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Synchrotron photoemission investigation of the initial stages of fluorine attack on Si surfaces: Relative abundance of fluorosilyl species

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The nature of fluorosilyl species existing on silicon surfaces during the initial stages of fluorine attack has been investigated with use of high-resolution soft-x-ray photoemission spectroscopy. In this study, several different silicon surfaces [Si(111)-(2×1), Si(111)-(7×7), Si(100)-(2×1), and silicon rendered amorphous by argon-ion bombardment] were exposed to fluorine via the dissociative chemisorption of XeF_2. For fluorine coverages in the monolayer regime we observed Si 2*p* levels chemically shifted by approximately 1, 2, and 3 eV corresponding, respectively, to SiF_1, SiF_2, and SiF_3. The relative abundance of the specific fluorosilyl species varied significantly among the different silicon surfaces. Recent experiments indicate atomic fluorine is the primary agent in reactive ion etching (RIE) of silicon by CF_4/O_2 plasmas. Based on such experiments several reaction models hypothesizing the existence of specific surface fluorosilyl species have been proposed, although no direct evidence for any of these surface species has been presented. The results presented here provide the first direct measurement of the composition and relative abundance of the fluorosilyl species remaining on silicon surfaces after exposure to fluorine.

I. INTRODUCTION

Production of (very-large-scale–integration) (VLSI) devices requires fabrication of silicon substrates with micrometer-scale anisotropic features. Currently, the method of choice for achieving the required level of profile control in these circuits is plasma etching. Plasma etching is performed by generating a discharge in a fluorocarbon containing gas. The resulting reactive atomic species, molecular ions, and free radicals react with the substrate to effect etching via the production of volatile silicon fluorides. Depending on the particular configuration, the substrate may also be subjected to energetic ion bombardment [in which case the process is frequently referred to as reactive ion etching (RIE)]. Clearly, from a mechanistic standpoint plasma etching is extremely complex. A wide variety of species of varying reactivities may impinge upon the surface, and once these reactants are adsorbed many bonds must be broken and formed before products may be desorbed. Given this complexity, it is hardly surprising that our understanding of the fundamental reaction mechanisms underlying this technology remains rudimentary. Considering the wide variety of potential reactants and reactions involved in plasma-etching processes, it is clear that simpler model systems must first be studied, so that the course of reaction between each individual gas-phase species and the silicon surface may be elucidated. Only then will it be feasible to address the more complex questions associated with the actual plasma-etching process.

Recently, several experiments have yielded strong evidence indicating that atomic fluorine is the primary reactive agent for the etching of silicon in CF_4/O_2 plasmas.[1–3] A first step towards understanding such etching is to investigate the nature of the interaction between fluorine atoms and silicon surfaces in the absence of other potential reactants. To date, such investigations have primarily addressed overall etching rates or the composition of the reaction products. Winters and Coburn found that XeF_2 etches polycrystalline silicon at a rate of 7000 Å/min at 1.4×10^{-2} Torr, and that the rate is linear in pressure.[4] The nature of the reaction products has been a subject of some controversy. Although minor disagreements remain, it is now generally agreed that SiF_4 is the predominant volatile product, but that a significant amount (10–30 vol %) of SiF_2 and SiF are also evolved.[5,6] Based on these kinetic data several models of the reaction mechanism have been proposed involving the existence of specific surface fluorosilyl species,[5,7,8] although no direct evidence for the existence of any of these has been found.

In order to experimentally address the question of what fluorosilyl species exist on silicon surfaces during the initial stages of fluorine attack, we have obtained the first high-resolution soft-x-ray photoemission spectra[9] of several different silicon surfaces exposed to fluorine [Si(111)-(2×1), Si(111)-(7×7), Si(100)-(2×1), and silicon rendered amorphous by argon-ion bombardment]. Exposure to fluorine was accomplished via the dissociative chemisorption of XeF_2. The results presented here show that the nature of the specific fluorosilyl moieties formed is strongly structure dependent, a variable not included in the above kinetic models and indeed not well controlled in some of the kinetic experiments. Surface structure is therefore seen to be an important variable which needs to be controlled in future experiments and included as a variable in future models of the reaction process.

II. EXPERIMENT

All photoemission spectra presented here were obtained at the IBM beamline of the National Synchrotron Light Source uv ring. Measurements were made using *S*-

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polarized light and a display-type photoemission spectrometer operated in the angle-integrated mode.[10]

The Si(111)-(2×1) surfaces used in these experiments were obtained by cleaving intrinsic ($10^{15}/cm^3$) silicon ingots in vacuum. The Si(111)-(7×7) and Si(100)-(2×1) surfaces were prepared on polished device-grade intrinsic silicon wafers. Immediately before insertion into the vacuum chamber, the wafers were etched in buffered HF and then rinsed successively in deionized water and methanol. A combination of argon bombardment and resistive heating to 1000 K sufficed to produce clean well-ordered surfaces as evidenced by sharp surface-state features in the valence-band spectra. In addition, broad-sweep photoemission spectra revealed no contamination of the cleaned surfaces.

Surfaces were dosed with fluorine by exposure to XeF_2 which chemisorbs dissociatively, leaving fluorine at the surface. Exposing surfaces to highly reactive gases such as XeF_2 requires special procedures designed to prevent sample contamination by gases liberated during exchange reactions at the vacuum-chamber walls. Even though the frequency of such reactions can be significantly reduced by pre-exposing the chamber walls to large quantities of XeF_2 gas, preliminary dosing attempts were uniformly marred by oxygen contamination (possibly in the form of adsorbed OH groups). This contamination manifested itself by the appearance of the oxygen 2*s* level in the spectra at -20 eV with respect to the valence-band edge. Clean dosing was achieved only after the construction of a special dosing chamber in which all of the surfaces line-of-sight to the sample could be liquid-nitrogen-cooled while the XeF_2 impinged directly on the sample surface through a copper nozzle. The dosing chamber which is all stainless steel has a volume of approximately 1 liter and is pumped by its own 20-l/s ion pump. A bakeable vacuum valve allows isolation of the dosing chamber from the main chamber. XeF_2 gas was obtained by sublimation from solid XeF_2 contained in a small capsule attached to a gold-on-sapphire leak valve. Before cooling the dosing chamber, its walls were passivated by exposure to 100 times a typical dose of XeF_2. Sample-exposure estimates were made by monitoring the rise in the ion-pump current, which was, in turn, calibrated against an ion gauge during the passivation process. Given the high reactivity of XeF_2 and the low pumping speed of xenon, stated exposure magnitudes should be regarded only as crude approximations. During XeF_2 exposure and the subsequent photoemission measurements, the sample remained at room temperature.

All spectra reported here were obtained subsequent to nominal 50-L (1 langmuir=1 L$\equiv 10^{-6}$ Torr s) exposures. We found this exposure to be typical of an apparent chemisorption saturation regime with about a monolayer of surface silicon atoms being bonded to fluorine. Broad energy scans of the exposed surfaces revealed the presence of no adsorbate other than fluorine. Specifically, no features due to xenon were observed, indicating that at room temperature XeF_2 dissociation is complete, in agreement with earlier x-ray photoemission spectra (XPS) results.[9] An extrapolation from the etch rate measurements of Winters and Coburn[4] indicates that this treatment was unlikely to have resulted in any significant etching, assuming that the same mechanism and rate law describes the reaction at XeF_2 pressures of 10^{-6} Torr as in the (10^{-4}–10^{-2})-Torr regime. This conclusion is supported by systematic exposure studies on the (111) surfaces. There, smaller exposures, nominally 10 L, produced similar spectra with only a very slight decrease in the fluorine-induced features. Repeated additional exposures of 50 L produced no further spectral changes. These surfaces should therefore be characteristic of the initial reaction phase, before product volatilization. The base pressure of the spectrometer chamber was 1×10^{-10} Torr. Under these conditions the fluorine-treated surfaces could remain in the chamber for several hours without noticeable degradation. Measurements on several different wafers and cleaves were made. The reproducibility of the spectra from surface to surface was excellent, with the specific exception of results from highly stepped cleaves, as noted in the next section.

III. RESULTS

A. Clean Si(111)-(2×1) surface

Figure 1(a) shows the Si 2*p* core level of a Si(111)-(2×1) cleaved surface at $\hbar\omega=130$ eV. Atoms at the sur-

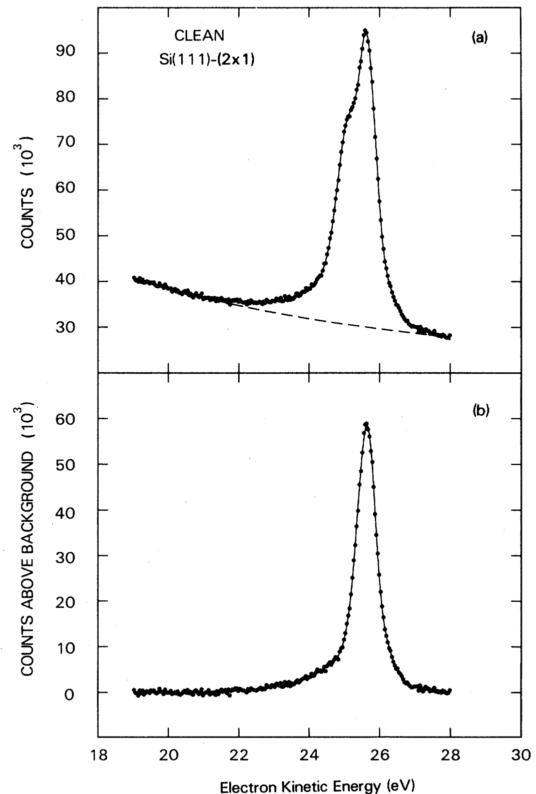

FIG. 1. Upper panel shows the 2*p* photoemission spectrum of a clean Si(111)-(2×1) cleaved surface. Dots represent actual data points and the dashed line a background subtracted for further analysis. The lower panel shows just the $2p_{3/2}$ contribution of the measured spectrum after a numerical removal of the $2p_{1/2}$ component from the background-subtracted spectrum.

face do not share the same coordination and bonding geometry as their neighbors in the bulk and consequently suffer small shifts in electron binding energy. As a result of the short mean free path for photoelectrons in the (25—35)-eV kinetic-energy range [4—5 Å (Refs. 11 and 12)], these shifted surface core levels provide a large contribution to the observed spectrum. The silicon $2p$ core level is spin-orbit-split by 0.61 eV with a statical branching ratio of 0.5. Since the instrumental resolution is approximately 0.2 eV, failure to clearly resolve the separate spin-orbit components is a consequence of different types of surface sites, each contributing its own slightly shifted core-level spectrum. Although sorting out contributions from the various surface sites would be quite difficult, their common spin-orbit splitting and branching ratio justifies use of a numerical procedure to separate the $2p_{3/2}$ and $2p_{1/2}$ components of the spectrum. Figure 1(b) shows only the $2p_{3/2}$ contribution to the measured spectrum assuming a spin-orbit splitting of 0.61 eV and a branching ratio of 0.52. Deviation from the statistical branching ratio of 0.5 is a consequence of slight differences in final-state densities at the different energies of detection. Removal of the $2p_{1/2}$ spin-orbit component is especially useful for visualizing Si $2p$ data with chemically shifted peaks since spin-orbit doublets congest the spectrum, making it difficult to separate features resulting from different chemical environments.

B. Fluorine-covered Si surfaces

The spectrum shown in Fig. 2(a) is characteristic of the Si(111)-(2×1) surface after exposure to 50 L of XeF_2. The most obvious change upon comparison to Fig. 1(a) is the new intensity on the high-binding-energy side of the $2p$ level. This shift of intensity results from silicon atoms which have been chemically bonded to fluorine. The fluorine—silicon bond involves transfer of electron density from silicon to fluorine, thereby shifting the silicon binding energy to a higher value. The magnitude of the shift for a given atom depends on the amount of electron transfer and, hence, on the number of fluorine atoms bonded to it. Since the silicon atoms participating in the fluorine bonds are surface atoms, some of the slightly shifted surface core levels, characteristic of the clean surface, are removed to higher binding energies. Removal of these surface core levels to energies significantly different from the unshifted spin-orbit doublet results in the clearer resolution of the $2p$ doublet for the fluorine-dosed surfaces. After background subtraction, the $2p_{1/2}$ component of the spectrum was removed using the same intensity and splitting parameters as for the clean surface, thereby isolating the $2p_{3/2}$ contribution shown in Fig. 2(b). A chemically shifted satellite peak at approximately 1 eV higher binding energy is clearly resolved. Comparison of these results with photoemission spectra of gas-phase silicon compounds,[13] with *ab initio* theoretical calculations,[14] and with XPS spectra of fluorine-doped hydrogenated amorphous-silicon bulk alloys,[15] allows straightforward assignment of the satellites as resulting from the formation of monofluorosilyl, difluorosilyl, and trifluorosilyl units, in order of increasing binding energy.

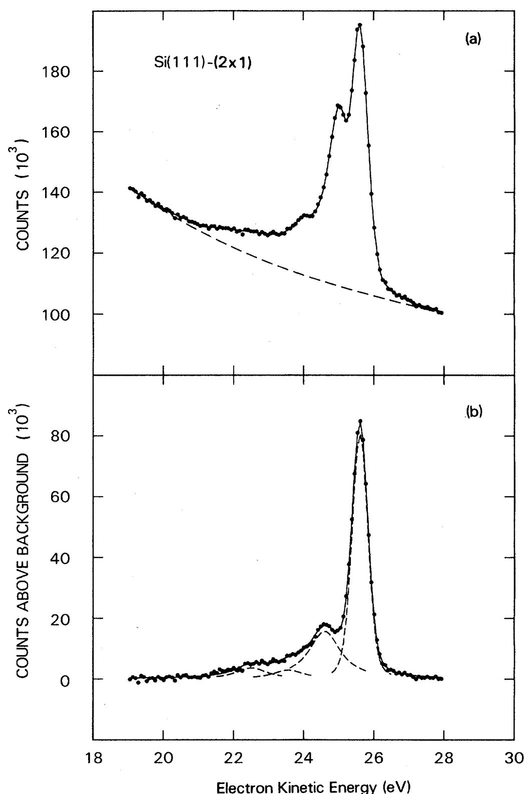

FIG. 2. Upper panel shows the $2p$ photoemission spectrum of the Si(111)-(2×1) cleaved surface after exposure to approximately 50 L of XeF_2. The lower panel shows the $2p_{3/2}$ component of the background-subtracted spectrum. In addition to the unshifted silicon $2p_{3/2}$ there are three chemically shifted satellites corresponding to SiF_1, SiF_2, and SiF_3, in order of increasing binding energy. The dashed lines show the separate components, and the solid line shows the sum of the four dashed components.

A least-squares-fitting procedure was employed to separate the spectrum in Fig. 2(b) into its various components, thereby obtaining accurate values for the energies and intensities of all its features. The resulting decomposition is illustrated in the figure by the dashed lines. The solid line through the data points is the sum of the dashed lines. The fit for this and all other surfaces was performed assuming three chemically shifted peaks of equal width. Line shapes were assumed to be Lorentzian-broadened by a Gaussian. The unshifted $2p$ component was allowed to have a different width from the chemically shifted components. Peak positions, widths, and intensities were adjusted, consistent with the above restrictions, to obtain the best fit. Derived peak positions and surface coverages calculated from their relative intensities are given in Table I, along with the analogous data for the other surfaces considered below.

The weak satellite intensity attributed to difluorosilyl and trifluorosilyl was found to vary significantly from cleave to cleave. The spectrum of Fig. 2 is typical, but on some cleaves these features were so small as to be virtually undetectable, suggesting that the difluorosilyl and tri-

TABLE I. Coverages and the magnitude of the chemical shift for chemically shifted peaks found on fluorine-dosed silicon surfaces. Coverages were calculated using a continuum model of the emission process and are listed in units of monolayers for SiF_1, SiF_2, and SiF_3 or units of 10^{15} atoms/cm^2 for fluorine. A monolayer is defined to be the number of atoms in the appropriate unreconstructed silicon surface.

	Coverage (monolayers)			Total F	Chemical shifts (eV)		
	SiF_1	SiF_2	SiF_3	10^{15} atoms/cm^2	SiF_1	SiF_2	SiF_3
Si(111)-(2×1)	1.01	0.19	0.23	1.62	1.00	2.04	3.09
Stepped Si(111)-(2×1)	0.72	0.31	0.23	1.56	1.07	2.16	3.22
Si(111)-(7×7)	0.47	0.31	0.31	1.58	1.08	2.09	3.17
Si(100)-(2×1)	1.16	0.39	0.11	1.56	1.04	2.11	3.36
Sputtered Si(111)-(2×1)	0.55	0.44	0.19	1.56	1.17	2.47	3.52

fluorosilyl components are associated with step or defect sites. To test this hypothesis, a deliberately bad cleave was made, in which the surface was clearly rough. The spectra thus obtained are shown in Fig. 3. It is apparent from these data that the intensity from difluorosilyl and trifluorosilyl is step or defect associated. This suggests that a perfect (111)-(2×1) surface would exhibit only the monofluorosilyl peak with a 1-eV chemical shift.

When the Si(111)-(7×7) surface (Fig. 4) was exposed to XeF_2, a dramatically different distribution of the fluorosilyl species was observed. In contrast to the (2×1) reconstruction, the (7×7) one supports larger amounts of difluorosilyl and trifluorosilyl. The position of the chemically shifted satellites is, however, in excellent agreement with the observations for the (2×1) surface.

Table I lists coverages for the various constituents found on the fluorine-dosed surfaces. Coverages were calculated using a continuum model of the emission process.[16] For the (111) surfaces a monolayer is defined to be the number of atoms in the unreconstructed Si(111) surface (7.81×10^{14} atoms/cm^2). For the (100) surface a monolayer is taken as the number of atoms on the un-

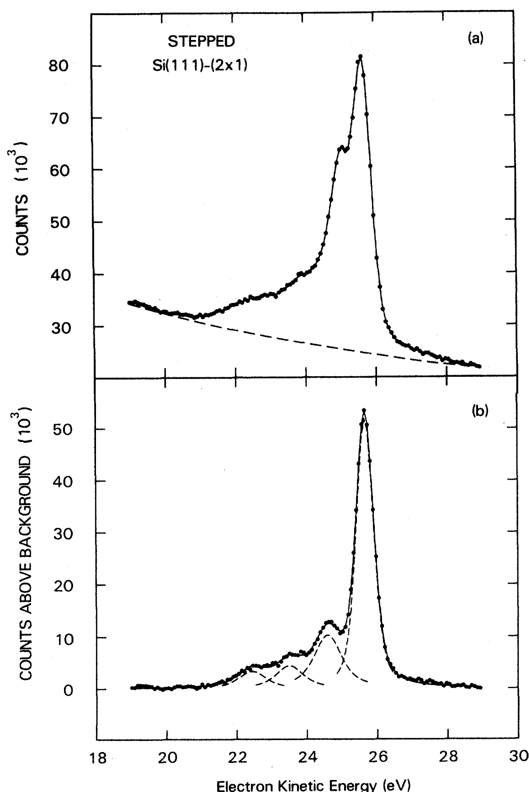

FIG. 3. Upper panel shows the $2p$ photoemission spectrum of a Si(111)-(2×1) stepped surface after exposure to 50 L of XeF_2. The lower panel shows the decomposition of the $2p_{3/2}$ portion of the spectrum into its different chemical components. Comparison with Fig. 2(b) suggests that the difluorosilyl and trifluorosilyl components (23.2 and 22.2 eV) are step related.

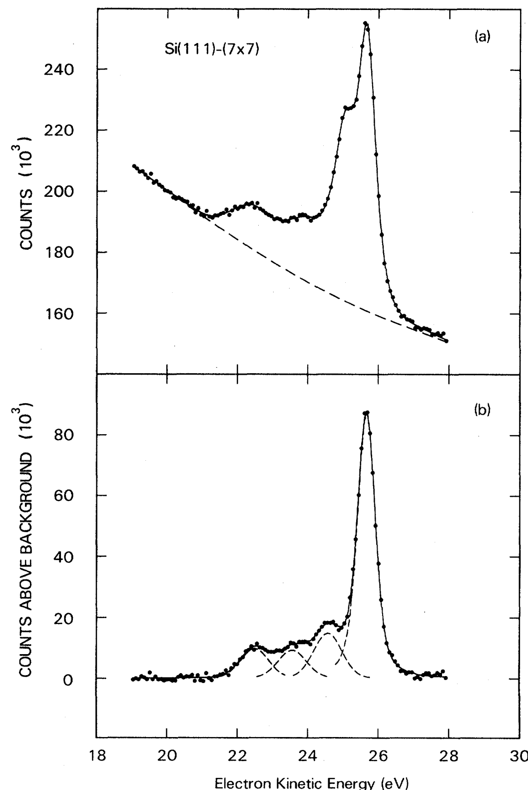

FIG. 4. Upper panel shows the $2p$ photoemission spectrum of a Si(111)-(7×7) surface after exposure to 50 L of XeF_2. The lower panel shows decomposition of the $2p_{3/2}$ portion of the spectrum into its different chemical components. The nature of the (7×7) reconstruction is such that it supports relatively more trifluorosilyl than the (2×1) surface.

reconstructed (100) surface (6.86×10^{14} atoms/cm^2). The first three columns show the number of monolayers of silicon atoms bonded to one, two, or three fluorines. Values in the fourth column correspond to the total coverage of fluorine atoms in units of 10^{15} atoms/cm^2. To compute the total amount of fluorine it is necessary to weight the difuorosilyl peak 2 times the monofluorosilyl, and the trifluorosilyl peak 3 times, resulting in total fluorine coverages of 1.62, 1.56, 1.58, 1.56, and 1.56×10^{14} atoms/cm^2. No possibility of double counting arises here since fluorine can form only a single covalent bond. The less than 10% variation in total fluorine coverage across the different surfaces is fully consistent with our observations of the saturation behavior observed with repeated dosings. It is also suggestive that repulsion between the fluorine atoms may be an important factor in determining the saturation coverage.

Results for the Si(100)-(2×1) surface after exposure to 50 L of XeF_2 are presented in Fig. 5. This spectrum appears to be distinguished by a nearly total lack of trifluorosilyl. In fact, this intensity is sufficiently small that structural defects cannot be completely ruled out as its source.

Amorphous surfaces were prepared by argon-ion bombardment of cleaved surfaces. The spectra thus obtained are shown in Fig. 6. Comparison with spectra obtained from the unsputtered surfaces (Fig. 2) shows that disordering of the surface affects both the total amount and the distribution among the different fluorosilyl species. Presumably due to inhomogeneity in the disordered lattice, the individual components in the satellite region appear to be less well resolved.

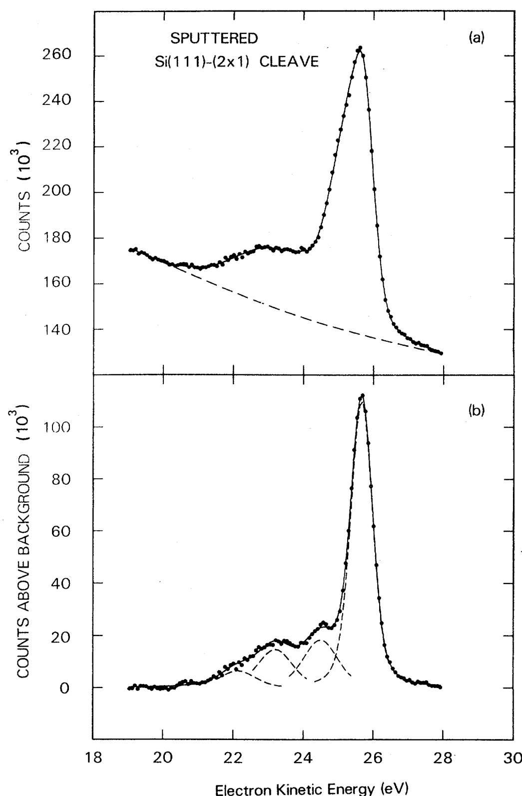

FIG. 6. Upper panel shows the $2p$ photoemission spectrum of a Si(111) cleaved surface rendered amorphous by argon-ion bombardment before exposure to 50 L of XeF_2. The lower panel shows the decomposition of the $2p_{3/2}$ portion of the spectrum into its different chemical components. This surface shows the largest relative concentration of difluorosilyl seen on any of the measured surfaces.

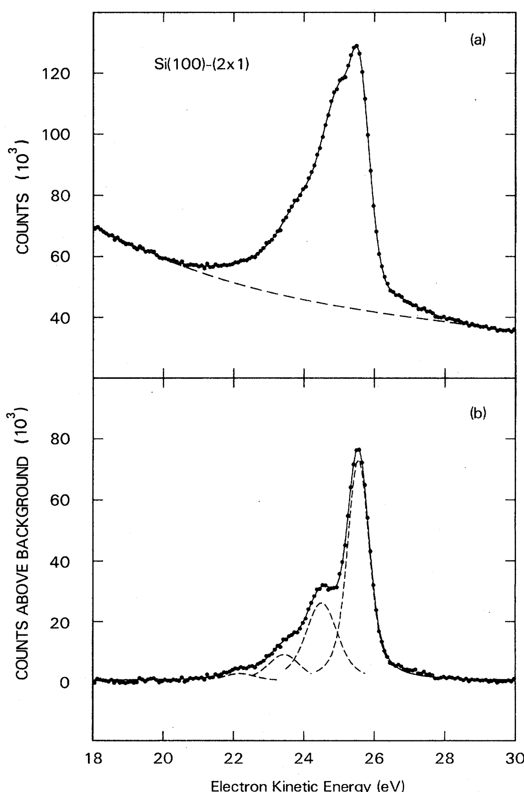

FIG. 5. Upper panel shows the $2p$ photoemission spectrum of a Si(100)-(2×1) surface after exposure to 50 L of XeF_2. The lower panel shows the decomposition of the $2p_{3/2}$ portion of the spectrum into its different chemical components. The small amount of trifluorosilyl may well be defect related.

In addition to the silicon $2p$ spectra, fluorine $2s$ spectra were obtained at $\hbar\omega=90$ eV. Somewhat surprisingly, these spectra showed little variation from surface to surface. A typical result, from the Si(111)-(7×7) surface, is shown in Fig. 7. The peak is well fitted by a single Gaussian with a full width at half maximum (FWHM) of 2.7 eV.

IV. DISCUSSION

The data of Table I indicates a great deal of regularity in the binding energies of the chemically shifted satellites, suggesting that, to first approximation, silicon chemical shifts depend only on the number of fluorines bound to a silicon atom and not on the surface structure. It is interesting to note that the greatest deviation from this simple behavior is exhibited by the sputtered surface, where a 1.17-eV shift of the monofluorosilyl peak is observed. This shift, while systematically larger than those found on

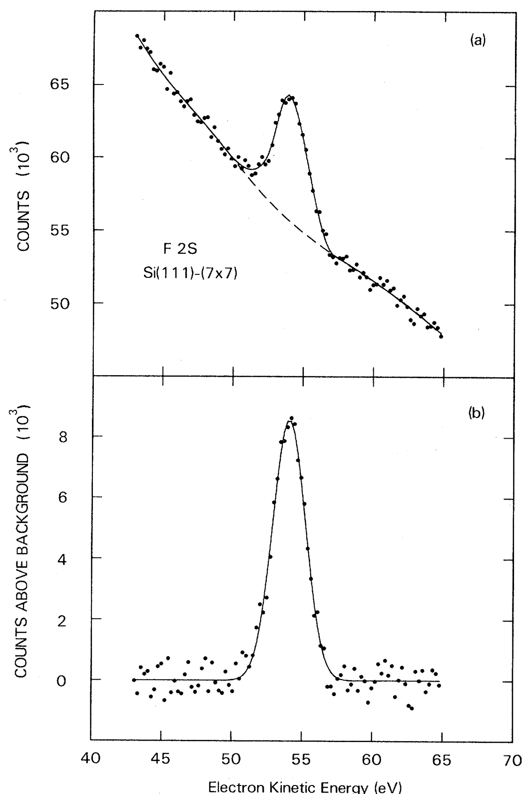

FIG. 7. Upper panel shows the $2s$ photoemission spectrum of a Si(111)-(7$\times$7) surface after exposure to 50 L of XeF_2. This spectrum is typical of all the fluorine-dosed surfaces studied and is well fitted by a 2.7 eV FWHM Gaussian.

ordered surfaces, agrees closely with the value of 1.15 eV deduced by Gruntz, Ley, and Johnson in their study of fluorine-doped hydrogenated amorphous silicon.[15] Agreement between these two results and their small deviation from the ordered-surface chemical shifts may result from the reduced density of the amorphous samples, resulting in less efficient screening of the core-hole state.

In addition to the fluorosilyl species, it is, of course, possible that fluorine exists on the surface in other configurations which affect the silicon $2p$ levels in a less dramatic fashion. Considering the reactivity of the silicon-fluorine system, interstitial fluorine may also be a possibility. Both of these cases have recently been considered theoretically by Seel and Bagus.[14] For a small cluster, they calculated *ab initio* orbital energies for fluorine bound in atop (monofluorosilyl) sites, in threefold sites above the surface plane, and in threefold sites below the surface plane (interstitials). For the monofluorosilyl site, they calculate a Si $2p$ binding-energy shift of 1.2 eV, in excellent agreement with experiment considering that relaxation has not been included. For the above-surface threefold site they predict a shift of 0.6 eV. In the spectra of Figs. 2 and 4 it is evident that there is no satellite peak of observable magnitude at this energy. Thus we conclude that no such binding state exists on either Si(111) surface. For the interstitial site, Seel and Bagus calculate a shift of only 0.3 eV. For this small splitting the situation is far less clear. Since the unshifted Si peak is quite symmetric, and not appreciably broadened with respect to the clean-surface peak, only a small feature could be concealed in the spectrum at this shift energy. If this shift were only 0.2 or 0.1 eV, however, significant amounts of this species could conceivably be obscured. Keeping the above caveats in mind, these spectra offer no positive evidence for the existence of interstitial fluorine.

Finally, we note that the fluorine $2s$ level is quite insensitive to the nature of the fluorosilyl species present on the surface. The splittings in this level which must occur in the polyfluoro groups must therefore be quite small with respect to the natural linewidth. Seel and Bagus have predicted that the fluorine $1s$ level would exhibit large binding-energy shifts if it were bound in interstitial or threefold surface sites. While this level was energetically inaccessible in our experiments, the F $2s$ level behaves somewhat like a quasi core level in its photoemission behavior.[17] The constancy from surface to surface and single-peak nature of this level is thus an additional argument against the occurrence of interstitial fluorine under the conditions considered here. This, of course, does not preclude the possibility that interstitial fluorine may be important under conditions in which steady-state reaction, as opposed to mere chemisorption, is taking place.

V. CONCLUSIONS

In conclusion, we have identified the types of fluorosilyl moieties formed by the initial attack of F atoms on clean silicon surfaces. The chemical shifts of approximately 1, 2, and 3 eV are characteristic of monofluorosilyl, difluorosilyl, and trifluorosilyl groups, independent of the structure of the particular surface considered. No evidence for interstitial or otherwise multiply coordinated fluorine atoms was found.

The distribution of the fluorosilyl species was, however, strongly dependent on the surface structure. This behavior may be understood in terms of simple activation energy arguments. While there are several plausible models for the structure of the (111)-(2$\times$1) surface, all of them involve a single recognizable residual dangling-bond state per surface atom, which interacts, albeit weakly, with the rest of the lattice. It should be both energetically feasible and kinetically facile to bond a single fluorine atom to each surface silicon. To fluorinate a given surface atom further would involve the breaking of at least one strong Si—Si bond. It is not difficult to believe that such a step would have a significant activation energy associated with it and would not occur to an appreciable extent with the exposures considered here. Similarly, the two dangling bonds per surface atom associated with bulk termination of the (100) surface are thought to reform with each other in the asymmetric dimerization giving rise to the (2$\times$1) reconstruction. These reformed surface bonds, however, have reduced overlap and are thus much weaker than bulk bonds. It is therefore quite plausible that fluorine atoms could easily insert into these weak bonds. Thus both monofluorosilyl and difluorosilyl units could easily be formed, but trifluorosilyl would be suppressed due to the necessity of cleaving a strong bulk

bond. In contrast to the (111)-(2×1) surface, steric effects on the (100)-(2×1) surface would be expected to play an important role in the distribution of chemisorbed fluorosilyl species in the monolayer regime. If all of the dimer bonds were to be terminated by fluorine atoms, a surface of all difluorosilyls would result. However, such a configuration would require either an unphysically short distance between fluorine atoms on adjacent difluorosilyls, or a severe distortion of the silicon—silicon bonds between the first and second layers. Both of these would be energetically unfavorable. It is therefore hardly surprising that the (100)-(2×1) surface exhibits more monofluoro than difluoro species. However, too much should not be made of the exact fluorosilyl distribution for the spectrum of Fig. 5. No systematic study of the exposure dependence has been made for this surface, and unlike the (111) results, this coverage does not necessarily represent a saturation value. Moreover, the spectra indicate that 1.7 monolayers of silicon atoms are fluorine bonded, indicating that disruption of the lattice may have already started. The structure of the (111)-(7×7) surface is less well understood, however, recent scanning-tunneling-microscopy results[18] indicate the presence of both "adatoms" and hollows on the surface. Depending on the specific structure of these features, either or both could involve surface atoms which could be subjects for facile trifluorination. The amorphous and stepped surfaces would almost certainly possess such atoms, and therefore the presence of trifluorosilyl species on these surfaces is as expected.

Finally, we note that a number of the kinetic models for the course of the surface reaction involve difluorosilyl units as the most prominent surface species, presumably because SiF_2 is a reaction product. Ironically, difluorosilyl is not the predominant species on any of the surfaces we have investigated. This suggests that these models are incomplete and that more emphasis might have to be placed on the reaction of trifluorosilyl groups. As a final note of caution, we wish to reemphasize that the results obtained here pertain to the initial attack of fluorine on the clean silicon surface, not to the conditions found on surfaces which have been subjected to substantial steady-state etching. Recent experiments in our laboratory have indicated dramatic differences between the results obtained for the initial stages of fluorine attack and those obtained from surfaces that have been exposed to sufficient XeF_2 to etch away significant amounts of silicon. These results will be the subject of a planned, forthcoming paper.

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[9]In an earlier study [T. J. Chuang, J. Appl. Phys. **51**, 2614 (1980)] low-resolution (FWHM of 1.5 eV) XPS spectra were reported for XeF_2 adsorption on an unspecified, but carbon- and oxygen-contaminated, Si surface. In was claimed that their XeF_2 surfaces supported predominately "SiF_2-like" units. While the direct comparison between their results and the results presented here for clean, well-characterized surfaces in not completely justified, our results indicate their claim is incorrect. In any event, due to lack of resolution, poor surface sensitivity of XPS measurements, and severe contamination problems, their conclusion was not, in our opinion, well supported by the evidence given. We therefore make no further mention of their work.

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