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ADSORPTION OF Br ON Si(111)-(1x1)

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X-RAY STANDING WAVE FLUORESCENCE MEASUREMENTS IN ULTRA-HIGH VACUUM:
ADSORPTION OF Br ON Si(111)-(1x1)

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Measurements with standing X-ray wave-fields were carried out for the first time under UHV conditions. Difficulties which were predicted for such measurements before were solved by using synchrotron X-radiation. The (111) Fourier component of the distribution function of 1 ML Br on a Si(111)-(1x1) surface was determined and reveals a Br position of $0.64 \cdot d_{111}$ perpendicular to the (111) planes, which favours a threefold ionic adsorption site. This adsorbate geometry differs markedly from the Br on-top position on a chemically prepared surface.

The feasibility to determine surface structures with standing X-ray wave-fields (SXW) was demonstrated by Cowan et al. in 1980¹. As was shown in this first paper, the results of such experiments reveal valuable information about adsorption sites of foreign atoms on single crystal surfaces. However, the use of conventional X-ray sources strongly limited the field of these measurements. The successful application of synchrotron radiation²⁻⁴, demonstrated that short measuring times (minutes) can be realized with a very high local precision ($\sim 0.01 \text{ \AA}$). This is essential for studies of well defined surface structures, to minimize contamination problems. Very small amounts of coverages (down to $6 \cdot 10^{13} \text{ atoms/cm}^2$)⁵ were studied as well, and the spectrum of possible substrate single crystals was broadened by using Ge and Cu⁶⁻⁷. This paper reports about the first successful study of an adsorbate under ultra-high vacuum conditions. Again, the limitations posed by using a fixed wavelength characteristic X-ray line were overcome by applying advantageously the free choice of wavelength from the white spectrum of synchrotron radiation.

The standing X-ray wave-field is excited during Bragg reflection, as an interference between incident and reflected beam. The spatial periodicity of this field is the same as the diffraction plane spacing. The phase difference between the diffraction planes and the standing X-ray wave-field is a function of the reflection angle and changes by about π over the angular range of a strong Bragg-reflection. Thus, if the E-field nodal-planes coincide at a given angle with the diffraction planes, they move to the position halfway between planes when the Bragg reflection condition is passed. The measurement of the fluorescence yield which is proportional to the local field intensity, as a function of reflection angle θ contains therefore information about the site of these atoms relative to the diffraction planes. If only one position is occupied, a maximum in the total X-ray fluorescence yield from the adatoms will be observed, when the anti-nodes of the standing wave-field and the atomic positions coincide. In general cases, a measurement with reflection H reveals the H-Fourier component of the atomic distribution function along the H direction⁵.

Several measurements of Bromine on chemically prepared ("real") (111) Silicon surfaces were reported previously^{2,3,8}. Real surfaces in this context means that the experiments were done under normal pressure and that the surface was not free from contaminants. In these studies Bromine was adsorbed on a Syton polished silicon



surface, out of a Br-Methanol solution. The maximum total coherent coverage reached was about 10^{14} atoms cm^{-2} corresponding to 0.2 monolayer. These experiments revealed an adsorption site of the Br at single-fold covalent on-top positions on an otherwise bulk-like outermost Si layer. The question whether another coherent position of a Br minority was hidden in the fraction of atoms assumed to be distributed incoherently was already raised² but could not yet be answered.

The measurement was carried out at the instrument ROEMO of the Hamburg Synchrotron Radiation Laboratory HASYLAB at DESY. Fig. 1 shows the experimental arrangement. The proper energy band of synchrotron radiation from the storage ring DORIS was selected by a double crystal monochromator, operating in a vertical reflection plane. The second crystal was asymmetrically cut, to obtain a small angular divergence⁹. Both crystals were mounted on goniometers equipped with piezo-electric elements for angular fine tuning. The monochromatic photon flux was monitored by an ionization-chamber and normalized on-line to the current of the storage ring. The reflectivity of the monochromator was kept constant by using the normalized output and a feedback control system¹⁰ coupled to the piezo-crystal of the first monochromator crystal. The crystal reflection curves (rocking curves) were measured by sweeping the angle of the second crystal linearly back and forth across the reflection range of the sample. The stability and linearity of this sweep was maintained by a capacitance type distance measuring system, coupled to a micro-angle servo control unit¹¹. In order to avoid the need for angular fine tuning of the sample crystal in UHV, the measurement of the rocking curves was done by rocking both monochromator crystals simultaneously. The joint action of the two feedback systems assures, that the relative alignment of the monochromator crystals is kept constant, while their emittance function is swept across the sample reflection curve by slightly changing the photon pass-energy. This procedure which is described in detail in ref. 12, provides the highest possible flexibility for the monochromator design as well as for the sample environment.

The monochromator is operated under normal pressure. The monochromatic beam, which enters the UHV-chamber through a 0.4 mm thick beryllium window, was reflected by the sample under Bragg-condition and left the chamber behind the second window. The fluorescence of the sample was recorded by an energy-dispersive solid-state

Si(Li)-detector. Since this detector was not constructed to operate under UHV conditions, a third Beryllium window with a thickness of 0.05 mm was mounted sideways close to the sample such that the Si(Li) detector looked onto the sample in the direction of the horizontal E-field vector of the synchrotron light.

The sample was mounted in the vacuum chamber on a one circle goniometer, to set the proper reflection angle with an angular precision of 10 arc. min.. Note, that this precision is sufficient since the wavelength can be chosen by the monochromator. The sample can be transferred to a second manipulator and moved in front of a combined LEED/Auger spectrometer for surface analysis. Cleaning of the sample can be done either by Argon-ion sputtering or by heating the sample with a direct current.

Deposition of Br on the sample surface can be done either through a fine-dosing gas inlet valve or by an electrolytical AgBr cell. In the latter case, Br can be released in controlled doses by measuring the current through the cell¹³. The vacuum system operates at a pressure down to $2 \cdot 10^{-8}$ Pa.

The first measurements were done on a Silicon(111)-(1x1) surface, covered with (1 ± 0.25) monolayer of Bromine. The total coverage was determined by measuring the Br fluorescence yield relative to the Si K_{α} yield from the substrate. Immediately before the Si crystal was inserted into the vacuum system, oxide layers were removed from the surface by an HF-etch. Subsequently, the surface was cleaned by heating the sample in a range 1000 to 1300°C at a pressure less than 10^{-6} Pa, until a (1x1) LEED pattern was observed. An Auger electron analysis showed afterwards, that the remaining contamination was mainly due to carbon.

The result of the standing wave measurement is shown in Fig. 2. The total Bromine K_{α} fluorescence yield is plotted versus reflection angle. The reflectivity of the sample is also shown for comparison. A photon excitation energy of 14 keV was chosen close to the Br K absorption edge at 13.5 keV to maximize the fluorescence emission. This energy, however, is sufficiently high to separate in the spectrum the thermal diffuse scattering peak and the inelastic Compton peak from the Br fluorescence peak. The best fit of the experimental data to a model which assumes one adsorption site plus randomly distributed atoms is obtained with a coherent fraction 0.35 ± 0.02 of atoms occupying a position of $(0.64 \pm 0.01)d_{111}$, where $d_{111} = 3.14 \text{ \AA}$ is the spacing of the Si(111) diffraction planes. This result shows, that Bromine is

in the present case not adsorbed at the position on-top of a bulk-like outermost surface Si atom, as was observed in earlier experiments^{2,3,8}. Inferring a Si-Br covalent bond length of 2.18 Å from SiBr₄¹⁴, gives for the on-top site a coherent position of $0.82 \cdot d_{111}$.

The result which was obtained under UHV-conditions can be due to the different preparation of the sample, which for example may cause a Si surface relaxation. Another possible explanation is that a phase change occurs when going to higher Br coverages. Measurements done on the same adsorbate at lower coverages showed only a low coherent fraction, which may indicate a coexistent mixture of sites.

Fig. 3 shows a model of the (111) surface looking along [112]. The measured position 2.01 Å is indicated by point-dashed lines. The dashed circle is centered at this distance above an open threefold coordination site and illustrates the close agreement between the measured adsorption site and a model in which Bromine is adsorbed ionically as Br⁻ with an ionic radius of 1.96 Å¹⁴. The measured coherent coverage of 0.35 ML is also in agreement with this model which allows at most one third of a monolayer to be adsorbed as long as adjacent sites are not occupied due to steric hindrance or electronic repulsion⁶.

No distinction can be made from our present data between the threefold open site (Fig. 3), the threefold eclipsed position above an atom of the second Si layer or a corresponding inner site below the second Si layer (lower point-dashed line in Fig. 3). As indicated by recent cluster calculations¹⁵ all three positions can play a role for the adsorption process of halogens on Si(111). This question, however, can presumably be solved by coverage dependent measurements and by studying the geometrical Br arrangement parallel to the (111) plane^{2,8}.

The present work has demonstrated that UHV measurements with standing X-ray wave-fields can be carried out routinely by using synchrotron radiation. This was demonstrated for an adsorbed Br monolayer on a clean Si(111)-(1x1) surface revealing that Br occupies ionically sites which are different from the covalent on-top position on a chemically prepared surface. This method therefore provides the mean to compare adsorbate structures in UHV with interfaces kept in an atmosphere under normal pressure or inside a liquid.

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Figure Captions

Figure 1 Schematic experimental arrangement for UHV standing wave measurements (for details see text).

Figure 2 Angular dependence of the Si(111) reflectivity and normalized Br K_{α} fluorescence yield. ●, ◆: experimental data; ---: least square fit to theory. In this case 45 L ($\approx 2 \cdot 10^{-7}$ mbar for 300 s) Br were deposited through the gas inlet valve. Measuring time was 30 minutes.

Figure 3 Side view of the unrelaxed Si(111)-(1x1) surface. The threefold open site of the adsorbed Br above the outermost Si(111) diffraction plane is indicated by a dashed circle.

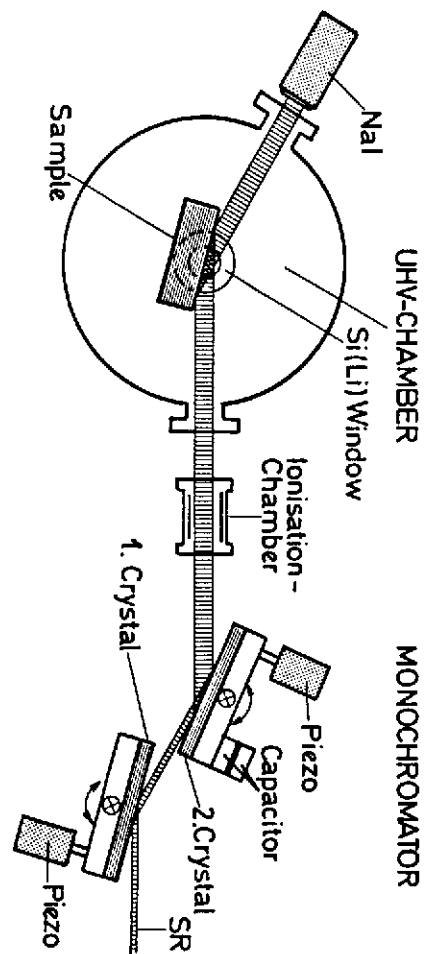
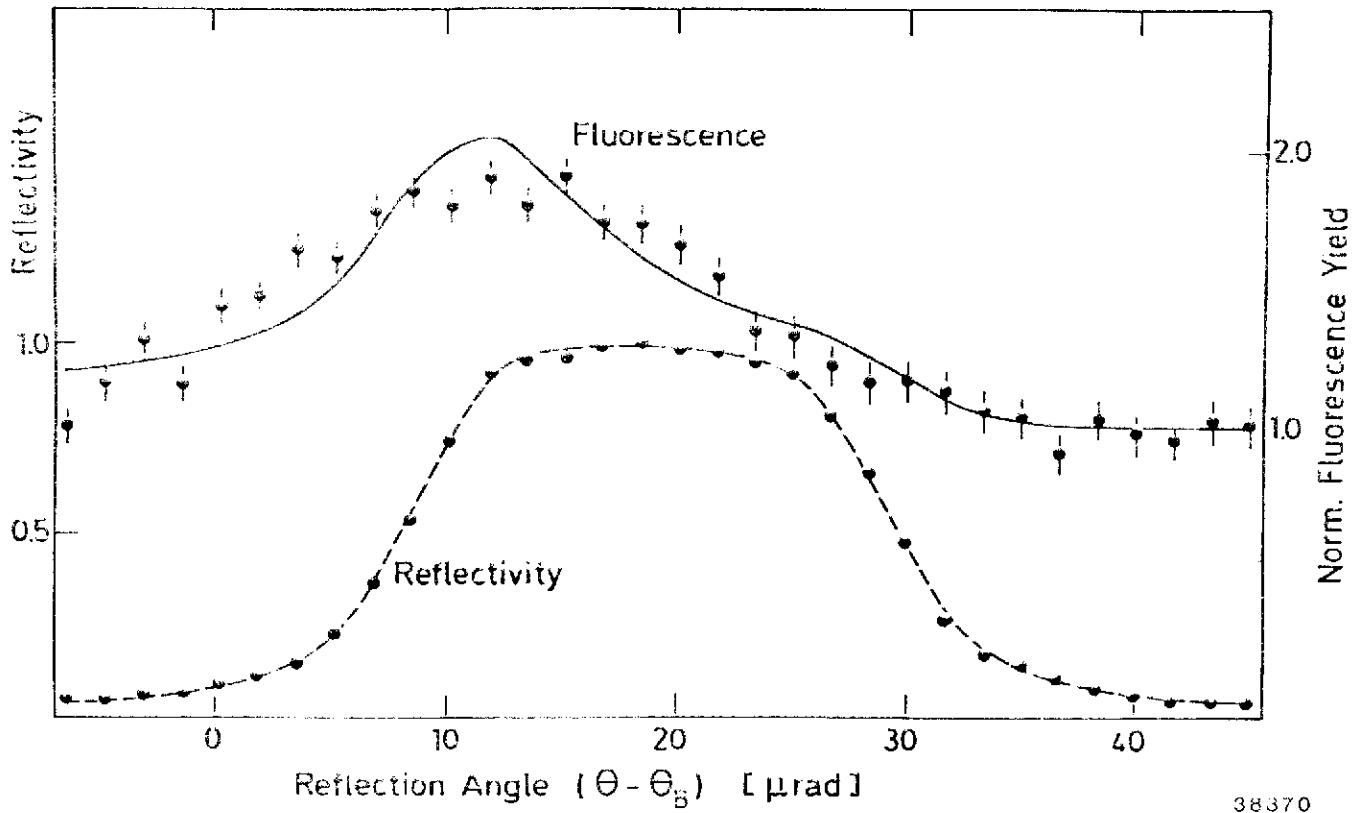


Fig. 1



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Fig. 2

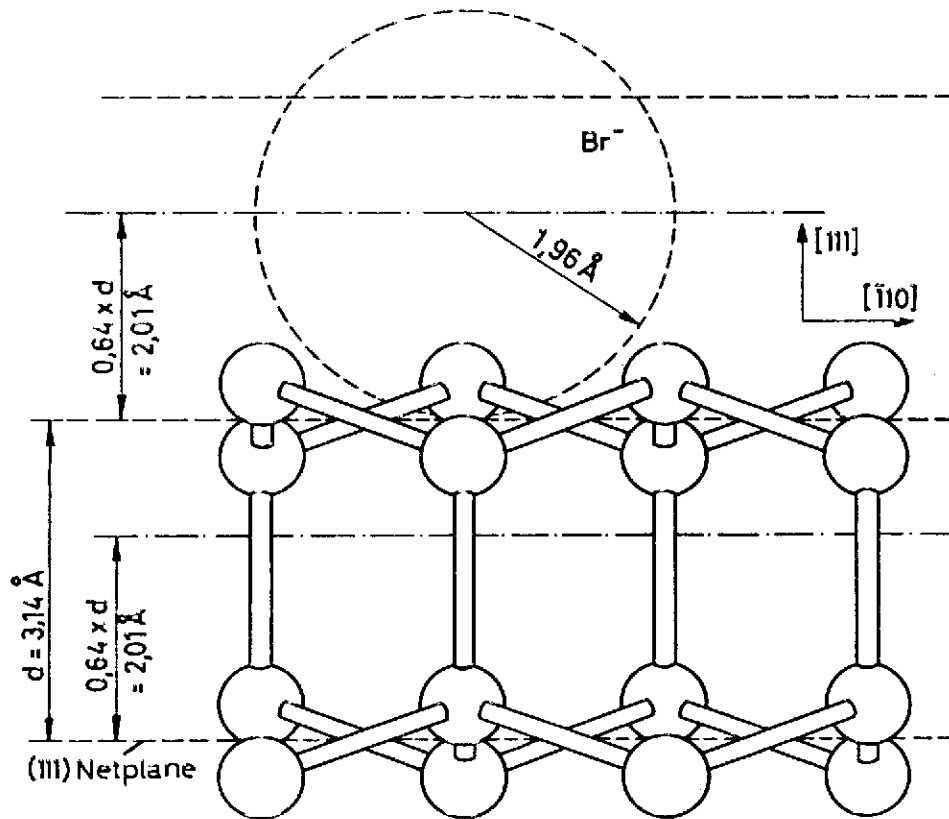


Fig. 3

