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Stabilization of Silica Gel Film Coated over the Scratched Silicon {111} Surface

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Changes in the adhesion and stability of dip-coated silica gel films due to surface flaws on the substrate artificially introduced by scratching were examined. The polished and scratched silicon {111} surface was coated with the silica sol from a tetraethyl orthosilicate solution by simple dipping. The similarities found between enhanced film–substrate affinity and preferential alkali leaching in the area in which there were concentrated dangling bonds are discussed with reference to the role of alcohol during etching and the mechanism of incipient interaction between Si and the OH group. © 1995 Academic Press, Inc.

1. INTRODUCTION

Dip coating on different substrates is now carried out routinely for the purpose of improving the mechanical and optical, as well as the electrical, properties of solid surfaces (1–4). A good affinity between the surface film and the substrate is of primary importance in obtaining a highly qualified film. Good contact between the film and the substrate has mainly been considered from the viewpoint of surface chemical affinity like a contact angle (5). However, it is also to be understood in the light of solid state chemistry, since the stability of the dried film after various heat treatments depends finally on the strength of the film–substrate interaction, which cannot always be a mere van der Waals type.

Solid state reactions are generally enhanced at points of lattice or structural defects. Imbalance of the chemical bond in the solid inevitably brings about instability of the bonding and distortion of the microscopic electrical field. All those phenomena are combined with the enhanced reactivity of the solids (6). In the fields of mechanochemistry and mechanical activation, the correlation between structural defects and enhanced reactivity has been thoroughly studied in relation to various kinds of reactions (7–9). Emphasis was laid in those studies mainly on the specific nature of the defects related to particular types of reaction. One of the typical examples is the enhanced leaching of locally amorphized silicon, silica, or minerals with caustic alkali or other solutions (10, 11).

The present study deals mainly with the formation and microscopic stability of dip-coated silica films on locally damaged silicon single crystals, i.e., those with local destruction and inelastic deformation in the vicinity of microcracks. To obtain practical information on a stable surface film is not a primary object of the present study. Instead, the specific preference of the solid state interaction of the surface film and the nature of surface damage are the main points to be elucidated in order to acquire basic knowledge of the mechanical activation of solids by using materials defined far better than conventionally used fine particles intensively stressed in a grinding machine (12).

2. EXPERIMENTAL

2.1. Preparation and Mechanical Treatment of the Substrate

A polished Si wafer (p-type with ⟨111⟩ 4° ± 1°) was kindly donated by Komatsu Electronic Metals Co. The 0.525-mm thick wafer was cut into rectangular pieces of dimensions 10 mm × 8 mm. After washing with acetone under ultrasonication, surface scratching was carried out using a simple device shown in Fig. 1. Emery paper (No. 2000) was used throughout the experiment. The rate of scratching was kept constant at 1.7 cm · s^{-1}. The direction of the scratching was chosen to be ⟨112⟩.

Annealing of the specimen was carried out by heating the scratched specimen at 800°C for 0.5 hr in a flow of N_2–4% H_2 at 1 dm^3 · min^{-1}. All the samples are summarized in Fig. 2 with their history and abbreviations.

2.2. Preparation of Silica Sol and Dip Coating

Silica sol was prepared by mixing 30 g tetraethyl orthosilicate (TEOS), 46.4 g ethanol, and 28.9 g 2.42 M HCl aqueous solution. The viscosity of the dipping sol was kept constant at 2.3 mPa · s by keeping the aging time at

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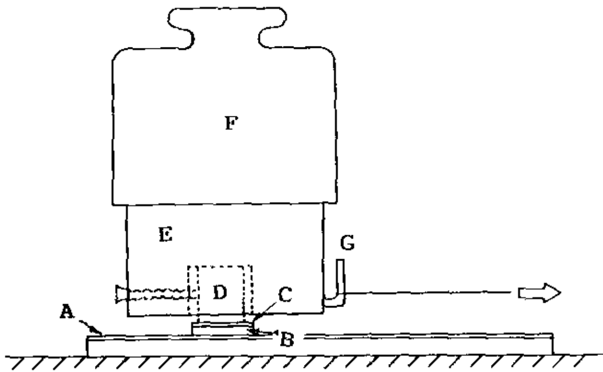

FIG. 1. Schematic diagram of a scratching apparatus. A, emery paper (No. 2000); B, specimen (silicon); C, double-adhesive tape, D, SEM specimen holder; E, adapter; F, weight; G, hook.

6 hr, under constant stirring with a magnetic stirrer at 300 rpm. The substrate was dipped into the sol for 2 min and pulled out at 1 mm · s^{-1}. After drying at room temperature for 24 hr, the gel film together with its substrate was heated linearly at 1 k · min^{-1} in a furnace in air up to 500°C, at which the specimen was held for 1 hr. The thickness of the silica film was ca. 1 μm. The heated specimen was then air-quenched.

2.3. Macroscopic Observation

Surface roughness of the scratched substrate was evaluated by profilometry with a surface roughness tester (Surfcom 302B, Tokyo Seimitsu). The extent of oxidation due to scratching, film formation, and firing was monitored by infrared and Auger electron spectroscopies. The

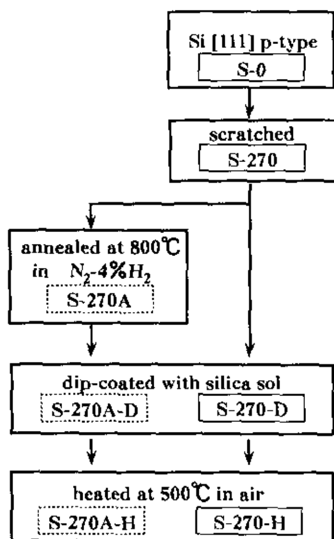

FIG. 2. Experimental flow and the sample names. The numerals given in the boxes denote the load during scratching, in kPa.

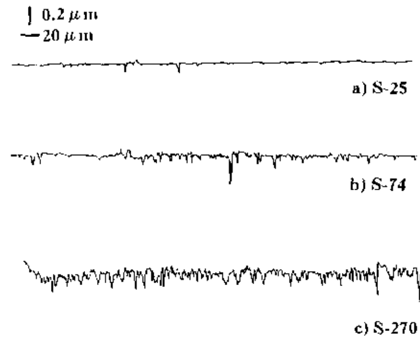

FIG. 3. Surface profilograms of Si scratched under varying normal load indicated by the inscription in units of kPa.

percent area of the film formed was determined on a macrophotograph. The adhesion strength of the gel film was evaluated from the relative peeling strength, which was determined from the resistance force during peeling of the film in the direction perpendicular to the specimen with the aid of freshly opened adhesive cellophane tape. While the surface gel film was detached from the substrate with adhesive tape, the rate of peeling differed, depending on the gel film–substrate adhesion force, which is smaller than that between the adhesive tape and the gel film.

We have measured the time needed for total peel-off using sample S-270-H as a reference standard, under a varying load, to obtain the peeling strength, F_p. By measuring the time needed, t_w, for total peel-off of the gel film on the different substrates under the load W_m, the corresponding load for the peeling of the reference standard at $t = t_w$ was obtained from the interpolation of F_p–t curve.

2.4. Chemical Treatment of the Substrate with and without Surface Film

Alkali leaching of the substrate was carried out using 0.3 *N* aqueous solution of KOH at 25°C for 5 hr. Half of the sample surface was masked with a paraffin film for the sake of comparison. The silica film formed on the substrate was leached by 0.1 *N* aqueous solution of HF at 25°C for 0.5 hr. The film–substrate interaction was evaluated mainly by observation under a scanning electron microscope (SEM) after the various treatments described above.

3. RESULTS AND DISCUSSION

3.1. Direct Consequences of Scratching

Surface profilograms perpendicular to the scratch direction are shown in Fig. 3. With increasing normal

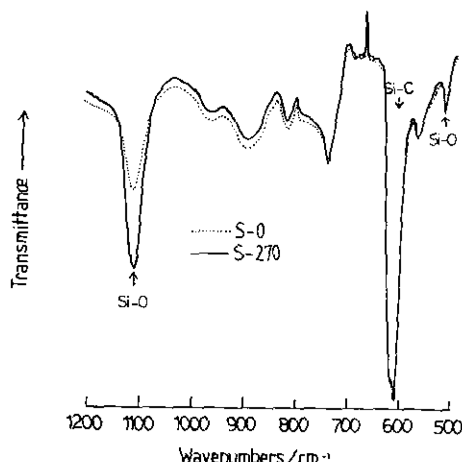

FIG. 4. Infrared spectra of the Si substrates obtained before (dotted line) and after (solid line) scratching.

stress, the scratch depth increased and the distance between the grooves decreased. This kind of sharp scratching is not available with an indenter or a diamond stylus with a well-defined scratching machine. The average scratch depth was 0.3–0.4 μm with the normal stress 270 kPa.

It is to be noted that the infrared adsorption bands at 1105 and 515 cm^{-1}, being attributed to the interstitial oxygen (13), increased as one of the direct consequences of the scratching, as shown in Fig. 4. This indicates that the scratching results in the breakage of the Si–O–Si bond spontaneously existing on the outermost surface of the polished silicon wafer. This breakage, in turn, entraps atmospheric oxygen atoms into the interstices of silicon tetrahedra. At the same time, it is to be kept in mind that the scratching brings about an increase in the density of dangling surface bonds.

3.2. Microscopic Observation of Scratched Substrates after Alkali Etching

The change in the surface morphology due to etching by a 0.3 N aqueous solution of KOH after scratching at 270 kPa is shown in Fig. 5. Preferred etching was observed at the periphery of the larger scratch, particularly at the mound parallel to the groove and near the microcrack tips developed perpendicular to the main groove of the scratch. The preferred reactivity with an alkali solution was reduced remarkably when the scratched silicon was annealed at 800°C for 0.5 hr under N_2–4% H_2 gas flow, in spite of the preservation of apparent surface textures. The recovery and recrystallization take place without any change in the texture, as far as the size range of several tenths of a micrometer is concerned.

The above-mentioned effect of annealing indicates that the enhanced solubility due to scratching cannot be attributed to the change in the surface geometry, e.g., to the increase in the effective area available as a reaction front due to increased surface roughness. Instead, the formation of dangling bonds along the crack wall and microplastic deformation at the crack tip should be responsible for the preferential local dissolution (12).

3.3. Macroscopic Stability of Dip-Coated Silica Film

When a silica film was formed on the nontreated, smooth {111} surface of a single silicon crystal, the surface film with microcracks was formed only on a few percent area of the total surface. A stable, crack-free film was never formed on the smooth {111} surface. With increasing

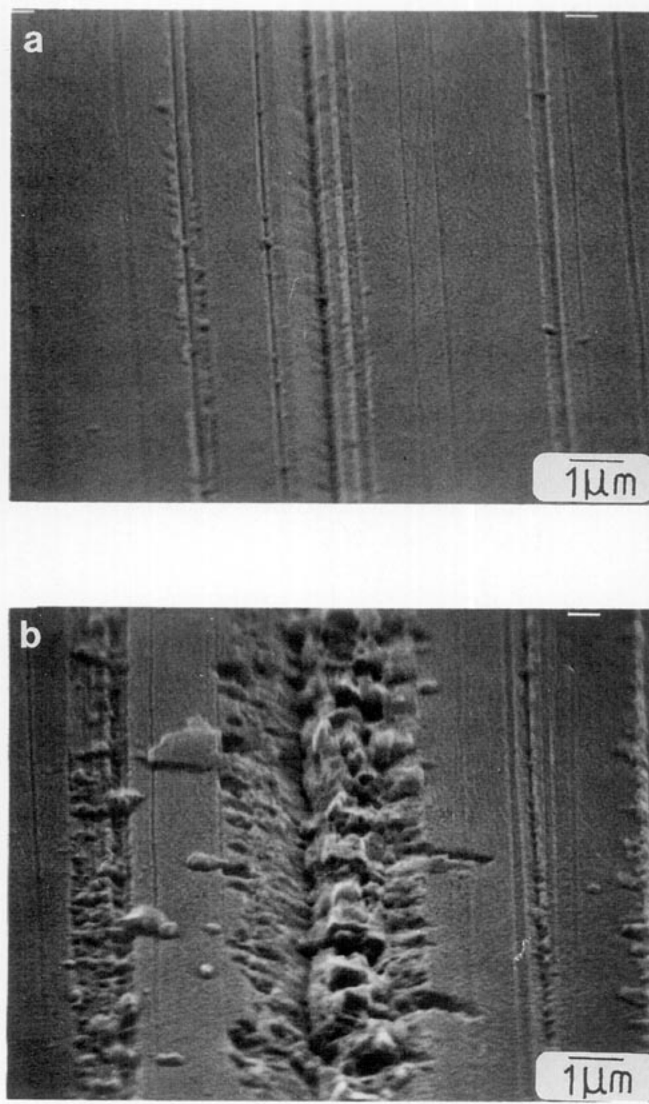

FIG. 5. SEM images of Si etched in a 0.3 *N* KOH aqueous solution after scratching at 270 kPa. (a) As-scratched (S-270); (b) Scratched (S-270) and etched in 0.3 *N* KOH.

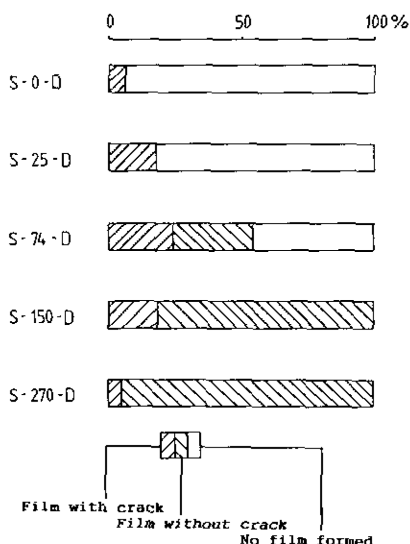

FIG. 6. Change in the proportion of the as-dried silica gel film with and without cracks on the substrates scratched with varying loads.

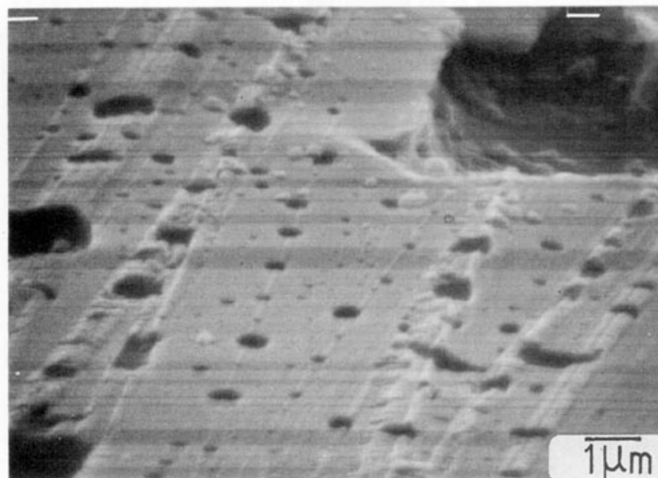

FIG. 7. SEM image of the replica of a part of the silica gel film transcribed on the adhesive film used for the peeling test.

normal stress during scratching, the percent area coated with a silica film increased, as shown in Fig. 6. A stable, crack-free film was available when the scratching load became as large as 74 kPa.

The percent area of the stable film was decreased by annealing. Since the real contact area between the film and the substrate, including the surface grooves due to scratching, is not changed significantly by annealing, it is obvious that the enhanced adhesion due to scratching cannot be attributed to the geometrical factor, i.e., the increase in the film–substrate contact area.

The increase and decrease in the film stability due to scratching and subsequent annealing, respectively, is not solely attributed to the corresponding increase and decrease of the wettability of the substrate by the dipping solution, which was actually observed. The crack in the coated film is formed as the result of poor attachment of the film on the substrate and resultant shrinkage. The firm attachment of the silica gel film takes place preferentially by increasing area density of the pinned spot of the film on the substrate. Further experiments were carried out in order to examine the preferred pinning of the gel film.

3.4. Peeling of the Surface Film

The peeling strength of the silica film on the S-270 substrate decreased from 81.8 to 61.3 N m^{-1} after annealing. The silica gel film did not detach evenly from the substrate. As shown in the electron micrographs in Fig. 7 taken from the replica of the film transcribed on the adhesive film used for the measurement of peeling strength, part of the substrate was recognized on the adhesive tape together with the detached silica film. It is important to note that the partial breakage of the substrate during the peeling test took place preferentially along the crack. This indicates that the enhanced adhesion of the film and the substrate took place at the periphery of the crack.

3.5. Etching of the Silica Surface Film by HF

As shown in Fig. 8, part of the silica film remained attached after the dissolution test using 0.1 *N* aqueous solution of HF for 0.5 hr. It is particularly important that the pattern formed by the rest of the nondissolved film is very similar to that of the relief obtained after etching by KOH solution, as shown in Fig. 3. This strongly suggests

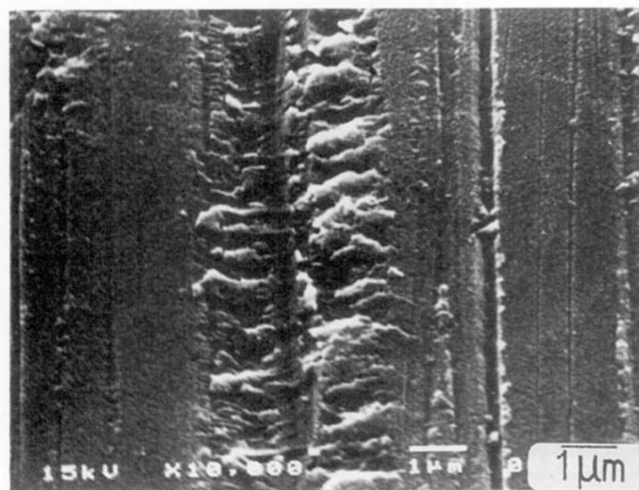

FIG. 8. SEM image of silica gel film remained attached on the substrate after etching in a 0.1 *N* HF aqueous solution.

that those structural defects which are sensitive for alkali etching are simultaneously sensitive for stronger adhesion of the silica film.

An incipient reaction of silicon with KOH was studied thoroughly by Seidel *et al.* (14). They explained the much higher rate of etching on Si{100} than on Si{111} by the higher density of dangling surface bonds. It is obvious that those spots where amorphization took place preferentially, i.e., at the crack tip on the periphery of the scratch, are rich in dangling bonds. The enhanced etching at those very spots are thus explained by the higher concentration of dangling bonds.

3.6. Active Center for TEOS Deposition

Palik *et al.* (15) reported that the addition of isopropanol to the aqueous solution of KOH reversed the preference of the etching rate between {100} and {111} in Si. They showed that the added isopropanol did not participate in the etching reaction but prevented OH^- from etching Si by covering the surface and decreased the rate of diffusion of OH^- (15). Since the preference of the etching rate between {100} and {111} was reversed by the use of isopropanol, it is obvious that the extent of coverage of alcohol on the Si surface is higher for {100}, where the dangling bond density was higher than {111}. The preferred coverage of alcohol thus seems to be those areas with higher density of dangling bonds, just as in the case of alkali etching.

In the case of dip coating from TEOS solution, the ethanol contained in the dipping solution can adsorb preferentially to the dangling bonds on the Si surface. The adsorbed ethanol was then attacked by H^+ contained in the etching solution, resulting in the formation of OH groups. This OH group, in turn, plays a significant role in forming a siloxane bond with the hydrolyzed alkoxide, providing the active spots for the polycondensation of TEOS to give an incipient deposition of silica gel. Condensation is thus initiated from the area where the film was attached most firmly, and hence most persistent against the subsequent dissolution test with an aqueous solution of HF. It is not appropriate to observe the preferential adhesion of silica gel as a surface chemical phenomenon, but to understand it as the consequence of the preferred ction of OH^- with Si at the spot with a higher dangling bond density.

4. CONCLUSION

The topochemical preferences of alkali leaching and silica gel deposition on Si{111} were found to be identical; i.e., these two reactions take place preferentially near the crack tip along the scratch groove. This was explained by a common mechanism, i.e., the preferred attack of OH^- to Si a the site of higher dangler bond density.

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