

## Surface Processes in Fluorine-Based Photochemical Etching of Silicon

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An ArF excimer laser light (193 nm in wavelength) was irradiated onto a silicon surface exposed to an  $\text{NF}_3$  gas to promote the photochemical etching reactions. The reaction products and their chemical states on the silicon surface were studied by in-situ x-ray photoelectron spectroscopy at each step of the photochemical treatment. It was found that  $\text{SiF}_X$  ( $1 \leq X \leq 4$ ) molecular units are existing on the etching surface and progressive fluorination of the Si-Si bonds results in the final surface products being mainly  $\text{SiF}_4$  and  $\text{SiF}_3$  molecular units. The fluorine-based etching is discussed on the basis of a valence electron transfer (VET) model.

### 1. Introduction

Photochemical etching technique is expected as a new procedure to obtain damage-free surfaces.<sup>1,2)</sup> The further progress in this new process technology needs more deep understanding of the etching mechanism. The photochemical etching of silicon has so far been achieved in a  $\text{Cl}_2$  gas.<sup>3,4)</sup> A possible mechanism of reactions between Cl and silicon surface is inferred to be as follows: Photodissociated Cl atoms adsorb on the surface, and they are negatively-charged as a consequence of tunneling of free electrons from the photoexcited silicon surface. Hence, a strong surface electric field induced by the dipole enhances Si/Cl reactions to produce  $\text{SiCl}_4$  as a final etching product.<sup>5,6)</sup> This model also explains the dramatic increase in the etching rate with increasing the bulk electron concentration.<sup>6)</sup> While the etching rate of silicon in an  $\text{NF}_3$  gas is almost independent of the bulk carrier concentration.<sup>7)</sup> This unique behavior in fluorine-based photochemical etching is not yet well understood. The purpose of this paper is to clarify the mechanism of the Si photochemical etching. The chemical states of silicon surface irradiated with an excimer laser in an  $\text{NF}_3$  gas have been investigated by in-situ x-ray photoelectron spectroscopy (XPS). It has been found that the final products on the etching surface are mainly  $\text{SiF}_4$  and  $\text{SiF}_3$ . The reaction

model is discussed in conjunction with previous work.<sup>8-10)</sup>

### 2. Experimental

After the removal of native oxide on silicon in BHF solution, the specimen was transferred into a reaction chamber connected with a XPS system. An ArF excimer laser light (193 nm) with a pulse energy of  $52 \text{ mJ} \cdot \text{cm}^{-2}/\text{shot}$  was irradiated at a repetition rate of 80 Hz onto the silicon surface in an  $\text{NF}_3$  gas at a pressure of 760 Torr. P-type and n-type Si(100) crystals with resistivities of  $0.3 \sim 0.7 \Omega \text{ cm}$  were used as substrates. At each step of photochemical treatment the specimen was transferred into the XPS chamber through two gate valves, and the chemical bonding features of the reacting surface were analyzed by XPS (Shimadzu ESCA 750). The construction of the apparatus has been reported elsewhere.<sup>11)</sup>

### 3. Results and Discussion

Typical Si(2p) and F(1s) spectra for photochemically etched silicon surfaces are shown in Fig. 1. The virgin surface exhibits only 99.5 eV peak due to Si(2p) photoelectron from the bulk silicon surface. The laser irradiation of more than 50 shots induces a new Si(2p) signal at the higher binding energies. A significant chemical shift occurs during the course of etching, and the signal intensity becomes higher

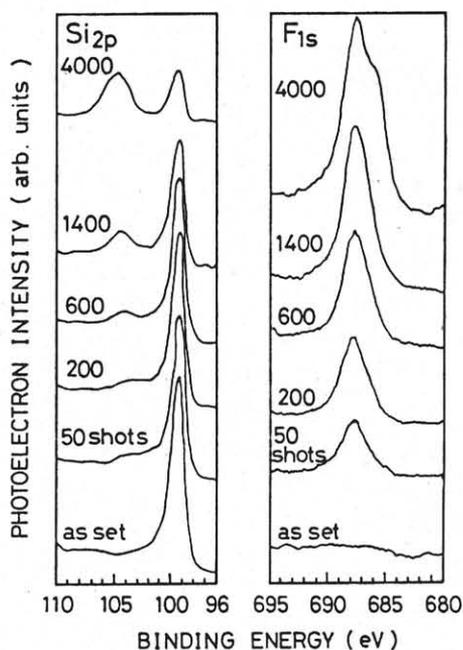


Fig. 1 XPS spectra of photochemically etched Si surface at each step of laser irradiation.

and higher. Correspondingly, the F(1s) main peak height appreciably increases and a F(1s) subpeak at a lower binding energy newly appears. The result of Fig. 1 shows that molecular units such as  $\text{SiF}_X$  ( $1 \leq X \leq 4$ ) are formed on the etching surface. In order to clarify the surface reaction products and their relative fractions, the observed Si(2p) spectra were deconvoluted. The chemical shift in the binding energy of core level electron for a specific atom in a covalent-bond material is basically proportional to the electronegativity sum of the nearest neighbour atoms.<sup>12)</sup> The measured chemical shift of Si(2p) for  $\text{SiF}_4$  is 5.6 eV with respect to bulk Si(2p) signal at 99.5 eV.<sup>9)</sup> Figure 2 represents the relationship between the Si(2p) chemical shift and the electronegativity sum for the case that the nearest neighbour atoms are fluorine and silicon. The chemical shifts for  $\text{SiF}_X$  ( $X=1,2,3$ ) units can be estimated by interpolating the measured data as indicated in Fig. 2. It is clear that the chemical shift caused by one Si-F bond is 1.4 eV and the Si(2p) binding energy for  $\text{SiF}_X$  ( $X=1,2,3,4$ ) molecular units are empirically determined as  $99.5+1.4X$  eV. According to the result of Fig. 2, typical deconvoluted spectra are found to consist of five Gaussian peaks respectively centered at  $99.5+1.4X$  eV as shown in Fig. 3. The relative

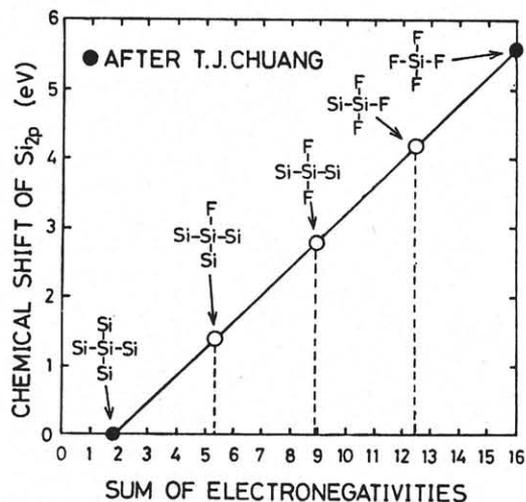
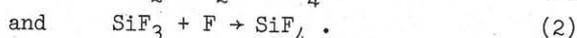
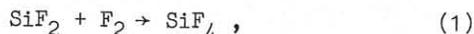


Fig. 2 Measured (solid circle) and estimated (open circle) chemical shifts of Si(2p) signals for  $\text{SiF}_X$  units plotted against the electronegativity sum of the respective molecules.

intensities of  $\text{SiF}_X$  units obtained from the deconvoluted spectra are plotted against the number of laser pulses as shown in Fig. 4. This indicates that the predominant reaction products at the beginning of etching are  $\text{SiF}$ ,  $\text{SiF}_2$  and  $\text{SiF}_3$ , while the final surface products are mainly  $\text{SiF}_4$  and  $\text{SiF}_3$ .  $\text{SiF}$  molecular unit is formed on the top surface at the beginning of photoreaction. It is also produced even in the deeper surface layer in the progress of the reaction because of the fast diffusion of fluorine atoms into the silicon matrix. Subsequent adsorption of fluorine radicals onto the surface results in further fluorination of  $\text{SiF}$  bonds to create  $\text{SiF}_2$  and  $\text{SiF}_3$  units. Therefore, the fraction of  $\text{SiF}_X$  unit at early stage of reaction is in the order of  $\text{SiF} > \text{SiF}_2 > \text{SiF}_3$ . It should be noted that  $\text{SiF}_4$  remains on the surface layer although it is volatile at room temperature.  $\text{SiF}_4$  molecules must be trapped within the reacting matrix, as observed by SOR for the case of ion-induced etching in  $\text{Si}/\text{XeF}_2$  system.<sup>10)</sup> It is likely that  $\text{SiF}_4$  molecules exist in the surface region underneath the top surface because fluorine atom has a small tetrahedral radius (0.672 Å) as compared with that of Si (1.173 Å)<sup>13)</sup> and can easily penetrate into the silicon network to form  $\text{SiF}_4$ .  $\text{SiF}_4$  molecular unit might be produced by the following reactions:



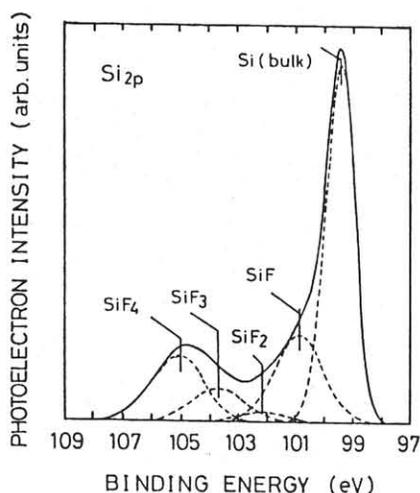


Fig. 3 Si(2p) spectra deconvoluted to five Gaussian peaks. The spectrum was taken after 1400 shots of laser pulses.

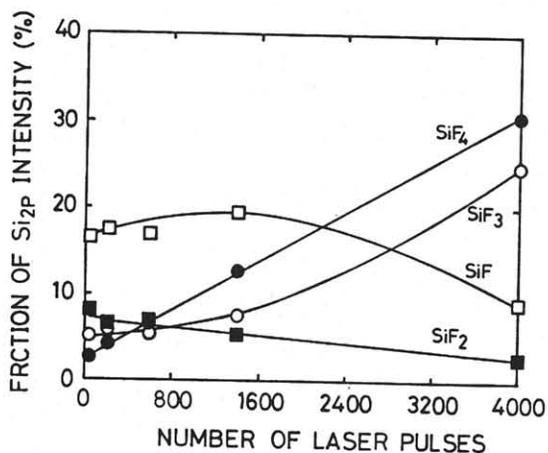


Fig. 4 Relative intensities of SiF signals plotted against the number of laser pulses.

The reaction (1) is likely to occur even in the deeper surface region because the deconvoluted F(1s) spectra clearly indicate the existence of F<sub>2</sub> molecule on silicon surface (Fig. 5). And also, F<sub>2</sub> molecule can easily penetrate into Si network because Si(100) surface has an atomic arrangement with an effective radius of atomic void  $r=1.54$  Å which is greater than the size of F<sub>2</sub> molecule (1.412 Å) as shown in Fig. 6. The fraction of F<sub>2</sub> molecules with respect to F-Si molecular units slowly decreases with increasing the number of laser pulses (Fig. 7), in consistency with the slow decrease of SiF<sub>2</sub> fraction as the number of laser pulses increases (see Fig. 4). Note that SiF<sub>2</sub> molecule can desorb from the surface.<sup>14)</sup> In fact, existence of SiF<sub>2</sub> radicals has been detected by using laser-induced fluorescence (LIF) during the down-stream etching of silicon with a remote

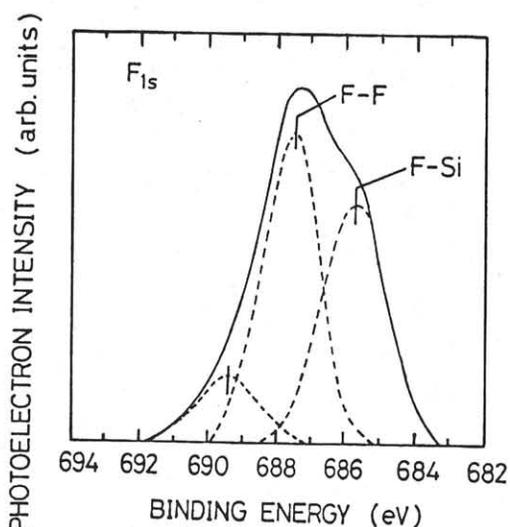


Fig. 5 F(1s) spectra deconvoluted to three Gaussian peaks. The spectrum was taken after 4000 shots of laser pulses.

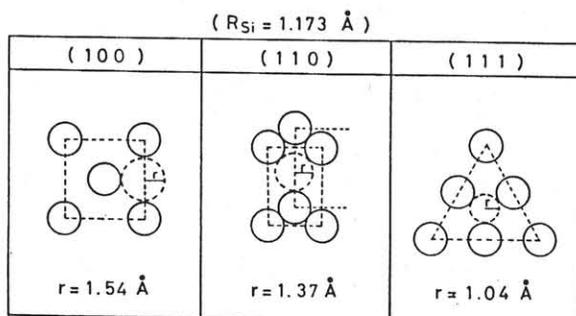


Fig. 6 Atomic arrangement on Si(100), (110) and (111) surfaces.  $r$  denotes the effective radius of atomic void.

microwave discharge of CF<sub>4</sub>+O<sub>2</sub>.<sup>15)</sup> This is a possible reason why the fraction of SiF<sub>2</sub> molecular unit is rather small. The reaction (2) can explain parallel increase of SiF<sub>3</sub> and SiF<sub>4</sub> with increasing the number of laser pulses. From the above discussion, the major reaction pathway which SiF<sub>4</sub> molecules are trapped in the deep surface region could be eq. (2). The F(1s) peak observed at 689.2 eV in Fig. 5 is not yet identified. Ninomiya et al.<sup>16)</sup> suggested that the peak at 689.2 eV arises from (CF)<sub>n</sub> polymer. However, this is not the present case because shifted C(1s) signal intensity decreases with laser irradiation time, while the F(1s) peak height at 689.2 eV increases. The etching rate is proportional to the laser pulse energy as shown in Fig. 8, indicating that fluorine radicals are produced by photon process and the flux intensity determines the reaction rate.

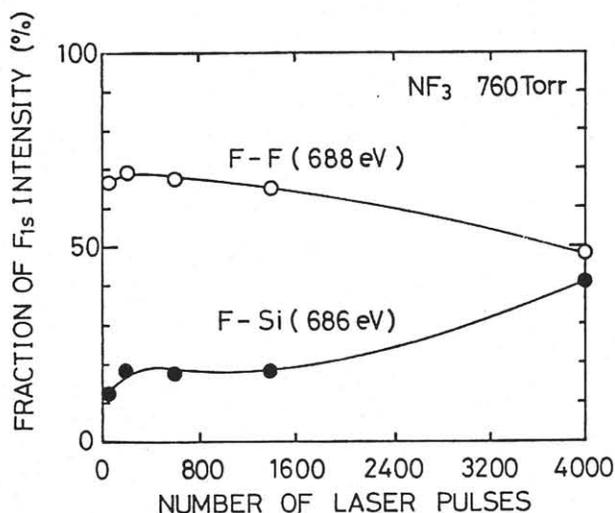


Fig. 7 Relative intensities of F-F and F-Si signals as a function of the number of laser pulses.

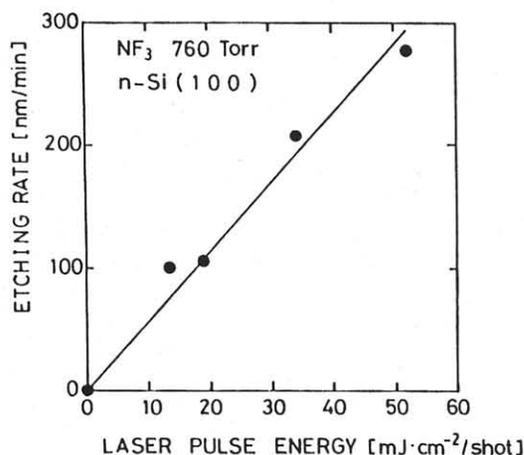


Fig. 8 Etching rate versus the incident laser pulse energy.

#### 4. Fluorine etching model

Houle<sup>8)</sup> claimed that photogenerated free electrons are important to promote etching reactions on silicon surface exposed to  $\text{XeF}_2$  under  $\text{Ar}^+$  ion laser irradiation, as in the case of Cl based etching of Si. However, the capture of conduction electron by adsorbed fluorine atom appears to be less important for initiating the etching reaction, because fluorine atom has the largest value of electronegativity ( $\chi_{\text{F}}=4.0$  in Pauling scale). Once fluorine atom adsorbs on the Si surface or is located near a Si atom site underneath the surface, the valence electron (not free electron) of silicon with  $\chi_{\text{Si}}=1.8$  moves to fluorine atom. This valence electron transfer results in breaking the Si-Si bond to form one Si

dangling bond and a covalent Si-F bond with a significantly large ionicity.<sup>17)</sup> When a silicon atom has a fluorine bond, the other three Si-Si bonds are weakened due to the valence electron transfer, and further fluorination reactions selectively proceed on such a silicon site. In the case of Cl etching, Si-Si bond can not be cleaved with Cl because the electronegativity ( $\chi_{\text{Cl}}=3.0$ ) is not large enough and hence conduction electrons become important. Therefore, the fluorine-based Si etching could be categorized as valence electron transfer (VET) type, and Cl etching as conduction electron transfer (CET) type.

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