A method for measuring the specular X-ray reflectivity with millisecond time resolution

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Abstract. A method for quick measurement of the specular X-ray reflectivity using a tapered undulator source is described. It uses a convergent X-ray beam with a one-to-one correspondence between X-ray energy and direction, which is produced by diffraction of a white X-ray beam at a curved silicon crystal. To increase the momentum transfer range, the sample is rotated 45° from the horizontal around the incident beam direction, so that both the X-ray energy and the incident angle change continuously with direction. The specularly reflected beam is observed with a two-dimensional detector. The X-ray reflectivity curve in a wide momentum transfer range can be observed in a single detector exposure with a time resolution in the millisecond range. Test measurements were done for a commercial silicon wafer and a gold thin film on silicon.

By measuring the specular X-ray reflectivity curve, the electron density profile of surfaces and interfaces can be determined [1]. This gives access to the thickness and roughness of thin films or multilayers, for example. In the most common method for measuring the X-ray reflectivity curve, the angle dispersive method, each point in the reflectivity curve is measured sequentially by scanning the incident angle and the detector. A high accuracy can be achieved with this method, but it is limited to only static or slowly changing samples, because a measurement takes from several minutes to hours or days.

Different methods have been developed in order to do time-resolved observations of structural changes caused by some stimulus. Nüske et al. have achieved a time resolution of 100 ps in a pump-probe experiment with the angle dispersive method, but this approach requires the structural changes to be reversible [2]. With the energy dispersive method, which uses a white X-ray beam and an energy-dispersive detector, a part of the reflectivity curve can be measured at once in seconds or less [3]. Previously, our group has developed a method using a convergent X-ray beam with a one-to-one correspondence between X-ray wavelength and direction in combination with an area detector (multiple wavelength dispersive method)[4, 5, 6]. With this method, short measurement times of less than one second were possible, but the momentum transfer range that was measured simultaneously was limited, because of a relatively narrow energy range. A recent improvement of the method, the multiple wavelength-angle dispersive method, widened the measurable momentum transfer range significantly by changing both the wavelength and the incident angle onto the sample for each direction in the convergent X-ray...
Figure 1. Schematic illustration of the geometry for specular reflectivity measurements. (a) Perspective view. $E_H$ and $E_L$ are the X-ray beams with highest and lowest energy, respectively. The shaded area between these beams represents the incident or reflected beam. The dashed lines indicate the transmitted beam. (b) View along the sample surface and perpendicular to the beam $E_L$, as indicated by the eye symbol. (c) Top view. (d) View along the beam $E_L$. (e) A detector image of the gold thin film sample. $x$ is in the horizontal and $y$ in the vertical direction.

beam [7]. This method has the advantage that it is possible to measure liquid samples, but it requires a white synchrotron beam with a large vertical divergence, making it mostly suitable for bending magnet sources. To reduce the measurement time, it is desirable to use undulator or wiggler sources, which have a higher photon flux but generally a small vertical divergence. Here, we describe a variation of the method, which is suitable for use with tapered undulator and wiggler sources, although it is limited to solid samples.

The specular reflectivity of X-rays is measured as a function of the momentum transfer perpendicular to the sample surface, $q_z$. The momentum transfer depends on the glancing angle $\alpha$ and the X-ray energy $E$ as

$$q_z = 4\pi \sin \alpha E / hc.$$  

The principle of the present method is illustrated in Fig. 1. A white X-ray beam with a large width is incident onto a cylindrically curved crystal (polychromator) in the Laue geometry [8]. The Bragg angle of the X-rays diffracted by the crystal is different for each point on the crystal, therefore the energy of the diffracted beam changes continuously from $E_L$ to $E_H$ along the crystal and the diffracted X-ray beam is focused onto the sample. The sample is rotated 45° from the horizontal around the direction of the beam with energy $E_L$. Therefore, the glancing angle onto the sample changes continuously across the incident beam from $\alpha_L = 0$ to $\alpha_H = \arcsin(\sin \beta \sin 45^\circ) \approx \beta \sin 45^\circ$, where $\beta$ is the convergence angle of the X-ray beam. The specularly reflected beam forms a vertical line on a two-dimensional detector downstream of the sample. The reflectivity in the range $q_L = 4\pi \sin \alpha_L E_L / hc$ to $q_H = 4\pi \sin \alpha_H E_H / hc$ can be determined from a single detector image by normalizing the reflected intensity at each pixel with the corresponding incident intensity.

The experiment was carried out at the tapered undulator beamline AR-NW2A of the Photon Factory, KEK. The setup and polychromator for crystal truncation rod (CTR) scattering described in Ref. [8] was used. A white X-ray beam was vertically focused by a mirror and higher order harmonic components were suppressed by reflection at two additional mirrors. The
convergent X-ray beam after the polychromator had an energy range from 15.6 keV to 23.2 keV and a convergence angle of $\beta=4.7^\circ$. This gives a maximum momentum transfer of $q_H=1.3$ Å$^{-1}$.

It should be noted that the X-ray energy is different for each $q_z$ value. Therefore, the energy dependence of the refractive index has to be included in the analysis. The reflected beam was observed 1 m downstream of the sample with a Pilatus-100K area detector (Dectris Ltd.) [9]. The whole reflected beam from $q_L$ to $q_H$ can be observed at once if the long side of the detector is oriented vertically. In the present experiment, however, the detector was oriented with the long side horizontally, which is the orientation used for CTR measurements. Therefore, two exposures with different detector angles $2\theta$ were needed to observe the whole beam.

For small glancing angles, the reflectivity is large, so the reflected X-ray beam easily saturates the detector. For this reason, the incident intensity was attenuated at small glancing angles with a tapered aluminum absorber with a thickness from 0 to 5 mm inserted before the sample.

Figure 1 (e) shows an example for a detector image. The incident beam would appear as a horizontal line at the bottom, but was stopped by the edge of a slit after the sample. The reflected beam forms a vertical line. Diffuse scattering from the sample is visible as well.

The reflectivity $R$ is obtained from the detector image by integrating the reflected beam at each $y$ position in the direction perpendicular to the sample, then normalizing it with the corresponding incident intensity $I_0$. The correspondence between positions in the incident and reflected beam is obtained by going diagonally to the right and down from a position in the reflected beam. The incident intensity without the tapered aluminum absorber and the X-ray energy at each pixel were determined as described in Ref. [8]. To determine $I_0$ for the glancing angles with the tapered absorber, the reflected intensities for different angles between sample and incident beam were compared as described in Ref. [7].

Figure 2 shows the X-ray reflectivity curves of a commercial (001) silicon wafer for different exposure times. Each curve was measured with two different detector angles, where the first angle covered the momentum transfer range from 0 to 0.4 Å$^{-1}$ and the second the range from...
0.3 Å\(^{-1}\) to 0.8 Å\(^{-1}\). The reflected beam was too weak to be reliably integrated above 0.6 Å\(^{-1}\). The lowest observable reflectivity for the 100 s exposure (curve f) was about \(2 \times 10^{-8}\), for the 1 s exposure (curve d) \(1 \times 10^{-7}\) and for the 0.01 s exposure (curve b) \(5 \times 10^{-6}\).

Figure 3 shows the X-ray reflectivity curves of a 15 nm-thick gold film on a silicon substrate. As in the case of the silicon sample, the curve was measured with two different detector angles. The lowest observable reflectivity was about \(5 \times 10^{-7}\) for the 1 s exposure (curve d), and \(1 \times 10^{-5}\) for the 0.01 s exposure (curve b). The Kiessig fringes were clearly observed even for an exposure time of 0.001 s (curve a). The difference in the lowest observable reflectivity to the silicon (001) sample is mainly caused by a higher background.

Curve f in Fig. 3 is a measurement of the same sample with the angle dispersive method conducted at beamline 37XU of SPring-8 [10]. Comparison of this curve with the one for the 10 s exposure shows that the reflectivity of the 10 s exposure curve is significantly larger than that of the angle scan curve. In addition, the reflectivity below the critical angle (below about 0.07 Å\(^{-1}\)) is larger than unity, which is physically impossible. The reason for this is likely an underestimation of the incident intensity caused by an instability of the optical system of the beamline due to a defect cooling water circulator.

For both samples, the lowest observable reflectivity was mainly limited by the height of the background for the exposure times of 1 s or longer. Reducing the background, for example by closing slits in front of the detector, would significantly lower the observable reflectivity. In addition, the incident beam could be used more efficiently by adjusting the \(q_z\) range to that which is needed for the experiment. This can be done by choosing an rotation angle of the sample smaller than 45°.

In conclusion, a method for quick X-ray reflectivity measurements was presented. For the test samples, the reflectivity could be measured down to the \(10^{-7}\) range in 1 s and down to below \(1 \times 10^{-5}\) in 10 ms. From the results, it can be expected that structural changes of surfaces or thin films can be observed with a time resolution from milliseconds to seconds with this method.

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