

Incipient Chemical Reaction on the Scratched Silicon {111} Surface with Ethoxy and Hydroxy Groups

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Incipient reactions on the scratched Si {111} surface with solutions containing KOH, ethanol, and tetraethyl orthosilicate (TEOS) were examined. *In situ* scratching in the TEOS solution was also carried out for comparison. A remarkable increase in the dangling bond concentration was detected on the scratched silicon surface by ESR. Similar hemispherical gel deposits were observed parallel to the uniformly coated gel film on the scratched sample after etching by an ethanol/KOH solution as well as by *in situ* etching in an ethanol/TEOS solution. The hemispherical deposition, being localized at the tip of branched cracks where KOH solutions also preferentially attack, indicates that the incipient chemical reaction on the scratched silicon {111} with ethoxy groups preferentially initiates at the crack tip, as a result of siloxane polycondensation after concurrence of competitive adsorption of ethoxy over hydroxy groups at the concentrated dangling bonds. © 1995 Academic Press, Inc.

1. INTRODUCTION

Solid state reactions preferentially take place at the spots where defects are concentrated. Defects play particularly important roles when the solid reactants are mechanically activated. Although most of the solid state reactions related with mechanical activation are carried out with the solid reactants in the form of fine particles, a well-defined single crystal surface is much more appropriate for the purpose of basic understandings of reactivity of mechanically activated solids.

In our previous studies we found that the crack tip of Si {111} is preferentially etched by KOH (1, 2). Recently, we have observed the firmer attachment of the silica gel film with stronger scratching under the higher normal stress by an emery paper (3). We also found that the film attaches preferentially at the same spots where KOH selectively attacks (3). It was therefore suggested that the crack tip with partial amorphization is active for OH groups. To elucidate the mechanism of formation of firmly attached

gel film on the silicon substrate, however, it is essential to know where and how the incipient interaction takes place between Si with topochemically well-defined damages and tetraethyl orthosilicate (TEOS).

The purpose of the present study is, thus, to examine the incipient reaction of scratched silicon with KOH, ethanol, and TEOS. More explicitly, we try to find out what kind of defects on the surface of silicon are preferentially active for the adsorption, hydrolysis, and polycondensation of chemical species supplied from a TEOS/ethanol solution.

2. EXPERIMENTAL

2.1. Equipment and Procedure of Scratching

A P-type nine-9 silicon wafer with a polished surface of [111] $4 \pm 1^\circ$, supplied from Komatsu Electronic Metals, was cut into pieces of 10×8 mm. After washed in acetone under ultrasonication for 10 min and mounted onto the sample holder of the scanning electron microscope (SEM), a sample piece of the wafer was subjected to scratching. A scheme of the pneumatically suspended scratching device is shown in Fig. 1. A dead weight was put onto the active pan of the built-in balance and the specimen was scratched by a diamond indenter with a radius of curvature $10 \mu\text{m}$ (Tokyo Diamond, 302D) at a constant rate ranging between 0.23 and 1.0 mm sec^{-1} . The effective force on the indenter was 0.065, 0.20, and 0.33 N, respectively, depending on the dead weight used. Some scratched samples were annealed at 800°C for 0.5 hr in a vacuum sealed silica tube prior to etching or dip coating.

2.2. Etching and Dip Coating

Scratched samples were etched at 25°C . A 0.3 N aqueous solution of KOH, dehydrated ethanol, or a mixture comprising 53.6 cm^3 ethanol and 26.4 cm^3 0.3 N KOH was used as an etching solution.

Silica sol coating was carried out by dipping a freshly scratched specimen into a dipping solution comprising a mixture with the molar ratio TEOS (1): ethanol (7): H_2O

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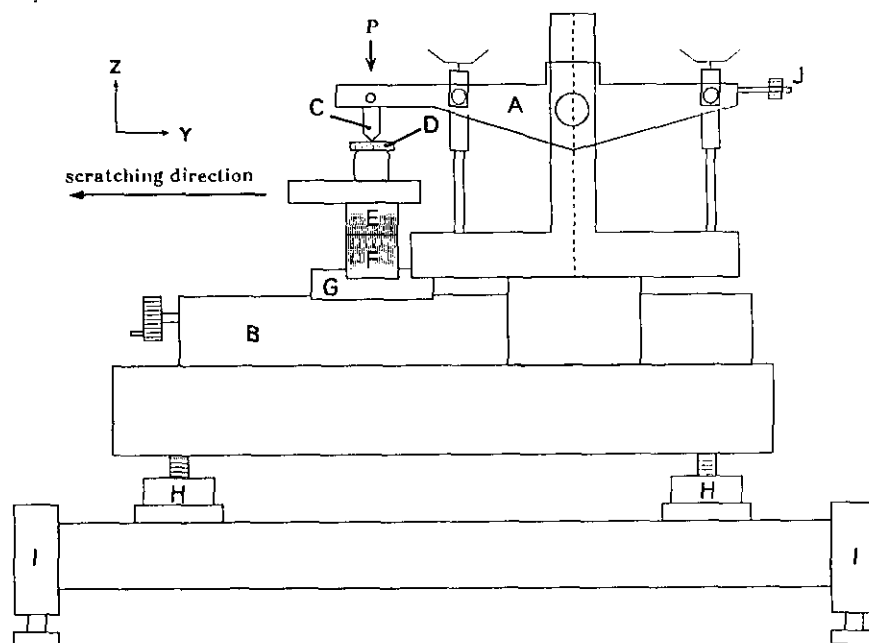


FIG. 1. Scheme of the air-suspended scratching device. A, loading beam; B, mortar drive slide; C, diamond cone; D, sample; E, x axis sliding stage; F, z axis sliding stage; G, y axis sliding stage; H, horizontal adjuster; I, air damper; J, fine balance adjuster.

(11):HCl (0.07). The dipping solution was carefully aged for 6 hr prior to coating in order to obtain the same state of preliminary hydrolysis. The viscosity of the dipping solution was always checked to be constant at 2.3 mPa sec at 30°C. Dipping time was varied between 2 and 120 sec, while the rate of pulling out was kept constant at 1 mm sec⁻¹. The coated specimen was dried at room temperature in air for 24 hr and subsequently cured under an air flow of 500 cm³ min⁻¹ at 500°C for 1 hr and then cooled in a switched-off furnace.

Some of the samples were scratched *in situ* in the dipping solution described above. After the specimen was pasted on the SEM specimen holder with a cyanoacrylate adhesive, 1 mm³ of the dipping solution was dropped on the surface of the specimen and scratched. Drying and heating were carried out in a similar manner to that for normally scratched and subsequently coated specimens, except that the adhesive was burnt out at 250°C for 0.5 hr between drying and cure heating. The specimens used are summarized in Table 1.

2.3. Characterization

Characterization was carried out mainly by using a surface roughness tester (Tokyo Seimitsu, Surfcom 302B), a scanning electron microscope (SEM, JEOL, JSM 5200), a Fourier transformed infrared spectrometer (FT-IR, Bio-Rad, FTS 65), and an electron spin resonance spectrometer (ESR, JEOL, JES-RE3X). A standard graphite (Weak

Coal, JEOL 42290217) was used for the purpose of calibration of the spin density.

3. RESULTS AND DISCUSSION

3.1. Dangling Bond Density

As shown in Fig. 2, the scratched {111} surface showed typical ESR resonance at $g = 2.005$, known to be typical from the dangling bonds in amorphous silicon (4, 5). The spin density per unit length of the crack obtained by scratching at 0.20 N and 1.0 mm sec⁻¹ was 1.85×10^{11} mm⁻¹. While the intensity of the ESR signal reduced to 22% of the original value after standing in an ambient atmosphere for 48 hr, the resonance entirely extinguished only after annealing the substrate at 800°C for 0.5 hr. The formation of high density dangling bonds by simple scratching is thus confirmed.

3.2. Precipitation of Silica Sol

The scratched silicon surface was observed under scanning electron microscope after immersing in a TEOS dipping solution for a varying period, dried, and cured by heating at 500°C for 1 hr. As shown in Fig. 3a, a film was not formed and the bare scratched surface remained when the period of immersion was only 2 sec. With an increasing immersion period, preferential attachment of the gel at the periphery of the main groove was observed, as shown in Fig. 3b with an arrow. The amount of the gel attached

TABLE 1
Samples

Name	Scratching		Coating
	Normal load (N)	Rate (mm · sec ⁻¹)	Dipping period (sec)
S-0	0	0	—
S-33h	0.33	1.0	—
S-20h	0.20	1.0	—
S-20m	0.20	0.50	—
S-20l	0.20	0.23	—
S-065l	0.065	0.23	—
S-33hA ^a	0.33	1.0	—
S-20hA ^a	0.20	1.0	—
S-20h-DC2	0.20	1.0	2
S-20h-DC120	0.20	1.0	120
S-20h-iC	0.20	1.0	<i>in situ</i> coating

^a Annealed at 800°C for 0.5 h after scratching.

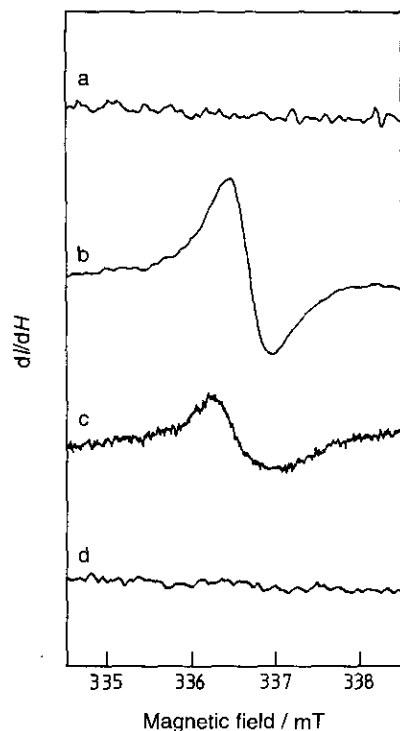


FIG. 2. ESR spectra of the samples (a) S-0 (intact); (b) S-20h (scratched at 0.2 N, 1.0 mm sec⁻¹); (c) S-20h after standing for 20 hr in air at room temperature; (d) S-20hA (S-20h after annealing at 800°C for 0.5 hr in a vacuum).

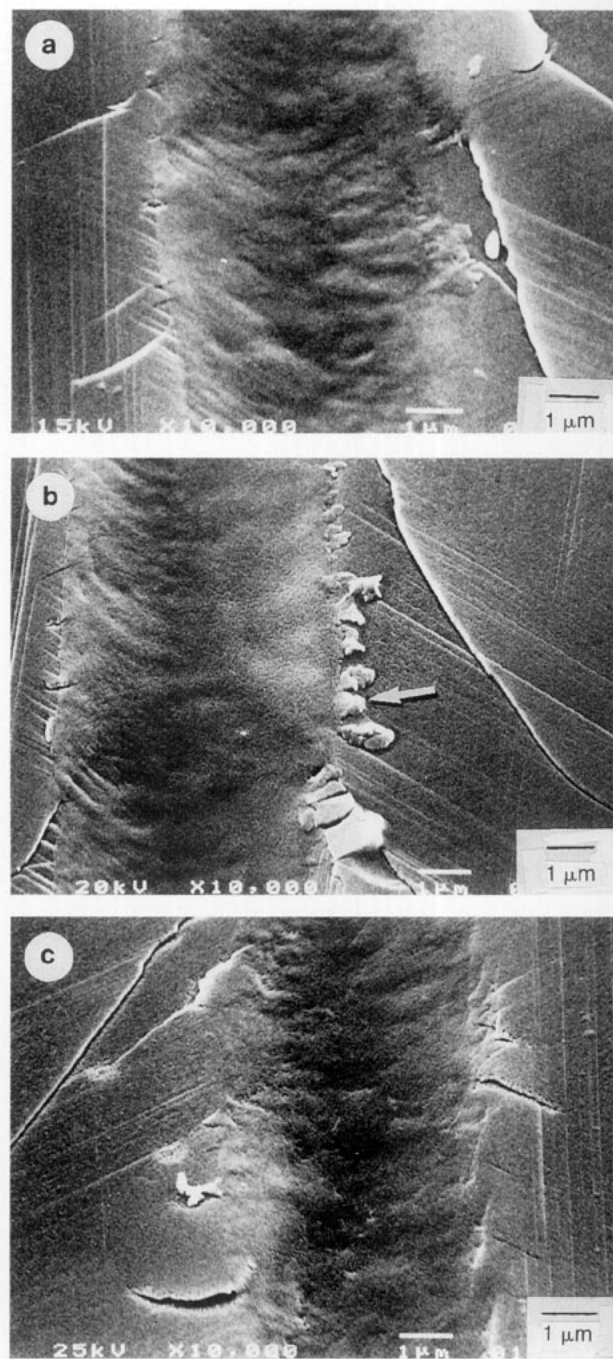


FIG. 3. Scanning electron micrographs of scratched silicon (S-20h) after dip coating of silica gel with varying dipping time: (a) 2, (b) 60, and (c) 120 sec. Peripheral frills appear on (b) as pointed by an arrow. These frills disappear again on further dipping time, indicating the entire coverage of the film.

increased with the increasing period of immersion. Disappearance of the peripheral frill of the gel shown in Fig. 3c, together with the change in the surface gloss or reflectance, indicates the formation of a fairly uniform film after immersing for 120 sec.

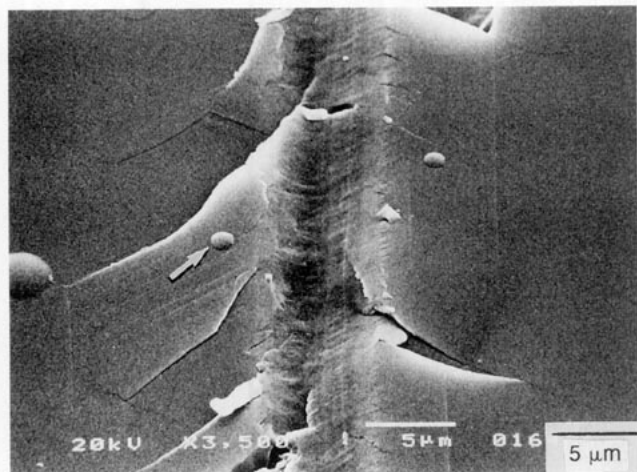


FIG. 4. Scanning electron micrographs of silicon scratching *in situ* (S-20h-iC). Hemispherical precipitates are deposited as marked by the arrow.

A silica gel film was also found around the scratched groove made *in situ* in the TEOS dipping solution, as shown in Fig. 4. When the TEOS dipping solution was washed off immediately after *in situ* scratching and annealed under the same condition, selective attachment along the periphery of the scratched grooves was still observed. It is important to note that some hemispherical precipitates were often deposited near the tip of the branched crack, as indicated by an arrow. Unfortunately, the chemical composition of the precipitates was not able to be determined because the amount of the precipitate was too small. However, it is reasonably anticipated to be the siloxane polymer, as a result of etching by KOH resulting in $\text{Si}(\text{OH})_4$ in the presence of ethanol, as further discussed below.

3.3. Etching with Ethanol/KOH Solution

Preferential etching at the crack tip was observed, as shown in Fig. 5a, when the scratched Si {111} was dipped into the 0.3 N aqueous solution of KOH, similar to the case of indented Si {111} (2) or Si {111} scratched by an emery paper (3). It is known from the literature (6) that the area of inelastic deformation develops along the crack, particularly at the tip of the branched crack and beneath the crack bottom. The etching proceeded into the interior of the crystal deeper into the median and the lateral cracks, and finally the entire region of the inelastically deformed part was etched off, as shown in Fig. 5b.

No sign of etching was detected when the scratched {111} specimen was subjected to immersion into pure ethanol. However, a slight local dissolution was observed when KOH was added to ethanol to give the concentration of KOH 1/3 of the pure KOH solution, as described in 2.2. The most important aspect of etching the scratched silicon with the ethanol/KOH solution is that several hemispheri-

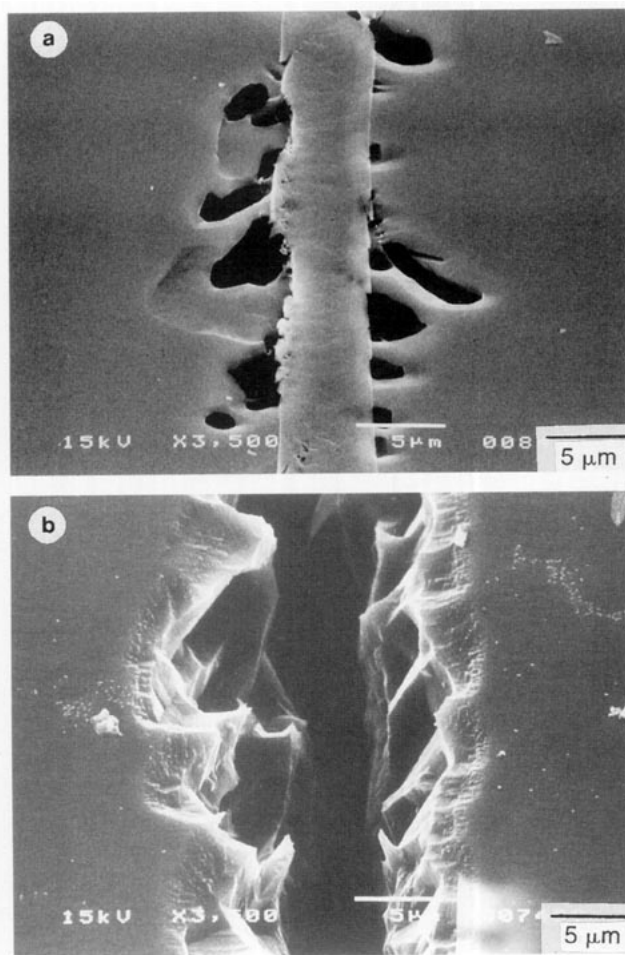


FIG. 5. Scanning electron micrographs of scratched silicon (S-20h) after etching in 0.3 N aqueous solution of KOH for (a) 3 hr; and (b) 4 hr.

cal precipitates are found, shown in Fig. 6 by an arrow, just like the case of *in situ* scratching in the TEOS dipping solution, as mentioned in the previous section and shown in Fig. 4. This was never the case on etching by an aqueous solution of KOH alone.

3.4. Triggering the Reaction by OH Groups

The processes of etching with KOH solution and the precipitation of silica sol from ethanol/TEOS, as well as ethanol/KOH, solutions are found to be topochemically similar. Erosion of silicon at higher pH with abundant OH^- is initiated by the attack of OH^- on the dangling bonds (7). When an electron is transferred from the adsorbed OH^- to the dangling bond, OH^- turns into OH radical to form a Si-O sigma bond. This induces polarization of the Si-Si back bonds.

Polarization, in turn, facilitates the formation of $\text{Si}(\text{OH})_2^{2+}$ complex ions, serving as a precursor of $\text{Si}(\text{OH})_4$ (7). When the silicon tetrahydroxide leaves the solid sur-

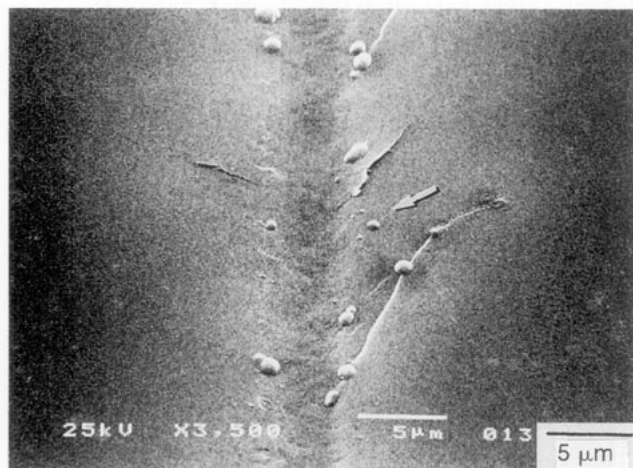


FIG. 6. Scanning electron micrograph of scratched silicon (S-20h) after etching in the C_2H_5OH/KOH mixture for 10 hr. Hemispherical precipitates are deposited as marked by the arrow.

face, it turns into $SiO_2(OH)_2^{2+}$ as a result of deprotonation, since $Si(OH)_4$ is not stable in an aqueous solution like vinyl alcohol.

In the presence of ethanol, stabilization of $Si(OH)_4$ also takes place partly by substituting OH groups with ethanol, resulting in the ethoxy groups, $-C_2H_5O$. This is also the case for the ethanol molecules which are adsorbed on the surface of silicon, preferentially at the concentrated dangling bonds.

It is to be reminded that the addition of ethanol to a KOH aqueous solution suppressed the preferential dissolution by OH^- . This cannot simply be attributed to the dilution of OH^- by ethanol to one third of the pure KOH solution. Instead, it is more likely to be attributed to the formation of ethoxy groups at the same spot, which takes place competitively with the dissolution via a mechanism given in the literature (7) and described above.

3.5. Adsorption of Ethanol and Formation of Ethoxide

As mentioned previously, we observed the topochemical similarity between the reactions of scratched Si {111} with

the ethanol/KOH and ethanol/TEOS solutions. For both of these cases, adsorption of ethanol takes place competitively on the same spot where OH^- groups attack, i.e., on the concentrated dangling bonds. Thus, silicon ethoxide molecules are concentrated at the crack tip while adsorbed. Those ethoxides are subject to polycondensation, as in the conventional process in a solution. This explains the preferential initial deposition of the polycondensed products at the crack tip. On those spots where the polycondensed siloxane phases are particularly concentrated, the hemispherical deposition was observed during *in situ* scratching in the ethanol/TEOS solution (Fig. 4) as well as during etching with the ethanol/KOH solution (Fig. 6) as a bulge of the deposited gel film.

The similarity of the formation of surface precipitates in the cases between TEOS/ethanol etching on the scratched Si {111} and *in situ* scratching in the presence of the TEOS/ethanol solution is thus explained consistently by assuming the accumulation of the excess polycondensed phase at the crack tip, where the deposition initiated.

4. CONCLUSION

Formation of the silica gel film on the scratched Si {111} is initiated by the siloxane polymerization preferentially at the crack tip, after competitive adsorption of ethoxy groups with OH groups at the area where dangling bonds are concentrated.

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