Depth-selective x-ray standing-wave analysis

M. J. Bedzyk and G. Materlik

Hamburger Synchrotronstrahlungslabor HASYLAB at Deutsches
Elektronen-Synchrotron DESY, D-2000 Hamburg 52, Germany

M. V. Kovalchuk

Institute of Crystallography, Academy of Sciences of the U.S.S.R.,
Moscow 117333, U.S.S.R.

(Received 18 May 1984)

Energy-dispersive electron emission yields from silicon crystals were measured while Bragg reflecting 15-keV x rays from the (111) diffraction planes. By combining the characteristics of the excited x-ray standing-wave field with the electron-energy-loss process, it was possible to probe the structure for lattice perfection as a function of depth and to determine an energy-loss-dependent electron escape length.

As predicted by the dynamical theory of x-ray diffraction,[1] a well-defined x-ray interference field is generated when an incident plane wave is Bragg diffracted by a perfect crystal. For the two-beam Bragg case, there is one Bloch-wave eigenstate of the photon excited for each angle of incidence. The spatial periodicity of this photon Bloch wave is identical to that of the diffraction planes, since it consists of two coherently coupled partial waves with wave vectors $\vec{K}_0$ and $\vec{K}_H = \vec{K}_0 + \vec{H}$, where $\vec{H}$ is the reciprocal lattice vector of the reflecting set of planes. The strong excitation of this photon Bloch wave also causes a drastic decrease of the effective crystal depth penetrated by the incident radiation (extinction effect).[2]

Advancing in angle through the strong Bragg reflection condition causes the phase of this standing-wave field to move in a continuous manner by π radians with respect to that of the diffraction planes. This corresponds to a movement of one-half of a diffraction plane spacing in the $-\vec{H}$ direction. On the low-angle side of the strong Bragg reflection, the antinodes of the wave field lie half-way between the diffraction planes and on the high angle side the antinodes coincide with the diffraction planes.

The existence of such standing-wave fields was first used by Borrmann[3] to explain the anomalous transmission of x rays in perfect crystals. Later, Batterman[4] demonstrated the motion of the interference field relative to the atomic planes by observing the variation of the fluorescence radiation being emitted by the atoms of the crystals. Recently, this radiation, which is characteristic for each atomic species, was also used to locate foreign implanted[5] and adsorbed[6] atoms relative to the host lattice. This determination is possible, since the fluorescence and electron yields from core-level electrons are proportional to the E-field intensity at the atomic nuclei.

The depth probed by using the fluorescence radiation emitted from atoms within the crystal depends on the ratio between the absorption length of these secondary photons and the extinction depth of the primary photons. If this absorption length is larger or comparable to the extinction length, the standing wave-field motion, and thus the structural information contained in the angular fluorescence yield, is masked by the drastic change of the probed depth below the crystal surface. For the opposite case, the absorption length of the reemitted photons and the fluorescence

detection take-off angle determine the crystal depth over which the structural information is integrated.[7] It is therefore difficult to use fluorescence measurements to obtain structural information about the substrate lattice as a function of depth, although this is of great interest, since local lattice relaxation around impurity atoms must be included in studies of bulk impurities.

Measurements of the modulation of the photoelectron emission process, induced by x-ray standing-wave fields, have also been reported. These have concentrated on the total secondary electron yield[8,9] and on the zero-energy-loss photoelectrons,[10] which again only contain depth integrated information. This situation can be changed by giving careful consideration to the energy lost by the electrons on their way out of the crystal. This energy loss is characteristic of the depth at which the electron was excited and also depends on the substrate composition, and on the electron take-off angle relative to the surface. Therefore, the energy resolved detection of photo and Auger electrons, under the standing-wave-field conditions, provides a depth selective microprobe for studying the structure of the lattice layer by layer. Furthermore, a characteristic escape length for the electrons can also be determined from this type of diffraction experiment.

The measurements were made at the instrument ROEMO of the Hamburg Synchrotron Radiation Laboratory HASYLAB at Deutsches Elektronen-Synchrotron DESY, with synchrotron radiation emitted by the DORIS storage ring. A double crystal monochromator[11] (Fig. 1, inset) with Si(111) crystals in a nondispersive arrangement was used for producing an $E_\gamma = 15$ keV x-ray beam incident on the Si(111) sample crystal. The second Si monochromator crystal was asymmetrically cut, thus serving as a plane-wave generator with a total angular emittance range of 0.7 arc sec. This width is approximately $\frac{1}{5}$ as wide as the angular acceptance range of the symmetrically cut Si(111) sample crystal.

The electron emission spectra from two different Si(111) crystals were analyzed in this study: one was an etched and polished perfect single crystal and the other was after polishing oxidized in a humid oxygen atmosphere above 1000 °C and thus was covered by a 0.6-μm SiO_2 disordered surface layer. The photoemission spectra were recorded with a low-resolution gas flow proportional counter.[9] As a sample crystal was scanned[12] in angle θ, back and forth over the
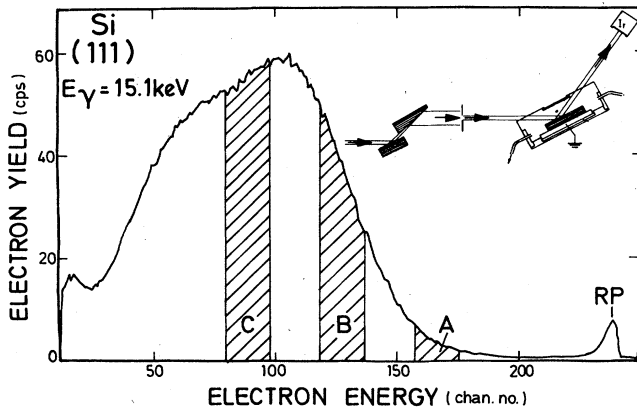
FIG. 1. Electron emission spectrum from perfect Si(111) sample collected with a gas-flow proportional counter (inset). A random-pulse (RP) generator was used for dead-time correction. The yield in region A is primarily from L photoelectrons with nearly zero energy loss. Regions B and C are from K photoelectrons with energy losses of 2 and 5 keV, respectively.

Bragg reflection, the photoelectron spectra (Fig. 1) and reflectivity values (Fig. 2) were simultaneously recorded at 32 equally spaced angular intervals of the Si(111) rocking curve with a narrow slit of about 0.1×0.1 mm^2 in front of the sample.

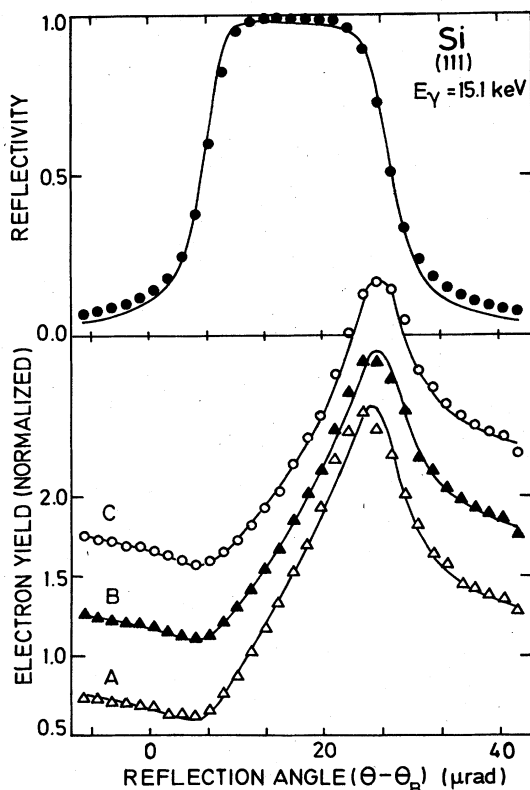Based on the relative values for the K, L, and M pho-

FIG. 2. The angular variation of the perfect Si(111) reflectivity and photoelectron yields for energy regions A, B, and C of the spectrum shown in Fig. 1. The electron yield scale corresponds to curve A. Curves B and C have been given a 0.5 and 1.0 vertical offset with respect to this scale. The solid lines are theoretical curves.

toelectric cross sections,[13] 93% of the initial photoelectrons are Si K photoelectrons. Approximately 95% of the resulting K-holes decay by emission of Si $K LL$ Auger electrons with initial energies of approximately 1.6 keV. However, due to the comparatively short escape depth for these low-energy Auger electrons and the reduction in the energy window of the detector at lower energies, the Si electron emission spectra shown in Fig. 1 corresponds primarily to Si K photoelectrons which have an initial energy of 13.3 keV. For the case of 15-keV x rays incident on SiO$_2$, only 15% of the electron yield will have been emitted by oxygen atoms.[13]

Due to the short mean free paths that the electrons have before they undergo, for example, electron-electron or electron-plasmon interactions, the emitted electrons reach the surface and are finally detected with an energy loss ranging from zero to several keV. To a first-order approximation, the depth dependence of this energy-loss process in silicon was calculated by χ^2 fitting the angular yields of the electron energy regions A, B, and C (Fig. 1) to the theoretical angular variation of the Si K-photoelectron yield[14] from ideal Si(111) atomic layers at a depth z within the crystal (see Fig. 2). This approximation assumes that all electrons in a given energy region originated from the same depth z. This is naturally a coarse assumption, since the depth distribution for a particular energy loss is not a delta function. However, since the actual distibution[15] tails off strongly at depths which are small or comparable to the x-ray extinction length, a delta function description is a reasonable first-order approximation for finding the average depth of this complicated distribution. The depth z enters into the theoretical angular variation of the photoelectric yield[14] by way of the extinction effect factor $\exp[-\mu_z(\theta)z]$ in the expression for the E-field intensity. The effective absorption length $1/\mu_z(\theta)$ is 56 μm at an off Bragg condition and reaches a minimum of 0.8 μm (the extinction length) in the center of the Si(111) 15-keV Bragg reflection curve. The yields for electrons originating from depths close to or greater than the extinction length are more strongly influenced by this change in the absorption. This effect can be seen in Fig. 2 by comparing the curvatures of yields A through C in the angular region of total reflection. Notice that curve A is almost a straight line in this angular region, whereas curve C is not. For these electron energy regions A, B, and C, the depth z was computed by our measurements to be 0.17 ± 0.06, 0.28 ± 0.02, and 0.37 ± 0.02 μm, respectively.

Also determined from this analysis[14] was an ideal fraction value f_I, which measures the average perfection of the contributing crystal region on a scale of 0–1. Parameter f_I is related to the slope of the photoelectron yield in the angular region of total reflection. This modulation in the yield is due to the movement of the standing-wave field with respect to the ideal atomic planes. For the perfect Si(111) sample, f_I was determined to be 0.94, 0.94, and 0.97 ± 0.05 for electron energy regions A, B, and C, respectively. The lack of any significant deviation from the ideal value of unity indicates that this sample had a uniform perfection over the probed depth.

This is in striking contrast to the measured results (Fig. 3) for the electron yields from the 0.6-μm SiO$_2$/Si(111) sample. The angular modulation of the electron yield from this crystal is strongly dependent on the electron-energy loss. Electrons escaping from this sample with a very-low energy loss, i.e., region A of Fig. 3, have primarily originat-
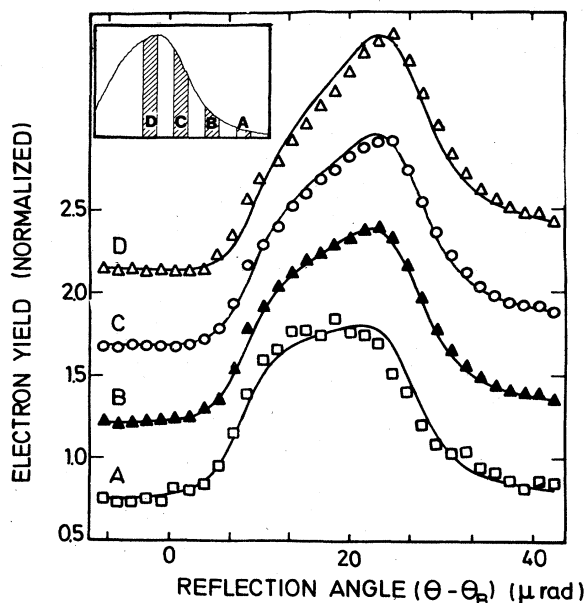
FIG. 3. The angular variation of the 0.6-μm SiO$_2$/Si(111) photoelectron yields for energy regions A–D of the emission spectrum (shown in the inset). The solid lines are theoretical curves.

ed from randomly distributed atoms in the disordered surface layer where $f_I = 0$. This is evidenced by the fact that the angular yield for this electron group closely resembles the shape of the reflectivity curve.

For the sample with the disordered layer, the ideal fraction f_I in energy regions A–D was determined to be 0.10, 0.23, 0.34, and 0.46 ±0.04, respectively. Since the measured reflectivity curve does not differ significantly from that of the ideal crystal, we can conclude that the imperfec-

tion as indicated by the $(1 - f_I)$ values give the percentage of electrons which originated from the disordered layer. Therefore, the relation between these f_I values and the thickness of the amorphous layer provides a means for characterizing the depth dependence of the energy-loss process in the solid.

By integrating the electron yield over the entire energy-loss range, the electron emergence length of the corresponding electron emission process, can be determined. The emergence length L_e is defined as the maximum range of an electron, with an initial energy E_i, in a given material in its initial velocity direction. L_e is determined[16] by relating the thickness t of the amorphous layer to the ideal fraction f_I^T inferred from the angular variation of the *total energy integrated* electron yield. This measured f_I^T value is 0.40 ±0.04 for the SiO$_2$/Si(111) sample and implies[16] an emergence length $L_e = 1.2$ μm for $E_i = 13.3$ keV, which is in reasonable agreement with empirically formulated values.[8,15]

In conclusion, we have shown how a low-resolution electron counter can be used for characterizing the x-ray-induced electron emission process in a solid and how the electron-energy-loss process combined with the standing-wave field can be used to measure the perfection of the lattice in a depth selective manner. By combining this depth sensitivity with the highly collimated synchrotron radiation, the potential for nondestructive three-dimensional probing of the lattice structure is demonstrated.

In closing, it should be noted that an ultimate extension of this experiment would be to differentiate between the angular yields from surface and bulk electron states. Such a measurement, which would require high energy and momentum resolution for the electrons and a high incident photon flux, could be used for discriminating between electrons from different atomic species and for determining positions of surface atoms (including low Z) with respect to the bulk atomic layers.

---

[1]M. v. Laue, *Röntgenstrahlinterferenzen* (Akademische, Frankfurt, 1960).

[2]The intensity of the total E field is derived from the sum of the two plane waves as

$$I(\theta) = |\vec{E}_0 \exp[-i(2\pi\vec{K}_0 \cdot \vec{r} - \omega t)]$$
$$+ \vec{E}_H(\theta) \exp[-i(2\pi(\vec{K}_0 + \vec{H}) \cdot \vec{r} - \omega t)]|^2 .$$

For our case the polarization direction of $\vec{E}_0$ is perpendicular to both $\vec{K}_0$ and $\vec{H}$. By setting $E_0 = 1$, $E_H(\theta) = \sqrt{R}(\theta) \exp[iv(\theta)]$, and $\mu_z(\theta) = 4\pi \operatorname{Im}(K_0)$:

$$I(\theta) = \exp(-\mu_z z)[1 + R + 2\sqrt{R} \cos(v - 2\pi\vec{H}\cdot\vec{r})] .$$

The angular variation of the reflectivity $R(\theta)$ can be seen in Fig. 2. As angle θ is advanced through the total reflection region, the phase $v(\theta)$ decreases in a continuous fashion from π to 0. The effective linear absorption coefficient

$$\mu_z(\theta) = [1 + \sqrt{R}(F_H' \sin v + F_H'' \cos v)/F_0'']\mu_0/\sin\theta_B .$$

For $E_\gamma = 15$ keV Bragg diffraction from Si(111), $\mu_0 = 23.57$ cm^{-1}, $F_H' = 59.55$, $F_H'' = 0.57$, and $F_0'' = 0.81$.

[3]G. Borrmann, Z. Phys. **42**, 157 (1941).

[4]B. W. Batterman, Phys. Rev. **133**, A759 (1964).

[5]J. A. Golovchenko, B. W. Batterman, and W. L. Brown, Phys. Rev. B **10**, 4239 (1974).

[6]J. A. Golovchenko, J. R. Patel, D. R. Kaplan, P. L. Cowan, and M. J. Bedzyk, Phys. Rev. Lett. **49**, 560 (1982).

[7]J. R. Patel and J. A. Golovchenko, Phys. Rev. Lett. **50**, 1858 (1983).

[8]M. V. Kruglov, E. A. Sozontov, V. N. Shchemelev, and B. G. Zakharov, Kristallografiya **22**, 693 (1977) [Sov. Phys. Crystallogr. **22**, 397 (1977)], and references therein.

[9]N. Hertel, M. V. Kovalchuk, A. M. Afanasev, and R. M. Imamov, Phys. Lett. **75A**, 501 (1980).

[10]T. Takahashi and S. Kikuta, J. Phys. Soc. Jpn. **47**, 620 (1979).

[11]A. Krolzig, G. Materlik, M. Swars, and J. Zegenhagen, Nucl. Instrum. Methods **219**, 430 (1984).

[12]A. Krolzig, G. Materlik, and J. Zegenhagen, Nucl. Instrum. Methods **208**, 613 (1983).

[13]J. H. Scofield, Lawrence Livermore Laboratory Report No. UCRL-51326, 1973 (unpublished).

[14]For this case, the yield is proportional to

$$\exp(-\mu_z z)[1 + R + 2\sqrt{R} f_c \cos(v)] .$$

This expression is derived from the sum of the E-field intensities (Ref. 2) at the two ideal lattice positions $\vec{H}\cdot\vec{r} = \pm\frac{1}{8}$. The coherent fraction $f_c = f_I \exp(-M)/\sqrt{2}$. For a perfect crystal

$f_I = 1$ and at room temperature the Debye-Waller factor $\exp(-M) = 0.989$. For a further explanation of this analysis, cf. M. J. Bedzyk, G. Materlik, and M. V. Kovalchuk, Phys. Rev. B **30**, 2453 (1984).

[15]S. Valkealahti and R. M. Nieminen, Appl. Phys. A **32**, 95 (1983).

[16]From simple geometrical scattering considerations, it can be shown (Ref. 8) that for electrons emitted at a depth z, the probability for escape is $P_e(z) = (1 - z/L_e)/2$. Based on this linear approximation with z, the fraction of electrons escaping from the perfect substrate crystal relative to the total electron yield is $f_f^T = 1 - a(2-x)/(x^{-1} + 2a - 2 + x - ax)$, where $x = t/L_e$ and $a = 0.54$ is the ratio of the density of electron emitters in SiO_2 to that in pure Si. f_f^T is measured from the energy integrated yield data and L_e can thus be calculated with $t = 0.6$ μm, or, vice versa, t if L_e was determined before.