates with Lewis bases such as F^- or OH^-, which are considered intermediate states in a variety of chemical reactions, owing to their high nucleophilicities.[15–19] Therefore, OH^- is considered to play the same role as F^- in CARE, as shown in Fig. 1(b), and to proceed an indirect dissociative adsorption of H_2O, i.e., an indirect hydrolysis. We have preliminarily tested the prospect of CARE with pure water.[20,21] In this paper, the feasibility of CARE of 4H-SiC with pure water was examined and discussed along the scheme of hydrolysis, relating the catalytic activity to the chemisorption state on Pt.

The experimental setup is shown in Fig. 2. A Pt film with a thickness less than 100 nm was deposited onto a polyurethane rubber pad with narrow grooves on its surface for

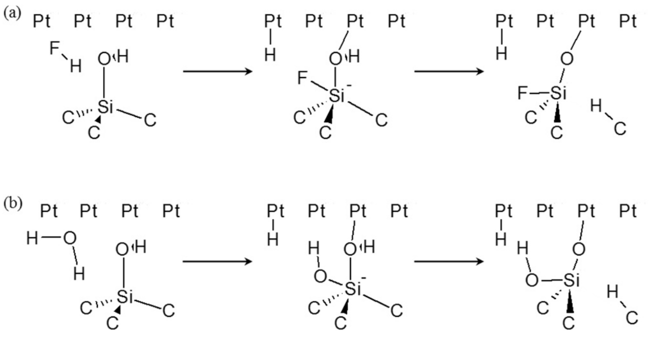

FIG. 1. Schematic of possible reaction pathways of (a) CARE with HF, which is theoretically considered to be a kind of indirect dissociative adsorption of an HF molecule that breaks the Si-C backbond and (b) CARE with pure water, which is expected to occur owing to the similarity of F and OH.

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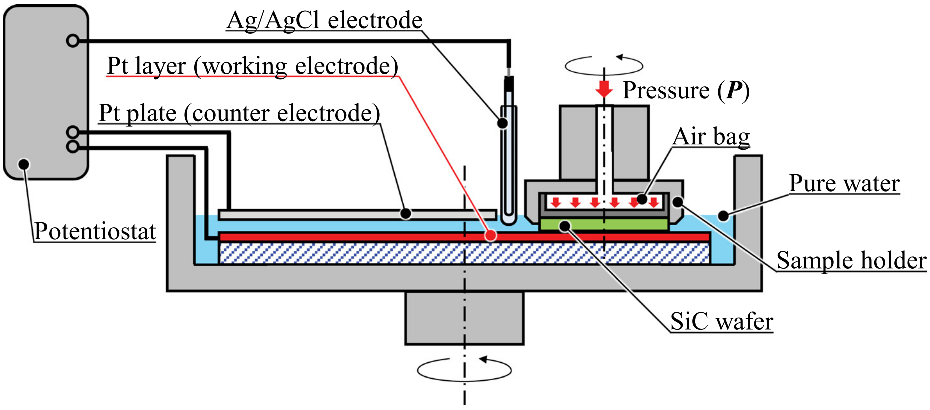

FIG. 2. Schematic of the experimental setup, which is basically similar to a conventional polishing machine. A SiC wafer and a polyurethane polishing pad are immersed in pure water. The wafer is set in the sample holder and faced toward the pad with pressure ***P*** by an air bag. A three-electrode system was equipped. As a reference, we employed an Ag/AgCl electrode.

supplying water to the wafer surface. The pad is fixed at the bottom of a processing tank by using a double-sided tape. The sample and the pad rotate independently on their own axes at nearly the same speed. The shape of the pad surface, which has the important role of being copied onto the wafer surface, was not atomically smooth. However, the topmost area on the wafer surface can interact with Pt more frequently and is preferentially removed. This is widely known as an averaging effect in conventional polishing methods, in which the independent rotations of the pad and the wafer play important roles to make the configuration random between the two surfaces. A wafer is set in the sample holder and faced toward the catalyst surface with an appropriate pressure by an air bag placed behind the wafer. The samples are immersed in pure water. To examine the dependence upon the electrochemical potential of the catalyst, a three-electrode system is equipped. As a reference, we employed an Ag/AgCl electrode.

First, we applied the method to the 3-inch n-type 4H-SiC (0001) on-axis and 4°-off-axis samples with a rotational speed of 30 rpm and an applied pressure of 800 hPa to understand the fundamental etching characteristics. The catalyst was placed under the open-circuit condition without potential control; the self-potential was measured to be 0.25 V. The processing time was 1 h. The processed surface was observed by using an atomic-force microscope (AFM). Figures 3(a) and 3(b) show the AFM images of the pre-processed and the processed samples of a 4H-SiC (0001) on-axis wafer, respectively. The view area is $2 \times 2\ \mu\text{m}^2$. The surface morphology was drastically changed after processing, and a straight step-and-terrace structure with a step height of approximately 0.25 nm was observed as shown in Fig. 3(c), which corresponds to the height of a bilayer of Si and C. This result shows that pure water can etch the 4H-SiC, similar to the HF solution, with the assistance of a Pt catalyst. The highly ordered surface indicates that the removal proceeds via a step flow and is based on a chemical phenomenon, similar to the case of CARE with the HF solution.[12–14] The material removal rates (MRRs) of the on-axis and the 4°-off-axis wafers were 1–2 nm/h and 19 nm/h, respectively. The MRR for CARE with the HF solution was known to be roughly proportional to the atomic-step density corresponding to the off-angle against the (0001) surface,[13] and thus, the MRRs obtained using pure water exhibited similar characteristics.

The dependence of MRR upon the electrochemical potential of Pt was examined to discuss along the scheme shown in Fig. 1. The potential determines the characteristics of chemisorption upon Pt, which affects the catalytic interaction. A potential ranging from −0.4 to 1.4 V was employed to exclude gaseous production of hydrogen and oxygen; hydrogen and oxygen bubbles were observed at potentials lower than −0.5 V and higher than 1.5 V, respectively. Pt potentials are shown using the voltage differences from the standard hydrogen electrode. pH was fixed at 7. The obtained results are summarized in Fig. 4(a). Two peaks are observed at 0.2 V and 1.0 V. A cyclic voltammogram was used to characterize the electrochemical state of Pt, as shown in Fig. 4(b). The sweep range was from −0.6 to 1.6 V at a rate of 0.5 V/s. The Pt surface is hydrogenated and oxidized when the potential is below −0.2 V and above 0.4 V, respectively. The Pt surface becomes bare between these ranges. At the first and second peaks, the Pt surface is bare and electrochemically oxidized, respectively. The AFM images of the processed surfaces at

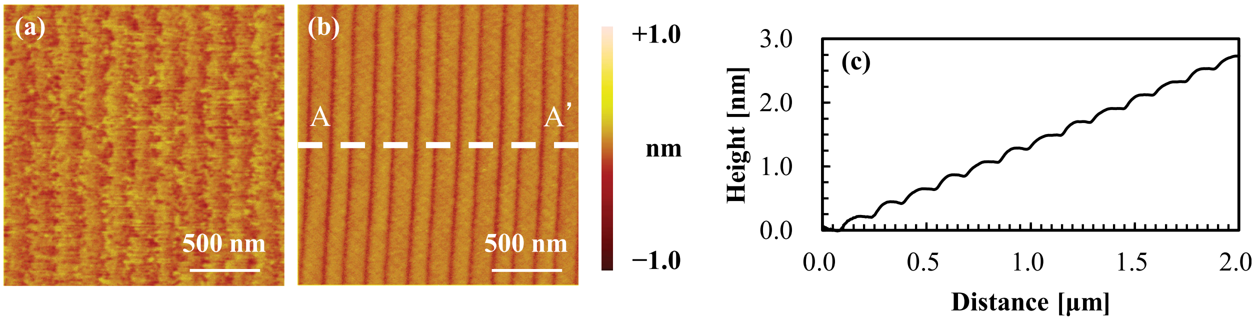

FIG. 3. AFM images of (a) pre-processed and (b) processed surfaces of a 4H-SiC (0001) on-axis wafer. (c) Cross-sectional image obtained along the dashed line between A and A′ in (b).

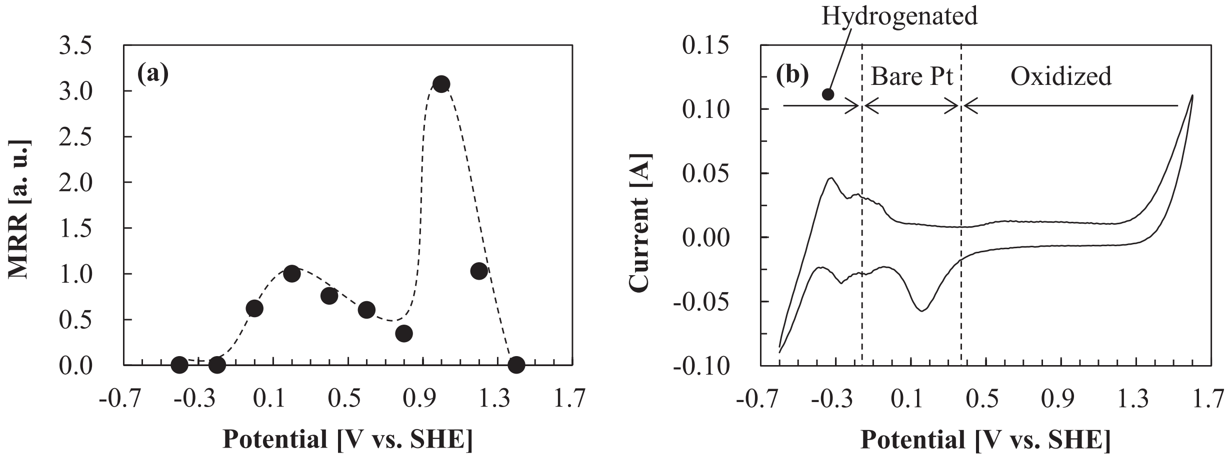

FIG. 4. (a) Dependence of relative material removal rates (MRRs) upon Pt potential; the MRR obtained at self-potential was determined to be 1.0. (b) The cyclic voltammogram of Pt measured with the scan rate of 500 mV/s. The characteristics of chemisorption on Pt are illustrated in (b).

0.2 V and 1.0 V are shown in Figs. 5(a) and 5(b). A highly ordered surface identical to that in Fig. 3 was obtained at 0.2 V, while the surface morphology degraded, and many pits were observed on the terrace at 1.0 V. Although step-flow etching is realized at 0.2 V, the etching also proceeds on the terrace at 1.0 V. Along the scheme shown in Fig. 1, bare Pt is considered to enhance the catalytic reactivity to produce the expected hydrolysis. At the potentials lower than −0.2 V, MRR quickly decreases with increasing hydrogen adsorption on Pt, which is supposed to block the reaction. In contrast, etching is tripled at 1.0 V, despite the fact that the Pt surface is covered by oxygen-related species. At this potential, the SiC surface is considered to be oxidized by taking on such species and to be dissolved in water through some as-yet-unknown mechanisms. The surface morphology significantly degrades at 1.0 V. The removal mechanisms at each of the two peaks are different, and the expected reaction is supposed to proceed at the first peak. The highly ordered surface shown in Fig. 3 is obtained at a self-potential of 0.25 V, which is close to the first peak, where the Pt surface is bare. Thus, the bare-Pt surface is crucial to catalytically enhance the indirect hydrolysis and to realize a geometrically and crystallographically highly ordered surface.

CARE with pure water was applied under the open-circuit condition to flatten an epitaxially grown 3-inch n-type 4H-SiC (0001) 4°-off-axis wafer. In the semiconductor fabrication process, the epitaxial layer is grown on the wafer to produce a high-crystallinity layer. However, the epitaxial growth induces surface waviness due to step bunching, which could significantly degrade the performance of the device.[5–11] The processing time was 3 min. Figures 6(a)–6(c) show the AFM images obtained over a $2 \times 2\ \mu m^2$ area of the pre-processed surface, and the surfaces processed at 2 and 3 min. The waviness appears to have been removed after 2 min, as evident from the topmost part in Fig. 6(b), and finally, the bunching was removed to yield a sufficiently smooth surface, the roughness of which was 0.051 nm rms within 3 min, as shown in Fig. 6(c).[20] From the results described above, CARE with pure water can etch the 4H-SiC wafer and atomically smoothen the surface. This method uses no chemical or slurry, unlike conventional mechanical and chemical polishing methods, thereby ensuring a higher compatibility with the processes used in semiconductor fabrication.

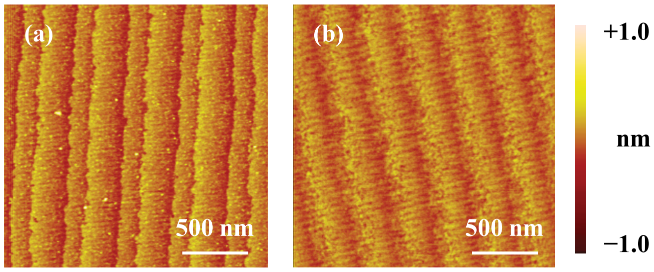

FIG. 5. AFM images of the processed surface at Pt potentials of (a) 0.2 V and (b) 1.0 V on the 4H-SiC (0001) on-axis wafer.

The MRR in pure water is acceptable for morphological and crystallographic ordering of surfaces as shown here but is more than ten times lower than that in the HF solution, although both OH^- and F^- have high nucleophilicity to Si. In the HF solution, the MRR of the 4H-SiC (0001) 4°-off-axis wafer can reach up to 300 nm/h under the same processing conditions noted above. This behavior can be attributed to the following three reasons. One is the frequency of the nucleophilic reaction of F^-, which is higher than that of OH^-, because the degree of ionization of a water molecule is much lower than that of HF. Another reason is the electronegativity. The strong electronegativity of F^- attracts more covalent electrons of Si at the backbond, as compared to the case of OH^-. Consequently, the backbond becomes easier to break when HF is used. The third reason is the strong affinity between Si and F, as compared with O; the bonding energies of Si–F and Si–O, in the case of Si, were calculated to be 540–570 and 370–450 kJ/mol, respectively.[22] The specific thermal stability of the Si–F bond is considered to make the five-fold coordination of Si more stable, leading to a lower reaction barrier. Regarding the first reason, the MRR of the 4H-SiC (0001) 4°-off-axis wafer was a few times higher than that in pure water, reaching 42 nm/h when a solution with higher pH, such as KOH, was added, but the MRR was still low when compared with that of CARE with the HF solution, indicating that all the above factors significantly contribute to MRR. The second and third

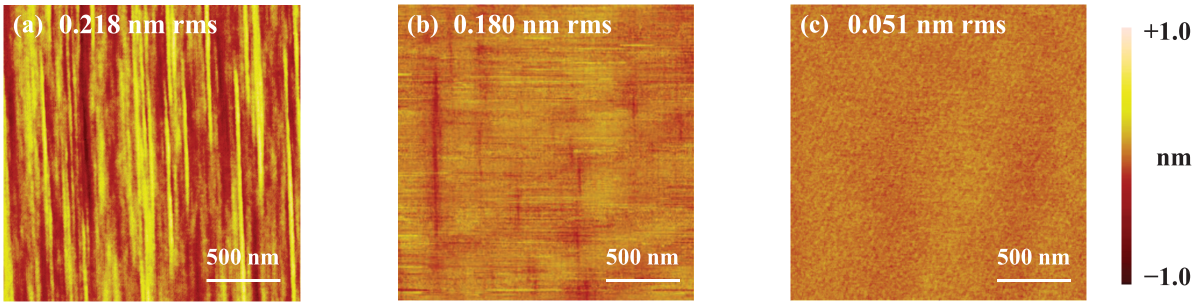

FIG. 6. AFM images of the (a) epitaxially grown surface, (b) 2-min processed surface, and (c) 3-min processed surface of the 4H-SiC (0001) 4°-off-axis wafer.

reasons should be investigated in detail using a first-principles-simulation study. Catalysts other than Pt can also be investigated because water is much less corrosive than the HF solution. In addition, the MRR can be improved by controlling the electrochemical potential of Pt to an oxidation condition, while CARE with bare Pt should be added as a finishing process to obtain a highly ordered surface.

Thus, we have found that CARE with pure water and a Pt catalyst can be used to etch the 4H-SiC and atomically smoothen the surface. This process may become an environmentally friendly and sustainable technology for the planarization of semiconductor devices.

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