

DESY SR-84-07

March 1984

X-RAY INTERFEROMETRIC SOLUTION OF THE SURFACE REGISTRATION PROBLEM

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ISSN 0723-7979

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Surface Registration Problem

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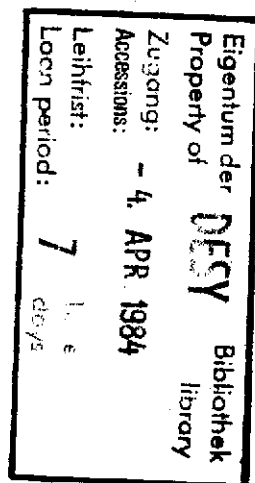
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Abstract

A Bonse-Hart x-ray interferometer was used to determine the (220) Fourier component of the distribution function of a chemisorbed submonolayer of Bromine on a (111) silicon surface. This measurement demonstrates not only the presence of an x-ray interference field above the crystal surface of the analyser of a Laue case interferometer, but when coupled with Bragg case standing wave measurements also provides the means to uniquely determine the position of surface atoms relative to the bulk lattice.

PACS numbers 68.20 +t, 61.10 Fr

published in Phys. Rev. Lett. 52, 441 (1984)

X-ray dynamical diffraction has been used recently to determine the position of adsorbed surface atoms on a perfect crystal substrate¹. The potentials of this method are best illustrated by reminding the reader, that under certain geometrical conditions two photon Bloch wave eigenstates are allowed solutions in a dynamically diffracting crystals. Each has two partial waves with wave vectors K_0 and $K_H = K_0 + H$, where H is the reciprocal lattice vector of the reflecting set of Miller planes. Therefore, the spatial periodicity of the standing wavefield equals that of the diffraction planes and one photon Bloch wave has nodes of the E field distributions which coincide with the maxima of the (h,k,l) Fourier component of the charge density distribution. The second solution has anti-nodes at the equivalent places and its nodes half-way between.

Changing the incidence condition by tuning the reflection angle of a crystal through the Bragg condition in a Bragg-case geometry, when incident and reflected wave are lying on the same side of the entrance surface, causes a continuous transition of the excitation of one Bloch waves solution to the other. This means a movement of the standing wavefield in the $-H$ direction by one half of a diffraction plane spacing from being in phase with the (h,k,l) charge density component to being out of phase by π radians. By measuring the fluorescence yield due to the decay of the photon excited in hole, a process which is proportional to the E field intensity at the sites of the nuclei, Batterman^{2,3} was able to verify this theory. Later Golovchenko et al.⁴ used the same technique to determine positions of foreign atoms in the direction of H . Although this technique is restricted to Bragg case measurements one can obtain projections of displacements of atoms in the surface plane by reflecting from diffraction planes which are not parallel to the surface and provide the basis for a triangulation technique⁵. For general cases this requires a careful consideration of the geometrical window function on the acceptance side of the crystal.

We shall show in this paper that a Laue case geometry, when entrance and exit surface of the incident and diffracted beams are different, allows a direct determination of atomic positions in a plane parallel to the surface. As is well known, standing interference patterns can be created by summing the amplitudes of two coherent plane waves. While this interference can be realized easily with optical waves, x-rays have such short wavelength and small coherence length that one has to take recourse to crystal diffraction in order to generate two coherent wave-trains.

Therefore, Bonse and Hart⁶, ingeniously used the Laue case of diffraction to excite two spatially separated coherent beams and were thereby able to manipulate their phases independently. This principle was used to construct successfully the first x-ray interferometer^{6,7}. The initial crystal splits the incident beam into two coherent waves, a second crystal in each of these beams consecutively acts as Laue case mirror to change the beam direction and to lead both beams to interference again. A third crystal finally serves to analyze the spatial distribution of the standing E field component of the resulting interference pattern.

Unlike the Bragg case of diffraction, the nodal and anti-nodal planes of this standing wave pattern are lying perpendicular to the surface and a phase difference induced between the incident beams will cause a shift of the pattern parallel to the surface plane. Also in a Laue case reflection two Bloch wave eigenstates of the photon inside the crystal are excited simultaneously at each angular position of a scan through the reflection condition. This causes interference which gives rise to "pendellösungs-effects"⁸.

However, close to the surface of the analyzer of a Laue case interferometer, the interference of two incident waves produces a standing wavefield with anti-nodal planes lying half-way between the scattering planes if the phase

difference is zero and a change of the relative phase by π radians will move these planes in a continuous manner by half a diffraction plane constant⁹.

The strategy of a position determination in the plane of the surface is similar to a Bragg case standing wave measurement. An adsorbate is deposited on the surface of the analyzer of an x-ray interferometer. The phase difference between the two incident waves is changed and the fluorescence from the bulk and surface atoms are registered simultaneously by a Si(Li) solid state detector.

The experiment was carried out by using the instrument ROEMO at the Hamburger Synchrotron Radiation Laboratory HASYLAB at DESY in Hamburg. The storage ring DORIS running at 3.7 GeV electron energy with a medium current of about 60 mA served as the source of synchrotron x-radiation (SXR).

The inset in Fig. 1 shows the experimental arrangement. The white SXR spectrum was initially monochromatized with a slightly dispersive double crystal monochromator which consisted of a symmetric Germanium (220) and an asymmetric Silicon (220) crystal. Because of the different refractive indices of Silicon versus Germanium, the higher order contamination is reduced considerably¹⁰. The first crystal also enhances the total intensity throughput because of the higher Germanium electron density. This increased emittance is utilized effectively by the second asymmetric silicon crystal, the acceptance of which at 15.4 keV is enlarged by a factor 3.5 to serve as a plane wave generator for the outgoing beam with a resulting width of 0.5 arc seconds. This width is small in comparison to the (220) Laue case reflection width of 2.6 arc seconds.

The plane wave like beam is divided in two coherent beams by the beam splitter of a monolithic Laue case Bonse-Hart x-ray interferometer. Both beams

consecutively pass through a parallel sided lucite phase shifter which can be rotated by a stepper motor in order to change the relative phases of these beams. This difference is zero when the plate is oriented parallel to the mirror surface and the rotation then produces a π radians phase shift by a rotation of two degrees¹¹. As shown in Fig. 1, four beams exist behind the second mirror and two of them are brought to interference again in the region in front of the analyzer crystal. The intensity in one of the non-interfering rays served, after registration by a NaI detector, as a reference signal to stabilize the angular alignment of the interferometer relative to the monochromator. An analog feedback servo-system¹² was used for this control as well as for keeping the monochromator crystals in a stable alignment.

A second NaI detector registered the intensity of the forward scattered interference beam (int). The Si(Li) solid state detector looked under grazing incidence on the front surface of the analyzer to collect the fluorescence scattering from the bulk (Si) and the adsorbate (Br) atoms.

The interferometer was cut from one dislocation free silicon bloc with three mirrors standing up, each with a thickness of 1.5 mm. The surface was oriented parallel to (111) Miller planes with (220) diffraction planes oriented perpendicular to the surface. After chemically etching the whole interferometer the analyzer surface was cleaned by a brief syton polish. The crystal was then dipped again in HF to remove oxide layers and finally Bromine was adsorbed from a wet methanol solution. During a measurement the interferometer was enclosed in a housing for thermal stabilisation and the built-in Moire was partly compensated by an electric heating from the side of the Si(Li) detector cool tip.

The result of a phase scan is shown in Fig. 1 for the intensity of the interfering beam behind the interferometer and for the fluorescence yields from the substrate and from the adsorbate. The total coverage of Br atoms

in this run was about 1/4 of a monolayer as was determined by comparison to an implanted standard sample.

The intensity transmitted through the analyzer is out of phase by about π radians relative to the fluorescence yield from the silicon atoms close to the front surface. This demonstrates the Borrmann effect¹³ since only the wavefield with anti-nodal planes of the electrical field intensity half-way between the diffraction planes reaches the backplane of the analyzer, while fluorescence from atoms near the entrance surface is maximized when the anti-nodes overlap with the inner core level states.

The Br fluorescence yield relative to the photon flux which was incident on the first interferometer mirror was about 1×10^{-9} . Even for the collimated high photon intensity from DORIS this only resulted in a count rate of 0.01 Br K_{α} photons per sec and per mm^2 of the illuminated analyzer surface. The total counting time needed for the set of data shown in Fig. 1 was 160 minutes with a sensitive detector area of 30 mm^2 in about 5 mm distance from the radiating spot.

The fluorescence yield from the Br adsorbate follows the substrate emission with a relative phase shift $\phi_{220}'' = (-0.008 \pm 0.018) 2 \pi$ radians. The contrast of this curve indicates the fraction of Br atoms which register coherently with the lattice parallel to the surface plane and was determined to be $f_{c,220}'' = 0.57 \pm 0.04$ ¹⁴.

These measured values represent the phase and the amplitude of the first Fourier coefficient of the Bromine distribution function relative to the (220) Fourier component of the substrate charge density. If the Br atoms are displaced relative to the (220) planes (see Fig. 2) in a single-sited position this result means that 57 % of all adsorbed atoms register

coherently with the (220) planes in a position $\Delta d_{220}^n = 0.01 \pm 0.03 \text{ \AA}$. This value indicates a substitutional position on the (220) netplanes, however, Fig. 3 shows that three different, highly symmetric positions (A, B and C) are still possible adsorption sites. All three positions lie on intersections of (220) planes and can, therefore, not be distinguished by one single distance measurement in the [220] direction.

To triangulate this position we have also performed a Bragg case measurement relative to the (111) diffraction planes to determine the distance Δd_{111}^\perp as illustrated in Fig. 2. For this measurement we have again used SXRF from DORIS and the instrument is described elsewhere¹⁵. Using the same chemisorption procedure as described above resulted in a phase $\theta_{111}^\perp = (0.82 \pm 0.02)2\pi$ radians and an amplitude $f_{c,111}^\perp = 0.77 \pm 0.01$ for the first Fourier coefficient of the Br distribution function in the (111) direction. Under the assumption of one single adsorption site this means that 77 % of the Br atoms occupy positions with a displacement $\Delta d_{111}^\perp = 2.57 \pm 0.06 \text{ \AA}$ which is in close agreement with earlier measurements^{1,5}.

Summing the atomic radii in a covalent bonding of the Si and Br atoms gives a Si-Br bondlength of 2.28 \AA . On the other hand Δd_{111}^\perp is measured relative to the (111) diffraction planes as shown in Fig. 2 and this implies for position A a Si-Br distance of $2.18 \pm 0.06 \text{ \AA}$ which is in good agreement with the covalent bondlength¹⁶. The values for the distances which are inferred from position B and C, however, are in distinctive disagreement with the value which is obtained from the sum of the atomic radii.

The comparison of the coherent fractions also shows reasonable agreement. Whether the remaining difference of about 15 % is caused by a distribution function of the Br in the (111) plane, relative to the (220) diffraction

planes with more than one adsorption site or whether the bonding angle in position A is not the same as in the bulk which makes from symmetry arguments several places in the (111) plane equivalent and will reduce the coherent fraction accordingly, cannot be answered from our present results. Measurements of higher orders¹⁵ and determinations of different Fourier components such as (422) in a (111) plane, however, can uniquely¹⁷ answer these questions.

One of us (C.M.) gratefully acknowledges many helpful discussions with J.A. Golovchenko in the early stages of this project .

References

1. P.L. Cowan, J.A. Golovchenko and M.F. Robbins, Phys. Rev. Lett. 44, 1680 (1980).
2. B.W. Batterman, Phys. Rev. Lett. 133, A 759 (1964).
3. B.W. Batterman, Phys. Rev. Lett. 22, 703 (1969).
4. J.A. Golovchenko, B.W. Batterman and W.L. Brown, Phys. Rev. Lett. B10, 4239 (1974).
5. J.A. Golovchenko, J.R. Patel, D.R. Kaplan, P.L. Cowan and M.J. Bedzyk, Phys. Rev. Lett. 49, 560 (1982).
6. U. Bonse and M. Hart, Appl. Phys. Lett. 6, 155 (1965).
7. U. Bonse and M. Hart, Z. Phys. 188, 154 (1965).
8. This means, for example, that the standing wavefield modulation becomes zero at certain depths within the crystal.
9. J.A. Golovchenko, D.R. Kaplan, G. Materlik, P. Funke, to be published.
10. U. Bonse, G. Materlik and W. Schröder, J. Appl. Cryst. 9, 223 (1976).
11. Note, that this requires a much less precise phase drive as for a Bragg case measurement, where the corresponding phase shift occurs over the width of a reflection curve.
12. A. Krolzig, G. Materlik, M. Swars and J. Zegenhagen, accepted by Nucl. Instr. and Meth.
13. G. Borrmann, Z. Phys. 42, 157 (1941).
14. This value was already corrected for a loss of contrast which is caused by the built-in Moire.
15. G. Materlik and J. Zegenhagen, to be published.
16. Note, that the positional accuracy of such measurement can still be increased if needed¹⁵.
17. Obviously, a unique position determination needs more than two distance measurements.

Figure Captions

- Fig. 1 Phase scan of the fluorescence yields from surface-near Silicon atoms (I_{Si}) and from adsorbed Br atoms (I_{Br}) relative to the transmitted intensity I_{int} . The inset shows schematically the experimental set-up in a side view.
- Fig. 2 Arrangement of Silicon atoms close to the (111) surface. Dashed lines give the (111) and (220) diffraction planes. Ad_{111}^{\perp} and Ad_{220}^{\parallel} are the distance of the adsorbed atom (dashed circle) determined by a Bragg case and by an interferometric measurement respectively.
- Fig. 3 Arrangement of Si atoms in the (111) surface of the analyzer relative to the three sets of (220) planes with spacing d_{220} . Closed and open circles indicate first layer and second layer atoms respectively. A, B and C are symmetric positions lying on intersections of (220) planes.

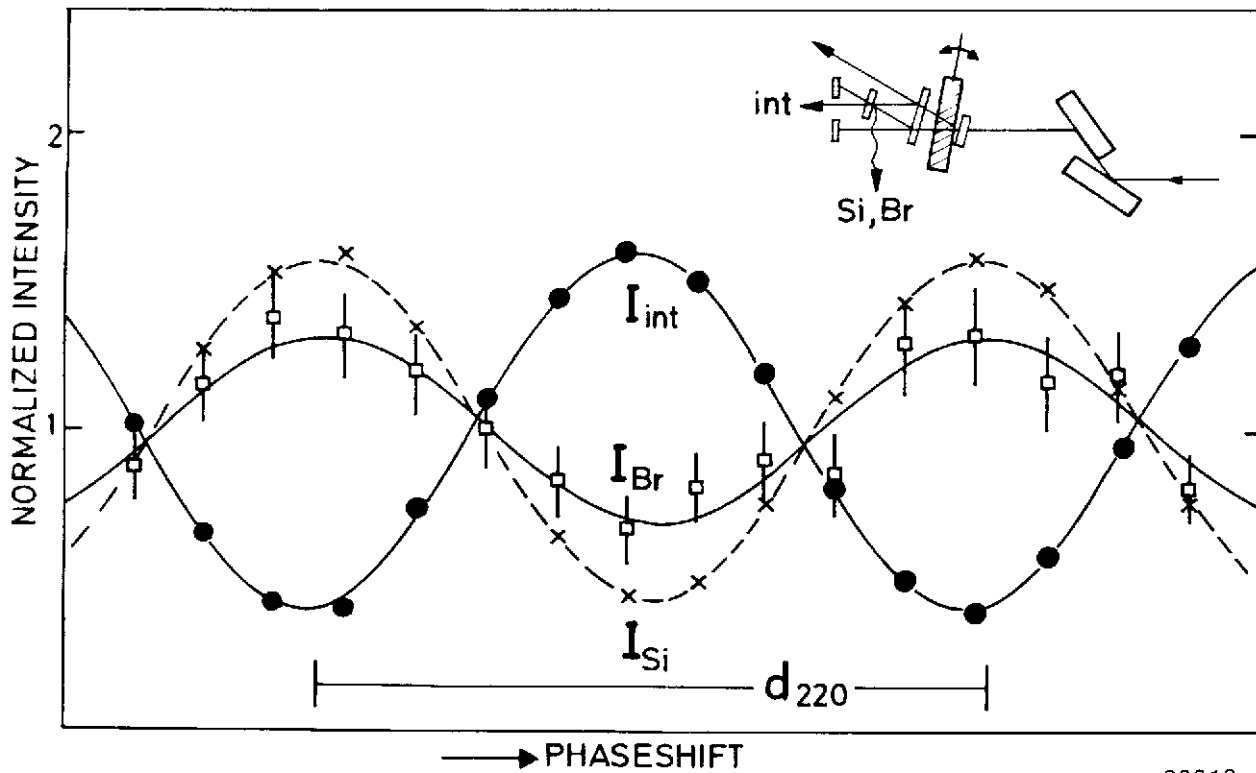


Fig. 1

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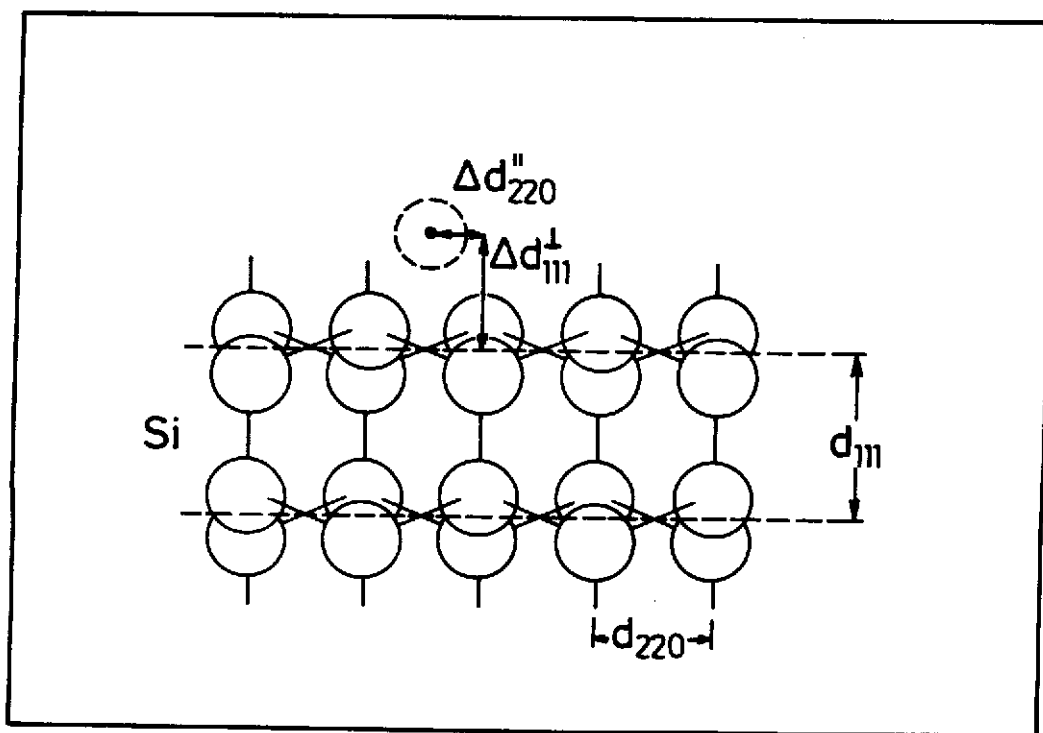
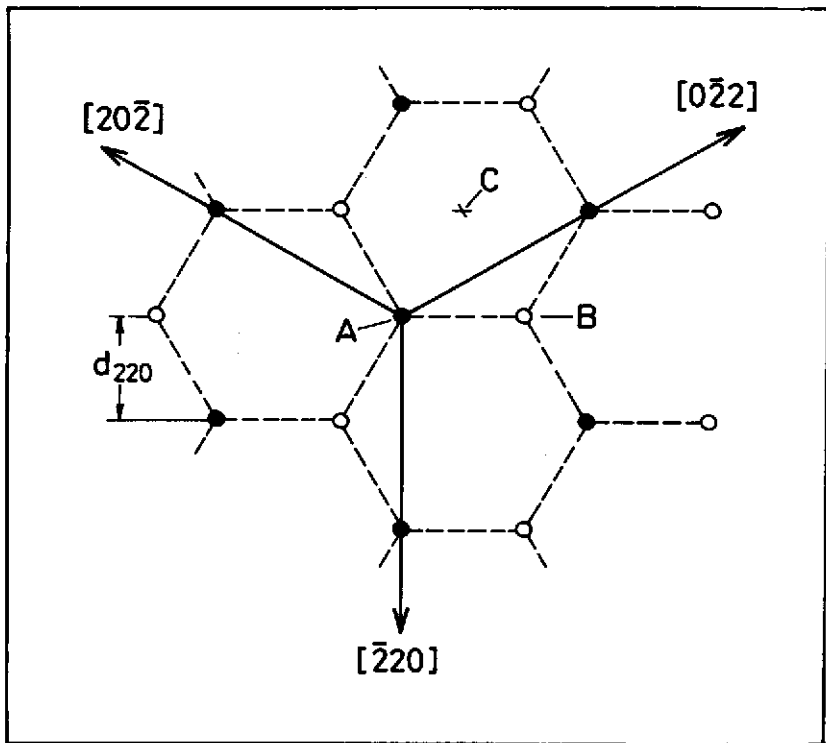


Fig. 2

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Fig. 3

