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Remote inductive effects in the Si 2p spectra of halogenated silicon

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Abstract

Si 2p spectra collected from fluorinated Si(111)-7×7 are analyzed to determine whether chemical shifts induced by remote F atoms are discernible. Although the traditional interpretation adequately accounts for the observed chemical shifts without considering remotely induced shifts, recent experimental evidence indicates that such shifts may occur for highly electronegative adsorbates. Thus, an extended scheme is outlined that is consistent with all known data, but which includes remotely induced shifts. It is found that, although they differ quantitatively, both approaches yield the same qualitative results for fluorinated Si.

Keywords: Halogens; Low index single crystal surfaces; Photoelectron emission; Silicon; Soft X-ray photoelectron spectroscopy

Because of their technological importance, halogen–silicon surface reactions have been investigated extensively [1]. Many of these studies employed core-level spectroscopies, since halogen bonds induce large, easily detectable Si 2p chemical shifts [2–20]. The results obtained demonstrate a variety of phenomena, including surface passivation [3–5,12–15], etching [2,6–11,16–20], the build-up of a reaction layer [6–8,10,20] and doping effects [8,20,21]. All of these findings, however, derive from an interpretation of Si 2p chemical shifts that considers only nearest-neighbor atoms.

Si 2p chemical shifts, which arise from the interaction of the core-level electrons with the outer valence electrons, primarily reflect the local chemical environment of the central (photoemitting) atom, and thus depend on the number and type of chemical bonds formed. Since the static dielectric constant of Si is large, long-range interactions are effectively screened out [22]. In addition, for electronegative adsorbates, the chemical shift per bond is nearly constant (~ 1 eV for F, ~ 0.9 eV for O or Cl, ~ 0.7 eV for I and ~ 0.6 eV for S), and roughly follows the trend that more electronegative adsorbates induce larger shifts [4,5,23]. This regularity, combined with the high degree of screening, has traditionally led to a consideration of only nearest-neighbor atoms in the interpretation of Si 2p chemical shifts.

Recently, however, a less conventional interpretation was put forth. In an investigation of silsesquioxane cluster (e.g. $SI_8H_8O_{12}$) adsorption on Si(100)-2×1, a Si 2p component 1 eV higher in

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binding energy (BE) than bulk Si was observed [24–26]. Since in the expected adsorption geometry there are no Si atoms bonded to single O atoms (the traditional interpretation for a 1 eV shift), the 1 eV shifted component was instead attributed to a surface Si atom attached to an –SiO$_3$ group in the cluster. In the traditional scheme, Si atoms in such configurations should not exhibit a measurable chemical shift, since they are attached solely to other Si atoms. Yet, by including the inductive effects of the second-nearest-neighbor oxygen atoms, the authors of Ref. [24] argued that an –SiO$_3$ group does indeed induce a shift of 1 eV. Their argument is based on a comparison to photoelectron spectroscopy measurements of gas-phase molecules, which do exhibit such effects [27]. However, since gas-phase molecules lack the high degree of screening that exists on a Si surface, a direct comparison may or may not be valid.

The goal of the present investigation is to determine, as a general rule, whether shifts arising from highly electronegative second-nearest-neighbor atoms need to be considered in the interpretation of Si 2p spectra and, if so, how this affects the results of previous studies of halogen–Si reactions. To that end, high-resolution synchrotron-based soft X-ray photoelectron spectroscopy (SXPS) was employed to investigate the possibility of remotely-induced shifts in the Si 2p spectra of fluorinated Si(111)-7 × 7. Fluorine was used as it is the most electronegative halogen and thus induces the largest shifts. Si(111)-7 × 7 was chosen because when it is moderately fluorinated, a large number of –SiF$_3$ groups are produced which, in analogy with –SiO$_3$ might induce chemical shifts of ~1 eV.

The data were collected on beamline U8-b of the National Synchrotron Light Source, using an angle-integrating ellipsoidal mirror analyzer. A detailed description of the apparatus and the sample preparation techniques can be found in Ref. [6]. To generate a surface containing primarily SiF, clean Si(111)-7 × 7 was exposed to 40 L of XeF$_2$ (1 L = 1 langmuir = 10^{-6} Torr·s), which produced SiF on the surface, along with small amounts of SiF$_2$ and SiF$_3$. The surface was then lightly annealed to remove the higher fluorides. A surface containing a significant amount of higher fluorides was generated by exposing the monoflu-

orinated surface to an additional 400 L of XeF$_2$, which is sufficient to form higher fluorides without causing the damage generated by larger exposures [6].

The greatest surface sensitivity is achieved for the Si 2p core level with ~130 eV photons, which produces ~25 eV photoelectrons. However, at 130 eV, fluorosilyl species in higher oxidation states exhibit enhanced photoabsorption cross-sections relative to those in lower oxidation states [6]. Thus, in this work, Si 2p spectra were collected with a photon energy of 170 eV, which is sufficiently high for such enhancements not to occur, but low enough to retain surface sensitivity.

The Si 2p spectra were fitted to a sum of Gaussian-broadened Lorentzian lineshapes using the procedure outlined in Ref. [6], with a spin-orbit splitting of 0.60 eV and a branching ratio of 0.50. The Lorentzian full-width at halfmaximum (FWHM) was fixed at 0.080 eV. Although this is larger than the value recently determined via high-resolution SXPS [28], it gives the best overall fit to the data, and has been used previously for data from the same beamline [23]. From the intensities of the chemically shifted components, coverages of each surface species are calculated using the same method as in Ref. [6], and are reported in Table 1.

The data and fits are shown in Fig. 1. Fig. 1a shows an Si 2p spectrum collected from monofluorinated Si(111), which has two contributions – one from bulk atoms and one from Si bonded to a single F atom (denoted SiF). Fig. 1b shows a spectrum collected from the same surface following additional fluorination, which generated higher fluorides, producing a total of three chemically shifted components ~1, 2 and 3 eV higher in BE than bulk Si (labeled A, B and C, respectively). Traditionally, these are attributed to mono-, di- and trifluorinated Si [9]. However, as discussed below, there may be additional contributions. The difference between the normalized spectra in Figs. 1a and 1b, which is also adequately fitted with three components at the same BEs, is shown in Fig. 1c. Note that no new spectral features appear in the 0–1 eV range following additional fluorination, which is important as it restricts any extension of the traditional interpretation scheme.

Table 1

The binding energy shift, Gaussian FWHM and area relative to the bulk Si 2p component determined from the fitting procedure for each of the core-level components shown in Fig. 1; also included is the coverage of each of the SiF$_n$ species, in monolayers (ML), where 1 ML is defined as the number of atoms on an unreconstructed Si(111) surface

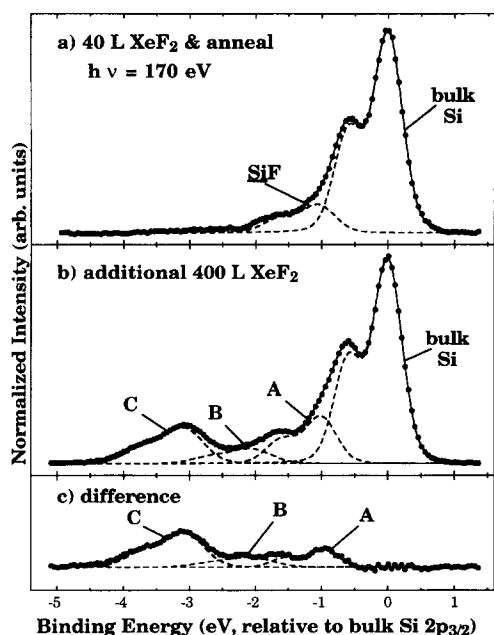|	Shift (eV)		Width (eV)		Area		Coverage (ML)	
	40 L and anneal	Additional 400 L	40 L and anneal	Additional 400 L	40 L and anneal	Additional 400 L	40 L and anneal	Additional 400 L
Bulk Si	—	—	0.47	0.46	1.00	1.00	—	—
A	−1.05	−1.00	0.55	0.51	0.16	0.25	0.49	0.69
B	−2.00	−2.04	—	0.65	—	0.09	—	0.25
C	−3.01	−3.07	—	0.63	—	0.22	—	0.52

Fig. 1. Si 2p SXPS spectra collected from (a) a Si(111)-7 × 7 surface exposed to 40 L of XeF$_2$ and then lightly annealed, and (b) the same surface following an additional 400 L XeF$_2$ exposure. Points are the background-subtracted raw data. Dashed lines are the individual chemically shifted components, as determined via fitting. Solid line is the sum of these components. Each spectrum is normalized so that the bulk Si component has unit area. (c) The difference between parts (a) and (b), fitted with the same components as in (a) and (b).

Fig. 2. Possible species present on Si(111) following moderate fluorination.

Some of the fluorosilyl species expected on the basis of previous investigations to form on a moderately fluorinated Si surface are illustrated in Fig. 2. Following light XeF$_2$ exposures, only small amounts of SiF, SiF$_2$ and SiF$_3$ form [9]. L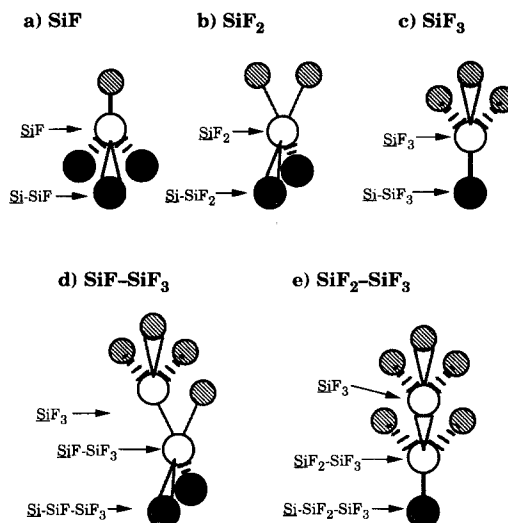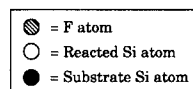arger exposures, however, generate a surface capped with −SiF$_3$ groups, some of which are thought to terminate tree-like structures, as shown in Figs. 2c and 2d [6].

For fluorinated Si, using the traditional approach, the shifts of ∼1, 2 and 3 eV are straightforwardly assigned to mono-, di- and trifluorinated Si, respectively. The 1 eV-shifted peak in Fig. 1a must be SiF; there is simply no other choice. Similarly, peak C must correspond to SiF$_3$; there is no other plausible way to account for such a

large BE shift. From these two considerations it follows that monofluorinated Si (S̲iF or S̲iF–SiF$_3$) and difluorinated Si (S̲iF$_2$ or S̲iF$_2$–SiF$_3$) are valid candidates for peaks A and B, respectively. Adopting these assignments, which exclude any remote inductive effects, it is clear that a proper proportion of the structures shown in Fig. 2 can account for the relative intensities of the shifted components in Fig. 1b.

We now construct a model that assumes, as in Ref. [26], that the remote inductive effects of second-nearest-neighbor F atoms are substantial. First, it is assumed that for relatively low exposures, as in Fig. 1, the substrate consists of predominantly unreconstructed (111)-like planes. It is also assumed that, since F and O atoms have similar electronegativities, and since they induce nearly identical Si 2p chemical shifts, the assignment rules for the oxide and fluoride systems are substantially the same. All of the conclusions concerning remote inductive effects given in Ref. [26] are therefore adopted, with –SiF$_x$ groups assumed to have the same effects as the corresponding –SiO$_x$ groups.

Proceeding on this basis, it is assumed that an –SiF$_3$ group induces a shift of 1 eV if it binds to either a substrate atom, as in the configuration shown in Fig. 2c, or to a monofluorinated species as in the configuration shown in Fig. 2d. The case of the configuration shown in Fig. 2e, the effect of an –SiF$_3$ group on an –SiF$_2$ group has no direct analog in Ref. [26]; the most consistent assumption is an additional 1 eV.

Two configurations in Fig. 2 involve a difluorinated silicon atom attached directly to a substrate atom. In Fig. 2b this happens directly, whereas in Fig. 2e it is part of a fluorosilyl tree. For the oxide case it was judged (in what was clearly a close call) that a single Si^{2+} neighbor induces a negligible shift. This view is also adopted in the present case.

The rest of the shifts illustrated in Fig. 2 are considered to be unresolvable from the bulk signal. The shift expected for S̲i–SiF Fig. 2a has a reasonably close analog in the S̲i–SiO configurations of Ref. [26], where it was concluded that the signal from Si atoms attached to two –SiO groups cannot be resolved from that of bulk Si. Si(111),

in contrast to Si(100), allows for three such neighbors. The surface giving rise to the spectrum in Fig. 1a, is however, only half covered so that, given a random site distribution, there should be relatively few such configurations. SiF coverages larger than that shown in Fig. 1a do not occur, as no more than about 0.3 ML of SiF forms, typically, before significant amounts of higher fluorides appear [6]. In any case, the operational definition of a non-zero shift is spectroscopic resolvability, which depends on the linewidth of the bulk Si component. In the oxide spectra this width is ~0.3 eV, whereas in Fig. 1a it is 0.47 eV, allowing substantially larger shifts to escape detection. Finally, the effect of attachment of the fluorosilyl tree of Fig. 2d on the S̲i–SiF–SiF$_3$ BE is also judged to be negligible, as this case is identical to S̲i–SiF if no more than second-nearest-neighbor atoms are considered.

With this expanded set of assignment rules, it is indeed possible to construct an alternative model that adequately describes the data. As before, the 1 eV-shifted peak in Fig. 1a must be S̲iF, as there is no other choice. To assign the features in Fig. 1b, a model employing the fewest moieties is proposed. From Table 1, it can be seen that 0.69 ML of 1 eV shifted Si, 0.25 ML of 2 eV shifted Si and 0.52 ML of 3 eV shifted Si must be accounted for. This can be done with three of the configurations in Fig. 2: 0.42 ML of the configuration shown in Fig. 2a accounts for 0.42 ML of 1 eV shift, 0.27 ML of the configuration shown in Fig. 2c accounts for 0.27 ML of 3 eV shift and an equal amount of 1 eV shift via remote induction, and 0.25 ML of the configuration shown in Fig. 2d accounts for 0.25 ML of 3 eV shift directly and 0.25 ML of 2 eV shift via a remote induction on S̲iF–SiF$_3$ (see Table 2). Clearly, there are other possibilities that would also give the same observed intensities. For example, one could include some portion of –SiF$_2$ or –SiF$_2$–SiF$_3$ groups. Note that as long as the surface remains reasonably smooth, there is little danger of forming configurations such as FSi–Si–SiF$_2$, which might yield chemical shifts of less than 1 eV.

Thus, it is possible to construct a model of the reacted F–Si surface using assignment rules that

Table 2
The coverage of each species contributing to the intensities of the three core-level components in Fig. 1b, representing a possible model which includes remotely induced shifts

	Component		
	1 eV	2 eV	3 eV
SiF (ML)	0.42	—	—
Si–SiF$_3$ (ML)	0.27	—	0.27
SiF–SiF$_3$ (ML)	—	0.25	0.25
Total	0.69	0.25	0.52

are expanded to include remote inductive effects in a manner consistent with the experimental data. Perhaps this is not too surprising, since this model is not very different from the standard picture. But, which of the two approaches is correct? The answer will probably have to wait for better characterization of the silsesquioxane adsorption geometry to determine whether the structure deduced in Ref. [24] is valid. Until then, it is comforting to note that the structural model for the F–Si system, with fluorosilyl trees capped by –SiF$_3$ groups, is at least qualitatively correct, if not entirely accurate in a quantitative sense.

In closing, there is insufficient experimental evidence at this time to warrant the universal adoption of an expanded set of assignment rules, as it relies entirely upon the observation and interpretation of an anomalous shift of 1 eV in the oxide cluster spectra. As discussed above, the acceptance of this interpretation at face value implies that a number of other configurations should also produce remotely-induced shifts. Unfortunately, there are as yet no well-defined model systems which can be used to evaluate these possibilities. Instead, a mixture of semi-empirical arguments and guesswork must be employed, which is clearly unsatisfactory. The primary reason for considering an expansion of the assignment rules is to have a single theoretical framework for two very similar systems. If the analysis of core-level spectra of the silicon oxide and silicon halide systems is governed by the same principles (as it should be), then a simple dismissal of the extended assignment scheme because of a lack of evidence leaves unresolved problems in its wake. The standard scheme,

although attractive by virtue of its simplicity, is confronted, in the Si–SiO$_3$ shifts for silsesquioxanes, with a result that appears directly to contradict its predictions. This result, whether or not one believes it arises from the remote inductive effects of second-nearest-neighbor atoms, still casts doubt on any quantitative conclusions derived using the standard scheme. Even if it is conceded not to arise from remote inductive effects and is somehow "anomalous", it remains imperative to understand the origin of the "anomaly" sufficiently well to predict where it will and will not occur.

Acknowledgements

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