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Preparation of highly planarized optical surface on Si substrate via catalyst-referred etching

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Abstract

In recent years, crystalline silicon (Si) has been used as a promising material for precision X-ray mirrors and Bragg optics. These devices require extremely well-ordered surfaces without crystallographic damage. Thus, we applied an ultra-precision polishing method called catalyst-referred etching (CARE) to planarize crystalline Si substrates. CARE is a catalyzed chemical etching method that uses pure water as an etchant and a catalytic pad that promotes the designed reactions. Owing to its abrasive-free nature, the polished surface reaches an atomic-level smoothness suitable for application to excellent optical devices, particularly in the X-ray regime. Understanding the mechanism of this method is essential for its wide practical application. CARE has been successfully applied to silicon dioxide (SiO_2) optical glasses, and the removal mechanism has been clarified to be an indirect hydrolysis reaction using first-principles calculations. In the case of Si CARE, because Si is easily oxidized by dissolved oxygen (DO) in pure water, the removal pathway may involve oxidation reactions, which may be similar to the removal mechanism of SiO_2 CARE. Clarifying the role of DO is essential for understanding the mechanism of Si CARE. In this study, we evaluated the processing characteristics under different DO concentrations and investigated whether the accompanying oxidation induced by DO is critically required. It was observed that Si CARE does not require oxidation. The surface roughness was observed to be drastically improved in low-DO water. We conclude that the etching mechanism of Si CARE is different from that of SiO_2 CARE. Thus, a first-principles investigation is possible, except for the O_2 molecule from relevant reactions.

Si, X-ray mirror, Bragg optics, catalyst-referred etching, indirect hydrolysis reaction

1. Introduction

In recent years, crystalline Si has been used in X-ray reflective optics and Bragg optics owing to its excellent crystallographic properties and precision machinability. In Si-based X-ray optics, the optical surface must be smooth at the atomic level without any crystallographic damage. Chemical mechanical polishing and elastic emission machining are generally used to produce precision surfaces of Si [1]. However, these surfaces are still rough, leading to a reduction in their X-ray reflective efficiency. Here, we propose the application of an abrasive-free polishing method called catalyst-referred etching (CARE) for crystalline Si substrates [2]. CARE employs pure water as an etchant and an elastic pad with a thin platinum (Pt) film deposited on its surface as a catalyst to induce an etching reaction. Etching occurs only at the sample surface in contact with the catalyst. Accordingly, the topmost site of the sample is preferentially etched off, leading to an effective ordering of the surface. We have already applied CARE to silicon carbide, gallium nitride, and quartz to obtain an atomically smoothed surface with a step-and-terrace structure [3]. Recently, an ultra-precision surface of Si(100) has been realized using CARE, as shown in **Fig. 1**. An atomically ordered surface is expected to produce excellent optical properties, particularly in the X-ray regime. Understanding the mechanism of CARE is critical for its wide application.

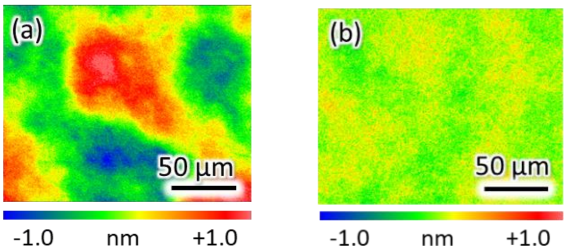

Figure 1. Optical profiler images of the (a) preprocessed surface (peak to valley (P-V): 2.48 nm, root mean square (RMS): 0.44 nm) and (b) CARE-processed surface of Si(100) (P-V: 1.02 nm, RMS: 0.08 nm)

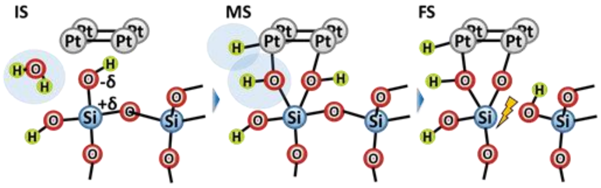

Figure 2. Reaction pathway of SiO_2 etching under the Pt catalyst in pure water

The removal mechanism of SiO_2 CARE has been clarified to be an indirect hydrolysis reaction using first-principles calculations, and the corresponding reaction pathway is shown in **Fig. 2** [4]. The Pt surface assists the dissociation of water molecules, and OH^- is adsorbed at the step-edge Si atom as a strong Lewis base and forms a hypervalent silicate. The back-bond of Si becomes unstable and weakened, leading to cleavage. In the case of crystalline Si, the Si surface, particularly the Si(100) surface, is easily oxidized in pure water by dissolved oxygen (DO). To understand the reaction pathway of Si CARE, it is important to know whether the accompanying oxidation is critical and whether the removal mechanism is related to that of SiO_2 CARE.

In this study, to investigate the role of DO in Si CARE, we designed a CARE apparatus with a degassing system that can adjust the DO concentration in the CARE process and evaluated the characteristics of the etching rates and surface properties in relation to the DO concentrations.

2. Experimental methods

The schematic of the experimental setup with the degassing system is shown in **Fig. 3**. Pure water circulates between the CARE machine, rotor pump, pre-filter, and degassing module connected by polybutylene terephthalate tubing, which has low oxygen permeability. The degassing module consists of hollow fibers with the inner and outer diameters of 100–140 µm and 180–220 µm, respectively. In this module, pure water flows inside the hollow fibers, and high-purity nitrogen flows outside them to reduce the DO concentration through Henry's law. The DO concentration was monitored in situ and adjusted using the flow rate of pure water. By maximizing the flow rate, the DO can be reduced below 9 ppb. At this concentration, the hydrophobicity of the Si surface does not change even after immersion for longer than 20 h, enabling an investigation of the CARE characteristics without surface oxidation. Hereafter, a concentration of less than 9 ppb is defined as 0 ppm.

The details of the CARE apparatus and the processing parameters are shown in **Fig. 4** and **Table 1**, respectively. A p-type Si(100) substrate with a size of 30 mm was polished using CARE. The Si substrate was placed in the processing tank and was in contact with a catalytic pad at a pressure of 60 kPa. Both the substrate and pad were immersed in DO-controlled pure water and rotated independently around their own axes. The etching rate was calculated from the depth of the etching mark as the footprint of the pad on the substrate. The surface morphologies of the Si substrate before and after the CARE process were observed using an atomic force microscope (AFM, Shimadzu; HT 9700).

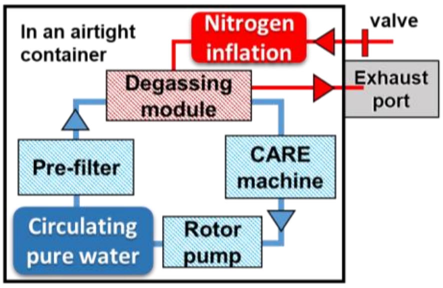

Figure 3. Schematic of the experimental setup with the degassing system

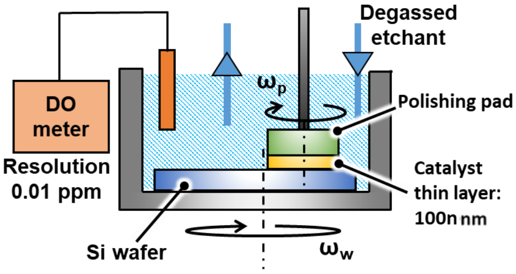

Figure 4. Schematic of the CARE apparatus

Table 1. Processing parameters

Dissolved oxygen Concentration	0 ppm, 2.5 ppm, 5.0 ppm, 7.5 ppm
Processing pressure	60 kPa
Relative speed	5.0 cm/s
Processing time	2 h

3. Results and discussion

The etching rates at different DO concentrations are shown in **Fig. 5**. The etching rates were normalized to that at 0 ppm. The etching rate decreased as the DO concentration decreased, but these two parameters did not have a strong relationship. Moreover, nearly the same rate is observed also at 0 ppm, the removal rate of which is about 5 nm/h. The results show that Si was etched without accompanying oxidation. **Figure 6** shows the AFM images before and after the CARE process in low-DO water. As expected, the surface roughness was markedly improved.

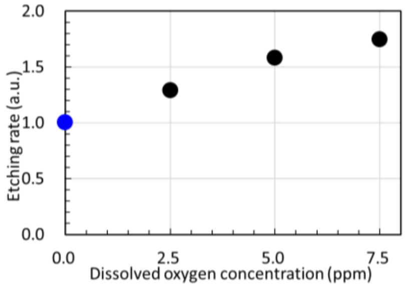

Figure 5. Dependency of the etching rate of Si(100) on the dissolved oxygen concentration

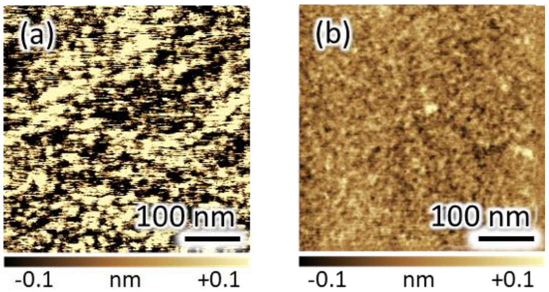

Figure 6. AFM images of the (a) preprocessed surface (P-V: 1.56 nm, RMS: 0.178 nm) and (b) CARE-processed surface (P-V: 0.345 nm, RMS: 0.035 nm)

4. Summary

The CARE method, which is an abrasive-free chemical etching method, can realize the atomic-scale planarization of Si(100) surfaces. It has been applied as a promising method for producing high-precision X-ray optical elements for next-generation synchrotron radiation sources. In this study, to confirm whether there is a similarity between the CARE processes of Si and SiO_2, we investigated whether the accompanying oxidation induced by DO is critically required. It was observed that Si CARE can proceed only with water molecules without DO and that the removal mechanism is different from that of SiO_2 CARE.

In preparation for future studies, we are attempting to reflect this result to propose a guess model of the reaction pathway for first-principles simulations. At the EUSPEN conference, we will present the performance and removal properties of Si CARE, including the latest status of the simulation research. The full elucidation of the mechanism will enable the wide application of this method not only to optical devices but also to the field of atomically controlled precision surfacing.

References

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