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Paper:

Photoelectrochemical Oxidation Assisted Catalyst-Referred Etching for SiC $\langle 0001 \rangle$ Surface

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In a previous study, we developed an abrasive-free polishing method named catalyst-referred etching (CARE) and used it for the planarization of silicon carbide (SiC) $\langle 0001 \rangle$. In this method, Si atoms at step edges are preferentially removed through a catalytically assisted hydrolysis reaction to obtain an atomically smooth and crystallographically well-ordered surface. However, the removal rate is low ($<$ nm/h) and needs to be improved. In this study, we proposed an ultraviolet (UV) light assisted CARE method. In this method, UV light is irradiated onto a SiC surface to generate holes and oxidize the surface. The oxidized area, consisting of SiO_2, can be quickly removed to form a nano-pit owing to the higher removal rate of SiO_2 compared to that of SiC. The periphery of the nano-pits works as a reaction site, leading to a higher removal rate. To enhance the oxidation rate and form nano-pits, we applied electrochemical bias to the SiC substrate. However, the removal rate did not improve significantly when the bias voltage was higher than 3.0 V. This is because the electrochemical potential of Pt increased with the anodic potential of SiC, which oxidized the Pt surface and degraded the catalyst capability. To avoid this issue, we modified the catalytic pad, where an in-situ refreshment of the Pt surface is possible. As a result, the removal rate increased up to 200 nm/h at a bias of 7.0 V, which is 100 times higher than that of the CARE without UV irradiation. The proposed method is expected to contribute to the enhancement in the productivity and quality of next-generation SiC substrates.

Keywords: catalyst-referred etching, silicon carbide (SiC), photoelectrochemical oxidation (PEC), ultraviolet light

1. Introduction

Silicon carbide (SiC) has attracted attention as a new semiconductor material for the substrate of next generated power devices owing to its excellent physical properties, such as wide bandgap, high breakdown voltage, and high thermal conductivity. SiC allows the production of low power-loss devices [1]. To fully exploit the properties of SiC in an electric device, its surface needs to be crystallographically and geometrically well-ordered. However, this is difficult owing to the high hardness, brittleness, and chemical inertness of SiC.

Generally, chemical mechanical polishing (CMP) is utilized to polish semiconductor materials [2–4]. In CMP, a slurry including chemical and an abrasive is utilized. The workpiece surface is first chemically modified and then mechanically removed [5–7]. However, because abrasives are used, mechanical damage is unavoidable [8, 9]. To avoid this, we developed an abrasive-free polishing method named catalyst-referred etching (CARE) [10–12]. This method is based on chemical etching assisted by a catalytic reaction. Only the part of the workpiece that contacts the catalyst surface is removed chemically. A catalyst metal is plated on an elastic pad, the surface of which works as a reference surface to be averaged and transferred onto the work surface similarly to the conventional polishing pad used in CMP.

In the CARE method, Pt and pure water are employed as catalyst and etchant, respectively. Neither chemicals nor abrasives are used, making the method more environmentally friendly. Crystallographically and geometrically highly ordered surfaces have been obtained with a step-and-terrace structure in crystalline materials, such as SiC [13], GaN [14], crystal quartz [15], and zinc oxide. Furthermore, CARE can atomically smoothen amorphous materials such as optical glasses [15]. However, the removal rate of CARE is lower than that of the conventional polishing technique. Especially, the removal rates of SiC and GaN with the CARE method are only several nm/h, which is 200 times lower than that of SiO_2.

The step-and-terrace structures observed on the surface of SiC suggest that the atomic removal proceeds at the step edge, not on the terrace. The removal rate of the 8° off-axis-cut SiC substrate is much higher than that of the on-axis-cut substrate [16]. These observations indicate that the removal rate strongly depends on the step density on the surface. We have already determined that additional step edges were generated by photoelectrochemical oxidation and the removal rate was improved [17]. This method is entitled photoelectrochemi-

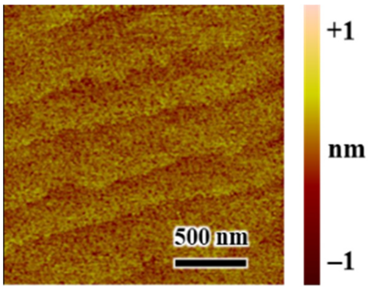

Fig. 1. AFM image of UV irradiated and HF solution treated surface of a 4H-SiC (0001) on-axis-cut wafer. Plenty of atomic size pits can be both at the step edge and on the terrace.

cal CARE (PEC-CARE).

In the present work, to realize a higher removal rate, we attempted to enhance the PEC oxidation by optimizing the electrochemical potentials of the SiC substrate and Pt catalyst.

2. Basic Theory of PEC-CARE

When the surface of SiC is irradiated by UV light with photon energy higher than the bandgap energy, electron-hole pairs are generated in the surface layer. In the case of UV irradiation in an aqueous solution, holes can oxidize the surface according to the following chemical equation [18]:

$$\mathrm{SiC} + 8\mathrm{h}^+ + 4\mathrm{H_2O} \rightarrow \mathrm{SiO_2} + \mathrm{CO_2} + 8\mathrm{H}^+ \quad . \; . \quad (1)$$

Figure 1 shows an atomic force microscope (AFM) image of an on-axis-cut 4H-SiC (0001) surface irradiated in a hydrofluoric acid (HF) solution. As can be seen in the figure, many atomic size pits formed on the terrace because the oxidized area, which consists of $\mathrm{SiO_2}$, is simultaneously etched off in the HF solution. This kind of pit is expected to be generated also during CARE with the UV irradiation because the removal rate of $\mathrm{SiO_2}$ is much higher than that of SiC. The peripheries of the pits are expected to enhance the removal rate as additional step edges and reaction sites.

3. Experimental Method

Figure 2 shows the experimental setup of the PEC-CARE. A Pt layer with a thickness of less than 100 nm was deposited on an elastic pad as a catalyst. The workpiece was set in a holder and pressed onto the pad surface. The workpiece and pad rotated independently around their axes. The work surface was irradiated with UV light using a light source (HAMAMATSU L9588-02A) placed in front of the workpiece. The catalytic pad had many holes with a diameter of 5 mm through which UV light passed onto the SiC surface. The pad was fixed on a silica glass with high UV transparency. A Pt wire was placed beneath the pad as a cathode and was connected to the backside of the workpiece. The pressure and relative speed between the surfaces of the workpiece and pad were 40 kPa and 70 mm/s, respectively. The workpiece surfaces before and after CARE were observed by AFM (SHIMADZU 9700HT) with a view area of $2.0 \times 2.0\ \mu\mathrm{m}^2$. The removal rate was calculated from the weight difference of the workpiece before and after processing.

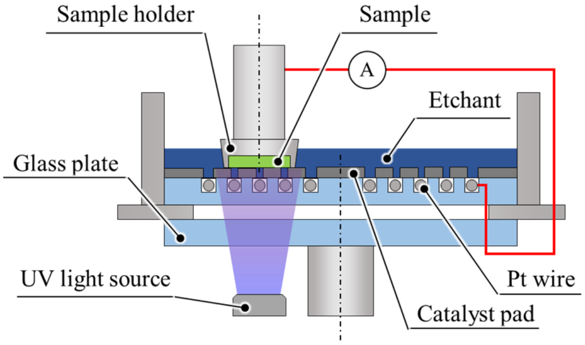

Fig. 2. Schematic of PEC-CARE system. To irradiate the SiC surface with UV light, many holes are made on the polishing pad and the bottom of the tank is made from glass.

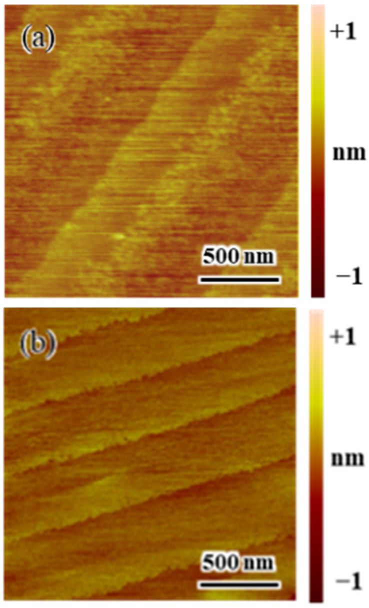

Fig. 3. AFM images of PEC-CARE processed surfaces of (a) 4H-SiC (0001) on-axis-cut wafer and (b) GaN (0001) on-axis-cut wafer.

4. Result and Discussion

4.1. Characteristics of PEC-CARE

We applied PEC-CAER to 2-inch n-type 4H-SiC (0001) on-axis-cut and 2-inch n-type GaN (0001) on-axis-cut substrates. **Figs. 3(a)** and **(b)** show AFM im-

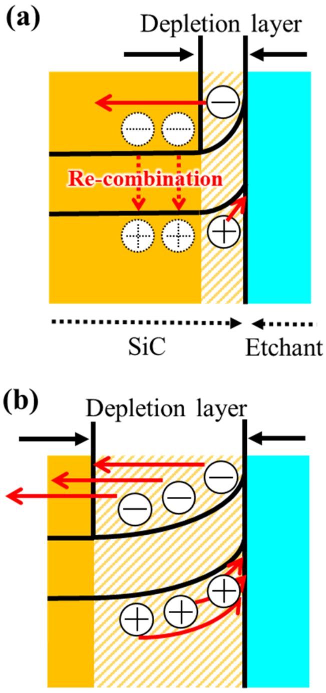

Fig. 4. Schematic of band structure at the interface between SiC and etchant (a) without bias and (b) with bias. This bias expands the depletion layer to effectively transport the generated holes to the SiC surface, contributing to the PEC oxidation reaction.

ages of the processed 4H-SiC (0001) and GaN (0001) substrates, respectively. It can be seen that both surfaces are characterized by striate steps and terraces similar to those obtained using CARE without UV irradiation. The removal rate of GaN was found to be 50 times higher after PEC-CARE, while that of SiC did not change significantly. This observation can be explained by the UV absorption coefficients. **Figs. 4(a)** and **(b)** show a schematic of the band structure at the interface between SiC and the etchant without and with applied bias, respectively.

Because SiC is an indirect transition semiconductor, the penetration depth of UV light is much wider than the width of the surface depletion layer. Thus, the holes generated in the layer deeper than the depletion layer cannot efficiently assist the oxidization of the SiC surface. To drag the holes to the surface, we tried to expand the depletion layer by applying a bias between the SiC substrate and the etchant. The removal rate was found to increase nearly proportionally with the applied bias. We named this method bias-assisted PEC-CARE (BPEC-CARE).

4.2. Characteristics of BPEC-CARE

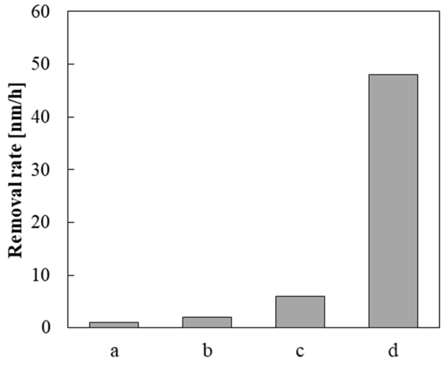

Fig. 5. Removal rates of 4H-SiC (0001) on-axis-cut wafer under several conditions; (a) conventional CARE; (b) PEC-CARE in pure-water; (c) PEC-CARE at pH 3; (d) BPEC-CARE at pH 3 with a bias of 3.0 V.

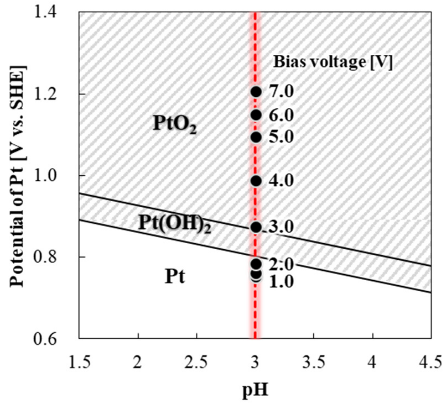

Fig. 6. Potential-pH diagram of Pt. Black dots indicate the electrochemical potential of Pt under several applied bias.

A DC power supply was utilized to apply a bias. The power supply was placed in the circuit between the workpiece and the Pt wire. SiC was positively biased against the wire. A nitric acid (HNO_3) solution with a pH of 3 was employed as an etchant to reduce the electric resistance of the solution. An additional reason for using the solution is that the removal rate at a pH of 3 is 2 or 3 times higher than that at a neutral pH, the mechanism of which is not clear so far. Note that, in this experiment, the etchant was not pure water. The removal rates are summarized in **Fig. 5**. As shown in the figure, under the applied bias of 3.0 V, the removal rate is drastically improved and reaches 50 nm/h on the on-axis-cut substrate, which is 50 and 25 times higher than those of the CARE without UV irradiation and PEC-CARE, respectively. The removal rate on the 4° off-axis-cut substrate increases to 125 nm/h. However, they saturated at biases higher than 3.0 V, both the on-axis-cut and 4° off-axis-cut substrates. In the setup configuration shown in **Fig. 2**, the Pt catalyst contacts with the SiC surface so that the electrochemical potential of Pt increased with the bias of the SiC. **Fig. 6** shows a potential/pH diagram of Pt [19]. The vertical and horizontal axes respectively indicate the electrochemical potential and pH. The potential is defined relative to the standard hydrogen electrode. Each line shows an equilibrium state between neighboring compounds. This diagram indicates that at an electrochemical potential higher than 0.8 V and a pH of 3, Pt is covered with oxygen-related species, such as OH and O, i.e., it oxidized. **Fig. 6** also shows the electrochemi-

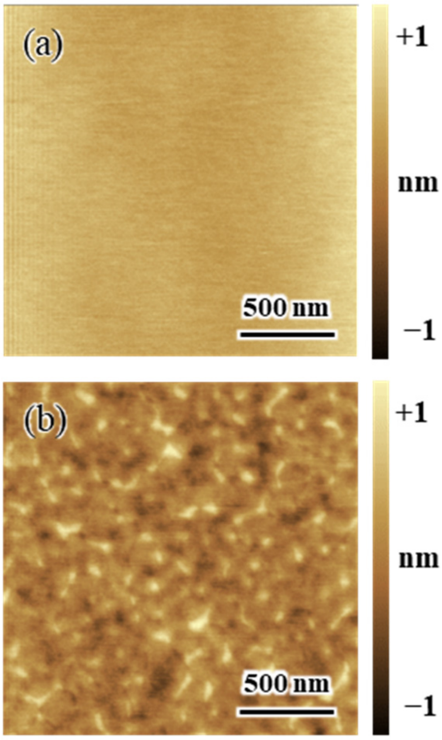

Fig. 7. AFM images of 4H-SiC (0001) surface obtained by BPEC-CARE with a bias of 7.0 V. (a) and (b) indicate the surfaces before and after HF treatment, respectively.

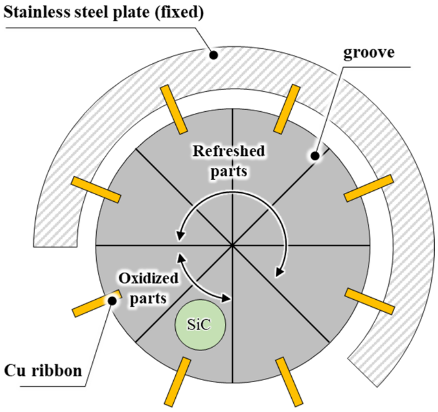

Fig. 8. Schematic of the modified BPEC-CARE. The catalytic pad was electrically divided into eight parts by narrow grooves. Each isolated part has a Cu ribbon. The outer plate is fixed outside of the processing vessel.

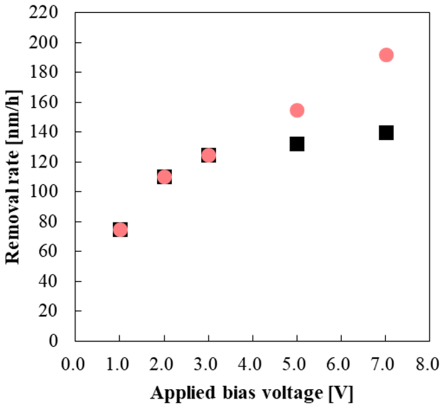

Fig. 9. Plot of the removal rate of 4H-SiC (0001) 4°-off-axis-cut wafer as a function of the applied bias voltage. The dots and squares indicate the removal rate using the divided pad and the not divided pad, respectively.

cal potential of the Pt catalyst at various biases. As can be seen in the figure, when the applied bias is lower than 2.0 V, the electrochemical potential of Pt is 0.8 V, indicating that the Pt catalyst surface is bare. In contrast, under biases higher than 3.0 V, the Pt surface oxidizes. In this case, the catalytic nature of Pt degrades owing to the adsorptions of oxygen-related species. If the removal rate of SiO_2 is lower than the PEC oxidation rate, the oxide layer remains on the SiC surface during CARE. Even when the SiC surface is covered with oxide, the atomically smooth surface is prepared on the topmost surface of the oxide, as shown in **Fig. 7(a)**. However, the interface between the oxide layer and SiC becomes rough owing to the following reason. Oxide layers grown in aqueous solutions are generally not uniform, so their electric insulation property fluctuates often. If there is a low insulation path in the oxide layer, the oxidation of the SiC surface proceeds. It becomes an origin of pit formation and roughening on the SiC surface. Even in this case, just after CARE, the surface is atomically smooth; however, the SiC surface obtained after the removal of the oxide layer could be rough. **Fig. 7(b)** shows a typical AFM image of the pit-induced roughness on the SiC surface. To realize a smooth surface even at a higher bias, the removal rate of SiO_2 should be higher than that of PEC oxidation. In other words, it is necessary to keep the catalyst surface bare even under higher biases. To achieve this, we tried to divide the pad electrically and control the potential of each part individually. The electrochemical potential of the part, which is not in contact with the SiC substrate, should be reduced to a non-oxidation condition for a refreshment of the Pt surface and the recovery of its catalytic property.

4.3. Characteristics of Modified BPEC-CARE

Figure 8 shows a schematic of the modified pad and the experimental setup. A polishing pad was electrically divided into eight parts by narrow grooves. Each part had a copper ribbon to touch the outer plate connected to the Pt wire. A part not in contact with the SiC substrate can touch the plate, and the electrochemical potential of the part is reduced to the spontaneous potential of the Pt wire at a pH of 3, leading to the recovery of its catalytic nature. To evaluate the processing characteristics of the modified BPEC-CARE method, we applied it to the 4H-SiC (0001) 4°-off-axis-cut substrate. The removal rate increased proportionally with the applied bias even when the bias was higher than 3.0 V, as shown by the dots in **Fig. 9**. At a bias of 7.0 V, it reached 190 nm/h, which was 100 times higher than that of the CARE without UV irradiation, whereas

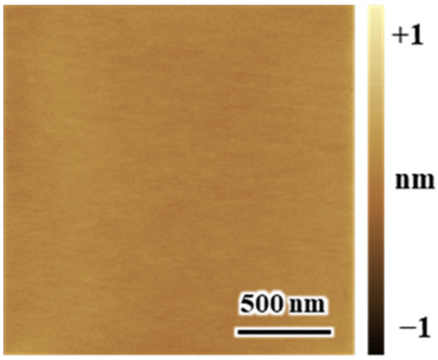

Fig. 10. AFM image of BPEC-CARE processed surface on 4H-SiC (0001) 4°-off-axis-cut wafer after immersed in HF solution (PV: 0.203 nm and RMS: 0.045 nm).

it saturated at higher biases in the case of conventional pad, as shown by the squares in **Fig. 9**. **Fig. 10** shows the morphology of the 4H-SiC (0001) surface. It can be seen that the surface has the same smoothness as the surface obtained by the conventional CARE method. The weights of the substrates before and after HF cleaning did not change, indicating that an oxide layer was not formed during modified BPEC-CARE.

5. Conclusion

We developed a PEC-CARE method utilizing UV irradiation. The photoelectrochemically oxidized part on the SiC surface is quickly removed, forming nano-pits; the periphery of the nano-pits is a kind of step-edge that acts as an additional reaction site for CARE, leading to a higher removal rate. To further enhance the surface oxidation rate, we applied a bias between the SiC and etchant during PEC-CARE and named the modified method BPEC-CARE. The removal rate increased proportionally with the bias, and a significantly high removal rate was obtained. However, at biases higher than 3.0 V, the removal rate saturated. This is because the electrochemical potential of Pt rises with the bias of the SiC surface. The higher electrochemical potential of the Pt catalyst was found to degrade catalytic ability owing to the oxidation of the Pt surface. To avoid degradation, a modified pad consisting of eight electrically isolated parts was developed. The parts other than those in contact with the workpiece were intentionally biased at a lower potential to prevent the oxidation of Pt and to recover the catalytic capability. Using this pad, the removal rate increased proportionally to the bias voltage up to a bias of 7.0 V and became 100 times higher than the conventional CARE method. The obtained surface morphology was confirmed to be atomically well-ordered.

Recently, smaller off-cut angles are set to reduce the cost of the substrate [20, 21]. This leads to a lower removal rate of CARE because the step density of the surface decreases with the decrease in the off-cut angle. BPEC-CARE is expected to achieve a high removal rate independently from the off-cut angle and to contribute to the enhancement in the productivity and quality of next-generation SiC substrates.

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