

# Penetration of fluorine into the silicon lattice during exposure to F atoms, F<sub>2</sub>, and XeF<sub>2</sub>: Implications for spontaneous etching reactions

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The purpose of this article is to present evidence about the quantity and distribution of fluorine in silicon after and during spontaneous etching with F atoms, F<sub>2</sub>, and XeF<sub>2</sub>. X-ray photoelectron spectroscopy spectra were analyzed using the method developed by Sven Tougaard designated in this paper as "ST." It is found that fluorine penetrates deeply into the silicon lattice during the etching reaction. It is shown that the surface concentration of fluorine (first 10 Å) is relatively independent of whether F atoms or XeF<sub>2</sub> were used and is also relatively independent of doping level. In contrast, the amount of fluorine in the silicon lattice does depend upon these parameters. It is suggested that the fluorine in the lattice exists primarily as negative ions. Fluorine on the surface (top 10–20 Å) is probably SiF<sub>x</sub> ( $x=1-3$ ). The authors' data are consistent with the data and interpretation of Lo *et al.* [J. Vac. Sci. Technol. A **11**, 2054 (1993)] who found the surface concentration of F at saturation to be  $\sim 1.7 \times 10^{15}$  F/cm<sup>2</sup> (1.7 ML,  $1.1 \times 10^{15}$  F/ML). They found that SiF<sub>3</sub> was the dominant species on the surface at saturation. The concentration of F<sup>-</sup> ions in the lattice is so large [ $\sim 10^{20}$  to  $4 \times 10^{21}$ /cm<sup>3</sup>] that they probably neutralize holes and donor sites and also are likely to dope the system with deep lying acceptor states which lead to an increased concentration of holes at the valence band maximum. A *p-n* junction may be created. In addition, the total quantity of fluorine in the lattice is estimated. These new values are derived from previously published work using a more reliable calibration. They are about 2.5 times higher than the original estimate. It will also be shown that the etch properties are influenced by the negative ions in the silicon lattice. The ions adjust their concentration and depth distribution to fit the etch conditions. The time constant for this adjustment is undetermined but is many minutes at room temperature and moderate fluxes [see Fig. 15 of Ref. 3(a)]. © 2007 American Vacuum Society.  
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## I. INTRODUCTION

It was discovered in 1979 that XeF<sub>2</sub> would spontaneously etch silicon<sup>1</sup> and that ion bombardment significantly enhanced the etch rate.<sup>2</sup> XeF<sub>2</sub> is now used in several manufacturing and analytical applications. It has also been frequently studied as an easy method to learn (by analogy) how F atoms may react on silicon. There are many similarities and some differences between the two systems. Much has been learned since 1979 with papers by several groups being particularly enlightening.<sup>3–26</sup> In our opinion, and despite much research, a detailed pathway for the etching reaction of fluorine with silicon has not been discovered.

The multibillion dollar per year semiconductor industry universally uses fluorocarbon gases to etch silicon compounds and in some instances silicon itself. Other materials are also etched using fluorocarbon gases. F atoms are often the most important reactant in such processes. Moreover, one of the breakthroughs in the growing microelectromechanical system industry was the introduction of XeF<sub>2</sub> as an etch gas

into the manufacturing process. Investigators which do quantitative analytical work with ion and electron beams often use XeF<sub>2</sub> to enhance the removal of material, e.g., in depth profiling. Despite its practical importance and the interesting scientific questions it generates, there is still a lack of understanding of how fluorine reacts with silicon even after almost 30 years of research and development. Spontaneous etching of silicon with F atoms is one area where additional knowledge is needed to understand the complicated chemical reaction pathways. One purpose of this article is to demonstrate how the surface concentration and the distribution of fluorine in the lattice may influence the etching reaction. These results will be used in a subsequent paper as input to a plausible model, which quantitatively explains the etching of silicon by the halogens.

The term spontaneous etching as used in this article is defined to mean the process whereby neutral species (including radicals) in the absence of energetic radiation interact with a surface to produce volatile products. Experiments on etching reactions were performed in an ultrahigh vacuum system where x-ray photoelectron spectroscopy (XPS) spec-

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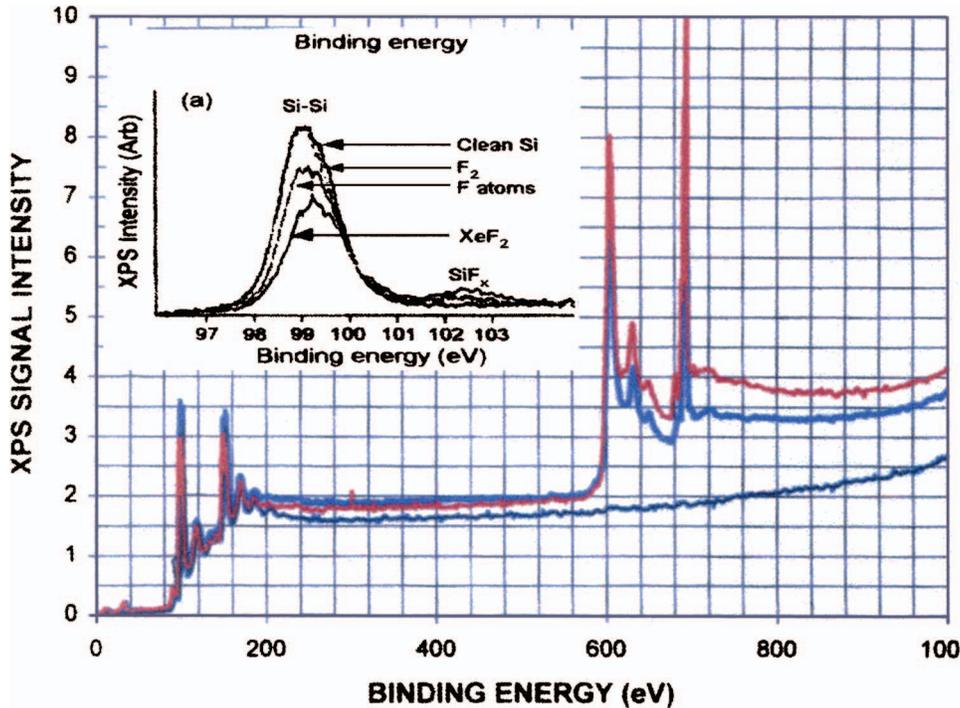


FIG. 1. XPS intensity vs binding energy. Black: clean silicon taken after the sequence of experiments. Blue: silicon exposed to a fluence of  $7.5 \times 10^{19}$  F atoms/cm<sup>2</sup>. Red: silicon exposed to a fluence of  $2.2 \times 10^{19}$  XeF<sub>2</sub>/cm<sup>2</sup>. Sample characteristics: Si(111),  $2 \times 10^{-3} \Omega \text{ cm}$ ,  $\sim 5 \times 10^{19}$  dopants/cm<sup>2</sup>, *p* type. F atoms were generated from F<sub>2</sub> gas using a microwave discharge and an Evenson cavity. The sample was bombarded with argon ions and annealed to  $\sim 800$  K before each experiment. The three spectra are overlapped at 0–10 eV binding energy so that the reader can judge the difference in the spectra in the F(1s) region. The insert is a higher resolution XPS spectrum taken on a Si(111),  $2 \times 10^{-2} \Omega \text{ cm}$ , *p*-type, sample. It is believed that all samples investigated are approximately represented by these data; i.e., the fluorine bonded to silicon is always a small fraction of the total fluorine. The large change in background intensity after the F(1s) peak indicates a concentration of F deep in the lattice independent of analysis. Si(2*p*) 99.15 eV, Si(2*s*) 153 eV, F Auger 599 eV, and F(1s) 686 eV.

tra could be obtained both during and after etching. The samples were never exposed to air. They were simply rotated from the mass spectrometer position to the XPS position where a custom valve was opened and spectra were obtained. The experimental system has been described previously.<sup>3(a)–3(c)</sup> The sample could be exposed to F atoms using either F<sub>2</sub> or XeF<sub>2</sub> gas flowing through a microwave discharge. The incident flux to the surface was calibrated using a stagnation detector<sup>3</sup> and the silicon leaving the sample was calibrated with a quartz crystal microbalance covered by a thin film of silicon. This procedure has been previously described in Ref. 3. F<sub>2</sub> was  $\sim 85\%$  dissociated and the XeF<sub>2</sub> was almost 100% dissociated by the microwave discharge. The gas approaching the surface was at or near room temperature because of multiple collisions on 300 K tube walls before entering the main vacuum chamber. Comparisons between “XeF<sub>2</sub>,” “F<sub>2</sub>,” and “F atoms” were obtained by simply turning the microwave discharge on or off while observing the modulated beam mass spectrometry signal or the XPS intensity. All reactions were examined in the absence of wall collisions, i.e., particles that had hit a wall were not detected with the mass spectrometer.

It will be demonstrated in this article that fluorine penetrates the silicon lattice to a distance greater than can be detected by the XPS. The total quantity of fluorine on or in the silicon will be estimated. The results will be used to discuss various possible etch mechanisms.

## II. DEPTH DISTRIBUTION OF FLUORINE

Figure 1 shows the XPS spectra for clean Si(111) before exposure to fluorine. It also shows the spectra after a fluence

of  $7.5 \times 10^{19}$  F atoms/cm<sup>2</sup> and a fluence of  $2.2 \times 10^{19}$  XeF<sub>2</sub>/cm<sup>2</sup>. The spectra are overlapped at low kinetic energies so that the changes in peak structure and background are evident for all three situations. The intensity at the peak energy and in the background region of inelastically scattered electrons varies for both the Si and the F peaks. The reason is that the depth distribution of Si and F atoms are different in the different samples. Thus, electrons that are photon excited at atoms deeper in the solid have a larger chance of being inelastically scattered compared to electrons excited at atoms near the surface. They will therefore give smaller intensity at the peak energy and a larger intensity in the background of inelastically scattered electrons. The presence of a large background on the high binding energy side of the fluorine peak, such as that shown in Fig. 1, indicates fluorine deep in the lattice independent of analysis. The distribution of emitted electrons in a wide energy region around the peak is thus characteristic for the depth distribution of the atoms. Tougaard has developed one technique that takes advantage of this to give information on the depth distribution of atoms by analyzing both the peak structure and the background.<sup>27–29</sup> This technique has been applied to several systems. It is thus easy to determine whether the distribution of F is localized in a thin layer near the surface or in an exponential decaying distribution with depth.

It is important to note that this technique is not influenced by surface roughness when the analyzer axis is near the surface normal. The determined depth distribution is measured along the direction of the analyzer axis, which is normal to the surface in this case. For a rough surface, where the angle of the analyzer axis varies over the analyzed surface area, the

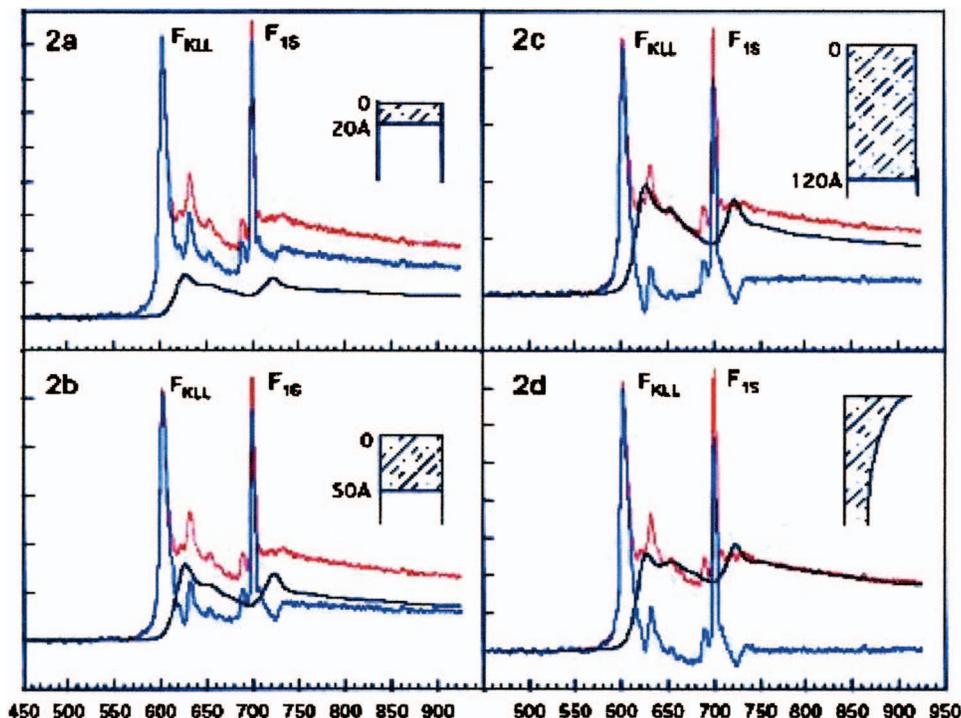


FIG. 2. XPS intensity vs kinetic energy. The sample was [Si(111),  $2 \times 10^{-3} \Omega \text{ cm}$ ,  $p$  type] exposed to  $\text{XeF}_2$  to saturation before the spectra were taken. The same spectra with the background subtracted and the background are also shown. The analysis was accomplished using ST techniques using the QUASES software (Ref. 29). Analyses with different assumed F atom depth distributions are shown. Three assume a uniform distribution at the surface. The fourth assumes an exponential distribution followed by constant concentration of F in the bulk lattice. It is clear that an exponential distribution which extends deep into the bulk gives the best agreement for the intensity over a wide energy range.

determined depth distribution is therefore an “effective” one (i.e., modified by an effective cosine factor), and the actual depths measured along the local surface normal will tend to be correspondingly slightly smaller. Under these conditions, roughness-induced shadowing effects are nonexistent. This is because the technique relies only on the energy distribution of emitted electrons measured for a single emission angle. Therefore, it determines the depth distribution counted from the outermost surface and down. For a rough surface, this means that the determined distribution is the depth distribution of atoms where the surface is the top of the rough surface for each point in the analyzed area.

This is illustrated by the following thought experiment: Assume a silicon wafer with an  $\sim 10 \text{ \AA}$  layer of gold uniformly deposited on the surface. The analysis is done assuming a  $60^\circ$  detection angle (to simulate a rough surface) and is compared with the same situation for detection normal to the surface. The calculated number of gold atoms contained in the surface region remains unchanged but the depth distribution is modified. The general conclusions made in this article are not influenced by these considerations. There is considerable uncertainty (about a factor of 5) in the absolute value of the fluorine concentration deep in the lattice, but it is quite clear that there is a large quantity of fluorine in the lattice.

There are two inputs into the Sven Tougaard (ST) calculation: the inelastic electron mean free path (IMFP) and the cross section for inelastic electron scattering. We have taken the cross section for inelastic electron scattering as well as the IMFP to be those of  $\text{SiO}_2$ . This is not critical for the analysis since a variation of IMFP will lead to a change in the relative depth scale but leave the structure unchanged, and a small change in the cross section will lead to a small change in the position of the loss structure but will not affect

the quantification significantly. Thus, the  $\text{IMFP} = 26 \text{ \AA}$  was estimated from Ref. 30 and the three-parameter cross section valid for  $\text{SiO}_2$  (Ref. 31) was used.

Figure 2 shows an example of this analysis (spectrum 4b, see Table I) for different assumed F depth distributions. In each case, the original spectrum, the inelastic background, and the difference are shown. The latter is the spectrum at the point of excitation in the solid and must consequently have near zero intensity in a wide energy range on the low kinetic (high binding) energy side of the peak. Figure 2 shows analysis assuming that F forms a layer at the surface. The layer thickness is varied from  $20 \text{ \AA}$  in Fig. 2(a) to  $50 \text{ \AA}$  in Fig. 2(b) and  $120 \text{ \AA}$  in Fig. 2(c). From this it is clear that the fluorine concentration must be significant to large depths to account for the inelastic background because the fit gets progressively better for larger thickness. However, even though there is a reasonable account for the intensity in the near-peak region for  $120 \text{ \AA}$ , there is a poor account for the electron intensity in the background at larger energy loss which implies that there is a significant amount of F at depths  $> 120 \text{ \AA}$ .

This is confirmed in Fig. 2(d) which shows an analysis where the F concentration  $c(z)$  is taken to be exponentially varying with depth  $z$ :

$$c(z) = C_b + (C_s - C_b)\exp(-z/L), \quad (1)$$

where  $C_s$  and  $C_b$  are the concentrations at the surface and in the bulk and  $L$  is the decay length. In Fig. 2(d) (valid for sample 4b),  $C_b/C_s = 0.45$  and  $L = 10 \text{ \AA}$  (see Table I) and Eq. (1) becomes

$$c(z) = C_s[0.45 + 0.55 \exp(-z/10)]. \quad (2)$$

TABLE I. Description of analyzed samples.

Sample	$\Omega$ cm	Gas	Incident flux/cm <sup>2</sup> s	$C_b/C_s$	$L$ Å	1–10 Fit quality <sup>a</sup>	Total F atoms top 200 Å	Total F atoms top 10 Å	Total F atom top 100 Å
1a	2E-2 p		1.53E+16			6	3.69E+15		
1b	2E-2 p	F <sub>2</sub>	5.25E+16	0.37	20	7	4.84E+15	3.72E+14	2.1E+15
2	2E-3 p	XeF <sub>2</sub>	5.00E+14	0.35	10	10	1.10E+16	1.09E+15	4.15E+15
3	2E-2 p	F	1.50E+17	0.20	17	10	7.68E+15	1.15E+15	3.36E+16
4a	2E-3 n	XeF <sub>2</sub>	1.50E+16	0.40	16	10	1.27E+16	1.20E+15	4.9E+15
4b	2E-3 p	XeF <sub>2</sub>	1.50E+16	0.45	10	10	1.37E+16	1.14E+15	5.05E+15
5a	11 n	XeF <sub>2</sub>	4.50E+14	0.30	10	10	9.59E+15	1.06E+15	3.7E+15
5b	11 n	F	9.00E+14	0.15	7	8	5.15E+15	8.63E+14	2.1E+15
Ja	2E-2 n	XeF <sub>2</sub>	8.95E+15	0.15	8	9	2.15E+16 <sup>ab</sup>	1.41E+15	
Jb	2E-2 n	XeF <sub>2</sub>	8.95E+14	0.15	8	9	2.31E+16 <sup>ab</sup>	1.52E+15	

<sup>a</sup>Visual estimate.<sup>b</sup>600 Å.

This is seen to account for the intensity both in the near-peak region and in the full energy range up to  $\sim 250$  eV below the peak energy. The small negative intensities in the near-peak region are attributed to deviation in the cross section from that applied (see above) but this will not affect the general results. The analysis in Fig. 2 shows that the F is distributed as an exponential and that the F atoms are present to very large depths (at least 250 Å). An analysis similar to that in Fig. 2 was done for silicon samples prepared under various conditions. In all cases, it was found that the exponential distribution gives a much better account for the peak shape in a wide energy region than does a uniform distribution in a thin surface region. This procedure determines  $C_s/C_b$  and  $L$ . Quantification of  $C_s$  was done by using the F(1s) and Si(2p) peak intensities and the Scofield cross sections<sup>32</sup> and TPP-2M values for the IMFP.<sup>30</sup>

The technique discussed above is believed to be the only technique that can reliably describe depth profiles to about 250–600 Å for the fluorine-silicon system. Electron or ion-based analytical techniques (e.g., Auger or secondary ion mass spectroscopy) change the composition and distribution of fluorine so rapidly that reliable measurements are not deemed possible. Angular-resolved photoemission could yield some information, but it is not applicable to rough surfaces and even for flat surfaces it is limited in depth to two or three mean free paths, or  $\sim 60$  Å.

The surface concentration of fluorine is of course a boundary condition for the depth distribution of fluorine and is a somewhat controversial quantity. Some investigators believe there is only a thin layer near the surface.<sup>4,6,10</sup> Other investigators have evidence of what they thought was a thicker layer of fluorine.<sup>3,17–19</sup> Recently, the opinion of most investigators has been leaning toward the thin surface layer model.

Figure 3 shows the concentration of fluorine as a function of depth based upon the ST analysis. Table I provides parameters for each sample. There is a thin  $\sim 5$ –15 Å surface layer of SiF<sub>x</sub>. It contains about  $1.5 \times 10^{15}$ – $2.0 \times 10^{15}$  F atoms/cm<sup>2</sup>. There is also a more dilute layer of fluorine that extends deep into the lattice as far as the XPS

can see. The concentration of the “surface fluorine” is about the same for F atoms and for XeF<sub>2</sub> and is relatively independent of doping concentration or type of dopant. In contrast, the dilute bulk concentration does depend on these parameters. A dilute concentration of unreacted, interstitial fluorine was suggested by Roop *et al.*<sup>18</sup>

### III. EVIDENCE FOR NEGATIVE IONS

The insert in Fig. 1 indicates that only a small fraction of the visible fluorine is bonded to silicon or that there is a dilute concentration of SiF<sub>x</sub> which extends deep into the silicon lattice. The first interpretation is more reasonable as will be demonstrated later in this article. If this were not the case, there should be a larger intensity in the shifted peak between 101 and 103 eV. Moreover, one would not expect fluorine that is bound to silicon to be mobile, fluorine bound to sili-

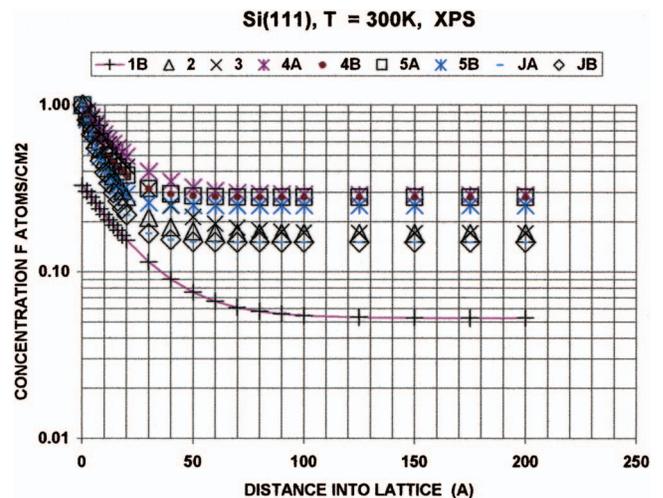


FIG. 3. Concentration of fluorine as a function of distance into the silicon sample based on ST analysis of ten samples. The absolute value is obtained by multiplying the value in this figure by the concentration in the top 10 Å (see Table I) and using Eq. (1).

con would be expected to create a thin  $\text{SiF}_x$  layer at the surface followed by the undisturbed silicon lattice. Oxides frequently exhibit that type of behavior.

Whereas most of the silicon is not bonded to fluorine, the large  $F(1s)$  peak in Figs. 1 and 2 would suggest one fluorine for each two to ten silicon atoms as judged from atomic sensitivity factors. A reasonable interpretation of Fig. 2 would be that there exist several monolayers of  $\text{SiF}_x$  near the surface. On the contrary, these two observations taken together suggest a large quantity of unbonded fluorine in the silicon lattice along with a thin (probably insulating)  $\text{SiF}_x$  surface layer. A reasonable interpretation for the data is that the fluorine existing within the silicon lattice is mostly negative ions. This is not an unexpected possibility. The assumption<sup>3,20</sup> that the lowest energy state for fluorine in silicon was  $F^-$  is supported by calculations. Both Van de Walle *et al.*<sup>8</sup> Bagus *et al.*<sup>20</sup> arrived at the conclusion that fluorine in the lattice (if it exists) would be negatively charged and quite unreactive. Chuang reported that he observed two different kinds of fluorine.<sup>21</sup> The two types were most likely fluorine bonded to silicon and fluorine negative ions sitting in the lattice. One would not expect a large shift in the fluorine peak in this situation. The fluorine bonded to silicon and many other materials is highly ionic, so the environment of the fluorine core electrons should be similar for both the bonded and the negative ion cases. Indeed penetration<sup>20</sup> and mobility of F (Ref. 22) have been proposed as important steps in the reaction process. Finally, it has been shown in electrochemical experiments that fluorine is dispersed throughout the entire wafer under the influence of an electric field.<sup>23</sup> These experiments seem to indicate that negative fluorine ions are very mobile and move throughout the surface region of silicon.

The fact that some  $\text{SiF}_4$  is trapped within the lattice is easily understood based on the present results. A few of the negative ions in the silicon lattice may react in a stepwise manner leading to  $\text{SiF}_x$  trapped in the lattice. [Our experiments, which use mostly data from the  $F(1s)$  region, cannot differentiate between  $F^-$  and F bonded to silicon.] The fact that the concentration of fluorine is rather flat at depths greater than  $\sim 50 \text{ \AA}$  suggests that diffusion driven by a concentration gradient is not the migration mechanism for F in the bulk. If it were, one would expect a concentration gradient to a depth where the fluorine becomes undetectable. Instead, a diffusion mechanism driven by an electric field or possibly by point defects may be operative. Those negative ions on the immediate surface generate an electric field in the silicon, which tends to drive other negative ions deeper into the bulk. This probably creates a depletion region near the surface, which reduces the electric field and thus avoids breakdown. The picture that is derived from this analysis is a thin  $\text{SiF}_x$  layer on the immediate surface followed by an exponentially decreasing function, which probably neutralizes (at least partially) the holes that accumulate at the Si– $\text{SiF}_x$  interface due to the electric field. This is followed by constant concentration of fluorine, which exists for at least  $200 \text{ \AA}$ .

The belief that fluorine exists as  $F^-$  in the lattice is not derived directly from our experiments. It is, however, consistent with the observation that the  $F(1s)$  peak from a Si sample shifts very little during fluorine exposure. The evidence for negative ions can be summarized as follows:

- (1) Calculations by Van de Walle *et al.*<sup>8</sup> and Bagus *et al.*<sup>20</sup> suggest that fluorine in a silicon lattice would exist as negative ions.
- (2) The experimental work of Lo *et al.*<sup>6</sup> showed a very large change in work function upon exposure to fluorine,  $\sim 5$  to  $6.4 \text{ eV}$ . This can be interpreted as caused by a dipole layer induced by negative ions in the surface region.
- (3) Fluorine is very electronegative and is expected to form negative ions.  $\text{SiF}_3$  centers and other types of surface or bulk site may also trap electrons.
- (4) The depth profile measurements indicate that fluorine in the lattice is highly mobile. One would not expect fluorine bound to silicon to be mobile nor would one expect fluorine atoms trapped in the silicon lattice to remain unreacted. Therefore, the characteristics of fluorine in the lattice resemble the behavior expected for  $F^-$ .
- (5) Simple image potential arguments along with the known electron affinity of fluorine ( $\sim 3.4 \text{ eV}$ ) suggest that the affinity level of fluorine on the silicon surface or in the lattice would lie below the valence band maximum.<sup>12</sup> Hence it is energetically favorable for them to be negatively charged.
- (6) Electrochemical experiments show that  $F^-$  is unreactive and highly mobile under the influence of relatively small electric fields.<sup>23</sup>
- (7) The earliest investigators assumed that negative ions would influence the etch reaction.<sup>19,33</sup>

The picture of a large quantity of mobile  $F^-$  in bulk silicon has important implications. It may induce a depletion layer near the surface by neutralizing the  $n$ -type donor impurities (i.e., the silicon is compensated) as well as neutralizing the hole population. The free electron population may also be small because the heavier negative ions take their place. If the concentration of  $F^-$  is sufficiently large, it may produce a degenerately doped  $p$ -type region. If the original wafer were heavily doped  $n+$  or  $n++$  silicon, a  $p$ - $n$  junction or even a tunnel diode might be the result. It has also been suggested that the etch rate is proportional to the concentration of negatively charged centers on the surface.<sup>12</sup> [Winters believes this to be the key to understanding the etching reaction.] The concentration of these charged centers would be influenced both by the thickness of the  $\text{SiF}_x$  surface layer and the concentration of negative ions in the bulk silicon.

#### IV. TOTAL FLUORINE CONTENT

Winters *et al.* found that exposing a silicon-covered quartz crystal microbalance to  $F_2$  at high pressure produced a surface coverage of at least  $6 \times 10^{15} \text{ F atoms/cm}^2$ .<sup>19</sup> Winters and Coburn also used XPS and temperature programmed desorption (TPD) to relate the total quantity of fluorine in

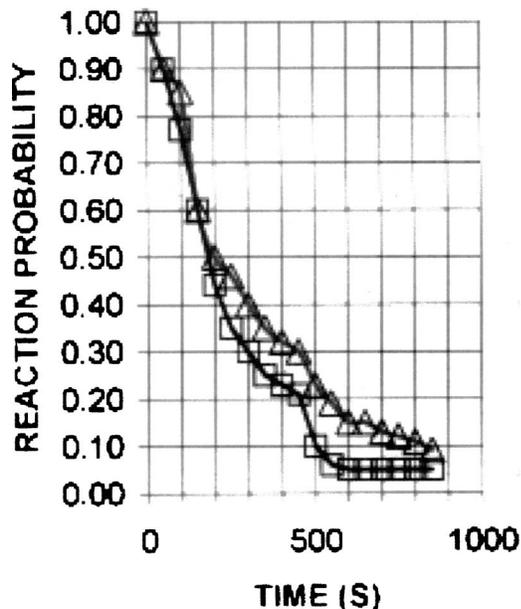


FIG. 4. Reaction probability vs time. Si(111), 300 K. The reaction probability was measured as a function of time for  $F_2$ . The product of the reaction probability and calibrated flux was integrated over time. Since  $F_2$  etching is negligibly small, the result obtained from this procedure is the quantity of fluorine in the sample. The values are  $3.8 \times 10^{15}$  and  $4.1 \times 10^{15}$  F atoms/cm<sup>2</sup>. The reaction probability was measured by comparing the reflected  $F_2$  “modulated beam mass spectrometer signal” from silicon with the same quantity from  $SiO_2$ . See Ref. 12.

single crystal silicon to the XPS ratio of the  $F(1s)/Si(2p)$  XPS intensities. They then assumed, based on the work of Lo *et al.* and McFeely *et al.*, that exposure to 50 L of  $XeF_2$  produced approximately  $1.62 \times 10^{15}$  F atoms/cm<sup>2</sup>. This number was used to normalize the TPD results to produce the absolute data presented in Fig. 13 of Ref. 3(a). It is now believed that those estimates are low because the work of Lo *et al.* probably missed most of the bulk fluorine. This was a consequence of tuning the photon energy to be particularly sensitive to the immediate surface region and not being able to address the  $F(1s)$  intensities with low photon energies.

$F_2$  is particularly interesting as a calibration gas because etching at room temperature is very slow. Most of the gas that reacts remains on or in the silicon. Reaction probabilities for  $F_2$  on Si(111) were measured as a function of fluence and the results are shown in Fig. 4. The techniques used were those described in Ref. 3(a). This technique assumes that the reaction probability is independent of the incident angle. It compares the quantity of the incident gas reflected from an inert surface ( $SiO_2$ ) to that reflected from silicon. This has proven to be an accurate technique in the few instances where it could be compared with a direct calibration.

Analysis of this type of data (integration of the product of flux times reaction probability) for  $F_2$  yields concentrations of fluorine, which are  $4.06 \times 10^{15}$  and  $3.81 \times 10^{15}$  F atoms/cm<sup>2</sup> for these two runs. These values are lower limits since the surface was not saturated. The ST analysis results for  $F_2$  shown in Fig. 3 give a value of  $\sim 4.96 \times 10^{15}$  F atoms/cm<sup>2</sup>, which again is a lower limit be-

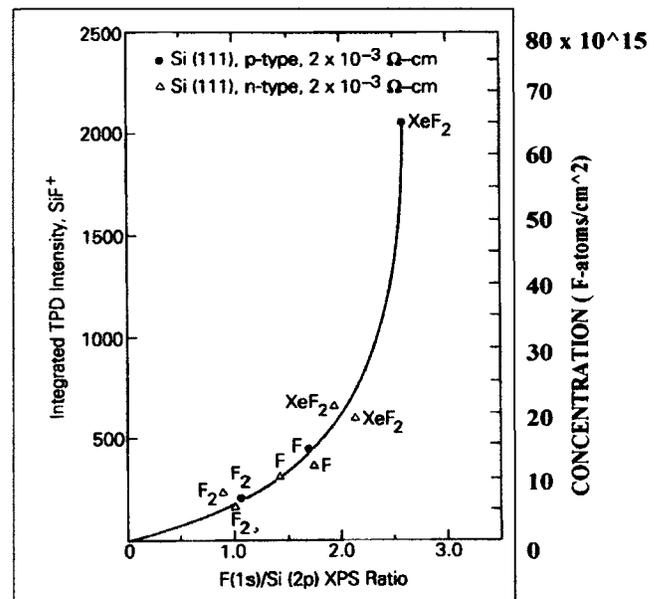


FIG. 5. Integrated temperature-programmed desorption (TPD) intensity vs  $Si(1s)/Si(2p)$  XPS ratio. The right hand axis gives the fluorine concentration put on an absolute scale by assuming the saturated  $F_2$  value to be  $6 \times 10^{15}$  F atoms/cm<sup>2</sup>. See text for justification.

cause the maximum depth sampled by this method is approximately ten IMFP ( $\sim 250$  Å in this case). These experiments (microbalance with  $F_2$ :  $6 \times 10^{15}$ , SP integration:  $4.06 \times 10^{15}$ ,  $3.81 \times 10^{15}$ , ST analysis of the XPS data:  $4.84 \times 10^{15}$ ) suggest that the saturation value for silicon exposure to  $F_2$  may be  $\sim 6 \times 10^{15}$  F atoms/cm<sup>2</sup>. It should be noted that XPS is relatively insensitive to surface roughness (see above) and yet it gives data which are consistent with results obtained by other techniques which are more sensitive to roughness. It is assumed that long exposure to  $F_2$  produces a concentration of  $6 \times 10^{15}$  F/cm<sup>2</sup>. This number was used to renormalize the data of Fig. 13 of Ref. 3 and the results are presented Fig. 5. They are larger than the numbers originally published by about a factor of 2.5. We expect these values to be good to within a factor of  $\sim 2$ . If anything, they are probably on the low side of the real value. In any case, this is the best that can be done with the available data. It is clear that there is a large quantity of fluorine in the lattice—much more than could be accommodated in a thin (10 Å) surface layer—during and after etching of silicon with fluorine.

Vugts *et al.*<sup>4</sup> get approximately the same results as the present work although it is interpreted differently. Their saturation value is about  $2 \times 10^{16}$  F atoms/cm<sup>2</sup> (30 ML,  $6.86 \times 10^{14}$  F atoms/ML). This is about the number we expect from the ST (top 200 Å) analysis which indicates a value of  $9.6 \times 10^{15}$  F atoms/cm<sup>2</sup> for  $n$ -doped 11 Ω cm Si(111) exposed to  $XeF_2$ . Our recalibrated TPD data shown in Fig. 5 give the same number as Vugts *et al.* for the same type of sample. Surface roughness or experimental error in our experiment or theirs could account for some discrepancy between the two sets of data.

The concentration of fluorine on the immediate surface (top 12 Å) is relatively constant at  $\sim 1.5$

$\times 10^{15}$  F atoms/cm<sup>2</sup>, as seen in Fig. 3. (The one exception being F<sub>2</sub>, which has a surface concentration of  $\sim 4.5 \times 10^{14}$ .) This is the same magnitude of surface concentration that was determined by Lo *et al.*,<sup>16</sup> and notably in the molecular dynamics simulations of Humbird and Graves.<sup>10,11</sup> While these simulations did predict a steady-state surface concentration of F along with steady etching of Si, migration of F (as F<sup>-</sup> ions or otherwise) into bulk Si was not considered due to the limitations of the computational technique. However, one might imagine a modification to these simulations that considers some arbitrary loss mechanism for surface fluorine, which creates new dangling bonds that are saturated by incident F atoms with a high sticking coefficient. Such a loss mechanism would thus allow the etch reaction probability to be manipulated without significantly affecting the surface concentration. Similarly, a reasonable way to model the (F atom or XeF<sub>2</sub>) reaction probability is to assume an insulating SiF<sub>x</sub> reaction layer of 10–15 Å as input to a model similar to the one published by Winters and Haarer.<sup>12</sup>

## V. SPECIFIC RESULTS

Conclusions based on the type of data shown in Fig. 3 are now summarized.

- (1) TPD measurements indicate  $6 \times 10^{16}$  F atoms on heavily *p*-doped Si(111). This type of experiment while not highly accurate should produce values that are proportional to all of the fluorine in the silicon. XPS measurements on this type of sample indicate  $\sim 1.8 \times 10^{16}$  F atoms, which is about 30% of the number measured by TPD. This result suggests that 66% of the total fluorine ( $\sim 4 \times 10^{16}$  F atoms) lies deeper than 200 Å. Consider sample 4b in Table I. If the concentration remains constant with depth, then the total thickness of the fluorinated layer would be  $\sim 700$  Å, i.e.,  $\{(4 \times 10^{16}) / (1.14 \times 10^{15})\} + 200$  Å.
- (2) When the exponential decrease in fluorine concentration is observable for depths less than 50 Å, which seems to always be the case, it is likely that 50 Å is the region where the F<sup>-</sup> mimics and neutralizes the hole population. If this hypothesis is correct, then the depletion width could well be  $\sim 700$  Å and the field across the insulator generates most of the surface charge.
- (3) XeF<sub>2</sub> produces the highest fluorine incorporation rates. TPD measurements indicate a concentration of  $\sim 1.37 \times 10^{16}$  F atoms/cm<sup>2</sup> for *n*-type silicon. XPS measurements give a value of  $1.50 \times 10^{16}$  F atoms/cm<sup>2</sup>, which is  $\sim 100\%$  of the total fluorine.
- (4) The total quantity of fluorine in the first 200 Å is similar for both *p*- and *n*-doped silicon. This result indicates that the fluorinated layer goes much deeper in heavily *p*-doped silicon than it does in heavily *n*-doped silicon because the TPD quantity is much larger than the XPS measurement. This suggests a model of the fluorine etching reaction where the surface charge is influenced by the width of the depletion layer, or the depletion layer adjusts its width to accommodate the surface charge.
- (5) Curves 5a and 5b in Fig. 3 compare the etching with XeF<sub>2</sub> to that of F atoms for lightly *n*-doped 11 Ω cm silicon. There is only a slight difference ( $<$  factor of 2) in the fluorine distribution within the silicon for these two gases.
- (6) There is only a small difference in the bulk concentration of fluorine for lightly doped *n*-type silicon and heavily doped *n*-type silicon (compare Fig. 3 curves 5a and 4a).
- (7) The total quantity of fluorine depends to a small extent upon the incident flux. The only difference in Fig. 3 between samples Ja and Jb is the flux:  $8.95 \times 10^{15}$  and  $8.95 \times 10^{14}$  XeF<sub>2</sub>/cm<sup>2</sup> s. There is about 8% difference in the total fluorine content of these films, with the higher flux having the lower fluorine content. This difference may be within the experimental error.
- (8) If a reasonable density is chosen for the SiF<sub>x</sub> layer ( $1 \times 10^{15}$  F atoms/cm<sup>2</sup> in 10 Å,  $4 \times 10^{21}$  F atoms/cm<sup>3</sup>), then from Fig. 4, the bulk concentration is between  $6 \times 10^{20}$  and  $3 \times 10^{21}$  F atoms/cm<sup>3</sup>. This large concentration of F<sup>-</sup> should produce a degenerately doped region near the surface. This might lead to a *p-n* junction with a thin insulator at the surface, i.e., a MIS diode and in some cases a tunnel diode.

As a chemical system, the etching of silicon with fluorine has many unique characteristics. Some of these are discussed in 1–8 above; others are seen in the work function experiments of Lo *et al.*,<sup>6</sup> the doping experiments of Winters and Haarer,<sup>12</sup> the modeling of Humbird and Graves,<sup>10,11</sup> and the reaction probability measurements of several groups: Beijerinck and co-workers,<sup>4,5</sup> Flamm *et al.*,<sup>14</sup> Coburn, and Winters (unpublished). Taken as a whole, these results tightly constrain the type of model that can be used to explain spontaneous etching.

It is believed that the ultimate model for etching silicon with fluorine is likely to be some variant of the “Harpoon Mechanism” described in Ref. 34, p. 15. An electron on the surface tunnels into the affinity level of an incoming fluorine atom. Electrons can also probably tunnel from the conduction or valence band to form negative ions. The resulting ion is accelerated by the image potential and gains the activation energy which is needed for the surface reaction to proceed. The F<sup>-</sup> ion reacts with a SiF<sub>3</sub> center to form SiF<sub>4</sub> or with a back bond to form Si<sub>2</sub>F<sub>6</sub>. The extra electron is lost to the bulk silicon during the reaction which forms these volatile gases. In other cases, the energy gain allows the F<sup>-</sup> to penetrate the thin SiF<sub>x</sub> layer which covers the surface. It then becomes highly mobile and moves freely depending on the electric field that exists at its position.

## VI. CONCLUSIONS

Silicon exposed to F atoms, F<sub>2</sub>, or XeF<sub>2</sub> will have a dilute concentration of fluorine distributed an indefinite distance ( $>200$  Å) into the lattice. The concentration of fluorine in the bulk is 0.1–0.4 times the surface concentration depending on the incident gas, the type and concentration of the dopant, and presumably the temperature. The concentration of fluo-

rine in the bulk depends upon etching conditions. The concentration of fluorine on the surface ( $<15 \text{ \AA}$ ) is about  $1.5 \times 10^{15} \text{ F atoms/cm}^2$ . This is relatively independent of doping level and whether the etch gas is F atoms or  $\text{XeF}_2$ . Arguments are presented suggesting that the lattice fluorine is primarily  $\text{F}^-$ . A graph showing the “quasisaturation value” for what is believed to be a quantitative description (within a factor of 2) of the amount of fluorine in Si(111) as a function of dopant concentration and type of incident gas has been presented. It is concluded that the lattice fluorine quite likely controls or strongly influences the etching reaction. There is only a small difference for the saturation values of lattice fluorine between lightly and heavily *n*-doped silicon.

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