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Atomically smooth Si surface planarized using a thin film catalyst in pure water

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Abstract
A catalytically assisted etching method was applied to planarization of Si surfaces for the ultra-precision fabrication of X-ray mirrors. The study demonstrates that an atomically smooth surface with less than 0.1 nm root-mean-square roughness could be achieved on a Si substrate using a thin metal film and pure water as the catalyst and etching solution, respectively. The removal rate using a Pt catalyst can reach to over 500 nm/h. Density functional theory calculations is carried out to understand the initial steps of the catalyzed hydrolysis reaction at catalyst-Si interface during the planarization. The removal mechanism is expected to be similar to that in SiC and SiO_2.

Catalyst-referred etching (CARE), planarization, catalyst, X-ray mirror, hydrolysis

1. Introduction

There is a growing demand on ultra-precision optical components for scientific and industrial applications, especially in extreme ultraviolet (EUV) and X-ray regimes. Using the short-wavelength light, scientific imaging of cutting-edge materials/biological samples and nanoscale lithography have become possible thanks to the ultra-precision optical components [1, 2]. Low thermal expansion materials such as glass and Si are still the main materials used for fabricating optical components. Compared to glass, Si possesses more attractive properties, such as higher cleanliness, machinability, and workability. Accordingly, ultra-precision surface machining for Si surfaces has been achieved significant advances in accuracy and smoothness. A highly ordered surface with a root mean square (rms) roughness at the level of several tens of picometer is greatly desired for the highest reflectivity and the lowest unwanted scattering [3, 4].

Chemical mechanical polishing (CMP) is generally employed as a final polishing method to finish these surfaces. CMP method employs a slurry containing chemicals and abrasives to machine the surface. The mechanical effects are primarily contributed to the removal. Accordingly, mechanical damage and irregularities can be induced on the finished surface that potentially decreases the device's performance [5, 6].

Thus, an abrasive-free polishing method employing catalyzed chemical etching, known as catalyst-referred etching (CARE), has been developed [7-10]. CARE employs a catalytic pad by depositing a thin catalyst film on its surface. The etching only takes place chemically at contact areas of a work piece and the catalyst pad. Accordingly, the topmost parts are preferentially etched, ensuring a highly ordered surface.

This method with Pt and pure water as the catalyst and the etching solution has successfully applied to planarize SiC, GaN and SiO_2 glass [8-10]. Atomically smooth surface with the step-and-terrace structure having a one bilayer step height was obtained. The removal mechanism of CARE for SiC and SiO_2 has been clarified to be hydrolysis reaction using first-principles calculations, as shown in Fig. 1 [9, 10]. Pt catalyzed the hydrolysis reaction via the assistance with water dissociation and stabilization of the hypervalent state through chemical Pt-O bond at the interface.

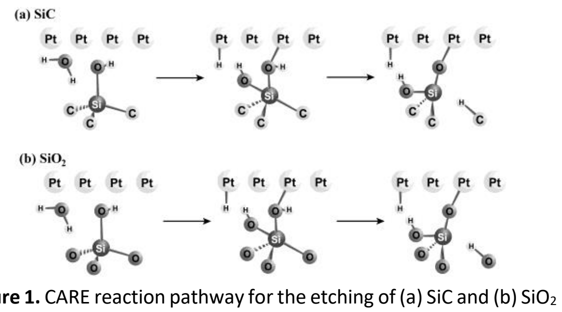

Figure 1. CARE reaction pathway for the etching of (a) SiC and (b) SiO_2 using Pt catalyst and water.

The CARE method is expected to be applicable to Si because the Si-Si bond is a weak chemical bond which is more vulnerable to a chemical attack (Fig. 2). Therefore, this study is to demonstrate the potential of Si planarization using CARE in water and understand the removal characteristics. Additionally, the removal mechanism of Si is also discussed using first-principles calculations.

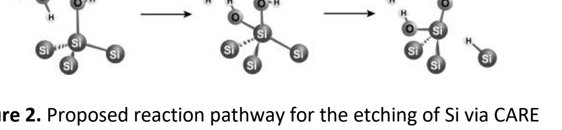

Figure 2. Proposed reaction pathway for the etching of Si via CARE

2. Experimental methods

A 2-in. Si(100) wafer is employed as a typical surface used for X-ray mirrors. The schematic of CARE setup is shown in Fig. 3. A Pt thin film was deposited on an elastic pad. The sample was placed into a wafer holder and pressed onto the pad with a pressure of ca. 40 kPa by an airbag. The sample and the pad were immersed in pure water and independently rotated at a speed of 20 rpm. The rotational speeds of the sample and the pad were slightly different to maximize the randomness of the contact areas between that sample and the pad. Thanks to the random effect of the contact areas, a highly ordered surface could be achieved.

The pre-processed and processed surface via CARE were observed with a phase-shift interference microscope (ZYGO Newview 200CHR) and a scanning probe microscope (Shimadzu; SPM 9700).

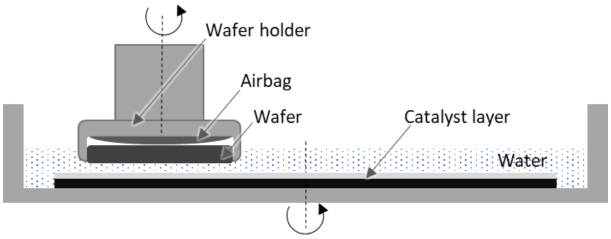

Figure 3. Schematic outline of CARE apparatus

3. Results and discussion

3.1. Surface planarization

Figures 4(a) and (b) show the surface topography of pre-processed and CARE-processed surfaces of the Si(100) surface, respectively. The roughness in peak-to-valley (P-V) and rms is markedly improved.

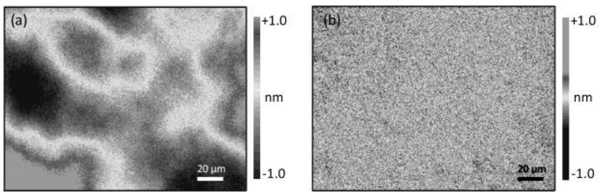

Figure 4. Optical profiler images of the (a) pre-processed surface (P-V: 4.244 nm, rms: 0.628 nm, Ra: 0.486 nm) and (b) CARE-processed surface of Si(100) (P-V: 1.252 nm , rms: 0.094 nm, Ra: 0.106 nm)

Figure 5(a) and (b) respectively show atomic force microscopy (AFM) images of pre-processed and CARE-processed Si surface. The surface roughness (rms and Ra) is markedly improved after CARE processing.

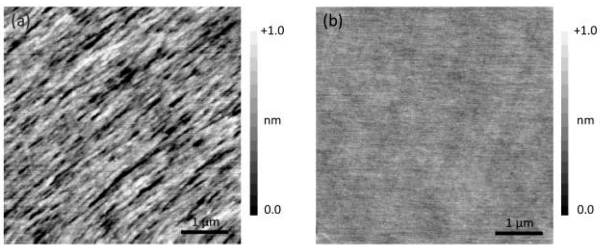

Figure 5. Atomic force microscopy images of the (a) pre-processed surface (rms: 0.225 nm, Ra: 0.175) and (b) CARE-processed surface (rms: 0.052 nm, Ra: 0.041 nm).

The removal rate is approximately 500 nm/h, which is faster than that for SiC and SiO_2 processing. The results suggest that the hydrolysis reaction on a Si surface might have a lower activation barrier than that on SiC and SiO_2 surfaces.

3.2. First-principles calculations

To confirm the hydrolysis reaction and role of the catalyst in CARE of Si, we performed first-principles calculations to estimate the activation barriers of the relevant reaction pathways. The calculation methods are explained elsewhere [9, 10]. At the first trial, we investigated the activation barrier of the reaction pathway without a Pt catalyst. The initial state (IS), metastable state (MS), and final state (FS) are shown in Fig. 6.

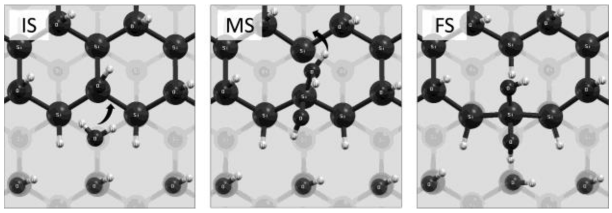

Figure 6. Atomic geometries of the initial state (IS), metastable state (MS), and final state (FS) for the reaction without a Pt catalyst.

The activation barrier of the reaction pathway in Fig. 6 is calculated to be 1.0 eV, which is smaller than that for SiC (1.9 eV) and SiO_2 (1.5 eV), indicating that the hydrolysis reaction on a Si surface is easier. The calculated results suggest the feasibility of the Pt-catalyzed hydrolysis reaction in Si processing via CARE. The removal mechanism of CARE of Si is expected to be similar to that of SiC and SiO_2.

4. Summary

The study demonstrated the feasible application of CARE planarization to Si substrates using a Pt catalyst in pure water. The CARE-processed surfaces were atomically smoothed with an rms roughness of less than 0.1 nm over the whole surface. From the first-principles calculations, the hydrolysis reaction is feasible, indicating that the similarity of the removal mechanism of CARE of Si is expected.

With the elucidated mechanism, the CARE of Si becomes not only a practical ultra-precision polishing method for X-ray mirrors but also an environmentally friendly and sustainable polishing technology because of its abrasive- and chemical-free character.

Acknowledgments
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