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Determination of the position and vibrational amplitude of an adsorbate by means of multiple-order x-ray standing-wave measurements

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For a submonolayer of Br atoms adsorbed onto a real Ge(111) surface, x-ray interference fields were used to determine the Br position with respect to the substrate (111) and (333) diffraction planes. The results from both the (111) and (333) measurements are consistent with the onefold-atop-site surface model. The increase in local sensitivity from using the (333) diffraction planes also enabled us to demonstrate the use of x-ray interference fields for determining the vibrational amplitude of an adsorbate.

The possibility of using x-ray interference phenomena to study the bonding geometry of surface adsorbates has recently been demonstrated by using dynamical diffraction in both the Bragg[1] and Laue[2] geometries. As shown in these demonstrations, an x-ray standing-wave field can be created in the surface region of a single crystal by the interference between two coherently coupled plane waves. The antinodal planes in this interference pattern are parallel to and have the same periodicity as the acting diffraction planes. Most importantly, the phase of the standing-wave field relative to the diffraction planes can be adjusted by changing the relative phase between the two plane waves. Thus the position of an adsorbate can be measured, relative to the substrate diffraction planes, by monitoring a characteristic fluorescence signal from the adsorbate, while moving the standing-wave field continuously across the atomic planes.

The high intensity of synchrotron x radiation (SXR) proved to be an essential requirement for the Laue-case measurement, since an x-ray interferometer is needed to generate the two coherent and independently traveling wave trains that impinge on the analyzed surface. For the Bragg case, there are certain favorable measurements that can be carried out with a conventional x-ray source, but the necessary measuring periods of at least 10 h are rather long for performing systematic surface studies. With the high brilliance of SXR, such favorable measurements can be reduced down to minutes.

Until now, standing-wave measurements on surface adsorbates have used only the fundamental diffraction planes. By going to higher-order harmonics, the spatial periodicity of the excited standing wave field is reduced and therefore one is able to obtain higher-order Fourier components for the spatial distribution of the adsorbate atoms. This additional information is necessary for completely describing the adsorbate distribution, when there is more than one preferred position, and for measuring the kinetics of an adsorbate atom in terms of its vibrational amplitude. In our present investigation we have used two reflection orders for a Bragg-case x-ray standing-wave analysis of the Br/Ge(111) surface adsorbate system.

Prior to Br deposition, the symmetrically cut Ge(111) sample crystal was Syton polished and etched in hydrofluoric acid. The sample was transferred into a 0.05% by volume Br methanol solution and treated with a Br-methanol nonabrasive-pad polishing procedure[3] followed by a thorough rinse in methanol. The sample was then kept in a dry-nitrogen atmosphere until the end of the measurement.

The experiment was carried out with the x-ray standing-wave setup installed at the ROEMO instrument[4] of the Hamburg Synchrotron Radiation Laboratory. Using the tunability of this instrument, the measurements were performed at an optimal incident photon energy just above the Br K absorption edge. This choice in energy, partially reduced[5] the overpowering influence of the Ge $K\alpha$ and $K\beta$ fluorescence (at 9.9 and 11.0 keV) relative to the $K\alpha$ fluorescence yield (at 11.9 keV) from the Br. As illustrated in Fig. 1, a double crystal monochromator was used to prepare the incident plane wave for the sample crystal. The indicated combination, of a symmetrical first crystal and an asymmetrical second crystal, reduces the angular emittance range and allows one to detune unwanted higher-order harmonics from the output beam.[6] Such a detuning was used for the Br/Ge(111) experiment. For this measurement a pair of Si(111) single crystals were used in the monochromator, with an asymmetrical angle of $\phi = 7°$ for the second crystal. At the selected energy of $E_\gamma = 13.7$ keV, the angular emittance range from the second crystal was 5.6 μrad as

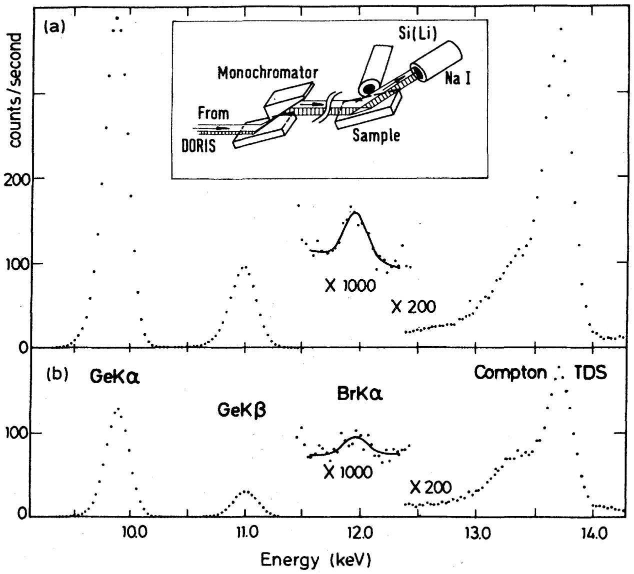

FIG. 1. Br/Ge(111) x-ray spectra collected with a Si(Li) detector (shown in inset). Spectra (a) and (b) were accumulated in angular intervals 15 and 8 of Fig. 2, respectively.

compared to 44.3 μrad for the acceptance angular range of the Ge(111) sample crystal.

As the Ge sample crystal was repetitively rocked[7] in angle θ, the reflected intensity, as monitored by the NaI detector shown in Fig. 1, and the fluorescence spectra, were collected in a multi-spectrum-scaling mode, which subdivided the angular scan range into 16 equally spaced intervals. Spectra (a) and (b) in Fig. 1 were accumulated in angular interval 15 and 8, respectively, during the 7.5-h Br/Ge(111) experiment. The reflectivity data and Br fluorescence yield data for all 16 angular intervals of this scan are shown in Fig. 2.

For the Br/Ge(333) standing-wave measurement it was necessary to eliminate the nearby (444), (555), (777), and (888) harmonics, as well as the (111) fundamental. Since asymmetrical detuning, as previously described, was not sufficient, we chose to use a pair of monochromator crystals with d spacings similar to Ge(333), but with nonmatching (h,k,l) indices. Thus we used a Ge(440) reflection at the first crystal and a Si(333) asymmetrical reflection at the second crystal. With an asymmetrical angle of $\phi = 21.5°$ and a selected energy of $E_\gamma = 13.6$ keV, the angular emittance range from the monochromator was 1.3 μrad as compared to 9.2 μrad for the Ge(333) sample. The corresponding theoretical curves and experimental data are shown in Fig. 3.

For a perfectly collimated monochromatic x-ray beam being Bragg diffracted by a symmetrically cut single crystal and polarized perpendicular to the reflection plane, the angular variation of the K fluorescence yield from a specific type of atom near the surface is

$$Y_H(\theta) = 1 + R_H + 2\sqrt{R_H} f_{c,H} \cos(v_H - 2\pi\Phi_H) \ . \qquad (1)$$

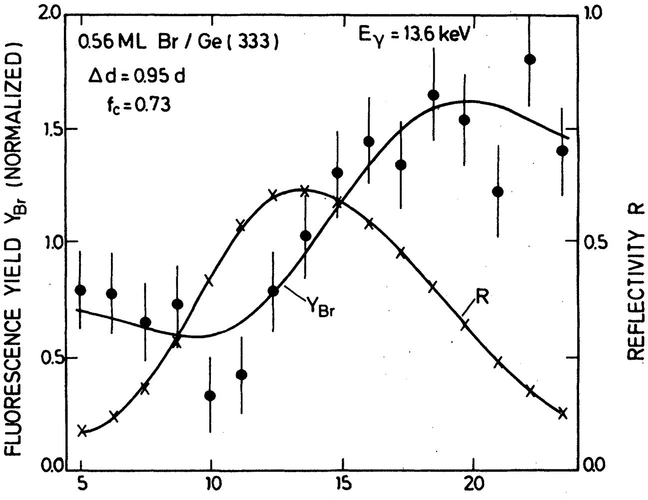

FIG. 3. Experimental data and theoretical curves for the Br K fluorescence yield and Ge(333) reflectivity vs Bragg reflection angle.

The angular dependence of Eq. (1) is contained in variables $R_H(\theta)$ and $v_H(\theta)$, which correspond to the intensity and phase of the diffracted plane wave relative to the incident. The phase v_H decreases continuously by π radians when the crystal is advanced in angle θ through the total reflection condition. Since the photoeffect for core electrons is proportional to the E-field intensity at the center of the atom, parameters $f_{c,H}$ and Φ_H, in Eq. (1), are the amplitude and phase of the (h,k,l) Fourier component $A_H = f_{c,H} \times \exp(-2\pi i \Phi_H)$ for the normalized distribution of fluorescence-selected atoms. $f_{c,H}$ and Φ_H, which are referred to as the coherent fraction and coherent position, respectively, are determined from the χ^2 fit of Eq. (1)[8] to the normalized fluorescence yield data as shown in Figs. 2 and 3.

From the Br/Ge(111) data, the coherent position of the Br atoms with respect to the underlying perfect Ge(111) diffraction planes was determined to be $\Phi_{111} = 0.80 \pm 0.01$. And from the Br/Ge(333) data, the coherent position with respect to the Ge(333) diffraction planes was $\Phi_{333} = 0.95 \pm 0.03$. In Fig. 4 the Φ_{111} and Φ_{333} scales are shown along with a bulklike Br/Ge(111) surface model. This

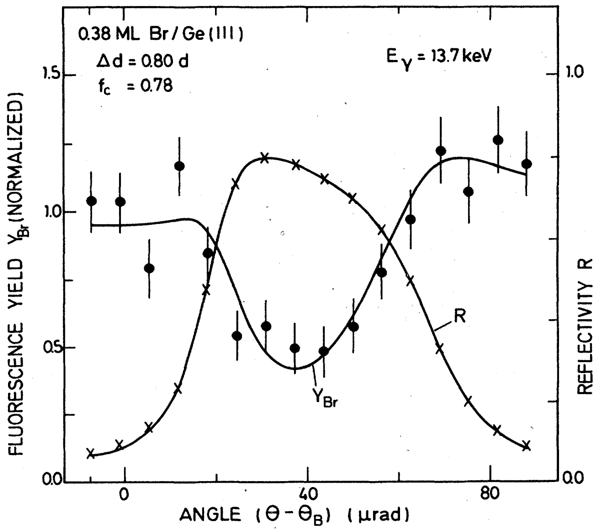

FIG. 2. Experimental data and theoretical curves for the Br K fluorescence yield and Ge(111) reflectivity vs Bragg reflection angle.

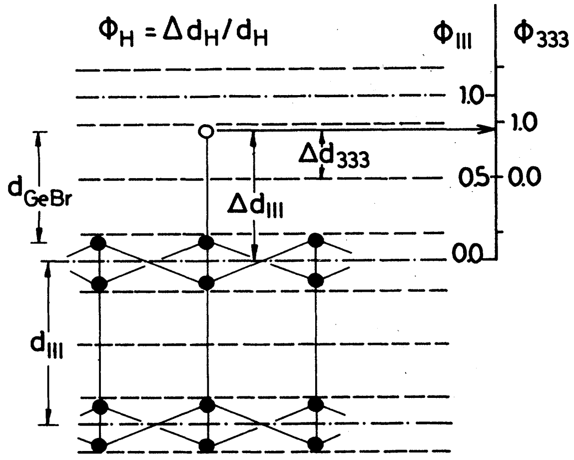

FIG. 4. Br/Ge(111) bulklike surface model, showing Br atoms (○) covalently bonded to Ge(111) surface atoms (●) which are in ideal lattice positions, where $d_{111} = 3.27$ Å and $d_{GeBr} = 2.27$ Å (Ref. 9). The (111) (— · — ·) and (333) (— — —) diffraction planes are positioned to sense the maximum in the x-ray scattering electron density.

model assumes that monovalent Br atoms saturate the dangling bonds of Ge surface atoms and thus occupy onefold-atop positions on a locally unreconstructed and unrelaxed Ge(111) surface. Using bulk Ge and $GeBr_4$ geometrical parameters, this model predicts that the coherent positions would be $\Phi_{111} = 0.82$ and $\Phi_{333} = 0.96$. This is in very good agreement (difference < 0.03 Å) with our measured values,[10] whereas the threefold bridging sites on this idealized surface would place the Br atom several tenths of Å inward with respect to the onefold position.[11] The atop-site bonding geometry is also consistent with standing-wave measurements[2,12] of the chemically prepared Br/Si(111) "real" surface and with surface extended x-ray absorption fine-structure (SEXAFS) measurements[13,14] of the Cl/Ge(111) and I/Ge(111) "ideal" surfaces prepared in ultrahigh vacuum. Note that the inferred adsorbate bonding configuration from these measurements is identical for both surface preparations. This is attributable to the high stability of this configuration.

The relationship between the two scales shown in Fig. 4 is defined by the transformation $\Phi_{333} = 3\Phi_{111} + \frac{1}{2}$ (mod 1). The fact that our measured Φ_{111} and Φ_{333} values obey this transformation combined with the high coherent fractions indicates that there is only one preferred position in the [111] direction. The measured coherent fractions for the two separate experiments were $f_{c,111} = 0.78 \pm 0.03$ and $f_{c,333} = 0.73 \pm 0.06$. For such measurements, the coherent fraction can be divided into three fundamental factors as $f_{c,H} = C a_H D_H$. In this expression C represents the commensurate (nonrandomly distributed) fraction of Br atoms, a_H is a geometrical factor which equals unity for the case of one preferred position, and D_H is the Debye-Waller factor for the adsorbed Br atom in the **H** direction. In terms of the mean square of the vibrational amplitude $\langle u_H^2 \rangle$ $D_H = \exp(-2\pi^2 \langle u_H^2 \rangle / d_H^2)$. Since the commensurate fraction C is approximately the same for both measurements[15] and since $a_{111} = a_{333} = 1$ is corroborated by the high f_c values, the Br vibrational amplitude can be determined from $f_{c,111}$ and $f_{c,333}$. From this we conclude that the chemisorbed Br atoms vibrate in the [111] direction with an amplitude of (0.067 ± 0.053) Å at room temperature. In comparison, bulk Ge atoms at room temperature have $D_{111} = 0.987$ and $D_{333} = 0.889$ corresponding to $(\langle u_{111}^2 \rangle)^{1/2} = 0.084$ Å.

The total coverage of Br on the sample surface for the two different preparations was determined by comparing its off-Bragg Br fluorescence yield with a Ge sample with a known implanted dose of Br. From this comparison the Br coherent coverage was 0.30 ± 0.03 monolayer (ML) for the Br/Ge(111) measurement and 0.41 ± 0.06 ML for the Br/Ge(333) measurement. These values, which are obtained by multiplying the coherent fraction times the total coverage, are significantly higher than the Br/Si(111) coherent coverages of 0.20 ML.[2,12] This increased coherent coverage can be explained by the slightly larger Ge-Ge lateral distance for two adjacent Ge atoms in conjunction with the filled-shell radii of two Br atoms. ($d_{110}^{\mathrm{Ge}} = 4.00$ Å, $d_{110}^{\mathrm{Si}} = 3.84$ Å, and $2r_{\mathrm{Br}^-} = 3.90$ Å.[16]) For the bulklike Br/Si(111) surface, adjacent Br atoms would slightly overlap, thus sterically forbidding the coherent coverage to exceed $\frac{1}{3}$ of a monolayler.

In conclusion, the use of multiple-order x-ray standing-wave measurements with SXR has enabled us to determine that the structure of Br chemisorbed onto a realistic Ge surface is described by a one-sited Br distribution function. As demonstrated, this method can also be used for measuring the vibrational amplitude of an adsorbate atom. Since x-ray standing-wave measurements have already been carried out in a temperature-controlled environment,[2] no obstacles are foreseen for such experiments at higher or lower temperatures.

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[10] Note, however, that even these two Fourier components of the Br distribution function cannot *a priori* serve to unambiguously describe the adsorbate geometry. This calls for additional characterization of the Ge top atom layer. Although such a problem can be studied with standing waves, this challenge has not yet been met successfully.

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