Origin of X-ray photon stimulated desorption of Cl\(^+\) and Cl\(^{2+}\) ions from Cl/Si(1 1 1)-(1 \times 1)

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Abstract

In this paper we investigate minority adsorption sites on Cl/Si(1 1 1)-(1 \times 1) with the X-ray standing wave technique. By a combination with X-ray photon stimulated desorption, we show that the coordinates of the desorption-active chlorine minority adsorption site can be determined analytically if standing wave difference spectra are recorded at the chlorine 1s absorption edge. Furthermore, the direct and indirect contributions to the total Cl\(^+\) and Cl\(^{2+}\) ion desorption yields above the chlorine K edge can be separated and the ratio of the atomic desorption cross-sections can be estimated. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The detailed understanding of chemical etching processes has attracted a lot of interest in the last two decades. Special focus has been dedicated to spontaneous and assisted etching reactions for the silicon–halogen system [1,2] which forms the basis of modern semiconductor manufacturing and processing. In many cases, scanning tunneling microscopy provided insight into the changes of the surface morphology on an atomic scale, revealing striking anisotropies in assisted etching [3–5] as well as in chemical vapor deposition growth [6]. Briefly summarizing, the key role in the etching process is played by surface steps and their specific configuration. For halogen-terminated Si(1 1 1) surfaces, the \{1 1 2\} directions are strongly favored with so-called A-type step edge reconstructions which are characterized by a dimerization of the upper silicon bilayer atom of the upper terrace with a silicon atom of the lower terrace [6]. Interestingly, this configuration is preserved even for step edges oriented in the \{1 1 2\} directions by implementation of a stacking fault on the upper terrace [7,8]. In both cases, the resulting dangling bond of the silicon atom that defines the step edge is saturated by a chemisorbed halogen atom [6]. However, a detailed knowledge of this step edge
geometry and its local electronic structure is still lacking.

At this point, the capability to determine adsorption sites with high precision offered by the X-ray standing wave (XSW) technique is of great advantage. In combination with X-ray photon stimulated ion desorption, it is also possible to shed light upon the site specificity of stimulated desorption cross-sections which in turn reflect the electronic nature of the local environment. The information of how the photoabsorption in a specific electronic level influences the stimulated desorption yields can be gathered by taking XSW difference spectra at the photoelectric absorption edge under investigation [9]. Also, the dominating desorption process can be uniquely identified. Additionally, the evaluation of the data allows the analytical determination of the desorption-active site. In this paper, a detailed analysis of the extensively-studied Cl/Si(1 1 1)-(1 × 1) surface [10–17] at the chlorine K absorption edge will be presented.

2. Experimental

The following XSW experiments were carried out at the undulator beamline BW1 at the Hamburg Synchrotron Radiation Laboratory HASYLAB. A non-dispersive double crystal Si(1 1 1) monochromator was used of which the first crystal was water-cooled and symmetric and the second one was cut asymmetrically. The reflectivity of the sample crystal was recorded while tuning the incident photon energy through the Bragg condition of the sample and keeping the incident angle fixed. At the same time, photoelectron yields or positive ion yields were monitored as secondary signals for the standing wave measurements. For photoelectron detection, the ultra-high-vacuum chamber was equipped with an energy-dispersive electron analyzer. The desorbing ions could be identified by means of time-of-flight (TOF) spectroscopy, making use of the periodic time structure of synchrotron radiation. With the storage ring DORIS III operating in double bunch mode, a detection time interval of 482 ns offered an enhanced ion mass resolution, see Fig. 1 for an exemplary TOF spectrum.

The analysis of the experimental data for the reflectivity and the respective secondary yields was performed according to the dynamical theory of X-ray diffraction [18,19]. With (hkl) diffraction planes used in the measurement, the thus-obtained coherent fraction $f_{c}^{hkl}$ and coherent position $\Phi_{c}^{hkl}$ are the amplitude and phase of the (hkl) Fourier component of the distribution function of the atoms contributing to the signal under investigation. A detailed description of the evaluation of XSW data can be found elsewhere [20].

The in situ sample preparation was done as follows: as a starting point, the RCA-cleaned [21] Si(1 1 1) substrate crystals were heated by direct current to 870 °C for 5 min. After a slow cooldown to room temperature, the resulting (7 × 7) reconstruction of the clean Si(1 1 1) surfaces was confirmed by low-energy electron diffraction (LEED). Subsequently, the samples were chlorinated at room temperature by a 5 min exposure to molecular chlorine provided by a AgCl electrochemical source. Annealing the saturation-dosed samples at 580 °C for 30 s always induced a sharp (1 × 1) LEED pattern.
3. Results and discussion

In Fig. 1, a typical TOF spectrum is displayed. The two sharp, most intense peaks labeled “hv” stem from scattered photons, therefore, they define the time window and their distance reflects the periodic time structure of the exciting synchrotron radiation. Due to the slightly asymmetric filling of the storage ring DORIS III in double bunch mode, the peak to the right is split into two components with the characteristic distance of ≈4 ns, in very good agreement with the two distinct time intervals of 480 and 484 ns between two adjacent bunches in the ring. The identification of the other peaks as given in the spectrum can be achieved by using the relation

$$\frac{(\Delta t_1)^2}{(\Delta t_2)^2} = \frac{(m_1/q_1)}{(m_2/q_2)}.$$  \hspace{1cm} (1)

with \(\Delta t\), \(m\) and \(q\) denoting the flight time, the ion mass and the ion charge of the particle under consideration, respectively. Additionally, the electrical field between the sample and the TOF detector was varied for cross-checking purposes and in order to eliminate ambiguities arising from the convolution of the TOF spectra with the periodicity of the synchrotron radiation. Finally, the small sharp peak marked as “a” represents scattered photons produced by parasitic bunches.

The first question which naturally arises concerning the use of a distinct secondary signal in XSW experiments is whether the selected signal has to be classified as a primary emission channel (PEC) or secondary emission channel (SEC) [22]. With PECs, as e.g. fluorescence photons and core-level photoelectrons, the structural interpretation of XSW experiments is in principle straightforward since the information contained in the data is direct. With SECs, the initial excitation and its final emission need not occur in just one place, i.e. the selected signal may not be triggered exclusively by the X-ray interference field. For example, the stimulated desorption of ions might be initiated by several desorption mechanisms as direct core-level excitation, nearest-neighbor excitation or photo-absorption in the substrate bulk crystal followed by stimulated desorption induced by secondary electrons. Only in the first of the three named cases, the XSW data will hold direct information of the atomic species, or the adsorbate, under investigation; in the latter cases it is impossible to pinpoint the adsorption site solely by the standing wave data. For the majority of adsorbate systems, the observed ion yield may originate from a superposition of PECs and SECs, and information about the dominating contribution is needed for a correct interpretation of the data.

To address this issue for the stimulated desorption of positive Cl\(^+\) and Cl\(^{2+}\) ions from Cl/ Si(1 1 1)-(1 x 1), the respective ion yield was recorded as a function of the incident photon energy near the chlorine K absorption edge, see the inset of Fig. 2. From these spectra, edge jumps (i.e. the ratio of ion yields above and below the absorption edge) of ≈3.2 for Cl\(^+\) ions and ≈7.1 for Cl\(^{2+}\) ions can be deduced. Consequently, the contribution of indirect desorption processes for Cl\(^{2+}\) ions amounts to ≲14% while the corresponding fraction for Cl\(^+\) ions is ≲30%. Therefore, at least the Cl\(^{2+}\) ions can be regarded as a PEC within a good first approximation.

When performing XSW experiments above the Cl K absorption edge, employing Cl\(^{2+}\) ions as a secondary signal, the measured coherent fraction \(f_{Cl^{2+}}^{111}\) and coherent position \(\Phi_{Cl^{2+}}^{111}\) will therefore directly reflect the distribution of Cl atoms. As photoelectrons are an ideal PEC, this also holds for \(f_{Cl\,1s}^{111}\) and \(\Phi_{Cl\,1s}^{111}\) obtained from XSW data recorded using Cl 1s photoelectrons. Hence, similar results are expected for experiments with Cl\(^{2+}\) ions and Cl 1s electrons, respectively. Nevertheless, as shown in Fig. 2, the ion yields are in strong contrast to the electron yield. From both, the Cl\(^+\) ion yield and the Cl 1s yield, high coherent fractions of \(f_{Cl^{+}}^{111} = 0.86\) and \(f_{Cl\,1s}^{111} = 0.81\), respectively, are obtained (the statistical errors are given in the inset of Fig. 2). This indicates that for both signals almost all Cl atoms contributing to each signal occupy a unique adsorption site, the coordinate of which along (1 1 1) is then given by the coherent position. Interestingly, the values of \(\Phi_{Cl^{+}}^{111} = 1.20\) and \(\Phi_{Cl\,1s}^{111} = 0.78\) are in very strong contrast to each other. This result is explained as follows: As the cross-section for core-level photoemission well-above the absorption edge is independent of the environment of the Cl atoms, the majority of these atoms occupy the on-top adsorption site.
corresponding to $\Phi_{\text{Cl}1s}^{111} = 0.78$ [23]. However, there is a minority adsorption site which is almost “invisible” to Cl 1s photoelectrons due to its small population. This adsorption site, in spite of its small population, dominates the ion signal due to its high desorption cross-section, which in contrast to the photoemission cross-section can be very site specific [24,25].

In order to analytically determine the different contributions to the ion yields for both ionic species and the coordinate in [1 1 1] direction of the new adsorption site, XSW experiments have been performed below ($h\nu = 2800$ eV) and above ($h\nu = 2860$ eV) the chlorine K absorption edge (2822 eV). The corresponding results are shown in Fig. 3. For both species, a distinct shift in the coherent positions has to be noted, i.e. they change from $\Phi_{\text{Cl}1s}^{\text{below}} = 1.02$ and $\Phi_{\text{Cl}1s}^{\text{above}} = 1.06$ below the Cl K edge to $\Phi_{\text{Cl}}^{\text{above}} = 1.15$ and $\Phi_{\text{Cl}2^+}^{\text{above}} = 1.19$ above the absorption edge. Likewise, the coherent fraction for the Cl$^{2+}$ ions takes a significant leap from $f_{\text{Cl}2^+}^{\text{below}} = 0.51$ to $f_{\text{Cl}2^+}^{\text{above}} = 0.81$.

For the quantitative evaluation of the data, a concise mathematical description for the XSW results near the absorption edge has to be introduced: let $A$ and $B$ be the two adsorption sites for Cl/Si(111)-(1 $\times$ 1) with the corresponding coherent fractions $f_A$ and $f_B$ and the corresponding coherent positions $\Phi_A$ and $\Phi_B$, respectively. Then the measured Fourier component of the adsorbate distribution function $F_{111}^{111}$ can be written as the weighted superposition

$$F_{111}^{111} = n_A F_A^{111} + n_B F_B^{111} + n_{\text{ind}} F_{\text{ind}}^{111}.$$  \hspace{1cm} (2)

The weight parameters $n_A$ represent the count rates of the desorbing ions originating from the sites $A$ and $B$ by direct processes initiated by excitation of the chlorine L shells or higher electronic levels located at the adsorbate. The weight parameter $n_{\text{ind}}$ denotes the count rate of events produced by indirect desorption processes. Neglecting the Debye–Waller factor and assuming no statistical disorder on the surface, the coherent fractions for the adsorption sites are both equal to 1, thus their Fourier components may be represented as $F_{A,B}^{111} = \exp(2\pi i \Phi_{A,B}^{111})$. 

![Fig. 2. XSW data and fit (solid lines) of Cl 1s (□) photoelectron yield, Cl$^+$ (○) and Cl$^{2+}$ (▲) ion yields and reflectivity (×) of Cl/Si(111)-(1 $\times$ 1) as functions of the incident photon energy in (1 1 1) Bragg reflection at a photon energy of $E_{\text{Bragg}} = 3350$ eV. The Cl$^+$ (+0.5) and the Cl$^{2+}$ (+1) ion yield are shifted, for clarity. Inset: normalized Cl$^+$ and Cl$^{2+}$ (shifted +1) ion yields as functions of the incident photon energy around the Cl K absorption edge (2822 eV).](image-url)
Analogously to Eq. (2), the measured Fourier component above the Cl K absorption edge may be expressed as

$$F_{\text{above}}^{111} = n_K \Phi_{\text{Cl}^+}^{111} + n_K \Phi_{\text{Cl}^{2+}}^{111} + n_L \Phi_{\text{Cl}^+}^{111} + n_L \Phi_{\text{Cl}^{2+}}^{111} + n_{\text{ind}} \Phi_{\text{ind}}^{111},$$

(3)

Here, $n_K^A$ and $n_K^B$ denote the site-specific contributions to the ion yield originating from direct processes initiated by excitation of the K shell. The previously discussed edge jump, which will be called $\eta$ here, can be defined in terms of count rates as

$$\eta = \frac{n_K^A + n_K^B + n_L^A + n_L^B + n_{\text{ind}}}{n_K^A + n_K^B + n_L^A + n_L^B + n_{\text{ind}}},$$

(4)

Then the following relation can be derived from the Eqs. (2)–(4) (the indices “1 1 1” for the Bragg reflection geometry are omitted from now on):

$$\frac{1}{\eta - 1} (\eta \Phi_{\text{above}} - \Phi_{\text{below}}) = \frac{1}{n_K^B + n_L^B} (n_K^A \Phi_{\text{Cl}^+} + n_K^B \Phi_{\text{Cl}^{2+}}) \equiv \Phi_{\text{XPSD}}.$$  

(5)

The complex plane offers a graphical interpretation for these relations. The left-hand side of Eq. (5) can be regarded as a complex number lying on the straight line defined by $\Phi_{\text{above}}$ and $\Phi_{\text{below}}$. Its meaning can be understood from the term in the middle of the same equation. This term represents the idealized case in which the direct desorption signal excited by chlorine K shell ionization solely determines the ion yield in an XSW experiment. Therefore, the straight line determined by the two (not yet known) Fourier components $\Phi_A$ and $\Phi_B$ must include this particular point in the complex plane since this very connection between these two Fourier components comprises all possible superpositions of direct processes originating from the sites A and B. The second point by which this straight line, which we will call $g$ in the following, is utterly fixed can be gained by considering the results of the XSW measurement with Cl 1s photoelectrons as secondary signal. With $\Theta_A$ and $\Theta_B$ denoting the coverage of the adsorption sites A and B, these results can be written as

$$\Phi_{\text{Cl}1s}^{111} = \frac{\Theta_A \Phi_A^{111} + \Theta_B \Phi_B^{111}}{\Theta_A + \Theta_B}.$$  

(6)

Thus the two Fourier components $\Phi_A$ and $\Phi_B$ and thereby the coherent positions $\Phi_{\text{Cl}^+}$ and $\Phi_{\text{Cl}^{2+}}$ can finally be computed as the intersections of $g$ with the unit circle or, in general, with a circle around the origin with the radius $r = 1 - c$, where $c$ denotes the fraction of incoherently adsorbed chlorine atoms, i.e. the statistical disorder of the adsorbate. The situation for Cl$^-$ ions as secondary signal is depicted in Fig. 4 with the special case of $c = 0$ describing a perfectly ordered surface.
With the knowledge of the two adsorption sites, it is possible to calculate the coverage ratio 
\[ \Theta_B/\Theta_A = \frac{|F_{\text{XPSD}} - F_A|}{|F_B - F_{\text{XPSD}}|} (\Theta_A/\Theta_B). \]  
(8)

From Eq. (5), the edge jump can also be expressed as
\[ \eta = \frac{|F_{\text{below}} - F_{\text{XPSD}}|}{|F_{\text{above}} - F_{\text{XPSD}}|}, \]
which is equal to the ratio of \((y_1 + y_2)/y_1\) in Fig. 4. Additionally, the parameter \(\lambda_K\) which describes the portion of stimulated desorption induced by chlorine K shell excitation can also be deduced graphically to become
\[ \lambda_K = \frac{n_A^K + n_B^K}{n_A^K + n_B^K + n_A^L + n_B^L + n_{\text{ind}}}, \]
where \(n_A^K\) and \(n_B^K\) are the counts of chlorine K shell excitation for ions A and B, respectively.

The results of the calculations for both ionic species for a perfectly ordered surface \((c = 0)\) and for a \(c\)-value of 0.10 are displayed in Table 1. The value \(c = 0.10\) can be regarded as a reasonable upper limit for the portion of incoherently adsorbed Cl atoms if the high coherent fraction for Cl\(^{2+}\) ion desorption of \(f_{\text{Cl}^{2+}} = 0.86\) is taken into account. First of all, the well-known on-top site is very-well reproduced by the adsorption site A with a bond length of 2.02 Å. The coherent position of the other adsorption site B is \(\approx 0.21\), likewise showing only a very weak dependency of the fraction \(c\) of incoherently adsorbed chlorine atoms. The value of \(\Theta_B/\Theta_A \approx 0.06\) establishes the notion that B is a minority site. As can be seen from the results for the parameter \(\hat{\Gamma}_K\), which is by virtue of Eq. (10) independent of \(c\), the portions of direct desorption processes, i.e. desorption induced by chlorine K shell excitation, are dominating for both ion charges. In the case of Cl\(^{2+}\) ion

Table 1
Overview of the results of the analytic evaluation of the XSW difference spectra

<table>
<thead>
<tr>
<th>Ion</th>
<th>(c)</th>
<th>(\phi_A^{111})</th>
<th>(\phi_B^{111})</th>
<th>(\hat{\Gamma}_K)</th>
<th>(\Theta_B/\Theta_A)</th>
<th>(\sigma_B/\sigma_A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl(^{+})</td>
<td>0.00</td>
<td>0.77</td>
<td>0.21</td>
<td>0.69</td>
<td>0.11</td>
<td>40</td>
</tr>
<tr>
<td>Cl(^{2+})</td>
<td>0.00</td>
<td>0.77</td>
<td>0.21</td>
<td>0.87</td>
<td>0.11</td>
<td>1.4 \times 10^3</td>
</tr>
<tr>
<td>Cl(^{+})</td>
<td>0.10</td>
<td>0.77</td>
<td>0.21</td>
<td>0.69</td>
<td>0.06</td>
<td>90</td>
</tr>
<tr>
<td>Cl(^{2+})</td>
<td>0.10</td>
<td>0.77</td>
<td>0.20</td>
<td>0.87</td>
<td>0.06</td>
<td>2 \times 10^3</td>
</tr>
</tbody>
</table>

For the explanation of the symbols, see text.
desorption, these make up almost 90% of the total ion yield. The highly favored desorption from the minority site $B$ is impressively demonstrated by the large values for the site-specific atomic desorption cross-sections, e.g., for $c = 0.1$, $(\sigma_B/\sigma_A)(\text{Cl}^+)$ ≈ 90 and $(\sigma_B/\sigma_A)(\text{Cl}_2^+)$ ≈ $2 \times 10^3$. These tremendous ratios of atomic desorption cross-sections point to a distinct change in the electronic structure located at the adsorption sites $B$ with respect to the electronic environment of the on-top sites $A$. However, it has to be noted that these ratios are strongly correlated with $c$, therefore the presented values should at least reveal their approximate orders of magnitude.

For the determination of the minority adsorption site $B$, XSW measurements in (111) Bragg geometry are not sufficient, as only information in the direction normal to the surface is obtainable in this geometry. From additional measurements employing the (220) Bragg reflection (i.e., with a non-vanishing lateral component of the scattering vector), it is concluded [23] that the minority site $B$ can be attributed to a bonding geometry in which Cl atoms terminate the dangling bonds of so-called $A$-type step edges. These step edges are characteristic of halogen-terminated Si(111) surfaces [7].

It has to be noted that the statement that a minority site dominates the Cl$^+$ ion yield due to a highly-favorable desorption cross-section is contradictory to the findings of Purdie et al. [26] and McGrath et al. [27] who claimed an on-top site origin of the Cl$^+$ ion yield on the basis of their surface extended X-ray absorption fine structure and near-edge X-ray absorption fine structure (NEXAFS) results. However, this type of step-edge structure is similar to a tilted on-top arrangement and should be very difficult to distinguish from the on-top site with NEXAFS.

4. Conclusions

In the present study we investigated the origin of the X-ray photon stimulated desorption of Cl$^+$ and Cl$^{2+}$ ions from Cl/Si(111)-(1×1). Tuning the incident photon energy through the chlorine K absorption edge resulted in edge jumps of 3.2 and 7.1 for Cl$^+$ and Cl$^{2+}$ ions, respectively, clearly indicating a prevailing direct desorption process, especially for Cl$^{2+}$ desorption. Although both ion signals should therefore contain direct information of the adsorbate structure when utilized in XSW experiments, the XSW data with Cl$^+$ and Cl$^{2+}$ ions clearly pinpoint to a second adsorption site utterly differing from the on-top site which has been determined by XSW measurements with Cl$^+$ photoelectrons as secondary signal. By taking XSW difference spectra at the chlorine K absorption edge with both ion charges as secondary signal, it is possible to analytically determine the coordinate in [111] direction of the second site. Furthermore, the calculated relative coverage of the second site of $\approx 0\%$ leads to the characterization as a minority site, which can be attributed [23] to an adsorption site terminating the dangling bonds at reconstructed step edges. This step edge structure is therefore concluded to be the reason for the tremendously higher desorption cross-sections for stimulated desorption of positive chlorine ions from this minority site in comparison to the stimulated desorption arising from the majority on-top site.

References