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X-RAY STANDING WAVE ANALYSIS WITH SYNCHROTRON RADIATION APPLIED FOR SURFACE AND BULK SYSTEMS

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X-Ray Standing Wave Analysis with Synchrotron Radiation Applied for Surface and Bulk Systems

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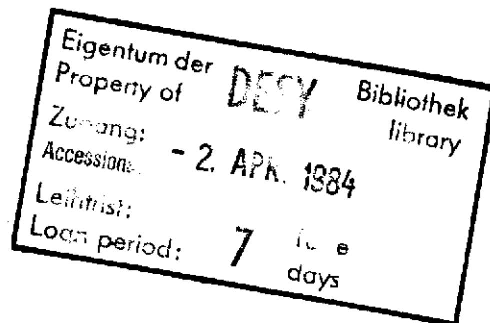
The advantageous use of synchrotron radiation for X-ray standing wave measurements is demonstrated. For bulk-like systems As implanted in Si was analysed with two reflection orders (220) and (449) which shows that lattice relaxation around the As atom can be measured. The case of Br chemisorbed on Si(111) illustrates the accomplished decrease in measuring time and increase in precision.



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Inelastic scattering processes, which result from the decay of photon excited atoms attracted over the past decade a strong, steadily increasing interest caused by the availability of high intensive, pulsed synchrotron radiation from storage rings [1], which has a continuous spectral distribution from the infrared to the hard x-ray region. Photoemitted electrons, scattered photons and desorbed ions are studied with high energy and momentum resolution as well as time resolved.

Although the photon cross section drops off rapidly with photon energy, the frontiers of these measurements of emission processes are continuously advancing into the short wavelength part of the spectrum, revealing new scattering and new spectroscopic applications.

In this context scattering caused by spatially modulated electromagnetic wavefields, which have the local periodicity of a crystalline lattice, has become specially exciting. Such x-ray standing wave measurements were introduced by Batterman [2] who studied the yield of fluorescence radiation from atoms interacting with a periodic interference pattern which was generated under the condition of dynamical Bragg diffraction. The interference of the coherently coupled incident and reflected waves produces a standing wave pattern with nodal and anti-nodal planes parallel to the (h,k,l) diffraction planes. When passing the strong Bragg reflection condition by changing the reflection angle Θ, the nodes of this interference field move by half a plane distance from being in phase with the (h,k,l)-Fourier component of the electron charge density to being out of phase by π radians at the high angle side.

Following this work several groups started to investigate other inelastic channels such as thermal diffuse scattering [3,4], Compton scattering [3,5,6], electron emission [7,8], luminescence excitation [9] and internal photoeffect [10].

An important application of this movement of the interference pattern on a crystal lattice constant scale was realized by Golovchenko, Batterman and Brown [11] who measured the characteristic fluorescence radiation from As impurity atoms, implanted in a Si host lattice to determine atomic positions relative to the bulk diffraction planes. Later on [12] it was shown that the position of adsorbates on crystalline surfaces can be measured with a high spatial resolution even for sub-monolayer coverages.

In this paper we report the first measurements with synchrotron x-radiation (SXR) in this field. By studying two different applications, we demonstrate the advantages which were realized by applying the properties of SXR in an adapted way.

Our instrument is installed at the ROEMO station of the Hamburger Synchrotron Radiation Laboratory HASYLAB in Hamburg and uses radiation from the DORIS storage ring. The inset in Fig. 1 shows a schematic lay-out in a side view. Synchrotron radiation is first monochromatized by a double crystal diffractometer for which a variety of perfect Si and Ge crystals was prepared with different orientations which can be used in various combinations. Since the monochromatic beam has to have an angular emittance which is small in comparison to the sample reflection width, asymmetrically cut crystals [13] with different asymmetry parameters are used as second crystals with a small angular emittance which goes in hand with a large angular acceptance. To gain maximum intensity, this acceptance range has to be illuminated by a proper first crystal. This combination also has to reduce the spectral contamination arising from harmonics. A Ge/Si combination [14] fulfills these requirements over a wide range of applications. The angular collimation of the monochromatic beam can be changed continuously via the Bragg angle, thus slightly tuning the photon energy. During a measurement an analog feed-

back system can be used to keep the monochromator crystals aligned [15].

The monochromatic plane wave like beam is reflected from a sample crystal which is mounted on a goniometer. The angle is changed across the narrow range of Bragg reflection by a piezoelectric crystal which is under control of an electronic feedback system [16] to assure a linear angle drive over a well defined angular range. A NaI (Tl) detector measures the reflectivity and a Si(Li) solid state detector records the fluorescence radiation in an energy dispersive manner. The data are stored as a function of angle into a multi-channel analyzer operating in a multi-spectrum scaling mode.

To demonstrate the possibilities of this instruments we have chosen examples in the areas of bulk impurities and adsorbed surface layers which can be compared with results from measurements with conventional x-ray tubes, namely the cases of As implanted into Si [17] and Br adsorbed on Si [12,18]. However, with a higher reflection order we demonstrate one of the new possibilities which can be realized routinely by using SXR. The As and Br data were recorded with DORIS running at an energy of 5.0 and 3.7 GeV and a medium current of 25 and 40 mA, respectively. Fig. 1 shows the measured reflection curve and As fluorescence yield data versus angle from a sample with 10^{15} As atoms/cm^2 implanted at 60 keV ion beam energy. The (220) diffraction planes are oriented parallel to the surface and the crystal was annealed for 0.5 hours in a dry N_2 atmosphere at 775°C. The monochromator consisted of a symmetric (220) Ge and an asymmetric Silicon (220) crystal. The result of a least square fit to the fluorescence data can be expressed as a coherent fraction $f_{c,220}$ of As atoms which register coherently with the Silicon (220) planes and by a position Δd_{220} measured as an offset perpendicular to the (220) planes [19]. For the case shown, this analysis gives $f_{c,220} = (79.3 \pm 1.2)$ % and $\Delta d_{220} = (0.022 \pm 0.003) * d_{220}$. The time needed to record this scan was

30 minutes with an illuminated crystal area of 14 mm^2 irradiating an acceptance angle of the Si(Li) detector of roughly 0.3 srad.

The high degree of linear polarization with an electric field vector lying horizontally was used to improve the statistical precision of the fluorescence data. Looking with the Si(Li) detector into the direction of the electric field vector reduced the background due to Compton- and elastically scattered photons specially far out in the tails of the reflection curve. In this way the statistical error remains almost constant across the reflection width.

The periodicity of the standing wave pattern is changed by using higher reflection orders. Applying the high photon intensity from SXR offers the possibility to compensate for the corresponding intensity loss. Fig. 2 shows a (440) scan of the same sample, which was again taken in 30 minutes at E_γ = 15.2 keV with a result $f_{c,440}$ = (66.3 ± 3.3) % and Δd_{440} = (0.041 ± 0.01) x d_{440}.

The standing wave analysis determines the amplitude $f_{c,hkl}$ and the phase $\Phi_{hkl} = 2\pi\, \Delta d/d_{hkl}$ of the (hkl)-Fourier component of the impurity distribution function. Therefore, a foreign atom in a centrosymmetric crystal always gives a position answer 0.0 x d_{hkl} or 0.5 x d_{hkl} as long as the distribution function remains, as in the present case, symmetric with respect to the diffraction planes. The measured offset $\Delta d_{440} = \Delta d_{220}$ = 0.04 Å is thus induced by an expansion of the Si lattice in the region of the shallow [17] implanted Si/As layer. Since the wavefield periodicity is only defined by the underlying perfect Si lattice this position offset determines a mean integrated lattice relaxation [20]. The local lattice expansion also depends on the impurity concentration which affects the number of atoms with a certain one directional displacement relative to the bulk lattice planes. This influences the amplitude

f_c [21]; however, this dependence is negligible for the As results.

The width of the distribution function with one lattice place being coherently occupied by an impurity atom can be derived from the amplitudes of the Fourier components. If the As atoms occupy coherently exclusively substitutional places and if the remaining portion is incoherently distributed, a width of $\langle u^2\rangle + \sigma_D^2$ = 0.01 Å^2 is inferred from the data [21] with 16 % of the atoms being randomly distributed. This width contains contributions from the mean square vibrational amplitude $\langle u^2\rangle$ and possibly also from a distortion profile which cannot be excluded from the present data and was assumed to be Gaussian like with standard deviation σ_D.

If we further examine the result for a distribution function with two possible sites, the measured off-plane position is Δd = 0.6 Å with less than 10 % of all As atoms occupying this site, while the substitutional fraction remains the same as above. This result is valid as long as 0.004 Å$^2 \lesssim \langle u^2\rangle + \sigma_D^2 \lesssim$ 0.01 Å^2. In view of the Si bulk mean square amplitude, $\langle u^2_{Si}\rangle \approx$ 0.006 Å^2, this requirement is safely satisfied. Such minority position can be caused by an As-vacancy coupling. The relaxation of a Si atom towards a single vacancy was calculated [22] to be 0.6 Å, which is in fair agreement with the determined As off-position.

To prove this model unambiguously and to characterize the bulk impurity distribution function completely, additional higher order measurements as well as studies at temperatures other than room temperature should be carried out.

Another system where position answers may be obtained directly is an adsorbed sub-monolayer on a crystal surface. Fig. 3 shows the result for Br chemisorbed from a liquid solution of Br in methanol on a Si(111) surface. The high precision of the measurement is reflected by the result being

$\Delta d_{111} = (2.61 \pm 0.01)$ Å and $f_{c,111} = (74.7 \pm 1.0)$ %. The whole measurement on the 0.02 monolayer thick adsorbate was recorded in 1 hour. This result agrees well with former measurements [18] and confirms the assumption of a single-fold on-top Br position on the Si(111) substrate.

Concluding we like to sum up that SXR has proven to bring the gain in precision, sensitivity [23] and measuring time which is needed to make routinely measurements of inelastic scattering out of interference fields with periodicities of the lattice netplanes. Also new applications become routinely possible, such as higher order measurements, which are necessary to draw a complete picture of bulk impurity and adsorbate distribution functions.

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Figure Captions

Figure 1 Measured (+,*) and calculated (---,—) Si(220) reflectivity and As K_α fluorescence yield data versus reflection angle, with a Bragg angle Θ_B. The inset shows schematically the experimental arrangement with an angular collimating second Si crystal. Asymmetry parameter $b = 0.08 = \sin(\Theta_B - \varphi)/\sin(\Theta_B + \varphi)$, where φ is the angle between the surface and the diffraction plane.

Figure 2 As Fig. 1, however, the Si sample crystal was reflecting in second order (440) and the second monochromator crystal has an asymmetry parameter b = 0.2.

Figure 3 Measured (+,*) and calculated (---,—) Si(111) reflectivity and Br K_α fluorescence yield data from a chemisorbed 0.2 monolayer of Br. The second monochromator crystal has an asymmetry parameter b = 0.07.

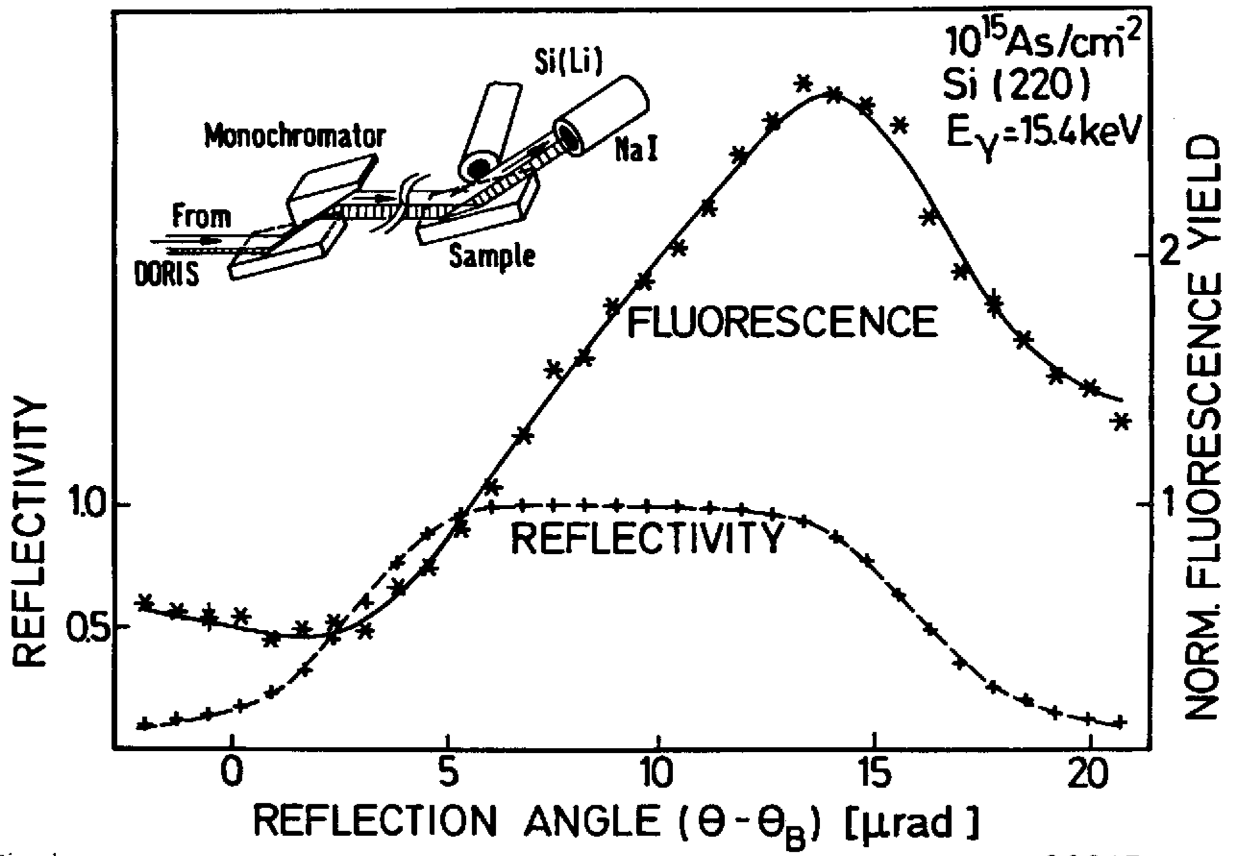

Fig. 1

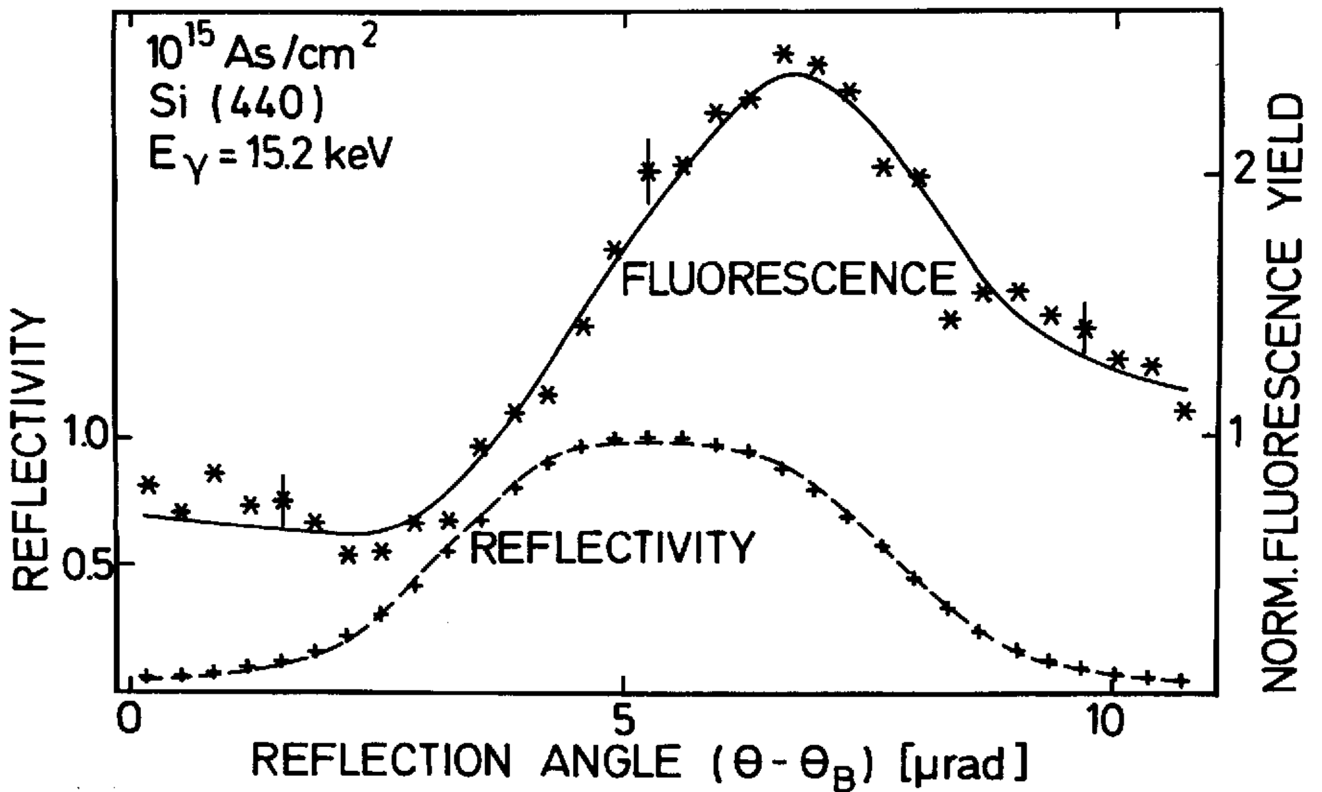

Fig. 2

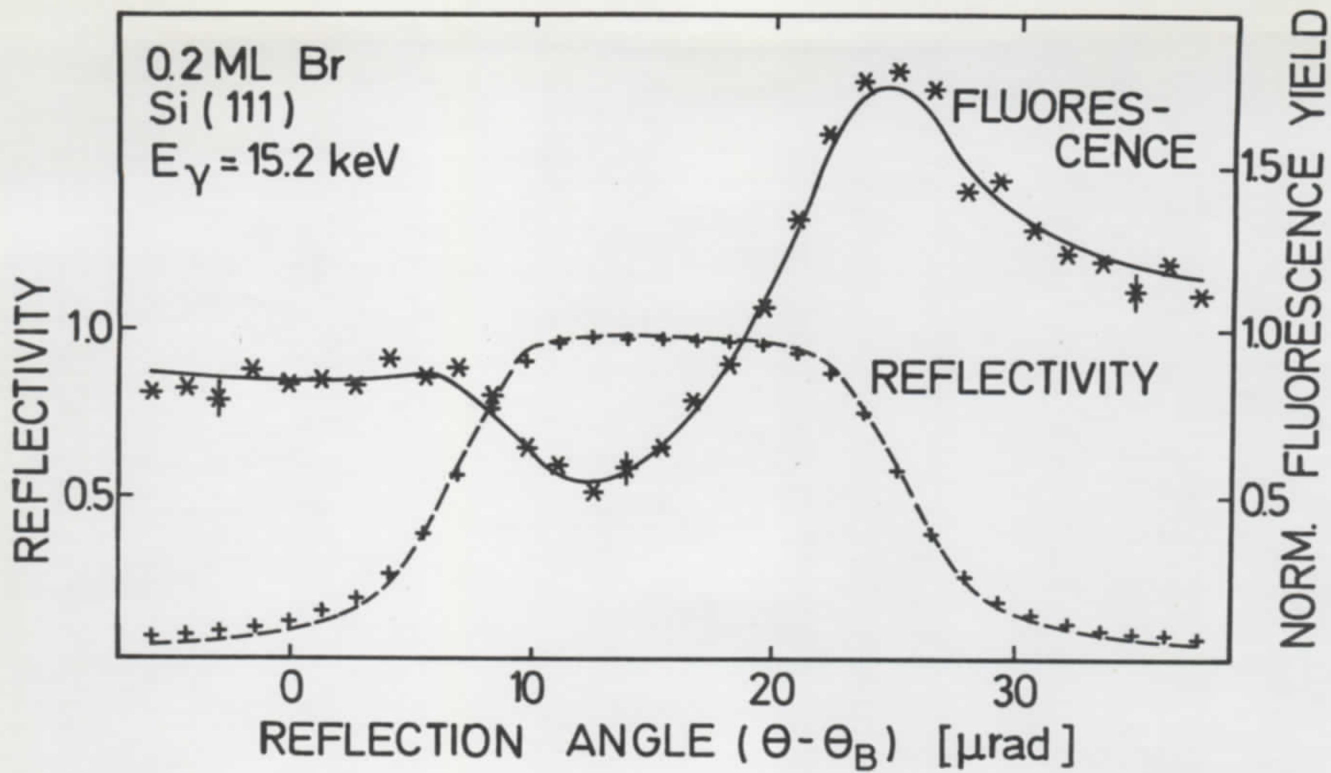

Fig. 3