

## The Role of Fluorine Termination in the Chemical Stability of HF-Treated Si Surfaces

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The principal role of silicon-fluorine bonds in the chemical nature of HF etched Si surfaces has been investigated by angle resolved x-ray photoelectron spectroscopy. The native oxide growth kinetics and the fluorine coverage have been systematically measured as functions of HF concentration, pure water rinse time, air or  $N_2+O_2$  gas exposure time and gas phase  $H_2O$  concentration. It is shown that the native oxide growth is strongly suppressed by the existence of Si-F bonds of about 0.12 monolayers on the surface. This is explained by a model in which Si-F bonds chemically stabilize the surface reactive sites such as atomic steps as supported by the result of the layer by layer oxidation of Si.

### 1. INTRODUCTION

One of important issues in the microfabrication of ULSI devices is to completely retard the native oxide growth on silicon wafer surfaces. It is known that the HF treated Si surface is less reactive and stable against oxidation in room air<sup>1-4)</sup> and that the surface is passivated mainly with Si-H bonds which are chemically stable compared to Si-Si bonds<sup>1-5)</sup>. In fact, the Si-H back bond is first oxidized and subsequently the Si-H bond is changed to Si-O-H<sup>6)</sup>. Si(100) surfaces cleaned in HF solutions with concentrations of more than 0.5% are covered by fluorine of more than 10% of the surface Si atoms and the amount of Si-F bonds decreases with pure water rinse time. Considering that the Si-F bond energy (129.3 kcal/mol) is extremely large compared to that of Si-Si (42.2 kcal/mol), Si-H (70.4 kcal/mol) and Si-O (88.2 kcal/mol), a small amount of Si-F bonds might play an important role in the chemical stabilization of the surfaces. This paper examines the correlation between the native oxide growth kinetics and the behavior of surface Si-F bonds and tries to reveal a possible retardation mechanism of oxidation reaction

on silicon surfaces passivated with Si-H and Si-F bonds.

### 2. EXPERIMENTAL

P-type CZ Si(100) wafers ( $\sim 10\Omega\text{cm}$ ) were used as substrates. They were cleaned in organic solution, in  $H_2O:H_2O_2:HCl=86:11:3$  and finally in  $H_2O:H_2O_2:NH_4OH=7:3:3$ . The chemically cleaned wafer was dipped in an HF solution whose concentration was changed from 0.5 to 50% and in most cases fixed at 4.5%. The HF treated wafer surfaces with and without pure water rinse were characterized. The pure water rinse was carried out by using a 300 cc teflon beaker at a flow rate of 900 cc/min and a temperature of 16°C. The resistivity of pure water was held above 16 M $\Omega\text{cm}$  and the DOC was estimated to be about 9.5 ppm from the equilibrium dissolved oxygen at 16°C. The wafer was stored in a clean bench or in the constant flow of a dew point controlled  $N_2:O_2=4:1$  ambient. At each step of storage time the chemical bonding feature of the Si surface was measured by x-ray photoelectron spectra (XPS) of  $Si_{2p}$  and  $F_{1s}$  core levels. The angle between the photoelectron detector axis and the direction normal to the Si surface was kept at 75° for

surface sensitive measurements.

### 3. DETERMINATION OF FLUORINE COVERAGE AND OXIDE THICKNESS

The surface fluorine concentration is obtained by the ratio of the integrated  $F_{1s}$  photoelectron intensity  $N_F$  and the  $Si_{2p}$  intensity  $N_{Si}$  which corresponds to the one monolayer of Si(100) surface and their ionization cross sections  $\sigma_F$  and  $\sigma_{Si}$  as well as the spectrometer functions  $S_F$  and  $S_{Si}$ . The fluorine coverage  $\theta$  is described as:

$$\theta = (N_F / \sigma_F S_F) / (N_{Si} / \sigma_{Si} S_{Si}) \quad (1)$$

The oxide thickness  $d_{ox}$  is given by the integrated photoelectron intensity of chemically shifted  $Si_{2p}$  spectrum  $N_{ox}$  and that of metallic Si signal  $N_{Si}$  as follows:

$$d_{ox} = \lambda_{ox} \cos \theta \ln \left( k \frac{N_{ox}}{N_{Si}} + 1 \right) \quad (2)$$

Here,  $\lambda_{ox}$  is the escape depth of  $Si_{2p}$  photoelectron from  $SiO_2$  (25 Å)<sup>6</sup>. The value of  $k=2.086$  is estimated by the atomic density of Si and  $SiO_2$  and their photoelectron escape depths.

### 4. RESULTS AND DISCUSSION

Fluorine coverage on an Si surface is dependent upon the HF concentration and water rinse time as shown in Fig 1. It should be noted that the two orders of magnitude HF concentration variation causes rather little change in the fluorine coverage. This suggests that the spatial distribution of surface Si-F bonds is not random, but chemically reactive sites such as atomic steps are selectively fluorinated. This idea will be further discussed later. Also, the fluorine coverage is significantly reduced by pure water rinse and hence the chemical stability of Si surface will be influenced with water rinse time. In fact the oxidation of Si in pure water occurs when the fluorine coverage is reduced down to about 5% as indicated in Fig. 2. For the purpose of examining the fluorine chemical states  $F_{1s}$  spectra were measured (Fig. 3). The peak energy ranges from 685.3 to 686.2 eV, indicating the existence SiF and/or SiF<sub>2</sub>

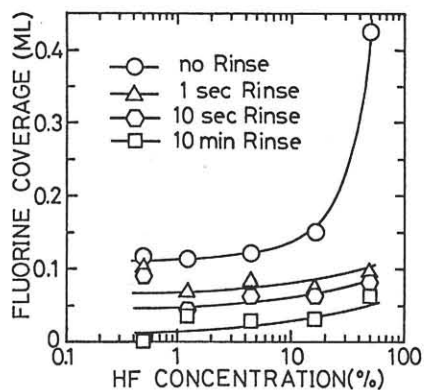


Fig. 1 Fluorine coverage as a function of HF concentration for different pure water rinse times.

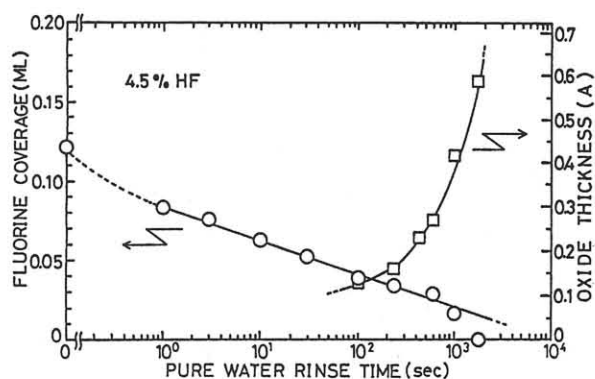


Fig. 2 Fluorine coverage and oxide thickness versus pure water rinse times.

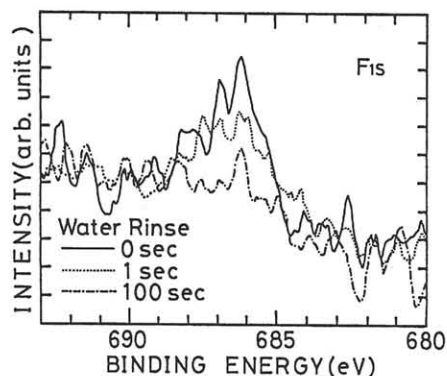


Fig. 3  $F_{1s}$  core level spectra of HF-treated Si surfaces prepared at different rinse times.

bonds on the surface<sup>8-11</sup>). This is consistent with the fact that the HF cleaned Si(100) surface without water rinse gives no  $Si_{2p}$  photoelectron yield due to SiF<sub>3</sub> (103.5 eV) and SiF<sub>4</sub> (104.9 eV) molecular units.

The fluorine coverage was determined by

assuming that Si-F bonds exist on the top surface even during the progress of oxidation. This assumption is verified from the XPS analysis of annealed wafers as discussed later.

#### 4.1 RETARDATION OF OXIDATION BY FLUORINE BONDS

The surface fluorine coverage can be controlled by water rinse time (Fig. 1). The native oxide growth on Si surfaces with different fluorine coverages has been measured at 25°C in an N<sub>2</sub>:O<sub>2</sub>=4:1 gas ambient with a flow rate of 1 l/min and an H<sub>2</sub>O concentration of 0.2~0.5 ppm. As clearly shown in Fig. 4, the onset time of oxide growth is strongly dependent upon the surface fluorine coverage. The existence of a critical amount of Si-F bonds (~12%) on Si dramatically suppresses the oxidation, and the decrease in F coverage enhances the oxidation rate. The fluorine coverage remains unchanged regardless of the N<sub>2</sub>+O<sub>2</sub> gas exposure time and oxide thickness, indicating again that the Si-F bonds are existing on the top surface of oxide. Even for an H<sub>2</sub>O concentration of 10~13 ppm in N<sub>2</sub>:O<sub>2</sub>=4:1 flow no oxidation occurs for the wafer without water rinse after HF cleaning. In the clean room air with an H<sub>2</sub>O content of 1.1% at 25°C the native oxide growth does not proceed for a few tens minutes when the fluorine coverage is about 12% as shown in Fig. 5, where fluorine is lost from the surface through reactions with H<sub>2</sub>O as in the case of Fig. 2. In the analysis of fluorine coverage we have assumed that Si-F bonds are located on the top of surface even after native oxide formation. In order to confirm the validity of this assumption the angle resolved XPS measurements of F<sub>1s</sub> signal intensity for Si wafers annealed at 1000°C in dry N<sub>2</sub> atmosphere has been carried out and compared with the result of model calculation (Fig. 6). Annealing at 1000°C in dry N<sub>2</sub> results in 23.7 Å thick oxide growth on Si because of unavoidable back diffusion of air into a reactor tube during the wafer loading.

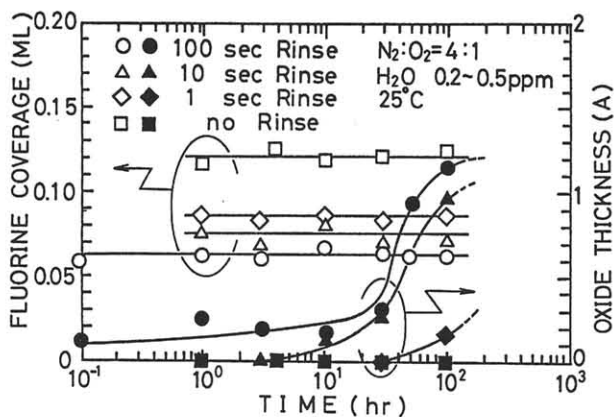


Fig. 4 Fluorine coverage and oxide thickness versus dry N<sub>2</sub>+O<sub>2</sub> exposure time for wafers with different fluorine coverages.

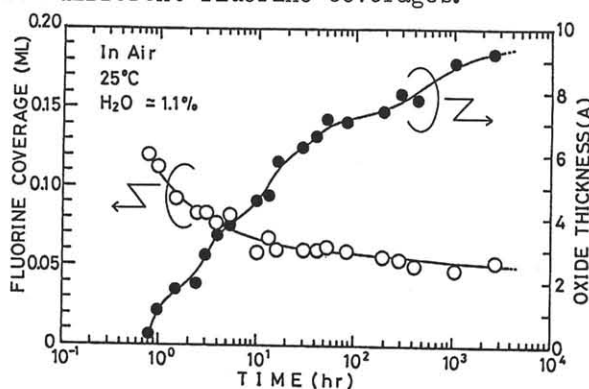


Fig. 5 Fluorine coverage and oxide thickness versus clean room air exposure time.

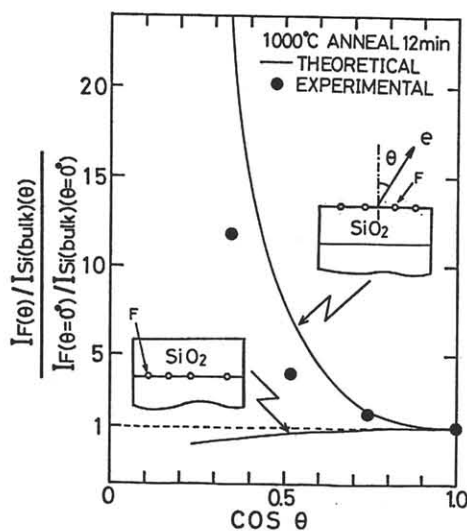


Fig. 6 Normalized F<sub>1s</sub> signal intensity for an HF-treated Si wafer annealed at 1000°C in dry N<sub>2</sub> plotted against the escape angle of photoelectrons. The larger value of θ refers to the surface sensitive measurement.

About 1% Si-F bonds are still detectable after 1000°C annealing and the model calculation, in which Si-F bonds are assumed to be located only at the oxide surface, well

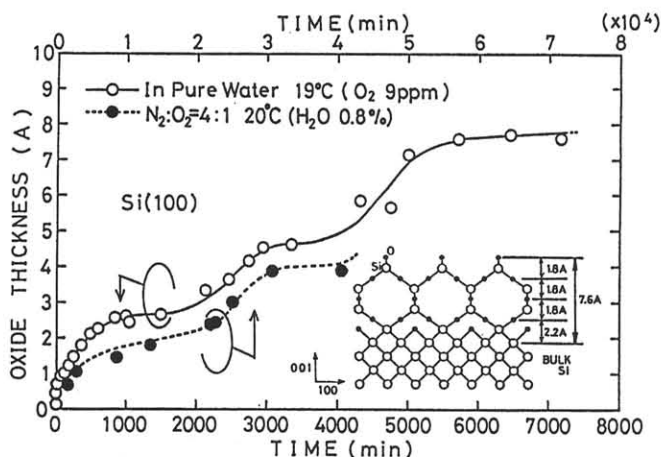


Fig. 7 Native oxide growth in  $N_2+O_2$  atmosphere containing 0.8%  $H_2O$  and in pure water as a function of exposure time. The inset is a possible  $SiO_2/Si$  interface model<sup>13)</sup>.

explains the experimental result. From the above the retardation time against oxidation is found to be strong functions of the fluorine coverage and the  $H_2O$  concentration in the atmosphere. It is also shown that oxidation proceeds through the fluorinated surface by leaving Si-F bonds on the top surface. This is quite consistent with the fact that the Si-H back bond is first oxidized<sup>1)</sup>. It is very likely that the fluorine bonds on Si does not enhance the oxidation rate at high temperatures, being different from the case of fluorine enhanced oxidation of Si, in which an  $NF_3$  gas is mixed with  $O_2$  and fluorine radicals are always existing in the gas phase and in  $SiO_2$  as well as the  $SiO_2/Si$  interface<sup>12)</sup>. This situation is completely different from the present case where stable Si-F bonds are located only on the surface.

#### 4.2 A PROPOSED MODEL OF OXIDATION RETARDATION

A possible mechanism of oxidation retarded by fluorine is as follows: Si-F bonds occupy the surface reactive sites such as atomic steps, where the etching reactions in HF solution proceed in such ways as  $\text{>Si-SiF}_3 + \text{HF} \rightarrow \text{>SiH} + \text{SiF}_4$  and/or  $\text{>Si-SiF}_2\text{-Si} \leftarrow + 2\text{HF} \rightarrow 2 \text{>SiH} + \text{SiF}_4$  to form surface SiH (or  $SiH_2$ ) bonds. It is also likely that partially fluorinated surface bonds SiHF

are produced. Such Si-F bond has strong ionic nature, inducing the charge transfer of valence electron cloud among neighbouring atoms. Hence, Si-H bonds located near the Si-F bond at the step site are also stabilized against attack of oxidant. This idea is supported by layer-by-layer oxidation of HF treated Si surface (Fig. 7). The oxidation reaction might proceed parallel to the surface from the atomic steps because the terrace is well passivated with Si-H bonds.

In conclusion, we proposed a model that the oxidation retardation on HF cleaned Si surfaces arises from the existence of ~10% SiF bonds which significantly stabilize the chemically reactive sites such as atomic steps.

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