

Chemical Selectivity in Photon-Stimulated Desorption of Fluorine from Silicon

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Photon-stimulated desorption of F^+ from Si(111) was studied with use of photon energies in the region of the Si $2p$ core level. Fluorinated surfaces with variable amounts of SiF_x groups were prepared, and distinct photon-stimulated-desorption thresholds in the Si $2p$ region were observed for F^+ desorption from SiF vs SiF_3 surface groups. In addition, the angular distributions of the ejected F^+ showed variations with respect to the Si(111) surface normal dependent on the bonding configuration, which were used to obtain local $2p$ absorption spectra for the individual SiF_x groups.

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The process of stimulated desorption of positive ions from surfaces has been used extensively as a means for the investigation of the local electronic structure and bonding geometries of adsorbed species.¹ We report here results from a study of photon-stimulated desorption (PSD) of F^+ from Si(111) in which desorption occurs as a direct result of the ionization of the $2p$ core level of the Si atom to which the fluorine is bonded. We observe that the desorption yield versus photon energy is dependent on the oxidation state of the bonding atom. This is the first observation of such a chemically selective mechanism in a stimulated-desorption process. In addition, the angular dependence of the PSD is used to obtain local absorption spectra at the different surface sites. This is the first demonstration of the use of PSD to obtain site-specific absorption spectra. These results suggest the use of synchrotron radiation for performing bond-selective chemistry.

Photoemission, photoabsorption, and PSD measurements were performed on beamline UV-8b at the National Synchrotron Light Source, employing an ellipsoidal mirror analyzer for the detection of both electrons and ions.² This analyzer is angle integrating with an 85° acceptance cone. Si(111) samples (p type, B doped, 1 ohm cm) were cleaned in ultrahigh vacuum (UHV) by thermal annealing to approximately 1050°C until Si $2p$ core-level and valence-band photoemission spectra representative of the clean Si(111)- 7×7 surface were obtained.³ Photoemission spectra were used to determine the oxidation states of the surface atoms in a way previously described,⁴ in which a shift of the Si $2p$ core level of approximately 1 eV per attached fluorine atom was observed. A 50-L XeF_2 exposure [1 L (langmuir) = 10^{-6} Torr sec] produced a surface composed of nearly equal amounts of SiF and SiF_3 units, along with a small amount of SiF_2 (see the bottom panel of Fig. 3). Annealing of this surface to 300°C resulted in the formation of a surface composed of only SiF groups (see the bottom panel of Fig. 1).

Photoabsorption measurements were made by monitoring of the yield of secondary electrons at a kinetic en-

ergy of 25 eV. This kinetic energy was chosen so as to maximize the surface sensitivity of the absorption measurements.⁵ PSD measurements were made by reversal of the polarity of the electron-energy-analyzer optics so that positive ions were detected. The positive-ion yield measured was due entirely to F^+ , as it is well known that the electron-stimulated-desorption (ESD) and PSD yields of F^+ are much larger than the yields of other species which could possibly contribute to the ion signal, such as oxygen or other halogens.⁶ Additionally, if there were other contaminants which could contribute to the desorption signal, they would have been observed on the surface with photoemission. ESD studies using mass analysis showed that F^+ (as opposed to a fluorosilyl species such as SiF_3^+) was the major species which desorbs from Si.^{7,8} As an additional check, no ion emission was observed from the clean surface, an indication that the ions were in fact a result of the XeF_2 exposures. The kinetic energy distributions of the ions which desorbed from these surfaces had a FWHM of approximately 1.5 eV and were centered at 2.2 eV, in agreement with Ref. 7.

The top panel of Fig. 1 shows the PSD excitation spectra, collected with the sample normal pointing directly into the analyzer, along with the photoabsorption spectrum for the sample which was exposed to XeF_2 followed by annealing to 300°C . The bottom panel of Fig. 1 shows the Si $2p_{3/2}$ and $2p_{1/2}$ photoemission spectra collected from this sample. The numerical spin-orbit deconvolution was performed in order to reduce the clutter of the data and to make the existence of a single type of fluorinated surface atom readily apparent. The photoemission spectra are shown with reference to the conduction-band minimum (CBM) so that they can be aligned with the absorption spectrum in the manner shown in Fig. 1.

The photoabsorption spectrum in Fig. 1 shows an onset at approximately 100 eV which corresponds to absorption of a photon from the bulk Si $2p_{3/2}$ core level to the CBM.^{5,9} There is a dashed vertical line drawn from the bulk Si $2p_{3/2}$ photoemission peak to the absorption

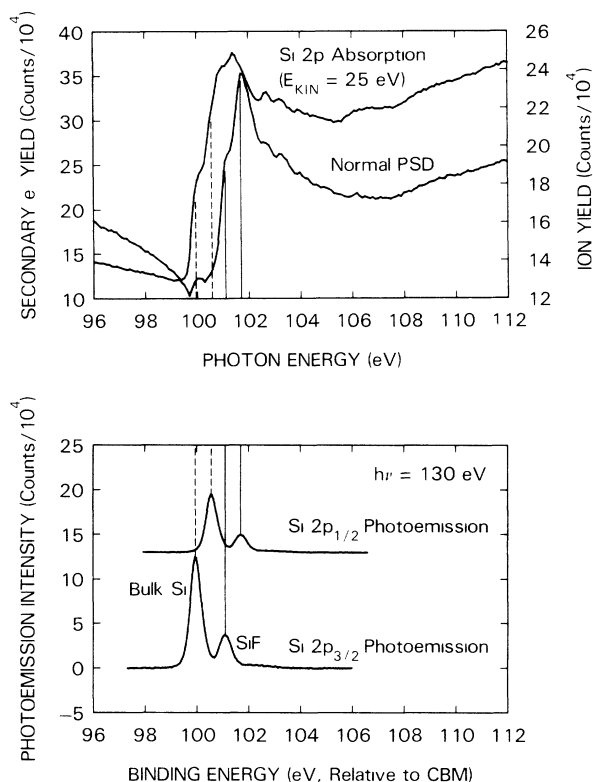


FIG. 1. Upper panel: Photoabsorption and normal PSD spectra of a Si(111) surface after exposure to 50 L of XeF₂ and annealing to 300 °C. Lower panel: Si 2*p* photoemission spectrum of this surface after background subtraction and deconvolution of the spin-orbit components.

edge to indicate this transition. The corresponding transition from the 2*p*_{1/2} level to the CBM is also shown with a dashed line. The shoulder which exists on the 2*p* edge is thus a result of the spin-orbit splitting (0.61 eV) of the 2*p* core level. The PSD spectrum in Fig. 1 shows a small peak at the same photon energy as the bulk 2*p*_{3/2} → CBM transition (≈100 eV) and a larger peak which shows the spin-orbit splitting in an analogous manner as the bulk 2*p* edge, but is shifted approximately 1 eV towards higher photon energy than the bulk 2*p* edge. The position of this peak corresponds exactly with the transition from the 2*p* level of the fluorinated Si atom to the CBM, as shown by the solid vertical lines in Fig. 1. Note that the intensities of both the absorption spectrum and the PSD spectrum do not drop to zero prior to the 2*p* onsets. This is due to absorption both by the valence band and by lower-lying core levels (e.g., F 2*s*). In fact, the desorption threshold for F⁺ from Si has been measured at about 28 eV.^{7,8}

There are two types of excitation mechanisms by which F⁺ desorption can take place at the 2*p* edge which are indicated by the data of Fig. 1. The first is an indirect desorption mechanism whereby the secondary electrons which are created upon the absorption of a

photon induce an ESD process. This mechanism should produce a desorption spectrum that is essentially identical to the absorption spectrum of the sample, since the secondary electron yield is proportional to the absorption. This indirect mechanism is responsible for only a small fraction of the observed F⁺ flux, however, as evidenced in Fig. 1 by the small peak in the PSD spectrum that has an onset at the same photon energy as the bulk absorption spectrum (near 100 eV).

The second PSD mechanism is a direct desorption process initiated by ionization of the 2*p* core level of the bonding Si atom. In contrast to the first PSD mechanism discussed, the second mechanism will produce a spectrum that is representative of the absorption of the individual Si atom to which the F atom was bonded. Since the position of the large peak in the PSD spectrum corresponds with the 2*p* → CBM transition of the shifted Si atom, it is reasonable to conclude that the F⁺ desorption associated with this peak is the result of the direct ionization of that atom. The Si 2*p* hole formed by this ionization process can decay by intratomic and interatomic Auger processes. Given the highly polar nature of the Si–F bond, in order for F⁺ desorption to occur, an interatomic process should place two holes on the fluorine.⁸ As recent calculations have shown,¹⁰ the resulting state is repulsive and would lead to F⁺ desorption.

The PSD yield is proportional to the probability for 2*p* ionization, and it is thus a convolution of the initial 2*p* core level and the local density of final states above the CBM. This is in contrast to photoemission, in which the final states are chosen far enough above the CBM so as to preclude any final-state distortions of the peaks. The width of the direct PSD peak shown in Fig. 1 is nearly the same as the width of the SiF photoemission peak, which indicates that there is little structure in the local density of final states for this species.

The preceding discussion implies that, with the exception of the small indirect desorption peak, the PSD spectrum of Fig. 1 is a measure of the photoabsorption of the monofluoride silicon atom. In principle, this conclusion can be verified by comparing the PSD spectrum to the difference of the absorption spectra for the clean and F-covered surfaces. In practice, however, this is a difficult procedure, particularly with respect to the manner in which the spectra are normalized. The top panel of Fig. 2 shows absorption spectra for clean silicon and for the monofluoride surface. These spectra were normalized to each other using the intensity just prior to the absorption edge and the intensity of the bulk 2*p*_{3/2} → CBM absorption edge. The latter is a bulk feature, and should thus provide a reasonable point for normalization, but the former is a baseline consisting of secondary electrons emitted as a result of exciting lower-lying states. This baseline is significantly different for the fluorinated and nonfluorinated surfaces, as the F 2*s* and 2*p* levels are responsible for some of this secondary-electron intensity.

The position of the first normalization point was thus chosen so as to produce a reasonable agreement with the PSD spectrum, as shown in the bottom panel of Fig. 2.

The absorption spectra in the top panel of Fig. 2 are thus shown with respect to each other after the employment of the above normalization procedure. Note that following the edge, the absorption is consistently higher in the fluorinated surface than on the clean surface. In the bottom panel, the difference between the two absorption spectra is shown as the solid line. The dip in the absorption difference just prior to 100 eV occurs because the surface state that existed on the clean Si(111) has been eliminated by the fluorine bonding. At about 101.8 eV, a peak is seen in the difference curve that represents the additional absorption due to the monofluoride species. Shown as a dashed line along with the difference plot is the PSD spectrum. The agreement between the absorption difference and the PSD spectrum indicates, at least qualitatively, the validity of employing PSD spectra as a measure of site-specific absorption. In effect, the PSD spectrum is a much better means for obtaining site-specific absorption than is the difference procedure, as there are no assumptions concerning the subtraction of the bulk absorption which can alter the results.

The data presented in Figs. 1 and 2 demonstrate how PSD can be used for localized absorption measurements, although the surface employed had only one type of fluorosilyl species present. The real utility of employing PSD in this manner is evident when one measures a sur-

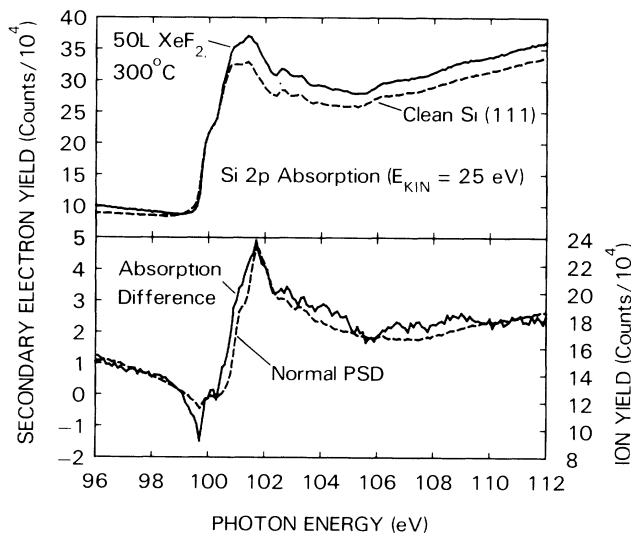


FIG. 2. Upper panel: Photoabsorption spectrum for the surface shown in Fig. 1 along with the photoabsorption spectrum collected from a clean Si(111)-7 \times 7 surface. These spectra were normalized to each other just prior to the 2*p* edge and at the feature which represents the bulk 2*p*_{3/2} edge. Lower panel: Difference between the two absorption spectra (solid line), and the PSD spectrum (dashed line).

face containing more than one type of adsorbate group, such as the surface resulting from a 50-L XeF₂ exposure prior to annealing. In this case, the angular distributions of the desorbing ions can be used to separate out the monofluoride from the trifluoride signal. It is well known from ESD studies that ions desorb from a surface along a direction which is related to the direction of the ruptured bond.^{7,11} This effect has also been observed in PSD.¹² Therefore, if the monofluoride species were to have a different bond direction than the multiple fluoride species, by the observation of the PSD along a particular exit direction, site-specific absorption at different surface sites can be directly measured with PSD.

The PSD spectrum collected in the normal direction from the surface containing SiF and SiF₃ (dashed line in the upper panel of Fig. 3) is, within the experimental accuracy, absolutely identical to the PSD spectrum collected from the purely monofluoride sample shown in Figs. 1 and 2, indicating that for normal collection, only F⁺ from SiF species is observed. Also shown in Fig. 3 is the PSD spectrum collected at off-normal emission from this surface. The off-normal data were collected by the rotation of the sample 65° from the normal collection position. Because of the large acceptance of the detector, however, the PSD of each particular type of adsorbed Si cannot be completely separated with this instrument. Therefore, the data labeled "Off-Normal PSD" in Fig. 3 were obtained by subtraction of the residual normal PSD contribution from the raw spectrum collected at 65°. The raw data are thus the sum of the normal and off-normal PSD shown in Fig. 3. (These curves are drawn to scale with respect to each other in the manner used for the subtraction.)

The difference in the photoabsorption between the clean Si(111) and the unannealed F-covered surface is shown in the upper panel of Fig. 3 as a solid line, with a similar background subtraction as in Fig. 2. Note that the difference spectrum in this case shows additional structure following the 101.8-eV peak relative to that found in the case where only monofluoride was present. This additional structure seen in the surface containing multiple fluorides correlates well with the portion of the PSD spectrum that is enhanced at the off-normal collection angle. The fact that this structure is shifted towards higher photon energies, and that a clear onset is seen at a photon energy about 2 eV above the SiF onset, indicates that the main contribution to this additional structure is from the PSD of F⁺ from SiF₃ units. The fact that this additional structure is not a single peak, as in the SiF PSD, indicates that the local density of final states in the region of the SiF₃ groups contains structure not present in the bulk silicon. This local structure is likely a result of the charge "cage" formed by the electronegative F atoms in the SiF₃ units, which leads to "inner well" resonances.¹³ These are quasimolecular excitations, for which, in the present case, a good correspondence is

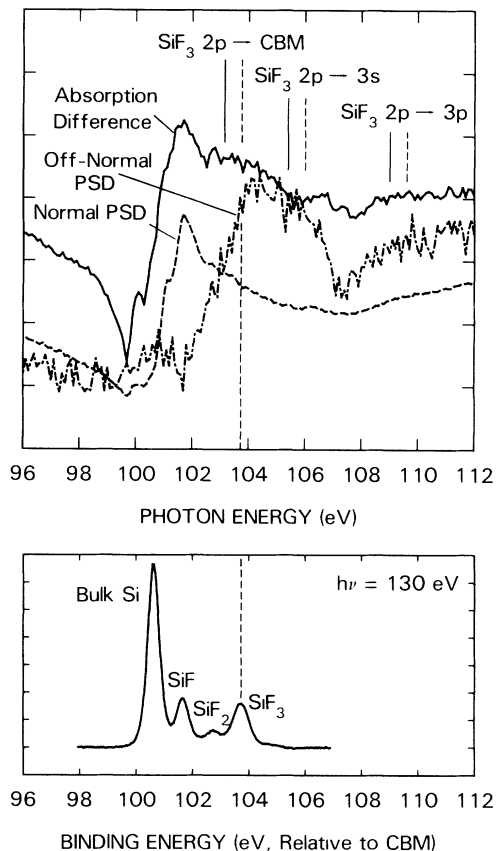


FIG. 3. Upper panel: Difference between the photoabsorption spectrum collected from a Si(111) wafer after a 50-L XeF₂ exposure prior to annealing and a spectrum of a clean Si(111)-7×7 surface (solid line), the PSD spectrum collected in a normal exit direction from this sample (dashed line), and the PSD collected at a 65° angle from normal for this sample (dot-dashed line) after subtraction of the normal component from the data. The vertical lines show the photon energies corresponding to the labeled transitions, with the solid vertical lines representing the 2p_{3/2} initial state and the dashed lines representing the 2p_{1/2} initial state. Lower panel: Si 2p_{1/2} component of the photoemission spectrum of this sample.

found between the structure seen in Fig. 3 and Rydberg-type 3s and 3p excitations observed in the SiF₄ molecule.^{14,15}

In conclusion, it has been demonstrated that a chemical selectivity operates in the photon-stimulated ion desorption of F⁺ from silicon at the Si 2p edge. The PSD excitation spectra obtained provide a direct measurement of the photoabsorption of the bonding atom. F⁺ from SiF species desorb in a direction normal from the sample, an indication that the bond direction for this type of Si-F species is perpendicular to the surface, while PSD from the trifluoride species occurs in an off-normal direction. The local density of final states was found to

be nearly flat for SiF species and to contain structure indicative of Rydberg-type final states for the quasimolecular SiF₃ species.

As the desorption of fluorine from a particular oxidation state is dependent on the photon energy, these results suggest the possibility of synchrotron-driven selective chemistry. By tuning of the radiation to the core-level binding energy of a species in a specific state, that species can be selectively desorbed from the sample. The data presented here demonstrate the feasibility of employing this chemical selectivity to modify the surface composition.

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