Desorption site-specificity and halogen minority sites on Si(1 1 1)

Jan Ingo Flege\textsuperscript{1,2,5}, Thomas Schmidt\textsuperscript{2}, Jan Bätjer\textsuperscript{1}, Mehmet Çakmak\textsuperscript{3}, Gerhard Materlik\textsuperscript{1,4} and Jens Falta\textsuperscript{2}

\textsuperscript{1} Hamburger Synchrotronstrahlungslabor HASYLAB/DESY, Notkestr. 85, 22603 Hamburg, Germany
\textsuperscript{2} Institut für Festkörperphysik, Universität Bremen, Postfach 330440, 28334 Bremen, Germany
\textsuperscript{3} Physics Department, Art & Science Faculty, Gazi Üniversitesi, 06500-Ankara, Turkey
\textsuperscript{4} Diamond Light Source Ltd., Chilton, Oxfordshire OX11 0QX, UK
E-mail: flege@ifp.uni-bremen.de

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Abstract. We identify the SiCl\textsubscript{3} bonding geometry as the most desorption-active site in x-ray photon-stimulated desorption (XPSD) of positive chlorine ions from chlorinated Si(1 1 1) surfaces due to their much higher desorption cross-section in comparison to the on-top majority site. The novel combination of x-ray standing waves (XSW), XPSD and density functional theory (DFT) allows to quantitatively determine this trichloride adsorption geometry with high spatial resolution and to deduce the site-specific desorption cross-sections for Cl\textsuperscript{+} and Cl\textsuperscript{2+} ions, respectively. Additionally, these SiCl\textsubscript{3} groups are shown to exhibit a preferential crystallographic orientation which is confirmed by both XSW and DFT. Moreover, the analogous identification of desorption-active SiBr\textsubscript{3} species for Br/Si(1 1 1) suggests a common physical origin of the site-specific desorption cross-sections.
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1. Introduction

Atomic defect sites are known to play a decisive role in solid-state electronics as well as in surface chemical and catalytic reactions. Up to now, their structural characterization with very high-spatial resolution has presented itself as a formidable task in experimental surface science. This is mainly due to the implicit averaging process of conventional spectroscopic and diffraction techniques which essentially results in a limited sensitivity to defect adsorption sites. If, however, the locally modified electronic structure of the defect adsorption geometry, which is the fundamental key to understanding the underlying physics, could be exploited in such a way that an increased detection efficiency to these sites is reached, then theoretical modelling using three-dimensional experimental data is feasible. In this paper, we will show both the dependence of the atomic-stimulated desorption cross-section on the local bonding geometry of the desorbate and how this phenomenon can be employed in determining the defect adsorbate structure of Cl/Si(111)-(1 × 1) and Br/Si(111)-(1 × 1) using a combined photon stimulated desorption (PSD) and x-ray standing wave (XSW) technique. These two ‘model systems’ have attracted a lot of attention in the study of halogen–silicon interactions [1] because of their possible application in surface passivation and dry etching. Our results not only demonstrate the existence of trichloride and tribromide species far above the commonly believed thermal desorption threshold [2–4], but also a pronounced orientational ordering of the SiCl$_3$ ‘molecules’ which is confirmed by our density functional theory (DFT) calculations.

We have reported earlier [5, 6] on the combination of XSW and PSD as a powerful experimental method for determining the fundamental desorption mechanisms following x-ray photo absorption. Here, we determine the absolute values of the site-specific PSD cross-sections for Cl ions and subsequently extract site-specific ‘escape probabilities’ based on theoretical photoelectric absorption cross-sections. Furthermore, we extend this methodical XSW–PSD approach to achieve structural probing with an extreme surface sensitivity which allows the direct determination of adsorption sites for defect concentrations in the range of a few percentage of a monolayer. The observation of Cl$^{2+}$-ion desorption emphasizes this aspect because these minority adsorption sites are in this particular case almost exclusively desorption-active. Moreover, since XSW for (hkl) Bragg reflections directly yields the (hkl) Fourier components of the corresponding
2. Experimental

The XSW–PSD experiments were performed under ultra-high-vacuum conditions \((p \approx 1 \times 10^{-10} \text{ mbar})\) at the undulator beamline BW1 at the Hamburg Synchrotron Radiation Laboratory HASYLAB using standard non-dispersive setups (see figure 1) at a photon energy of \(3.35 \text{ keV}\). Two pairs of Si(1 1 1) and Si(2 2 0) monochromator crystals, each consisting of a water-cooled symmetric first crystal and an asymmetrically cut second crystal, were used, implying corresponding Bragg angles of \(\Theta_{111} \approx 36^\circ\) and \(\Theta_{220} \approx 75^\circ\), respectively.

While tuning the incident photon energy through the Bragg condition of the sample crystal in a \(\sigma\)-polarized diffraction geometry, the reflectivity and the ion-desorption yield were recorded simultaneously. The desorbing ions were identified by means of time-of-flight spectroscopy [6]. The experimental data for the reflectivity, the photoelectron yield and the ion yield were analysed according to the dynamical theory of x-ray diffraction [7, 8]. Details regarding the structural interpretation of XSW data will be given in section 3.2.

spatial atomic distribution function, these may straightforwardly be compared to calculated Fourier components of defect Cl adsorption geometries as predicted by ab initio DFT.
The in situ preparation of the samples, which was routinely monitored by low-energy electron diffraction (LEED) and photoelectron spectroscopy, proceeded in the following way: Cl/Si(111)-(1 × 1) surfaces were obtained by Cl deposition onto Si(111)-(7 × 7) substrates either at room temperature followed by subsequent annealing at 580°C for 30 s or longer [6] or by Cl₂ saturation exposure at 600°C and 2 min annealing, respectively. Both procedures lead to a change from a sharp (7 × 7) to another sharp (1 × 1) LEED pattern, and no difference between the XSW results for either type of preparation was found.

3. Results and discussion

Before we turn to the analysis of the surface structure and to the topic of PSD, we introduce the Cl/Si(111) system by means of scanning tunnelling microscopy (STM). These STM data provide an easy access to the majority site adsorption geometry and serve to draw the reader’s attention to the existence and possible nature of structural defects. These will turn out to be crucial in the interpretation of the XSW data for photo-desorbed ions.

3.1. Scanning tunnelling microscopy

An STM image of a Si(111) surface chlorinated at 600°C is shown in figure 2. Clearly, the (1 × 1) reconstruction [9] is resolved, but also defects are visible. For clarity, just a few of the structural defects observed are marked by circles. Judging from the location of the defects with respect to the surface registry [10], the defects are located at the on-top position. Interestingly, many defects appear as ‘double peaks’ of non-equal height in the corresponding line scans (see inset of figure 2) along the atomic rows which hints to a rather complex defect geometry. Using a cut-off level which is chosen to separate the on-top sites and the minority sites at about half of their height difference, as indicated in the transparent inset of figure 2, a quantitative estimate yields a defect density of about 0.02 ML of the surface sites for the selected surface area (1 ML = 7.83 × 10¹⁴ cm⁻²). However, from the information gained from the STM image alone, an unambiguous identification of the defect adsorption site is by no means possible. Nevertheless, as the existence of dangling bonds or e.g. co-adsorbed hydrogen atoms seems very unlikely for the kind of preparation used, the presence of SiClₓ species is most probable. This issue will now be addressed employing the XSW technique in combination with PSD.

3.2. XSW and PSD

Although the basic XSW theory dealing with conventional inelastic signals, as e.g. x-ray fluorescence and photoelectrons, has been published elsewhere [11], we repeat the essential ingredients for a standard structure analysis of XSW data. Within this theoretical frame, we will be able to clarify how the conventional reasoning has to be modified if applied to photo-desorbed ions.

In the standard dipole approximation, the outcome of a standard XSW analysis are the so-called coherent fraction $f_{c}^{hkl}$ and coherent position $\Phi_{c}^{hkl}$ which represent the modulus and phase of the $(hkl)$ Fourier component of the distribution function of the atoms contributing to the signal.
under investigation [11], with \((hkl)\) diffraction planes used in the measurement:

\[
f_c^{hkl} \exp(2\pi i \Phi_c^{hkl}) = \frac{1}{N} \sum_{n=1}^{N} D_{n}^{hkl} \exp(i \vec{H} \cdot \vec{r}_n). \tag{1}
\]

Here, \(N\) denotes the total number of contributing atoms located at positions \(\vec{r}_n\) and \(\vec{H}\) the scattering vector, respectively. The site-specific Debye–Waller factor \(D_{n}^{hkl}\) accounts for thermal vibrations around these equilibrium positions, which will be neglected in the following. From equation (1) it is evident that only the non-integer part of \(\Phi_c^{hkl}\) is physically relevant. If only few crystallographically inequivalent bonding sites as defined by their ‘atomic’ coherent position \(\Phi_n^{hkl}\) contribute to the detected signal, then equation (1) may more conveniently be re-written in a so-called \(N\)-position model introducing the individual site-specific surface coverages \(\Theta_n\)

\[
f_c^{hkl} \exp(2\pi i \Phi_c^{hkl}) = \sum_{n=1}^{N} \Theta_n \exp(2\pi i \Phi_n^{hkl}) \quad \text{with} \quad \sum_{n=1}^{N} \Theta_n = 1. \tag{2}
\]

In contrast to equation (1), the sum is taken over all \(N\)-bonding sites which exhibit different \((hkl)\) Fourier components. Now, if one site is highly prevalent, then equation (2) may be replaced by
the following expression describing an effective one-position model:

\[ f_{c}^{hkl} \exp(2\pi i \Phi_{c}^{hkl}) \simeq c \exp(2\pi i \Phi_{1}^{hkl}). \] (3)

The parameter \(0 \leq c \leq 1\) yields the fraction of adatoms precisely located at the position \(\Phi_{1}^{hkl}\). In this special case, the relation \(c = f_{c}^{hkl}\) holds, hence the name ‘coherent fraction’. Equation (3) and its implicit assumptions often provide the basis for the structural interpretation of XSW data and facilitate a bonding site determination by straightforward triangulation.

For photoelectrons employed as the detected inelastic signal (also frequently termed ‘secondary signal’ in the literature), in general, non-dipole contributions have to be taken into account and a generalized expression for the XSW yield needs to be used [12] which may lead to erroneous information on the corresponding Fourier coefficients [13]. However, in our current XSW setup (see figure 1), these higher-order terms in the differential photoelectron absorption cross-section contribute only marginally to the measured photoelectron yield. This has experimentally been verified for the (1 1 1) Bragg geometry employing both Cl 1s photoelectrons and Cl K\(_\alpha\) fluorescence as secondary signals, yielding differences of 0.02 and smaller than 0.01 for the deduced coherent fractions and coherent positions, respectively, well within the error bars.

XSW measurements in (1 1 1) and (2 2 0) Bragg reflection were carried out with Cl 1s photoelectrons and Cl\(^+\) and Cl\(^{2+}\) ions as secondary signals. The associated data are shown in figure 3 along with the corresponding coherent fractions, coherent positions and experimental errors. A straightforward triangulation of the photoelectron data, given by \(\Phi_{Cl-1s}^{111} = 0.78\) and \(f_{Cl-1s}^{111} = 0.81\) in (1 1 1) Bragg reflection and \(\Phi_{Cl-1s}^{220} = 0.89\) and \(f_{Cl-1s}^{220} = 0.85\) in (2 2 0) Bragg reflection, respectively, in a one-position model in conjunction with the three-fold symmetry of the Si(1 1 1) surface confirms the well-known on-top configuration [14]. Here, we note that for on-top adsorption sites on Si(1 1 1), the relation \(\Phi_{on-top}^{220} = \frac{4}{3}(\Phi_{on-top}^{111} - \frac{1}{8})\) follows from basic geometry, in accordance with the XSW data. Additionally, a plane-wave DFT calculation\(^6\) using a supercell with (1 \times 1) surface periodicity yields the corresponding coherent positions \(\Phi_{Cl-1s}^{111} = 0.79\) and \(\Phi_{Cl-1s}^{220} = 0.89\) for the Cl on-top site, in very good agreement with the experimental data.

To elucidate the question what kind of structural information is obtainable with chlorine ions as secondary signal for XSW measurements, an analysis of the contributions of the prevailing desorption mechanisms is required. In the past, only a few PSD experiments following Cl 1s core-level excitation have been performed [15] in connection with a near-edge x-ray absorption fine structure (NEXAFS) analysis, leading to the conclusion that a direct desorption process from the Cl on-top site is preferred. In this contribution, however, we will show that the ion signal is dominated by minority sites which exhibit a geometry that is virtually indistinguishable from the on-top site if the NEXAFS signal is dominated by strong first-shell scattering [15].

As derived in a previous paper [6], in the case of Cl\(^{2+}\) ions direct processes strongly prevail. A comparison between the edge jump of the Cl\(^{2+}\) ion yield while crossing the Cl K absorption edge [6] and the corresponding edge jump of the calculated total Cl photoabsorption cross-section [16] show that almost all Cl\(^{2+}\) desorption events are induced by initial absorption in Cl atoms. For Cl\(^+\) ions, however, indirect contributions, such as x-ray-induced electron-stimulated

\(^6\) Details of the theoretical approach will be discussed in section 3.3 when applied to more complex surface geometries.
Figure 3. XSW data and fit (——) of Cl 1s photoelectron yield (⊙), Cl⁺ (★) and Cl²⁺ (♦) ion yields and reflectivity (×) of Cl/Si(111)-(1 × 1) as a function of the incident photon energy in (1 1 1) (left) and (2 2 0) (right) Bragg reflection at a photon energy of $E_{\text{Bragg}} = 3.35$ keV. All normalized yields are shifted for clarity (Cl 1s: +1, Cl⁺ :+ 2 , Cl²⁺ :+ 3).

desorption (XESD) or stimulated desorption mediated by neighbouring silicon atoms, of approximately 30% have to be considered.

Figure 3 displays the XSW results obtained with Cl⁺ and Cl²⁺ ions and Cl 1s photoelectrons as secondary signals in (1 1 1) Bragg reflection (left) and in (2 2 0) Bragg reflection (right) at an incident photon energy of 3.35 keV, i.e. well-above the Cl K absorption edge. Especially, the results in (1 1 1) geometry are striking since there is a sharp contrast between the photoelectron yield and the ion-yield data, i.e. the coherent position $\Phi_{111}^{\text{Cl}^2⁺} = 0.17$ seems contradictory to the value $\Phi_{111}^{\text{Cl}−1s} = 0.78$. Intriguingly, the measured coherent fractions $f_{111}^{\text{Cl}^2⁺} = 0.81$ and $f_{220}^{\text{Cl}^2⁺} = 0.73$ for Cl²⁺ ions almost meet the requirements of a single adsorption site which is definitely not compatible with the on-top position revealed by the conventional XSW data.

The only answer to this question is the following: besides the well-established on-top site, there exists a second adsorption site for Cl/Si(1 1 1) which exhibits a tremendously higher desorption cross-section than the on-top site, especially in the case of Cl²⁺-ion desorption. Hence, in the special case of ions as inelastic signal, the relative desorption probability $\sigma_n$ for the specific adsorption site $n$ (or, more precisely, excitation channel) has to be taken into account, leading to a more general form of equation (2) for each secondary signal and every measured Fourier component

$$f_{c}^{hkl}\exp(2\pi i \Phi_{c}^{hkl}) = \sum_{n=1}^{N} \kappa_n \exp(2\pi i \Phi_{n}^{hkl}) \quad \text{with} \quad \sum_{n=1}^{N} \kappa_n = \sum_{n=1}^{N} \Theta_n \sigma_n \equiv 1. \quad (4)$$

Thus, if a minority adsorption site exists and if it features a considerably higher desorption cross-section, this site can nevertheless dominate the total ion yield. This additional factor is the reason...
why the use of e.g. Cl 1s photoelectrons and Cl$^{2+}$ ions does provide complementary information about the adsorbate structure.

Based on equation (4), we can treat the present situation as the special case of an ion yield originating from two inequivalent sites labelled $\alpha$ and $\beta$ by direct processes with Fourier components $f_{hkl}^{\alpha,\beta} \equiv f_{hkl}^{\alpha,\beta} \exp(2\pi i \Phi_{hkl}^{\alpha,\beta})$ or resulting from excitations mediated by the Si substrate (XESD), leading to an effective three-position model

$$\mathcal{F}_{\exp}^{hkl} = (1 - \lambda)[\mathcal{F}_{\alpha}^{hkl} + (1 - \kappa)\mathcal{F}_{\beta}^{hkl}] + \lambda \mathcal{F}_{\text{Si}}^{hkl}. \tag{5}$$

The left-hand side of equation (5) represents the measured data. $\lambda$ denotes the fraction of indirect contributions to the signal and $\kappa$ is the contribution of site $\alpha$ to the direct signal. For simplicity, statistical disorder has been omitted. This general equation is valid for both photoelectrons and ions as secondary signals since we obtain the special case of photoelectrons by using $\lambda = 0$ and substituting $\kappa = \Theta_{\alpha}/(\Theta_{\alpha} + \Theta_{\beta})$ with $\Theta_{\alpha,\beta}$ denoting the surface coverage of the chlorine atoms belonging to $\alpha$ and $\beta$, respectively. However, for PSD as secondary signal $\lambda$ is in general nonzero, and $\kappa$ depends both on the coverage ratio $\Theta_{\beta}/\Theta_{\alpha}$ and the ratio of the desorption cross-sections $\sigma_{\beta}/\sigma_{\alpha}$ of the site $\beta$ versus $\alpha$

$$\kappa = \frac{\Theta_{\alpha}\sigma_{\alpha}}{\Theta_{\alpha}\sigma_{\alpha} + \Theta_{\beta}\sigma_{\beta}} = \frac{1}{1 + \frac{\Theta_{\beta}\sigma_{\beta}}{\Theta_{\alpha}\sigma_{\alpha}}}. \tag{6}$$

Hence, equation (5) can be applied to a complete data set consisting of the XSW spectra obtained for Cl 1s photoelectrons and Cl$^+$- and Cl$^{2+}$-ion desorption recorded in (1 1 1) and (2 2 0) Bragg reflection, consequently leading to a set of coupled equations.

From here, two different approaches for the data analysis may be taken. On one hand, the optimum parameter set fulfilling equation (5) can be determined model-free by least-squares fitting procedures in which the ‘atomic’ coherent positions, i.e. the atomic coordinates, are treated exactly in the same way as the mixing parameters $\kappa$ and $\lambda$. However, due to the limited number of independent equations only a few atomic coordinates may be refined in this scheme. On the other hand, a more sophisticated approach is to use positions $\Phi_{hkl}^{\alpha,\beta}$ as calculated by ab-initio DFT for trial defect geometries. Furthermore, if only contributions by XESD processes to the indirect desorption channel are considered, then $\lambda$ is given by the inverse edge jump $\lambda = 1/\eta$ [6]. If the effect of thermal vibrations is neglected as well, then only fitting of the mixing parameter $\kappa$ for each secondary signal is necessary.

Before we present the results of the XSW–PSD analysis, a detailed comment on the sources of possible uncertainties and experimental errors is required. Actually, the least important errors are the experimental errors due to the Poisson statistics arising from the data collection. These errors induce uncertainties in the coherent fractions and coherent positions smaller than 0.01 for the individual sample investigated. However, additional errors arise from possible fluctuations of experimental parameters during sample preparation such as deposition temperature or evaporation rate which are expected to have a substantial impact on the formation of structural defects. Hence, the errors given in figure 3 result from averages of nominally identically prepared samples. In this respect, it is noted that the errors for the coherent fractions are generally higher than for the coherent positions in case of photo-desorbed ions as secondary signal. Another source of errors in the structural analysis originates from mixing of several positions as laid out in equation (2), which leads to increased uncertainties $\delta f_{\alpha}^{hkl}$ and $\delta \Phi_{\alpha}^{hkl}$ for the calculated Fourier
coefficients. Consider e.g. two adsorption sites $\alpha$ and $\beta$ which differ in the respective coherent positions by $\Delta \Phi \equiv \Phi_{hkl}^{\alpha} - \Phi_{hkl}^{\beta} = 0.5$ and whose coherent positions $\Phi_{hkl}^{\alpha,\beta}$ bear uncertainties of $\delta \Phi_{hkl}^{\alpha,\beta} = 0.01$ each. Then, a mixture according to equation (2) results in errors of $\delta f_{c}^{hkl} = 0.06$ and $\delta f_{hkl} = 0.02$, respectively, simply due to Gaussian-error propagation. Concluding this paragraph on error analysis, the calculated coherent fractions are more prone to deviations than the respective coherent positions and thus have to be regarded less reliable.

3.3. DFT and structure models

The DFT calculations employing norm-conserving pseudo-potentials \cite{17, 18} were performed in a repeated slab geometry consisting of a $(4 \times 4)$ surface unit mesh and six Si substrate layers plus H passivation on the backside. Ground-state geometries were obtained using a plane-wave cut-off of 16 Ryd and a $(3 \times 3 \times 1)$ grid of $\vec{k}$ points. As possible point defects, mono-, di- and trichlorides were taken into account. Step-edge sites could be ruled out due to the very low-step density found in large-scale STM images (not shown here) as well as because of the large discrepancy between the calculated and the measured Fourier coefficients.

A side view and a top view of the DFT-relaxed structure for the SiCl$_3$ configuration are presented in figures 4 and 5 (left panel). This structural element was found to yield the best fitting to the experimental values as will be discussed in more detail in a later paragraph. The SiCl$_2$ model (see e.g. \cite{4}) could rigorously be excluded due to the very low calculated coherent fraction of $f_{220}^{\text{SiCl}_2} = 0.11$, which is utterly incompatible with the experimental results for $f_{220}^{\text{Cl}}$ and $f_{220}^{\text{Cl}_2}$. The bonding angle in the trichloride is very close to the tetrahedral angle as expected for an sp$^3$-like hybridization. Specifically, the trichloride species is found to be orientated in a way such that the projected bonds between the central Si and the surrounding Cl atoms point along the $(\bar{1} \bar{1} 2)$ directions (figure 5, left panel). This particular azimuthal orientation will be denoted as ‘A type’ in the following. The related SiCl$_3$ bonding geometry is defined by a 60° rotation around the vertical symmetry axis (see figure 5, right panel) and will be referred to as ‘B type’, accordingly.

The calculated coherent fractions and coherent positions for the optimal mixture of on-top sites and SiCl$_3$ species are given in table 1. The fitted relative coverage of Cl atoms

![Figure 4](http://www.njp.org/)

**Figure 4.** Side view of the SiCl$_3$ adsorption geometry as incorporated into a $(4 \times 4)$ supercell within the DFT calculations. Cl atoms at on-top sites and SiCl$_3$-A sites are marked by green- and blue-shaded circles, respectively.
A type B type

Figure 5. Top views (two BL substrate visible) of the SiCl$_3$-A (left) SiCl$_3$-B (right) adsorption geometries as incorporated into (4 × 4) supercells within the DFT calculations. Cl atoms at on-top sites and in SiCl$_3$-A/B geometry are marked by green- and blue-shaded circles, respectively.

Table 1. Theoretically and experimentally (in parentheses, with errors) determined XSW Fourier coefficients for a surface structure composed of Cl on-top sites as well as SiCl$_3$ defects. The experimental values have been obtained from averages over nominally identically prepared samples. For a discussion of the uncertainties of the calculated coherent fractions and coherent positions, see text.

|          | $f^{111}$      | $\phi^{111}$ | $f^{220}$      | $\phi^{220}$ |
|----------|----------------|--------------|----------------|--------------|
| Cl 1s    | 0.81 (0.79 ± 0.02) | 0.79 (0.78 ± 0.01) | 0.92 (0.85 ± 0.02) | 0.88 (0.88 ± 0.01) |
| Cl$^+$   | 0.47 (0.55 ± 0.01) | 0.14 (0.13 ± 0.02) | 0.46 (0.51 ± 0.03) | 0.87 (0.90 ± 0.01) |
| Cl$^{2+}$| 0.72 (0.82 ± 0.03) | 0.22 (0.19 ± 0.02) | 0.59 (0.73 ± 0.05) | 0.86 (0.89 ± 0.03) |

in trichloride coordination amounts to $\kappa_{\text{Cl} - 1s} \approx 0.09 ± 0.02$. Since $\kappa_{\text{Cl} - 1s}$ accounts for each of the three Cl atoms residing in trichloride coordination, dividing by three yields a SiCl$_3$ defect coverage of about 0.03 ML which is in good agreement with the coverage estimated from STM.

The sole mixture of the on-top site and the SiCl$_3$-B species resulted only in a very poor fit to the experimental data, which is easily realized by inspection of the calculated coherent position for the SiCl$_3$-B defect in (2 2 0) geometry, $\Phi^{220}_{\text{SiCl}_3\text{-B}} = 0.18$. Consequently, if contributions of on-top sites and both SiCl$_3$-A and SiCl$_3$-B groups are taken into account for the XSW analysis, then only a marginal fraction of about 16% of B-orientated SiCl$_3$ complexes is found according to the best-fit solution as presented in table 1. This fitting relies on the assumption that the probabilities for PSD from A-type and B-type species are identical. This constraint is reasonable since the DFT-calculated Si–Cl bond lengths within the SiCl$_3$ species and the Si–SiCl$_3$ back bond differ only by less than 0.01 Å for the A-type and the B-type bonding geometries. Therefore, the XSW analysis reveals a strong prevalence of the A-type orientation at room temperature, which
is supported by a binding energy lowered by 69 meV with respect to the B type. This rotational crystallographic ordering has neither been reported nor predicted yet for the halogen–silicon system.

3.4. Site-specific desorption cross-sections

Having established the trichloride adsorption site as the bonding geometry acting most favourably in PSD experiments, we now turn to the quantitative analysis of the site specificity. The best fit for the ion data was obtained with mixing parameters $\kappa_{\text{Cl}^+} \approx 0.79$ and $\kappa_{\text{Cl}_2^+} \approx 0.91$, respectively. From these values and using equation (6), the corresponding ratios $(\sigma_{\text{SiSiCl}_3}/\sigma_{\text{SiCl}})$ of the site-specific desorption cross-sections are calculated to be $34 \pm 7$ and $97 \pm 24$ for $\text{Cl}^+$ and $\text{Cl}_2^+$ ions, respectively. Furthermore, a separate measurement of the absolute incident photon flux $J$ using published experimental calibration data for the quantum efficiency of Au [19] allows us to calculate the absolute desorption cross-sections by virtue of the general definition:

$$\sigma_{X, \alpha, \beta} \equiv n_X/(J\Theta_{\text{Cl}}^{\alpha, \beta}) \quad \text{with} \quad X = \{\text{Cl}^+, \text{Cl}_2^+\},$$

Taking into account the detection rates $n_X$, the site-specific Cl coverage per unit area $\Theta_{\text{Cl}}^{\alpha, \beta}$ and the ion-detection efficiency $\varepsilon$. Hence, the absolute site-specific desorption cross-sections ($1\text{ b} = 10^{-28} \text{ m}^2$) amount to:

$$\begin{align*}
\sigma_{\text{SiCl}}^{\text{Cl}^+} &= (13 \pm 6)\text{b}, \\
\sigma_{\text{SiSiCl}_3}^{\text{Cl}^+} &= (460 \pm 210)\text{b}, \\
\sigma_{\text{SiCl}}^{\text{Cl}_2^+} &= (0.15 \pm 0.07)\text{b}, \\
\sigma_{\text{SiSiCl}_3}^{\text{Cl}_2^+} &= (14 \pm 7)\text{b},
\end{align*}$$

respectively.

Assuming that the initial photoabsorption and the desorption event following core–hole excitation may be treated as independent processes, we may define the site-specific probability for desorption $p_{\alpha, \beta}$ after photoexcitation as follows:

$$p_{\alpha, \beta} \equiv \sigma_{X, \alpha, \beta}/\sigma_{\text{ph}, \text{K}}.$$

Hence, using the calculated [20] photoabsorption cross-section in the Cl 1s level, $\sigma_{\text{ph}, \text{K}} = 5.95 \times 10^4 \text{ b}$, the respective desorption probabilities for the on-top site and the trichloride site can be obtained as:

$$\begin{align*}
p_{\text{SiCl}}^{\text{Cl}^+} &= 2 \times 10^{-4}, \\
p_{\text{SiSiCl}_3}^{\text{Cl}^+} &= 8 \times 10^{-3}, \\
p_{\text{SiCl}}^{\text{Cl}_2^+} &= 3 \times 10^{-6}, \\
p_{\text{SiSiCl}_3}^{\text{Cl}_2^+} &= 2 \times 10^{-4}.
\end{align*}$$

In order to explain this enhanced desorption probability for Cl ions from the SiCl$_3$ adsorption site, some general theoretical background on desorption induced by electronic excitations is provided: in essence, the atomic desorption cross-section is determined by the bandwidth $\Delta E$ for localized multi-hole states [21]. If $\Delta E$ is sufficiently small, the resulting lifetime $\Delta t \sim h/\Delta E$ for this localized excitation (also known as ‘small polaron’ in the literature) is long enough to

7 In a simple semi-classical model using Boltzmann statistics this would result in occupation probabilities at room temperature of 0.93 and 0.07 for the A and B type, respectively, strengthening the experimental result of a highly prevalent occupation of B-orientated SiCl$_3$ complexes.
allow for the desorption to proceed. Now, in a simple LCAO picture of molecular binding, the single-hole bandwidth is proportional to the overlap integral between adjacent atomic sites and the corresponding two-hole bandwidth to about its squared value, respectively.

In the present case of PSD from SiCl$_3$/Si(1 1 1), there are several indications in favour of this scheme to be valid qualitatively: firstly, the theoretical approach boils down to a very simple observation that the Cl atoms are much further away from the surface which manifests itself in a decreased overlap and hence a reduced probability for reneutralization or recapture. Secondly, assuming that relaxation/recombination processes are nearest-neighbour processes and that the number of ‘active’ nearest neighbours is given by the number of surrounding atoms covalently bonded to the excited atom, then the average Si coordination of the Cl atoms in the trichloride site is much smaller since there is only one second-nearest Si neighbour instead of three in the monochloride case. Thirdly, the decreased overlap between the trichloride and the substrate manifests itself in a stretched Si–SiCl$_3$ bond length of 2.42 Å (DFT) as compared to the Si–Si bulk value of 2.34 Å (DFT). Although the Si–Cl bond length in the SiCl$_3$ molecule is shortened by 0.03 Å, which points to a slightly more ionic character of the Si–Cl bond, the reduced overlap between the trichloride and the underlying substrate should be decisive.

3.5. Extension to Br/Si(1 1 1)

Finally, using the same XSW–PSD technique and following an analogous reasoning, we demonstrate that the phenomenon of an enormously enhanced desorption cross-section for
minority sites is also found for Br/Si(1 1 1)-(1 × 1), which can be prepared in a similar way by room temperature adsorption and subsequent annealing at 600°C. In figure 6, the corresponding XSW data taken in (1 1 1) Bragg reflection for Br 2p photoelectrons and Br⁺ ions are displayed. Again, the coherent fraction $f_{111}^{Br-2p} = 0.72$ and coherent position $\Phi_{111}^{Br-2p} = 0.84$ are in excellent agreement with our DFT calculations [22] for the established on-top site [23]. Likewise, the ion data $f_{111}^{Br+} = 0.85$ and $\Phi_{111}^{Br+} = 0.25$ can successfully be attributed to SiBr₃ minority species. Therefore, these results strongly suggest that increased stimulated desorption cross-sections due to a specific local-bonding geometry are indeed a common general feature of halogenated Si(1 1 1) surfaces.

4. Conclusion

Concluding, we reported the identification of Cl and Br minority sites on Si(1 1 1) under dry etching conditions. Applying a novel combination of PSD, XSW and DFT, these sites could be attributed to SiCl₃ and SiBr₃ species due to their significantly enhanced site-specific desorption cross-section. Furthermore, we have shown that these SiCl₃ sites orient along specific crystallographic directions which is corroborated by our results from ab-initio DFT calculations. For the first time, the XSW–PSD analysis was used to directly determine site-specific absolute desorption cross-sections.

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