Photon-stimulated desorption and x-ray standing waves

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Introduction

X-ray standing waves (XSW) using electrons and fluorescence photons as secondary signals has become a standard technique to determine adsorbate structures. However, when a sample is irradiated by intense light, desorption of ions is also a frequently observed phenomenon which is known as photon-stimulated desorption (PSD). But, this signal is of a fundamentally different physical nature. The identification of this process has been a persistent topic in surface science throughout the last decades [1]. By virtue of the inherent periodic time structure of synchrotron radiation, an efficient detection of positive ions emitted from the surface is feasible using time-of-flight spectroscopy. In this review, we will survey the relevant desorption mechanisms which initiate the prevailing processes. We will show that the combination of x-ray standing waves with x-ray PSD (XPSD) is a unique tool to identify the underlying desorption processes in a site specific manner.

In general, two distinct types of stimulated desorption processes were identified in the past, i. e. *direct* and *indirect* desorption processes. This classification is based on the nature of the initial excitation which sequentially leads to ion emission. For direct processes, the desorption-active photoabsorption is located at the atom which is finally ejected. For indirect processes, the primary photons are absorbed either at the bonding partner of the desorbing ion, which results in so-called nearest-neighbor PSD, or in the underlying bulk crystal, leading to the creation of secondary electrons which cause the ion desorption by valence excitation (x-ray induced electron-stimulated desorption (XESD)). Therefore, three primary desorption processes can be distinguished. While the details of the desorption mechanisms are in general highly specific to the system under investigation, it has to be emphasized that the dominating desorption processes can be identified by using synchrotron radiation. This is feasible through applying a combination of XSW and XPSD (XSW-PSD), since all three types can be related to distinct Fourier components of the atom distribution function. In the course of developing this method we have applied it to several systems, e. g. H/Pd(111), K/Ge(001), CsCl/Si(111) [2] as well as Cl/Si(001) and Cl/Si(113) [3]. In the following, we will deal with the systems Si(111)-(7x7), H/Si(111)-(1x1), Ge/Si(111)-(1x1):H [2], and Cl/Si(111) [4]. This choice serves to illustrate the peculiarities of the different kinds of desorption processes and to demonstrate the general approach to the interpretation of XSW-XPSD data.

Experimental

All the measurements presented here have been performed under ultra-high vacuum conditions at the undulator beamline BW1 at the Hamburg Synchrotron Radiation Laboratory (HASYLAB) using monochromatic x-radiation from a double-crystal

monochromator in a standard non-dispersive setup. The XSW experiments were carried out by tuning the x-ray photon energy through the Bragg condition of the sample. Simultaneously desorbing ions, photoelectrons and x-ray fluorescence spectra were recorded. With the DORIS III storage ring operating in single-bunch or two-bunch mode, desorbing ions were identified by time-of-flight (TOF) spectroscopy utilizing the time structure of the incident radiation, i.e., the extended time interval of 964 ns or 482 ns between two successive bunches. Applying a negative bias of more than 3 kV between the sample and the TOF detector leads to distinct flight times for each ionic species as a function of their characteristic m/q values, where m stands for the mass of the ion and q for its charge, respectively. Hence, the desorption products can be identified by varying the distance between the detector and the sample. Examples for the quality and resolution of the obtained TOF spectra will be given in the following section.

Results and discussion

We start our survey with the clean Si(111)-(7×7) surface. Its structure has been explained within the so-called dimer adatom stacking-fault (DAS) model as originally proposed by *Takayanagi* and co-workers [5]. In order to follow the subsequent discussion of the XSW ion data, it is sufficient to note that the (7×7) unit cell partially consists of a local (2×2) Si adatom structure in each triangular subunit separated by dimer rows. In the inset of Figure 1 a TOF spectrum is displayed identifying the desorbate as Si^+ ions created by irradiation at an energy of 5.1 keV. The corresponding ion yield measured in (111) Bragg reflection is given in the main part of the figure. The analysis yields a coherent position of $\Phi = 0.16 \pm 0.03$ and a coherent fraction of $f = 0.53 \pm 0.03$ which have to be compared to the calculated coherent position of the Si adatom since desorption of adatoms from the outermost atomic layer is most likely. Taking the theoretically calculated structure of *Qian et al.* [6] leads to a simulated atomic coherent position of $\Phi = 0.51$ and a coherent fraction of $f = 1.0$. Hence, the predominance of purely direct desorption processes initiated by photo absorption in the Si $1s$ level at the adatom can be excluded since both coherent positions should then closely match. Likewise, purely indirect desorption via the XESD mechanism can be ruled out because the coherent position of the Si bulk atoms would then be reproduced (see below). However, the experimental data can be successfully explained by a mixture of a direct mechanism and the presence of indirect processes via photo excitation of the three bonding partners beneath the adatom. In either case, the core hole predominantly relaxes via Auger decay and subsequently the chemical bonds are destroyed. Assuming a 1:3 ratio between direct and nearest-neighbor PSD, the XSW simulation yields a coherent position of $\Phi = 0.14$ and a coherent fraction of $f = 0.54$, reproducing the experimental data within the error bars. Concluding, we find that using the XSW technique with desorbing ions allows the identification of the prevailing stimulated desorption processes for a covalent system in the x-ray regime.

Figure 1. XSW data and fit (solid lines) of the reflectivity (o) and Si⁺ (◇) yield as functions of the photon energy E for Si(111)-(7×7) in (111) Bragg reflection. Upper left inset: TOF spectrum identifying the desorbing Si⁺ ions. For comparison, the hypothetical peak positions for the neighboring elements Al and P are displayed. Upper right inset: Adatom configuration for Si(111)-(7×7) in the DAS model.

Upon hydrogen adsorption on the clean Si(111) surface e. g. by wet-chemical etching or exposure at elevated temperatures, the hydrated Si(111) surface gradually transforms into a bulk-like (1×1) adsorbate structure with H occupying the on-top site [7], as depicted in the upper right inset of Figure 2. This atop geometry with a literature value of 1.51 Å for the Si—H bond length corresponds to an atomic coherent position of 0.61 for the H atom in (111) Bragg geometry. The XSW ion data for the H⁺ signal at a Bragg energy of 4.0 keV, however, reveal a coherent position of 0.01 and a coherent fraction of 0.66, bearing the characteristic of XESD processes to which corresponding values of 0.00 and 0.71 can be attributed, respectively. Physically, this result is expected since direct desorption induced by photoabsorption in the Si—H bond is negligible due to the very low associated photoabsorption cross section at x-ray energies. Therefore, the combined XSW and XPSD experiment with H⁺ ions as secondary signal from the saturated Si(111) surface reveals the dominant desorption mechanism, but includes no structural information on the atomic configuration of the adsorbed hydrogen atoms.

Figure 2. XSW data and fit (solid lines) of the reflectivity (o) and H^+ (◇) yield as functions of the photon energy E for $H/\text{Si}(111)-(1 \times 1)$ in (111) Bragg reflection. Upper right inset: Side view of the on-top adsorption geometry.

Interestingly, this situation changes drastically after deposition of 1.3 bilayers of germanium on the hydrogen-saturated surface at a temperature of 430°C. This was done in the course of an experiment aimed at studying the heteroepitaxial growth of $\text{Ge}/\text{Si}(111):\text{H}$. In Figure 3, the H^+ ion yield and the Ge K fluorescence yield are displayed as a function of the photon energy in the vicinity of the Ge K absorption edge. As clearly visible, the ion yield increases by a factor of more than 10. This proves that more than 90% of the desorbing ions are created by photo excitation of core holes in the Ge $1s$ level and direct desorption processes can be neglected. Since the ion desorption and the fluorescence signal rise at the same energetic threshold, electron-stimulated desorption by Ge $1s$ photoelectrons can be excluded. Hence, the most probable desorption mechanism involves an *inter-atomic* Auger decay following the initial photo absorption in the Ge K shell. This suggests that H^+ ions can be used as a probe to determine the adsorption sites of their respective germanium bonding partners in an XSW experiment.

Figure 3. H^+ (o) and $Ge K_{\alpha}$ (□) yields as functions of the photon energy at the $Ge K$ absorption edge. Inset: TOF spectrum for H^+ desorption.

The corresponding XSW data for the H^+ ion yield and the $Ge K$ fluorescence signal recorded at a Bragg energy of 11.5 keV are presented in Figure 4. The measured (111) Fourier components are 0.42 ± 0.02 and 0.99 ± 0.02 for the coherent fraction and coherent position of the fluorescence yield, respectively. Hence, the thin Ge film is fairly well-ordered. However, the ion signal exhibits a much higher coherent fraction of 0.92 ± 0.12 and a coherent position of 0.02. These values are not compatible with H^+ desorption solely from on-top sites since this would lead to an average coherent position between 0.18 and 0.23 for the Ge atoms on the “accessible”, hydrated terraces. Therefore, additional processes need to be taken into account in order to simulate the ion data, such as a more favorable desorption cross section from step edges or point defects. That site-specificity may indeed be pronounced in XPSD experiments will next be demonstrated for the $Cl/Si(111)$ system which is the last example in this review.

Figure 4. XSW data and fit (solid lines) of the reflectivity (o), Ge-K fluorescence (Δ) and H^+ ($\square$) yields as functions of the photon energy E for Ge/Si(111):H in (111) Bragg reflection.

The chlorinated Si(111) surface exhibits a geometric structure similar to the previously discussed system H/Si(111). In order to study the influence of photo absorption in the Cl $1s$ level on the desorption rate, PSD experiments were performed at the Cl K edge, as reproduced in Figure 5. Both the Cl^+ and the Cl^{2+} ion yield undergo a significant increase when tuning the photon energy across the absorption edge. The edge jumps of about 3 for Cl^+ and 7 for Cl^{2+} establish above the absorption edge the predominance of direct desorption processes for both types of charged ions. Consequently, Cl^{2+} ions in particular offer a high Cl elemental specificity if used as a secondary signal in combined XSW and XPSD measurements with Bragg energies above the Cl K edge. The desorption can proceed as follows: After the initial photo absorption the core hole induces an Auger cascade which leads to the excitation of localized multi-hole states at the Cl atom. Because of the high ionicity of the unperturbed Si-Cl bond, the neighboring Si atom carries a positive charge. Hence, the charge reversal of the highly-excited Cl atom causes a Coulomb repulsion which effectively disrupts the Si—Cl bond, resulting in the emission of a Cl^+ or Cl^{2+} ion.

Figure 5. Photon-stimulated desorption and time-of-flight spectra for $\text{Cl}/\text{Si}(111)-(1 \times 1)$. Main figure: Cl^+ and Cl_2^+ ion yields as functions of the photon energy near the Cl-K absorption edge. Inset: Raw TOF spectroscopy data (full spectrum).

The result of a typical XSW experiment for $\text{Cl}/\text{Si}(111)-(1 \times 1)$ in (111) Bragg reflection with Cl $1s$ photoelectrons and desorbing ions as secondary signals is shown in Figure 6. While the photoelectron yield nicely reproduces the coordinate of the well known on-top adsorption geometry, which is depicted in the upper left corner, both ion yields exhibit characteristics utterly different from the electron data. As pointed out above, within a first approximation especially the Cl_2^+ ions should reveal the atomic positions of the desorption-active chlorine sites. Therefore, the ion yields are a direct evidence for the existence of minority adsorption sites with a highly-favorable atomic desorption cross section. Due to their low coverage, these sites are virtually invisible to the XSW experiment with photoelectrons. However, they can precisely be determined as SiCl_3 species using desorbing ions as the secondary signal and several non-collinear Bragg reflections [8].

Figure 6. XSW data and fit (solid lines) of the reflectivity ($\times$), Cl-1s ($\square$), Cl^+ ($\circ$) and Cl^{2+} ($\diamond$) yields as functions of the photon energy E for Cl/Si(111)-(1 $\times$ 1) in (111) Bragg reflection. Inset: Side view of the (1 $\times$ 1)-reconstructed Cl/Si(111) surface.

Conclusions

In summary, we have demonstrated that x-ray standing waves are a unique tool to determine directly the type of the prevailing PSD processes and the desorption-active sites. In cases where the desorption signal provides site selectivity, XSW-PSD can be used to determine adsorbate structures which are neither accessible to conventional XSW with fluorescence/electron detection nor to standard x-ray diffraction scattering techniques.

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