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Study of initiation and development of local oxidation phenomena during anodizing of SiC

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ABSTRACT

Even though anodizing has been proved to be a highly efficient oxidation approach of single crystal SiC, the oxidation mechanism is still unrevealed. In this work, the initiation and development of the local oxidation phenomenon during anodizing of SiC have been experimentally studied. Local oxidation occurred on the charge carrier-rich areas like damaged areas and doping sites. The oxidation of the damaged areas has a higher priority compared with that of doping sites during anodizing of SiC. For anodizing of damaged areas, the protrusions generated by local oxidation gathered around the damaged areas. In contrast, protrusions were randomly distributed for anodizing of doping sites.

1. Introduction

Single crystal silicon carbide (4H–SiC) has many excellent electrical and chemical properties, such as a wide energy band gap, a high breakdown electric field, excellent thermal conductivity and strong chemical inertness. Therefore, it has been widely considered as one of the most promising third generation semiconductor materials for fabrication of power devices working with a high voltage, a high frequency and high temperature conditions [1–3]. As semiconductor devices will be fabricated on the wafer, a smooth surface without scratches and subsurface damage (SSD) is indispensable. However, flattening of SiC with good surface quality is challenging owing to its strong chemical inertness and high hardness.

In order to develop a new polishing method that can potentially provide a high material removal rate (MRR) with minimal subsurface damage, electro-chemical mechanical polishing (ECMP) [4–6], in which anodic oxidation and abrasive polishing are combined, has been proposed and applied. In ECMP, SiC was anodically oxidized to SiO_2 with a very high initial oxidation rate and then the oxide layer, which was much softer than SiC, was removed by polishing using soft abrasive like ceria or silica. As the hardness of the soft abrasive is much lower than that of SiC, only the soft oxide layer is removed and SSD is not introduced, making it possible to generate a damage-free surface. As reported, the MRR of ECMP for a diamond abrasive-polished SiC surface was 3.62 μm/h, which was more than seven times higher than that of the conventional CMP processes [5]. However, it was also found that anodizing of SiC was a nonuniform process and many "egg-like" SiO_2 protrusions appeared at the oxide/SiC interface [5]. As the abrasive polishing process only removes the oxide layer, the roughness of the oxide/SiC interface determines the surface roughness achieved by ECMP. Therefore, the generation of protrusion during anodizing limits the polishing capability of ECMP.

Since anodic oxidation plays a decisive role in the ECMP process, it is expected that figuring out the mechanism of the anodization of SiC will be highly advantageous for improving surface quality of the ECMP process applied on SiC. In this study, the initiation and development of the local oxidation phenomenon during anodizing of SiC are experimentally studied.

2. Experiments

Semi-insulating type 4H-SiC wafers (on-axis, n-type), with a thickness of 365 μm and a specific resistance of 0.0223 Ω·cm were used in this work. All experiments were carried out on the Si (0001) face, which is the most commonly used face for power device applications. Before and after anodic oxidation, the wafers were degreased by sonicating in ethanol for 10 min at 30 °C, followed by rinsing with deionized water and drying in the air.

Fig. 1 shows the experimental setup employed in this work. The experimental setup consisted of a three-electrode electrochemical unit with a platinum mesh as the counter electrode and an Ag/AgCl (1 M KCl) electrode as the reference electrode. The 4H-SiC wafer was attached on the side wall of the PTFE-made container. There was a circular aperture with a diameter of 10 mm on the side wall to realize the exposure of SiC to the electrolyte. Anodization experiments were carried out using a potentiostat (CS350H). KCl solution configurated from

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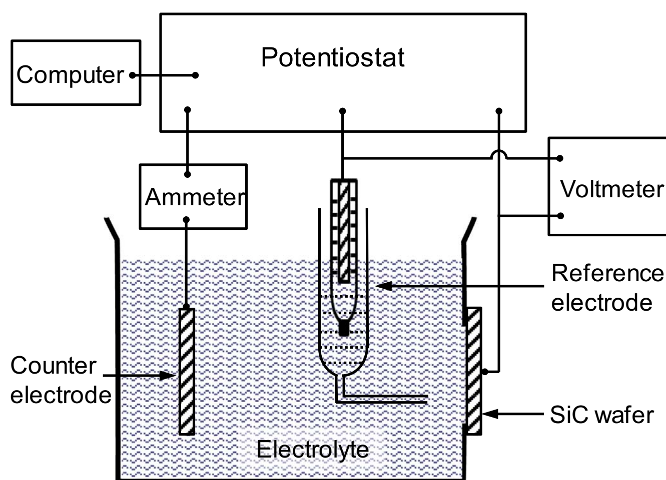
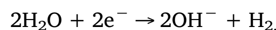


Fig. 1. Experimental setup of KCl-solution-based anodic oxidation of SiC.

10 g reagent grade KCl powders per 1 L DI water was used as the electrolyte. The electric conductivity was 146 mS/cm.

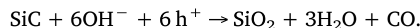
The electrochemical reactions occurring on the cathode (platinum electrode) and anode (SiC) can be summarized as follows:

At the cathode (platinum electrode),



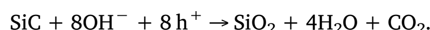
$$2H_2O + 2e^- \rightarrow 2OH^- + H_2.$$

For SiC [7],



$$SiC + 6OH^- + 6h^+ \rightarrow SiO_2 + 3H_2O + CO.$$

or



$$SiC + 8OH^- + 8h^+ \rightarrow SiO_2 + 4H_2O + CO_2.$$

According to the anodizing reactions on SiC, CO or CO_2 gases are generated as well as solid and insulating SiO_2 at the SiC/electrolyte interface. The formed CO, CO_2 release as gas bubbles while SiO_2 remains on the surface as an oxidation layer. The change of surface morphology during anodizing was confirmed using atomic force microscopy (AFM) (Asylum Research, MFP-3D-Stand Alone).

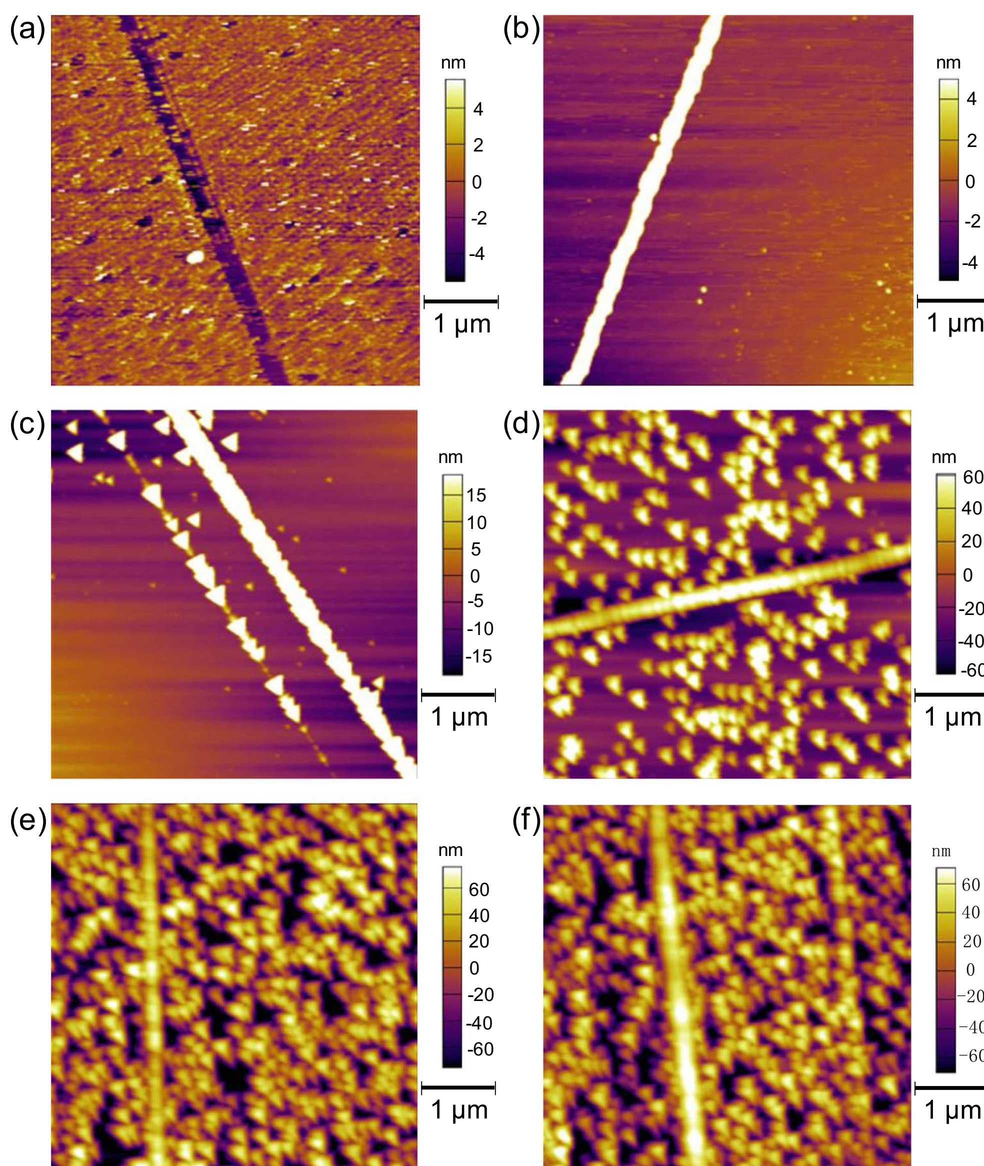


Fig. 2. Surface morphology change of as-lapped SiC during anodizing observed by AFM. (a) As-lapped surface (RMS roughness: 2.83 nm). (b) 10 s (RMS roughness: 4.39 nm). (c) 50 s (RMS roughness: 14.32 nm). (d) 100 s (RMS roughness: 30.90 nm). (e) 240 s (RMS roughness: 37.84 nm). (f) 450 s (RMS roughness: 35.81 nm).

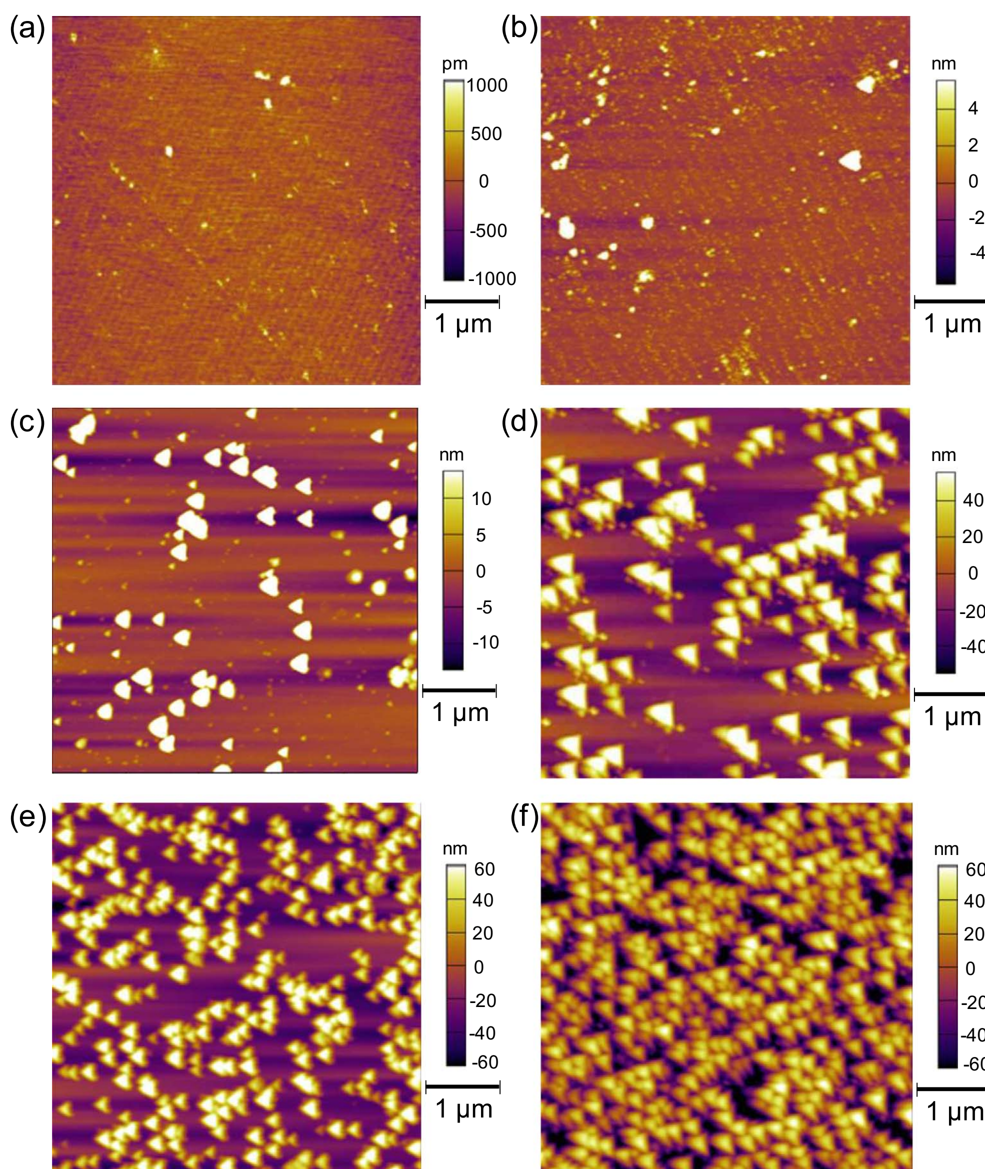


Fig. 3. Surface morphology change of CMP-processed SiC during anodizing observed by AFM. (a) As-received surface (RMS roughness: 0.14 nm). (b) 50 s (RMS roughness: 2.0 nm). (c) 120 s (RMS roughness: 7.32 nm). (d) 300 s (RMS roughness: 28.41 nm). (e) 450 s (RMS roughness: 38.29 nm). (f) 600 s (RMS roughness: 43.71 nm).

3. Results and discussion

As anodic oxidation is based on electron transfer on the electrolyte/SiC interface, the charge carrier density plays a key role in the SiC anodizing process. Therefore, crystalline damage and doping will greatly affect the anodizing process [8,9]. As semi-insulating wafers are used in this work, nitrogen doping is randomly distributed in the wafer, which is determined by the crystal growth process [10]. Meanwhile, crystalline damage can be induced by lapping using hard abrasives. Anodic oxidation on an as-lapped SiC surface with a few scratches was first carried out to investigate the anodizing process of SiC on a damaged and doped surface.

The change of surface morphology during anodizing of the lapped SiC wafer was measured by AFM as shown in Fig. 2. On the lapped surface, only a very few and shallow scratches were observed as shown in Fig. 2 (a). Scratches are formed by plastic deformation of SiC, thus, damage existed around the scratched areas [11–13]. After a short time of anodizing for 10 s, it was found that the scratched area was preferentially oxidized while oxidation was seldom observed on the scratch-free areas as shown in Fig. 2 (b). As SiC was oxidized to SiO_2, volumetric expansion with a ratio of 2.19 occurred during anodizing. Therefore, the scratch upheaved, which highlighted the trajectory of the scratch. At the timing of 50 s, protrusions formed by local anodizing were also observed on the scratch-free area as shown in Fig. 2 (c). As the anodizing time increased, the number of protrusions greatly increased and randomly distributed on the surface as shown in Fig. 2 (d). Finally, the whole surface was oxidized and covered by protrusions as shown in Fig. 2 (f). It was also found that the formed protrusions have very similar shape and dimensions. The height of the protrusions saturated at around 60 nm and irregular protrusions could not be observed.

The results shown in Fig. 2 revealed that the local oxidation process on the lapped SiC surface has different priorities. The scratched areas are preferentially oxidized, followed by the oxidation of scratch-free areas. During anodization, areas with more charge carriers preferentially induce current passing through owing to the application of electrical potential. Thus, anodization of the charge carrier-rich areas is selectively enhanced. As for the lapped substrate, both scratched areas and doping sites can be considered as the charge carrier-rich areas. Subsurface damage including stress layer and dislocations exists near

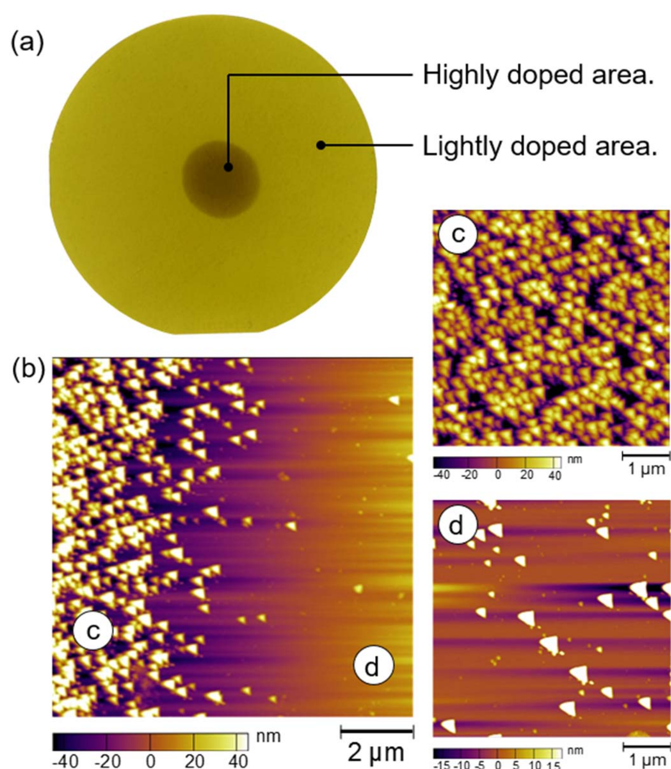


Fig. 4. Anodizing across the boundary of the highly and lightly doped areas conducted at a constant voltage mode (10 V) with 120 s. (a) Photo of the wafer. (b) AFM image of the anodized boundary area (RMS roughness: 19.94 nm). (c) AFM image of the anodized highly doped area. (d) AFM image of the anodized lightly doped area.

the scratches. Meanwhile, nitrogen doping is also randomly distributed in the SiC wafer owing to the crystal growth process [10]. As shown in Fig. 2 (b), when an as-lapped SiC wafer is anodized, scratched areas are firstly anodized and the formed protrusions gather along the scratches. Along the scratched areas, a large amount of covalent bonds formed by carbon atoms and neighboring silicon atoms are broken, which leads to the creation of a large number of dangling bonds, free electrons and holes [14,15]. As a result, the scratched areas have a high density of available charge carriers, which improves the conductivity of these areas to a large extent, thus leading to the preferential anodization of these areas. After the scratched areas are fully anodized, areas without scratches begin to be anodized as shown in Fig. 2 (d). It was found that the protrusions formed by local oxidation are randomly distributed without gathering. After a long period of anodization, the whole surface is oxidized and the surface is fully covered by protrusions as shown in Fig. 2 (f). As nitrogen doping is randomly distributed in the substrate, it is assumed that the randomly distributed protrusions are formed by local anodizing of doping sites.

In order to verify the speculation that the oxidation of doping sites occurred locally and randomly, anodizing was conducted on an as-received CMP-processed SiC wafer surface at a constant voltage mode (10 V) with different anodizing durations. CMP is a well-known damage-free polishing process, thus, it is considered that the CMP-processed surface is free of damage and the preferential oxidation of damaged areas can be excluded. Fig. 3 (a) showed the AFM image of the as-received CMP-processed Si-face. The Si-face was free of scratch and the step-terrace structure of Si-face was dimly visible. Fig. 3 (b–f) showed the AFM images of the anodized Si-face with different anodizing durations. It was found that oxidation layer as the form of SiO_2 protrusions single by single distributed randomly on the anodized surface, which deteriorated the RMS roughness of the surface. With the increase of the anodizing duration, the number of protrusions also increased. After anodizing for 600 s, the wafer surface was full of protrusions as shown in Fig. 3 (f). Similar to the anodizing process of the lapped surface, the shape and dimensions of the protrusions are very uniform and the saturated height of the protrusions is also around 60 nm. These results indicate that the anodic oxidation is a less homogeneous process than plasma oxidation and thermal oxidation [16–18]. Based on the results shown in Fig. 3, it is concluded that the anodizing of a CMP-processed SiC surface is a local and random oxidation process just like the distribution of doping sites.

To further verify that the existence of doping enhanced anodization of SiC, a SiC wafer with a highly doped area as shown in Fig. 4 (a) was used for a comparison study. Anodizing across the boundary of the highly and lightly doped areas was conducted at a constant voltage mode (10 V) with 120 s. Fig. 4 (b) showed the AFM image of the anodized boundary area. Obviously, the highly doped area has a much higher oxidation rate than that of the lightly doped area. Fig. 4 (c) and (d) showed the enlarged AFM images of anodized highly doped area and lightly doped area respectively. It was found that the area with high concentration of doping (area c) was almost fully covered by protrusions, while the area with low concentration of doping (area d) just began to anodize and only a few protrusions appeared on the surface. These results indicate that the existence of nitrogen doping selectively enhances the anodization of SiC and areas with higher concentration of doping are preferentially anodized.

4. Conclusions

Experimental investigation of the initiation and development process of local oxidation during anodizing of single crystal SiC has been conducted. During anodization, areas with more charge carriers preferentially induce current passing through under the application of electrical potential and these areas are preferentially oxidized. To summarize, the following conclusions can be drawn from this study:

1. No matter for a damaged or non-damaged SiC surface, anodic oxidation occurs locally and protrusions are formed.
2. For anodizing of damaged areas, local oxidation occurs preferentially around the damaged areas.
3. For anodizing of non-damaged areas, anodic oxidation occurs randomly owing to the random distribution of doping sites in the SiC wafer.

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