Quick X-Ray Reflectometry in the Simultaneous Multiple Angle-Wavelength Dispersive Mode

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Abstract. The whole profile of the specular X-ray reflectivity curve was simultaneously and quickly measured with no need to rotate the specimen, the detector or the monochromator crystal. A white synchrotron beam from a bending magnet source is incident on a bent-twisted silicon (111) crystal polychromator that produces a convergent X-ray beam with a continuously varying wavelength (energy) and glancing angle to the specimen surface. This convergent X-ray beam was specularly reflected in the vertical direction by the specimen placed at the focus. The normalized spatial distribution across the beam direction of the reflected beam represents a specular X-ray reflectivity curve because each position along the line recorded on the two dimensional detector surface corresponds to a different momentum transfer. Reflectivity curves from a (001) silicon wafer, a nickel thin film on a silicon substrate, and a water surface were measured with data collection times of 0.001-100 s, 0.01-100 s, and 1.0-1000 s, respectively. The simultaneously covered momentum transfer range was 0.03-0.52 Å⁻¹ for solid specimens and 0-0.41 Å⁻¹ for liquid specimen.

1. Introduction
Specular X-ray reflectivity is often used for characterizing surface and interface structures of materials [1]. In the conventional angle-scan method, the reflected X-ray intensity measurement is repeated many times by successively changing the glancing angle of X-rays. Time resolutions of time-resolved X-ray reflectivity measurements for studies of surface structural transient changes were limited to minutes [2, 3], except for a recent pump-probe experiment [4]. In another method, the energy dispersive method, the data collection time is sub-seconds to minutes [5], but counting loss becomes a serious problem at high count rates. For studying the structural kinematics or dynamics of samples induced by some stimulus, quicker methods for time-resolved measurement of the X-ray reflectivity have been desired. Especially for irreversible structural changes, it is better to be able to simultaneously measure the whole profile of the reflectivity curve and to successively measure the time dependent changes. To realize data collection times of milliseconds to sub-seconds, Matsushita et al. [6, 7] reported a simultaneous wavelength-dispersive method where a specular X-ray reflectivity curve in a wide range of the perpendicular momentum transfer $q_z$ can be recorded simultaneously without mechanical movement of the specimen, the detector or the polychromator crystal during measurements. Matsushita et al. [8] also reported a simultaneous angle-wavelength dispersive method where a convergent X-ray beam is realized by a bent-twisted crystal polychromator, so that both the wavelength and the glancing angle to the specimen surface of the incident X-ray beam change...
continuously at the same time as a function of direction. A slightly different approach using a polychromatic convergent beam at a tapered-undulator beamline was recently reported as well [9].

In this study, we have improved the previous design [8] of the polychromator, thereby widening the simultaneously covered $q_z$ range.

2. Principle

Figure 1 schematically shows the experimental arrangement of the present X-ray reflectometer. A synchrotron white X-ray beam from a bending magnet is incident on the polychromator crystal. An inclined slit with the shape of an ellipse arc is placed upstream of the polychromator crystal. The arc shape of the slit was designed to give a straight-line-shaped reflected X-ray beam downstream of the bent-twisted polychromator crystal. A beam through the upper end of the slit aperture hits a point A close to the upper-downstream corner of the polychromator crystal which is slightly above the electron orbit horizontal plane of the storage ring. A beam through the lower end of the slit aperture hits a point B close to the lower-upstream corner of the crystal which is deviating downward 13.7 mm from the plane including A. The footprint of the X-ray beam on the polychromator is along a curve connecting A and B.

The crystal is horizontally bent to give a horizontally focused X-ray beam at F in Fig. 1. Moreover, the crystal is twisted around a horizontal axis in such a way that the surface normal at any point on a vertical line through A is inclined downward, while that on a vertical line through B stays horizontal. By properly adjusting the twist angle of the crystal, the beam diffracted at A is deflected downward to F. At the same time, all the rays diffracted at points along the curve AB are also directed toward F. The beam is therefore horizontally focused and vertically condensed at F.

Compared to the previous polychromator design [8], the position where the beam from near the electron orbit plane hits the polychromator crystal was changed from the upstream side to the downstream side. In this way, the simultaneously covered $q_z$ range was widened compared to the previous design [8], because the glancing angle range of the X-ray beam along AF became larger.

The specimen is placed almost horizontally at F. The perpendicular momentum transfer $q_z$ for the beam from an arbitrary point along the curve AB on the polychromator crystal to F changes between $q_{\text{max}}$ and $q_{\text{min}}$, where $q_{\text{max}}$ and $q_{\text{min}}$ are the maximum and the minimum $q_z$'s for the X-ray beams along AF and BF, respectively. The reflected intensity distribution $I$ is measured along a line on a two dimensional pixel array detector. Without the specimen, the incident beam intensity distribution $I_0$ is measured along another line on the detector. By normalizing $I$ by $I_0$, the X-ray reflectivity curve profile is simultaneously obtained without any mechanical movement of the specimen, the detector or the polychromator crystal. The detailed method of measuring $I_0$ was discussed previously [8].

3. Experiment

A silicon (111) wafer (200×20×0.3 mm$^3$) in the reflection geometry was bent and twisted by sandwiching it between convex and concave water-cooled bronze blocks. The bending radius of the crystal was between 4.7 m (for shorter wavelengths) and 3.7 m (for longer wavelengths), and the twist angle was 10.3°. The surfaces of these metal blocks were configured to be tangential to a generating line of an ellipsoid for which the X-ray source and the focal point F are located at its two foci. To secure beam paths for the incident and reflected X-ray beams, grooves were cut into these blocks.
A white synchrotron beam from a bending magnet source of the 6.5 GeV electron storage ring PF-AR at KEK was incident onto the polychromator crystal 20.5 m downstream of the source. The X-ray beam size at F (451 mm from the center of the crystal) was horizontally 0.8 mm and vertically 0.15 mm. The specimens were a mechano-chemically polished silicon (001) wafer, a thin nickel film on a silicon substrate, and a water surface in a trough. They were placed horizontally at the focus position.

A two dimensional pixel array detector (PILATUS 100K) [10] was placed 858 mm downstream of the specimen. The sensitive area of the detector is $83.8 \times 33.5 \text{ mm}^2$ and the size of a pixel element is $172 \times 172 \mu\text{m}^2$. The wavelength region of the X-ray beam actually used was $0.561-0.648 \text{ Å}$ (energy 22.1-19.1 keV). It was calibrated by observing positions of absorption edges on the detector when several kinds of metal foils were placed at the focus position. For the water surface, the glancing angle varied from $-0.24^\circ$ to $1.22^\circ$ within the convergence of the X-ray beam, where the negative glancing angle region was not used. For solid specimens, the central glancing angle of the convergent beam could be changed by rotating the specimens around a horizontal axis.

4. Experimental results

4.1. Silicon wafer

Figure 2 shows X-ray reflectivity curves from a silicon wafer. Curves a-f were obtained in 100, 10, 1.0, 0.1, 0.01 and 0.001 s, respectively. Curves b-f are shifted upward along the vertical axis for clarity. The central glancing angle was changed to $0.32^\circ$ for curve a, $0.12^\circ$ for b and c, $-0.08^\circ$ for d and e, and $-0.28^\circ$ for f, respectively. The simultaneously covered $q_z$ range was from 0.03 to 0.52 Å$^{-1}$ for curve a. The measured minimum reflectivity was $1.4 \times 10^{-8}$ for curve b measured in 10 s.

4.2. Nickel thin film on a silicon substrate

Figure 3 shows X-ray reflectivity curves from a nickel thin film on a silicon substrate. Curves a-e were obtained with data collection times of 100, 10, 1.0, 0.1 and 0.01 s, respectively. Curve f is a calculation assuming NiO and Ni layers on a Si substrate and is shifted downward one order of magnitude.
calculated one assuming nickel oxide (2.3 nm) and nickel (25.2 nm) layers on a silicon substrate. The size of the detector pixel element was taken into account when calculating curve f.

4.3. Water surface
A water trough was placed on an anti-vibration table. Curves a-d in Fig. 4 are X-ray reflectivity curves from the water surface obtained with data collection times of 1,000, 100, 10 and 1.0 s, respectively.

5. Discussion and conclusions
As shown in Figs. 2 and 3, reflectivity curves up to \( q_{\text{max}} = 0.52 \, \text{Å}^{-1} \) were measured with a sufficient data collection time of 100 s. Curves with the same quality could be obtained in an even shorter time if stronger X-ray sources like multi-pole wigglers were used.

A small dip around \( q_z = 0.46 \, \text{Å}^{-1} \) of curve a for the silicon wafer in Fig. 2 is a result of the existence of a natural thin silicon oxide layer at the surface. Comparison of the present dispersive method with the angle-scan method was discussed in a previous paper [8], although the geometry of the polychromator crystal was slightly different. For the nickel thin film, interference fringes (Kiessig fringes [11]) were clearly observed. The calculated curve f in Fig. 3 reproduces the experimental curve reasonably well. For the water surface \( q_{\text{max}} \) was 0.41 Å\(^{-1}\) because there was no incident beam for \( q_z > 0.41 \, \text{Å}^{-1} \).

In conclusion, the present reflectometer will be suitable for studies of irreversible structural changes with a time resolution from milliseconds to tens of seconds. Much higher time resolutions would be possible in pump-probe experiments. The present reflectometer will be most suitable for studying reactions at liquid surfaces, because the specimen surface is kept horizontal and no movement of the specimen and the detector is required.

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