Instrumentation for X-ray reflectivity in micro area: present status and future outlook

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Abstract. X-ray reflectivity is sensitive to slight structural changes along the depth of layered materials in the order of sub-nanometers or even smaller. This property is extremely promising for the observation of buried interfaces, but the conventional X-ray reflectivity technique unfortunately lacks spatial resolution. The method looks at quite a large area, typically mm^2 ~ cm^2 of the sample, and this often makes it difficult to analyze realistic problems in modern nano sciences and technologies. The present article discusses instrumentation for upgrading the X-ray reflectivity technique to give it a much higher spatial resolution. Recent preliminary results with high-energy white X-rays are reported.

1. Introduction

For many years, X-ray reflectivity has been employed as a method to analyze non-destructively the structure along the depth of thin films and layered materials [1,2]. The method has the unique advantage of detecting very small changes to the thickness and the density of each layer, as well as the roughness of surfaces and buried interfaces. As such information is not easily obtained by other methods, especially non-destructively, X-ray reflectivity is one of the most important probes for buried layers, interfaces and the structures therein.

Unfortunately, however, the conventional X-ray reflectivity method has an apparent limitation - it lacks spatial resolution, and gives just 'average' information over quite a large area, typically mm^2 ~ cm^2. As illustrated in Fig.1, it is sometimes difficult to rely on this method. When the structures along the depth are not uniform and there exist several different layered structures depending on the location of the sample, then obtaining the 'average' generally does not make any sense. It is necessary to clarify each structure in detail and thus make a map of the whole sample. Even where the layered structure is almost uniform, the 'average' does not always present the key to resolving the problem. Much depends on whether the functions (or properties) of interest are determined by the majority of the structures in the sample, or not. If only a very limited number of extraordinary structures play a crucial role in the phenomena etc, conventional X-ray reflectivity becomes useless because of its excellent performance in analyzing the 'average'.
In contrast, on 3rd generation synchrotron beamlines, the use of micro beams is now almost standard, at least for other X-ray techniques, such as X-ray fluorescence [3] and X-ray diffraction [4]. Why have synchrotron micro beams not been used often for X-ray reflectivity measurements so far? One reason is that X-ray reflectivity usually employs parallel beams because of the need to obtain quite high angular resolution at an extremely small angle. The use of focusing optics, which makes an X-ray beam angularly divergent, is not ideal in this context. In addition, it could prevent the real irradiation area on the sample from becoming small enough, even if a micro beam is used. Assume the beam is a rectangle of width $x$ and height $y$, then the footprint of the beam on the sample, $h$, can be written as $h = \frac{x}{\sin \theta}$, here, $\theta$ is a glancing angle. If $\theta$ is 2.5 mrad, $h$ becomes 400 times larger than $x$. Furthermore, until now, unlike other X-ray techniques, X-ray reflectivity measurements have been done more popularly with an ordinary X-ray tube rather than with a synchrotron X-ray source. As a result, there is still a lag in introducing synchrotron micro beams to X-ray reflectivity.

The present article discusses how micro beams can change the capability of the X-ray reflectivity technique. Broadly, there are two different directions as shown in Fig.2; the use of focused monochromatic or parallel white X-ray micro beams. Both are significant and are used in different ways, depending on the type of application. The latter part of this article reports on recent preliminary experiments with a white X-ray micro beam from a high-energy synchrotron source.

![Figure 1](image1.png)

**Figure 1.** Why does the X-ray reflectivity technique need spatial resolution? (a) a non-uniform sample, where the 'average' does not make any sense, (b) case where significant changes that need to be observed are found in only a limited area.

![Figure 2](image2.png)

**Figure 2.** Typical layouts for micro area analysis by X-ray reflectivity technique with monochromatic (a1 and a2) or white (b1 and b2) micro beam.
(a1) A standard way to obtain reflectivity curve by $\theta/2\theta$ angular scan. The length of footprint, i.e., the analyzing area of the sample changes during the scan.
(a2) Reflectivity measurement with completely fixed geometry, by using quite large angular dispersion of the incident X-ray beam [5-8]. A 1D/2D detector is used.
(b1) So called energy-dispersive X-ray reflectivity technique [9-11]. A detector with high-energy resolution, such as a Si(Li) or Ge detector, is used.
(b2) Acquisition of reflection spectra by an analyzing crystal and a 1D/2D detector [12].
2. Consideration of micro area analysis by X-ray reflectivity technique

2.1. Spatial resolution

Spatial resolution concerns the size of the available X-ray beam and depends on the optics employed. Since the advent of highly brilliant synchrotron X-ray sources like undulators, the development of focusing optics has undergone remarkable acceleration. Zone plates [13], K-B mirrors [14], multilayer Laue lenses [15] and refractive lenses [16] are now able to reduce an X-ray beam size to 50 nm or even smaller. The use of a beam of at least 300–500 nm would be quite easy at many beamlines in 3rd generation facilities, such as the European Synchrotron Radiation Facility (ESRF), Advanced Photon Source (APS), and SPring-8. With the X-ray reflectivity technique, a parallel beam is generally desirable, but when such a micro beam with an angular dispersion in the order of mrad is used, the use of double-slits, crystal analyzers or another system before the detector is necessary in order to ensure the angular resolution in the measurement as shown in Fig.2 (a1).

On the other hand, a small parallel beam can be obtained, when one compromises on a beam size of 1–10 µm. Slits, pinholes and other similar components are used to collimate the beam [17, 18]. When a high-energy white beam is used, experiments at such a size become possible without having to move anything, i.e., the sample, detector, and all other equipment parts are fixed during measurement. Note that the analyzing area for X-ray reflectivity is large in the direction of the beam, as mentioned earlier. As the size perpendicular to the beam axis is small enough, repetition of measurements while rotating the sample (e.g., 90 deg.) could be sometimes a help.

2.2. Qz resolution

Here, \( Q_z = \frac{4 \pi \theta}{\lambda} \), where \( \theta \) is the glancing angle and \( \lambda \) is the X-ray wavelength. X-ray reflectivity is measured as a function of \( Q_z \) in any case. The resolution of \( Q_z \) is a kind of instrumental function, which smears out an ideal reflectivity curve.

When monochromatic X-rays are used, the measurement is usually done by a normal \( \theta/2 \) scan. In the case of Fig.2 (a1), the resolution is limited by the acceptance angle width for the detector, and it can be set at typically better than 0.1 mrad. As shown in Fig.2 (a2), there is a way of using quite large angular dispersion [5-8]. In this case, angular dispersion corresponds to the range of \( Q_z \), and the resolution is limited purely by geometrical factors and the spatial resolution of the one or two dimensional (1D/2D) detector.

When parallel white X-rays are used, the experiment measures the spectra of reflection at a certain angle. The resolution is limited by the energy resolution (\( E/\Delta E \), i.e., \( \lambda/\Delta \lambda \)) of the detector. For a normal Si(Li) or Ge detector (as shown in Fig.2 (b1)), \( E/\Delta E \) is about 40 for 6-10 keV X-rays, but becomes better than 100 at 40-100 keV. In wavelength-dispersive mode (Fig.2 (b2)), resolution usually becomes 10-30 times better at a lower energy (~25 keV), but is almost the same level at a higher energy (25~100 keV).

2.3. \( Q_x \) range

Basically, the layout shown in Fig.2 (a1) has no special limits regarding the \( Q_x \) range, because the measurement is simply a continuation of a \( \theta/20 \) scan. The \( Q_x \) range depends on how wide the scans are done, and is typically \( 0.7 Q_x \sim 14 Q_x \) (though sometimes extended to 20 \( Q_x \)), where \( Q_x \) is the critical angle observed in the reflectivity curve. For instance, \( Q_x \) for a silicon substrate is ca. 0.3 nm\(^{-1}\), and in this case, the range is 0.21~4.2 nm\(^{-1}\), which corresponds to 2.6~52 mrad (\( \theta \)) for \( \lambda = 0.154 \) nm X-rays.

In contrast, when white X-rays are used, the \( Q_x \) range depends on the spectral range of the incident X-rays. The \( Q_x \) range discussed above corresponds to 5~100 keV and 4~80 keV for \( \theta = 4 \) mrad and 5 mrad, respectively. When such high-energy X-rays are available, energy-dispersive X-ray reflectivity measurements (shown in Fig.2 (b1)) become competitive at this point.

On the other hand, in the layouts shown in Figs. 2 (a2) and (b2), the \( Q_x \) range is severely limited. As for Fig.2 (a2), the range mainly depends on the opening angle of the focusing optics, and it usually
cannot be that large, unlike Naudon’s pioneering experiments [5] that used natural angular dispersion from a laboratory linear X-ray source. In the case of Fig.2 (b2), a single analyzing crystal is unable to cover such a wide energy range, but the simultaneous use of several crystals is possible, although fairly challenging.

2.4. Range in reflectivity
Range in reflectivity concerns both the incident X-ray intensity available and the specification of the detector employed. Generally, ordinary X-ray reflectivity measurements are done in a range from 1 to $10^8$ (though an extension to $10^{12}$ has been reported [19]). The maximum counting rate for the scintillation detector is $10^5$ to $10^6$ counts/sec, but employing a suitable attenuator can help to extend the range. The layout shown in Fig.2 (a1) is a way of maintaining such a wide range when analyzing a small area. When synchrotron X-rays from a high-energy storage ring are used, one needs to beware of the influence of high-energy X-ray fractions. The use of several mirrors to reduce higher-order harmonics down to $10^8$ is necessary. For the energy-dispersive method (Fig.2 (b1)), incident X-ray intensity is not a limit at all, and saturation of the detector is the main problem. If the incident X-ray spectra are flat, the detector would simultaneously count strong X-rays (in the total-reflection region) and very weak X-rays (in the high Q_z region). Assuming the counting limit and the background level are $10^3$ counts/sec and 0.1 counts/sec, respectively, then the range is only $10^6$. However, when incident X-rays have some specific features so that their intensity strengthens at high energy and weakens at low energy, the range can be widened somewhat simply by accumulating counts. On the other hand, it is not easy to do experiments with such a wide range as $10^8$ with the 1D/2D detectors used in Figs. 2 (a2) and (b2). The typical detection range is 3–4 decades, but this can be sufficient in some cases, depending on the application. The advantage of using a CCD camera system is the potential for quick measurement by looking at specific changes in the reflectivity curve, which most likely requires only a limited range. As there is a limit to the number of counts but no limit to the counting rate, one can just shorten the measuring time to avoid saturation of the detector. This becomes clear when a highly brilliant X-ray source is available.

2.5. Measuring time
The measuring time is fairly different depending on the system. Obviously, fixed geometry is far superior. While an angular scan (shown in Fig. 2 (a1)) requires something like 0.5–1.5 h, in the case of fixed geometry, the measuring time for the system without angular scan (Figs. 2 (a2), (b1) and (b2)) should be typically 0.01 sec ~ 2 min. A more detailed discussion of quick measurement has been described elsewhere [20].

3. Preliminary experiments for small area analysis with high-energy white X-rays
In light of the above, the energy-dispersive reflectivity technique with white X-rays (shown in Fig.2 (b1)) is attractive in order to take measurements in quite a short time, to make a map of the whole sample efficiently, or to watch the changes at a specific point of interest. As discussed earlier, the ability of this technique is enhanced when combined with white X-rays from a high-energy synchrotron. The availability of a parallel small beam with sufficient photons, as well as the extension of the Q_z range is significant. In the present study, preliminary experiments [21] on X-ray reflectivity in a small area were performed at BL28B2, SPring-8 [22]. The distance from the source to the sample position is 44m.

To obtain a small beam in the high-energy region, fairly thick materials are necessary to prepare a pinhole, a slit or something similar. The thickness should be at least 2–3 mm even when using quite a heavy material such as tungsten or tantalum. When the target size is 10 µm or smaller, the aspect ratio is 200~300, and this has presented technical difficulties so far. Furthermore, in order to obtain a parallel beam (i.e., suppressing angular dispersion effectively), some new technologies for fabricating an extremely long and small pinhole would become important. In the present study, instead of a pinhole, a kind of slit is employed. As shown in Fig.3 [18], a pair of thick blades of tungsten is placed
in parallel, but not touching each other, in order to create a very narrow gap at the edge. The beam size at the sample position was estimated as $17\mu m \times 5.5 \mu m$ by X-ray intensity in comparison with that for the normal beam size. The profile of the X-ray beam was directly measured by GAFCHROMIC film, HD-810 (ISP Technologies Inc, USA), and it was found that the profile agrees well with above beam size. The special slits shown in Fig.3 were used on this occasion to reduce the vertical size, but it would be also possible to reduce the horizontal direction in the same way. Further experiments are under way.

Figure 4 shows one of the preliminary results. The sample measured here is a patterned chromium thin film deposited on the glass substrate. The observed area is a $10\mu m$ wide line, and the layer thickness is 100 nm. The setup used is schematically shown in the inset. A Si drift chamber (Rontec, XFlash, $5mm^2$ effective area, Peltier cooling $-10 \degree C$) and a silicon photo-diode were used for measurements and alignment, respectively. The data are processed by a digital processing unit (Seiko, MCA7600). To reduce background, a vacuum path is put between the sample and the detector. Receiving slits and direct beam stoppers are placed at both sides of the vacuum path. For alignment, RS2 and DBS2 are used, but during the measurement, RS1 and DBS1 are applied so that direct and reflected X-rays do not hit RS2 and DBS2. As the X-ray intensity is still too much for the detector, some attenuator (Al plate, $2mm$ thick) is used. The measurement was done at a glancing angle of $3mrad$. This means that the observed area was $17\mu m \times 1.8 mm$. The measuring time was 2 min.

One finds the following in Fig.4; (i) the critical energy is $17.5 keV$, indicating that $Q_C$ is $0.53 \text{ nm}^{-1}$, which agrees well with that of metallic chromium, (ii) interference fringes are clearly observed, and the frequency corresponds to 100 nm thickness, (iii) the spectra are smooth, and parasitic X-rays are not observed, probably because the vacuum path as well as the use of pairs of receiving slits and direct beam stoppers work well (though many spikes were observed in our previous experiments [23]), (iv) the measuring time was reasonable, but could be shortened further (e.g., $10-20$ sec), thus making ‘reflectivity mapping’ realistic, (v) there was no problem with the analysis of the layered structure in the present case, although the present data have only 3.5 decades.

Figure 3. Schematic view of the slits to reduce the vertical size of high-energy white synchrotron beam.
Figure 4. Preliminary obtained X-ray reflection spectra from small area in the patterned chromium thin film sample. The layer thickness of the observed area is 100 nm. Measuring time 2 min. The setup is illustrated as an inset. RS1, RS2: receiving slits, DBS1, DBS2: direct beam stoppers. SDD: silicon drift detector.

4. Conclusions
Developing the X-ray reflectivity technique in the micro area is extremely important. The technique will allow us to see the structure in a different scale, from each 'tree' to the whole 'forest'. It will become possible to discuss the unusual structural changes that take place only at a specific position, in addition to the 'average' structure for the sample. The use of advanced focusing optics at modern synchrotron beamlines could reduce the beam size to the 50~500 nm level. Furthermore, the combination of high-energy white beams and energy-dispersive X-ray reflectivity is attractive because of the potential for reasonably quick measurement. This combination is especially powerful when it is necessary to make a map of the whole sample efficiently, or to observe changes at the specific point of interest. During preliminary experiments at the SPring-8, we found the following: (i) A µ slit, consisting of a pair of thick blades of tungsten, works effectively in reducing the beam size to 5.5 µm, which could open up a new field for the application, (ii) However, it is still necessary to develop further methods and instruments to form an even smaller white beam.

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References
[1] J. Daillant and A. Gibaud Eds., "X-ray and Neutron Reflectivity: Principles and Applications", Springer (1999).
[2] K. Stoev and K. Sakurai, Spectrochim. Acta, B54, 41-82 (1999).
[3] K. M. Kemner, S. D. Kelly, B. Lai, J. Maser, E. J. O'Loughlin, D. Sholto-Douglas, Z. Cai, M. A. Schneegurt, C. F. Kulpa, Jr., K. H. Nealson, Science, 306, 686-687 (2004).
[4] J. S. Chung and G. E. Ice, “Automated indexing for texture and strain measurement with broadband x-ray microbeams”, J. Appl. Phys., 86, 5249-5255 (1999).
[5] A. Naudon, J. Chihab, P. Goudeau, J. Mimault, J. Appl. Cryst., 22, 460-464 (1989); A. Naudon, Analusis (France), 18, 122-122 (1992).
[6] U. Niggemeier, K. Lischka, W. M. Plotz and V. Holy, J. Appl. Cryst., 30, 905-908 (1997).
[7] L. N. Koppel, US patent No. 5,619,548, “X-ray thickness gauge” (1997), Date of Patent: 8 April 1997, Filing Date: 11 August 1995.
[8] K. Sakurai and M. Mizusawa, Japanese Patent No. 3903184; K. Sakurai and M. Mizusawa, in preparation for publication.
[9] Y. Nakano, T. Fukamachi, K. Hayakawa, Jpn. J. Appl. Phys., 17-2, 329-331 (1978).
[10] M. Bhattacharya, M. Mukherjee, M. K. Sanyala, Th. Geue, J. Grenzer, and U. Pietsch, J. Appl. Phys., 94, 2882-2887 (1993).
[11] T. Horiuchi, K. Ishida, K. Hayashi and K. Matsushige, Adv. in X-Ray Anal., 39, 171-180 (1995).
[12] J. W. White, A. S. Brown, R. F. Garrett, D. J. King and T. L. Dowling, Aust. J. Phys., 52, 87-100 (1999); R. F. Garrett, J. W. White, D. J. King, T. L. Dowling, W. Fullagar, Nucl. Instrum. & Methods, A467-468, 998-1000 (2001).
[13] W. Yun, B. Lai, Z. Cai, J. Maser, D. Legnini, E. Gluskin, Z. Chen, A. Krasnoperova, Y. Vladimirsy, F. Cerrina, E. Di Fabrizio, and M. Gentili, Rev. Sci. Instrum., 70, 2238-2241 (1999).
[14] H. Mimura, S. Matsuyama, H. Yumoto, H. Hara, K. Yamamuru, Y. Sano, M. Shibahara, K. Endo, Y. Mori, Y. Nishino, K. Tamakura, M. Yabashi, T. Ishikawa, and K. Yamauchi, Jpn. J. Appl. Phys., 44, L539-L542 (2005).
[15] H. C. Kang, J. Maser, G. B. Stephenson, C. Liu, R. Conley, A. T. Macrander, and S. Vogt, Phys. Rev. Lett., 96, 127401 (2006).
[16] C. G. Schroer, O. Kurapova, J. Patommel, P. Boye, J. Feldkamp, and B. Lengeler, M. Burghammer and C. Riekel, L. Vincze, A. van der Hart, and M. Kuchler, Appl. Phys. Lett., 87, 124103 (2005).
[17] K. Ohsumi, K. Hagiya, M. Uchida, N. Suda, M. Miyamoto, M. Kitamura, and M. Ohmasa, Rev. Sci. Instrum., 66, 1448-1450 (1995).
[18] Y. Imai, private communications.
[19] N. Awaji, Spring-8 Reserach Frontiers 2001B-2002A, 92-93 (2003).
[20] K. Sakurai, M. Mizusawa and M. Ishii, Trans. MRS Japan, 32, 181-186 (2007).
[21] K. Sakurai, M. Mizusawa and Y. Imai, to be submitted.
[22] Y. Chikaura, S. Iida, S. Kawado, K. Mizuno, S. Kimura, J. Matsui, M. Umeno, T. Ozaki, T. Shimura, Y. Suzuki, K. Izumi, K. Kawasaki, K. Kajiwara and T. Ishikawa, J. Phys. D: Appl. Phys., 34, A158 (2001).
[23] K. Sakurai, M. Mizusawa and Y. Imai, KEK Proceedings, 2006-3, 29-32 (2006).