

A new mirror-like finish method for oxide materials by catalytically induced chemical etching in pure water

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Abstract

We have developed a new mirror-like finishing method that does not entail the use of abrasives. This method, named catalyst-referred etching (CARE), requires only Pt as a catalyst and pure water as an etchant. In this study, we applied the CARE process to oxide materials, which are often employed in electronic and optical applications. A single crystal silicon dioxide (SiO₂) substrate was used to evaluate the feasibility of the proposed method. Their surfaces were examined by an atomic force microscopy before and after the CARE process. Surface roughness was improved from 0.42 nm rms to less than 0.13 nm rms, and a straight step-terrace structure was created. In addition, specialized lens materials such as fluorophosphate glass and lanthanum oxide glass substrates were smoothed and shaped with a removal rate and accuracy at a level practical for industrial use. The removal mechanism was also investigated by running a simulation based on first-principles calculations. The proposed reaction, hydrolysis at a backbond of a topmost Si atom of SiO₂, was confirmed to occur easily at room temperature in the presence of a Pt catalyst.

catalyst; etching; platinum; pure water; silicon dioxide; lens; the first-principles calculations

1. Introduction

Oxides are materials of considerable technical importance. Actually there are much glasswork made of oxide, such as camera and microscope lenses, displays, photomask substrates, and magnetic disk substrates. To provide much smaller, higher-performance, and more highly integrated devices, the oxide surface requires an atomic flatness without crystalline defects and a high accuracy of form. Because the final step of surface preparation is polishing, the performance of these devices unexceptionally depends on the accuracy of the polishing techniques. We propose a novel chemical finishing technique without the use of abrasives. In this study, we apply this method, named catalyst-referred etching (CARE) [1], to single crystal SiO₂ and to glass substrates used as optical lenses whose quality is affected eminently by the accuracy of their form, scratches, and optical strain.

2. Planarization method

2.1. Catalyst-referred etching

A remarkable difference between general polishing techniques and CARE is the persistence of abrasives. The CARE process requires only Pt as a catalyst and pure water as an etchant. Etching occurs only in the areas where the work material comes in contact with the Pt catalyst so that protrusions on the work surface are selectively removed. In other words, the surface shape of the pad carrying the catalyst can be transferred to the work surface by a chemical reaction. Because the work materials are removed by only chemical reactions, in principle, surface damage will not be induced. Therefore, the CARE technique can produce a flat surface without inducing crystallographic damage. CARE has realized atomically flat surfaces with straight step-terrace structure on semiconductor device substrates including

silicon carbide [2] and gallium nitride [3]. The factor associated with the removal reaction is only pure water; therefore, its mechanism can be attributed to hydrolysis [4]. CARE was expected to have applicability to oxide materials because they are fabricated by hydrothermal synthesis, the mechanism of which is opposite to that of hydrolysis.

2.2. Experimental setup

In this study, we applied the CARE process to single crystal R-face SiO₂ for a basic understanding the CARE of oxides, and to lanthanum oxide glass and fluorophosphate glass substrates for an optical fabrication usage. The apparatus of CARE is similar to that used in conventional polishing. The work substrate is set in the wafer holder, placed onto a catalyst plate, and then pressurized. A thin film of platinum deposited on a pad made of urethane was employed as a catalyst. Processing conditions are shown in Table 1. The processed surface qualities were evaluated by an atomic force microscope (SII Nanotechnology, Inc., Chiba, Japan, SPA400 + SPI3800N) and an optical interferometer (ZYGO Corp., CT; Middlefield, NewView 200 CHR). Removal rates were estimated from the weight loss of the substrate after CARE.

Table 1. Experimental conditions for each substrate

Sample	2 inch ϕ R-faced on single crystal SiO ₂ 35 mm ϕ Fluorophosphate glass Lanthanum oxide glass
Rotational speed	10 rpm (for SiO ₂), 300 rpm (for fluorophosphates)
Pressure	20 kPa
Time	5 min
Etchant	Pure water

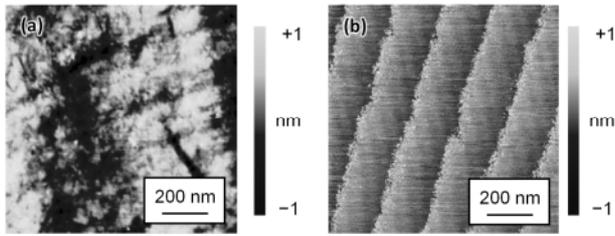


Figure 1. AFM images of (a) pre-process and (b) processed surfaces on a single crystal R-faced SiO₂ substrate. Surface roughness is reduced from 0.42 nm rms to 0.13 nm rms

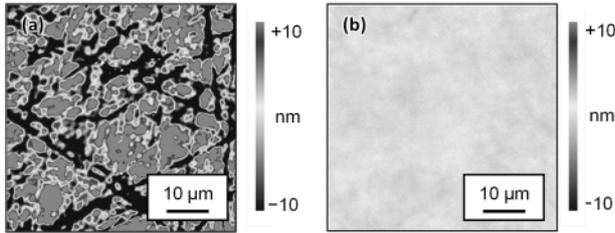


Figure 2. Optical interferometer images of (a) pre-process and (b) processed surfaces on a fluorophosphate glass substrate. Surface roughness is reduced from 11.9 nm rms to 0.36 nm rms

3. Results and discussion

3.1. Processed surface qualities and the removal rate

Figure 1 shows typical AFM images of the pre-process and processed surface on an R-faced single crystal SiO₂ substrate. The processed surfaces were atomically flat in the AFM area. A step-terrace structure with a straight step edge was observed. The step heights were equivalent to the single-bilayer thickness of SiO₂, 3.4 Å [5]. The typical optical interferometer images of the pre-process and processed surface on a fluorophosphate glass substrate are shown in Fig. 2. The observed area was 50 × 50 μm². Surface flatness was improved. Further, the surface flatness of a lanthanum oxide glass substrate was also improved at almost the same level, i.e., reduced to 1.1 nm rms. The removal rates of fluorophosphate glass and lanthanum oxide glass substrates were up to 250 and 1400 nm/min, respectively.

3.2. Proposed removal mechanism

In the CARE process, only pure water and a Pt catalyst are used; therefore, the removal mechanism should be a reaction between the work material and pure water. The straight step-terrace structure created on a single crystal substrate indicates that the removal proceeds from the step edges. On the basis of these facts, the removal mechanism is attributed mainly to the dissociative adsorption of water molecules at the Si–O bonds at the step edge, namely the hydrolysis at the backbond, and the reaction is promoted by the Pt catalyst. We investigated this inferred reaction by running a simulation based on the first-principles molecular dynamics calculations using the Simulation Tool for Atom Technology (STATE) code [7]. The activation energies of the hydrolysis at the backbond of a topmost Si atom at a step edge with and without Pt were calculated. Figure 3 illustrates the steps for the removal of a Si atom in the presence of Pt through indirect hydrolysis at the backbond of a Si atom. Figure 4 shows the energy diagram of the proposed reaction path, calculated by the nudged elastic band (NEB) method [6]. In both cases, the Si atom is terminated by OH at the initial state, as commonly understood. The energy at the initial state is set to be 0 eV. In the case with no Pt, the reaction barrier height was approximately 1.73 eV; therefore, direct hydrolysis reaction at a backbond of a topmost Si atom hardly proceeds at room temperature. With Pt, the proposed

removal occurs by indirect hydrolysis. At first, a water molecule adsorbs at

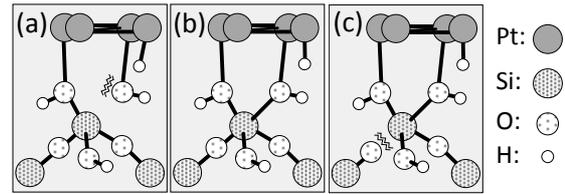


Figure 3. The steps for the removal of a Si atom in the proposed reaction path, i.e., indirect hydrolysis at the backbond. The images show (a) the dissociative adsorption of a water molecule at Pt, (b) meta-stable condition; OH and a topmost Si forming a five-fold coordination, (c) the cleavage of a backbond of a topmost Si.

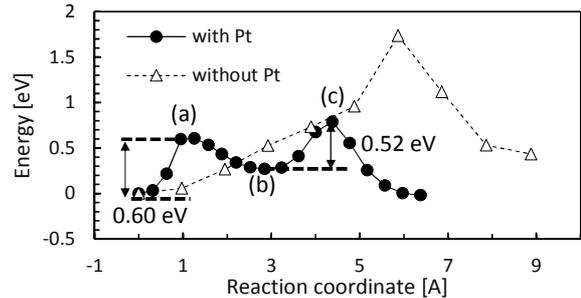


Figure 4. The energy diagram of activation energies at several states corresponding to each step shown in Fig. 3

at Pt ((a)). Herein, OH and a topmost Si form a five-fold coordination, in which the backbond is elongated and weakened ((b)), which is a meta-stable condition. Thereafter, a backbond of the Si is cleaved easily and H⁺ moves from the terminated OH to the cleaved bond ((c)). The reaction barrier height for the dissociative adsorption of water molecule at Pt ((a)) and that of the cleavage of a backbond of a Si atom at the step edge ((c)) are 0.60 eV and 0.52 eV, respectively. The activation energies are reduced sufficiently to less than 1.0 eV by the catalyst. This reaction was theoretically confirmed to proceed at room temperature with Pt catalysis. Therefore, hydrolysis is the main reaction of removal in the CARE process.

4. Summary

A new mirror-like finishing method without the use of abrasives, named CARE, was applied to some oxide materials. Surface flatness of all substrates was improved. On a single crystal substrate, a straight step-terrace structure was created. Hydrolysis at the backbond of a topmost Si atom was confirmed as the mechanism of material removal.

5. Acknowledgment

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References

- [1] Hara H, Sano Y, Mimura H, Arima K, Kubota A, Yagi K, Murata J, and Yamauchi K 2006 *J. Electron. Mater.* **35** L11
- [2] Isohashi A, Sano Y, Sadakuni S, and Yamauchi K 2013 *Mater. Sci. Forum* **740–742** 847–850
- [3] Murata J, Sadakuni S, Okamoto T, Hattori A, Yagi K, Sano Y, Arima K, Yamauchi K 2012 *J. Crystal Growth* **349** 83–88
- [4] Oue M, Inagaki K, Yamauchi K, and Morikawa Y 2013 *Nanoscale Res. Lett.* **8** 323
- [5] Sugiura T, Isohashi A, Yamaguchi W, Matsuyama S, Sano Y, and Yamauchi K 2014 *Proceedings of the 14th euspen international conference* **2** 351–354
- [6] Morikawa Y 1995 *Phys Rev. B* **51** 14802
- [7] Milles G, Jonsson H, and Schenter G K 1994 *Surf. Sci.* **324** 305