AFM Studies on the Difference in Wear Behavior Between Si and SiO₂ in KOH Solution

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Wear behavior between a Si tip and a SiO₂ film in KOH solution at various pH values has been examined by using an atomic force microscope. We found that the Si tip removal amount strongly depended on the solution pH value and was at a maximum at pH 10.2-12.5. This result indicates that wear behavior of the Si tip is similar to that of actual chemical mechanical polishing of a Si wafer. It was also found that the Si removal volume in moles was approximately equal to that of SiO₂ irrespective of the solution pH value. This equality implies that a Si-O-Si bridge is formed between one Si atom and one SiO₂ molecule at the wear interface, followed by the oxidation of the Si tip, and finally the bond rupture by the tip movement and the silica species including the Si-O-Si bridge is dissolved in the KOH solution.

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Chemical mechanical polishing (CMP)¹ is the final and thus the most important step of a Si wafer shaping process (after cutting, lapping, and chemical etching) to produce an atomically flat and defectfree surface for further electronic device manufacturing. The process of CMP consists of rotation of a soft polishing pad on a Si wafer with alkaline silica (SiO_2) slurry. It has been known that CMP is a complicated process, where mechanical wear by the SiO₂ particles and chemical corrosion by the slurry solution occur simultaneously. This complexity leads to the difficulty of analyzing a microscopic Si removal process that controls the polished surface morphology on an atomic scale. Schnegg et al. have proposed the removal process in which OH⁻ adsorption on the topmost Si atoms catalyze the corrosive reaction by H₂O, resulting in cleavage of Si back bonds.² Pietsch et al. have verified this mechanism by Fourier transform infrared (FTIR) spectroscopy of the Si surface immediately after CMP. They presented a removal mechanism, in which a silicic acid species, i.e., Si(OH)₄, (OH)₃Si-O-Si(OH)₃,... is formed by local oxidation by OH⁻ and frictionally removed by the mechanical action of the SiO₂ particles.³ Although the formation of silicic acid species has been identified, the frictional interaction between the SiO₂ particle and those species has not fully been understood.

In this study, we examine the origin of the frictional interaction by considering a chemical reaction between Si and SiO₂ during wear. We use an atomic force microscope (AFM), which is a powerful tool for atomic scale wear analysis.⁴⁻⁶ The wear test is performed by scratching a thermally oxidized SiO₂ film on a Si wafer with a Si AFM tip in KOH solution at various pH values. The chemical reaction between Si and SiO₂ is investigated by comparing the Si removal volume in moles with that of SiO₂ by the wear test, in order to clarify the Si removal mechanism on an atomic scale.

Experimental

A commercial-type AFM with a closed glass fluid cell was used in this experiment (Digital Instruments, Santa Barbara, CA).⁷ A four-sided pyramidal single-crystal Si tip, mounted on a microfabricated Si cantilever (Digital Instruments, Santa Barbara, CA) was used for both the wear test and AFM observation. The cantilever is 125 μ m long and has a spring constant of 20-50 N/m. A SiO₂ film was grown on a nondoping Si(100) wafer by thermally oxidizing (1000C°, 3 h) in a dry O₂ atmosphere. Prior to the thermal growth, the wafer was cleaned by using the RCA procedure.⁸ The thickness of the oxide film was approximately 100 nm. KOH solutions were prepared by mixing reagent grade chemicals and deionized water. The pH value of the solution was adjusted to add buffered solutions, H₃BO₃ (0.30 kmol/m³) and Na₂B₄O₇ (0.075 kmol/m³). After the solution was injected into the cell, the Si tip was brought to the SiO₂ film and scratched the film surface for the wear test. An area of $10 \times 10 \ \mu$ m was scratched with a tip scan speed of 20 μ m/s at normal loads ranging from 1 to 6 μ N for 3, 8, 18, and 38 cycles. Then, a larger SiO₂ surface area of $20 \times 20 \ \mu$ m was observed for imaging the wear mark by using the same Si tip at a normal load about 0.2 μ N. The SiO₂ removal volume was obtained from the product of the scratched area (100 μ m²) and the observed depth of the wear mark.

The Si tip was observed by a scanning electron microscope (SEM) before and after scratching the SiO₂ surface. The Si removal volume was estimated by the change of the tip apex shape. The removal volume of Si and SiO₂ were converted into the volume in moles by using the molar volume, Si: 12.059 cm³/mol and SiO₂: 27.311 cm³/mol, respectively. In order to clarify surface oxidation, the Si tip apex was observed by a transmission electron microscope (TEM) with a modified holder for wire specimens.⁹ An atomic scale image of the tip apex was obtained without any etching treatment, because the radius of the apex was less than 10 nm.

Results

Figure 1 presents a typical TEM image of the Si tip apex before scratching the surface of the SiO₂ film. The {111} lattice planes of the Si single crystal with a few native oxide layers is clearly visible. Figure 2a shows a SEM image of a typical Si tip after scratching the SiO₂ surface in the KOH solution. This SEM image shows that the apex of the Si tip has been removed uniformly and a flat surface is exposed at the end of the tip. As shown in Fig. 2b, the substrate mounting angle of the front edge of the tip is approximately 65° (Digital Instruments, Santa Barbara, CA), thus, the wear volume of the tip (V_{si}) is calculated as

$$V_{\rm si} = \frac{1}{3} SL \tan 65^{\circ}$$
 [1]

Here, *S* is the area of the flat surface and *L* is the distance between front and middle edges at the end of the tip. Figure 3 shows the dependence of the Si wear volume in moles in the solution pH at normal loads ranging from 1 to 6 μ N for 3, 8, 18, and 38 scratching cycles. It was shown that the Si wear amount peaked at the pH 10.2-12.5. This result is similar to polishing behavior in the actual Si CMP.^{2,3}

Figure 4 shows a typical AFM image of a wear mark on the SiO₂ surface. It is clearly shown that an area of $10 \times 10 \ \mu\text{m}$ is worn uniformly. Figure 5 shows the depth of the wear mark on the SiO₂ surface as a function of the number of scratching cycles at pH 12.5 and normal loads ranging from 1.89 to 2.40 μ N. It is obvious that the wear depth increased with the number of scratching cycles and the maximum depth is less than 30 nm, which is thinner than the initial SiO₂ film thickness. It was also shown that the depth per one scratch

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Figure 1. TEM micrograph of the Si tip apex before scratching the surface of the SiO_2 film. The {111} lattice planes of the Si tip with a few oxidized atomic layers is clearly visible.

ing cycle was less than 1 nm at all cycles. It suggests that an atomic layer removal from the SiO_2 surface takes place during the wear test.



Figure 2. (a, top) SEM image of a typical Si tip after scratching the SiO₂ surface in KOH solution. The apex of the Si tip has been removed uniformly, and the flat surface is formed at the end of the tip. (b, bottom) Design of the microfabricated Si tip. The substrate mounting angle of the front edge of the tip is approximately 65° .



Figure 3. The dependence of the Si tip removal volume in moles as a function of the solution pH at normal loads ranging from 1 to 6 μ N for 3, 8, 18, and 38 scratching cycles. The removal volume peaks at pH 10.2-12.5 at any cycle.

Figure 6 presents the relationship between the removal volume in moles of Si tips and that of corresponding SiO_2 films. Independent of the pH value and the number of scratching cycles, it is clear that the removal amount of Si is in good agreement with that of SiO_2 . It implies that one Si atom is removed per one SiO_2 molecule removal when the Si tip scratches the SiO₂ film in KOH solutions.

Discussion

The atomic process taking place during the wear test is now considered. The wear test is performed by scratching the SiO_2 surface by the Si tip in the KOH solution. As shown in Fig. 1, the initial Si tip apex is covered with a native oxide layer, which is a few nanometers in thickness. After the wear test, as shown in Fig. 2a, the apex of the Si tip is worn in a micrometer scale. Therefore, the native oxide



Figure 4. A typical AFM image of a wear mark on the SiO_2 film in KOH solution (pH 12.5), which is made by using the Si tip at a normal load of 1.9 μ N and eight scan cycles.



number of scratching cycle (times)

Figure 5. The depth of the wear mark on the SiO₂ surface as a function of the number of scratching cycles at pH 12.5 and normal loads ranging from 1.89 to 2.40 μ N. Note that the depth per one scratching cycle is less than 1 nm at any cycle.

layer is removed at the beginning of the wear test and then the SiO_2 is scratched by Si itself.

It has been well known that a very sharp Si tip will wear by fracturing when the tips are used with a contact mode AFM with high normal loads (F_n) on hard samples. E_{Si} /10 is an estimate for the the-



Figure 6. Relationship between the removal volume in moles of Si tips and those of corresponding SiO_2 films. Irrespective of the pH value and the number of scratching cycles, the removal amount of Si is in good agreement with that of SiO_2 .

oretical fracture strength ($\sigma_{\rm Si}$) of Si surface bonds.¹⁰ Here, $E_{\rm Si}$ is the Young's modulus of Si and $E_{\rm Si}$ is 162.9 GPa. At the beginning of the wear test, the Si tip will wear by fracturing, because the contact area between the tip and the SiO₂ surface is smaller than $F_{\rm n}/\sigma_{\rm Si}$ and therefore the pressure is higher than $\sigma_{\rm Si}$. When the contact area extends over $F_{\rm n}/\sigma_{\rm Si}$, on the other hand, the pressure is lower than $\sigma_{\rm Si}$ and tip wear would not occur by fracturing. In the present experiment, Si tips scratched SiO₂ surfaces at normal loads ranging from 1 to 6 μ N. Thus, $F_{\rm n}/\sigma_{\rm Si}$ is estimated at 6.1 \times 10⁻¹⁷ to 3.7 \times 10⁻¹⁶ m², which is much smaller than the observed flat area at the tip apex, on the order of 10⁻¹³ to 10⁻¹² m², as shown in Fig. 2a. This suggests that the Si tip would not wear by mechanical fracture except at the very beginning of the wear test due to the lower pressure than $\sigma_{\rm Si}$.

When the Si tip scratches the SiO₂ surface at the leading edge of the tip dissolution of the SiO₂ surface may take place due to an increased liquid temperature and a compressive stress in the SiO₂ network.¹⁰ Siloxane bonds (Si-O-Si) of the SiO₂ surface are broken by hydroxyl and form a hydrated silica surface,^{11,12} For water, this reaction may be simplified to^{10,13}

$$\equiv Si-O-Si \equiv + H_2O \rightleftharpoons 2 \equiv Si-OH$$
[2]

From neutral to alkaline pH, the surface hydroxyl equilibrium may be described by 10,12

$$\equiv Si-OH \rightleftharpoons \equiv Si-O^{-} + H^{+}$$
[3]

and the fraction of molar surface concentrations may be calculated by $^{10}\,$

$$[\equiv Si-O-]/[\equiv Si-OH][\equiv Si-O^{-}] = (10^{5.2 \log(pH) - 4.78})/4.6$$
 [4]

On the SiO₂ surfaces, therefore, equimolar concentrations of each species occurs at pH 9.8, and \equiv Si–O⁻ is dominated at the value of pH > 9.8. The opposite reaction occurs on the trailing edge due to a decreased liquid temperature and a tensile stress in the SiO₂ network. The reversal of Eq. 2 and 3, which is the network condensation, is described by^{10,11}

$$\equiv Si - O^{-} + \equiv Si - OH \rightleftharpoons \equiv Si - O - Si \equiv + OH^{-}$$
[5]

Consequently, silica species is precipitated on the SiO_2 surface again.

Here, the Si surface may be terminated by H, and the OH termination increases with solution pH.^{3,14} If the \equiv Si–OH of the Si tip reacts with \equiv Si-O⁻ of SiO₂ surface by Eq. 5, there is some probability that a Si-O-Si bridge is formed between the Si tip and the SiO₂ surface¹⁵ This Si–O–Si bridge weakens Si–Si backbonds of Si by strong polarization and facilitates a further attack by H_2O molecule,^{2,3,14} then the Si tip surface becomes oxidized in the lattice. As the tip scans over the SiO₂ surface, the Si-O-Si bridge and the Si-O backbonds both the SiO₂ film and the oxidized Si tip are strained, resulting in bond rupture. As shown in Fig. 6, the Si removal volume in moles is in good agreement with that of SiO2. This equality indicates that the strength of the Si-O-Si bridge is stronger than that of the Si-O back bonds of the SiO₂ film and the oxidized Si tip. Therefore, the Si-O-Si bridge will remain, leading to the Si-O back bond breakage. Finally, the silicic acid species, (OH)₃Si-O-Si(OH)₃, dissolves in the KOH solution. As shown in Fig. 5, the wear depth of SiO₂ per one scratching cycle is less than 1 nm, *i.e.*, on an atomic layer scale. This result suggests that only a few atomic layers of Si were oxidized16 and subsequently removed. The new Si surface generated by this layer-by-layer removal mechanism is again terminated by H and OH.

As shown in Fig. 3, the Si removal amount increases with the solution pH and peaks at pH 10.2-12.5, indicating that the reaction rate between Si and SiO₂ is varied with solution pH. According to Eq. 5, the concentration of $[Si-O^-]$ of the SiO₂ surface increases with the pH value. Further, the concentration of [Si-OH] of the Si surface is also increased with pH (Fig. 7a). Consequently, the number of the reaction by Eq. 5 must be increased (Fig. 7b), leading to a higher reaction rate.



Figure 7. Schematic showing the change in interaction at the wear interface due to a variation of solution pH.

Although the removal volume in moles of Si and SiO₂ is equal, a drop of the Si removal amount is observed at pH > 13, as shown in Fig. 3 and 6. As the solution pH increases, the oxidation of the Si tip by immediate condensation of adjacent \equiv Si–OH^{2,3,14}

$$\equiv Si-OH + HO-Si \equiv \rightarrow \equiv Si-O-Si \equiv + H_2O$$
[6]

prevail over the reaction between the Si tip and the SiO₂ surface, described by Eq. 5. \equiv Si–O⁻ dominates on the oxidized Si tip surface, thus the number of the reaction by Eq. 5 decrease (Fig. 7c). Consequently, the Si removal amount is decreased at very high solution pH > 13.

Conclusion

The atomic process during the wear test between the Si tip and the SiO_2 film in KOH solution at pH 6-14 has been examined by AFM. We have found that the pH dependency of the Si tip removal

amount is similar to the polishing behavior in the actual CMP of the Si wafer. It has been also shown that the Si tip removal volume in moles is in good agreement with that of the corresponding SiO_2 film. We discussed the chemical reaction at the wear interface between the Si tip apex and the SiO_2 surface, and proposed the surface Si removal mechanism in an atomic scale that involves the formation of the Si–O–Si bridge at the interface, followed by the oxidation of the Si tip, finally the bond rupture by the tip movement, the silica species including the Si–O–Si bridge is dissolved in the KOH solution. These results indicate that the formation of the Si–O–Si bridge at the interface is an important factor for controling the polishing behavior of the Si surface on an atomic scale.

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