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Recent Novel X-ray Reflectivity Techniques: Moving Towards Quicker Measurement to Observe Changes at Surface and Buried Interfaces

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The present paper reviews recent extensions of the X-ray reflectivity technique, which is a powerful tool for the non-destructive exploration of layered films and which can provide data on density, layer thickness, interface roughness, interdiffusion etc. With conventional X-ray reflectivity measurement, samples need to be sufficiently stable, and analysis is basically concerned with the static structure. In view of the growing need to observe changes to the buried interfaces of a variety of thin films and multilayers, it is crucial to develop novel methods and instruments that enable reflectivity measurements to be carried out much more quickly, preferably without any motion of the sample, the detector or the optics, i.e., without a $\theta/2\theta$ scan. One can observe structural variations by noting changes in the position of critical angles, the frequency of interference fringes, or the degree of decay of the curve. This paper introduces recent developments in such rapid X-ray reflectivity techniques, as well as some interesting applications.

Key words: total reflection, layered materials, surface, interface, thickness, diffusion, roughness, non-destructive

1. INTRODUCTION

Since the discovery of X-ray total-reflection by Compton in 1923 [1], and also interference fringes by Keissig in 1931 [2], X-ray reflectivity has been developed as a method to analyze non-destructively the structure along the depth of thin films and layered materials [3-8]. The method has a unique advantage in detecting very small changes to the layer thickness and morphology of surfaces and interfaces, as found by A. Segumular and L. Esaki [9,10] in the 1970s, i.e., in the pioneering era of modern nano science and technology. Therefore, the technique has been widely used for thickness monitoring in industries, for various types of semiconductor, magnetic and optical multilayers [11]. In addition, since the critical angle is a function of density, the technique has been used for determining the density at the near surface of thin films, which we would expect to differ slightly from that of bulk materials. One promising application is the evaluation of low-k porous thin films [12]. It is possible to determine porosity by comparing the density before and after the absorption of gas molecules by the pores of thin films. The roughness of surfaces and interfaces represents other significant information, which also can be obtained through reflectivity measurement [13-15]. As other methods cannot aid in the analysis of buried interfaces, the use of the reflectivity technique is important.

The most popular data acquisition method using X-ray reflectivity is the so-called $\theta/2\theta$ angular scan, which utilizes monochromatic X-rays, typically Cu Kα_1 (8.04778 keV) from an X-ray tube. The experiment is quite similar to powder diffraction except that the glancing angle is extremely small. Because of the need for a precise angular scan, the samples need to be sufficiently stable. However, recent progress in nano sciences and technologies requires information on what is happening exactly on an atomic scale during the growth, fabrication and operation of nano-structures [16]. As such, the analysis of structural variation assumes much more importance than the simple determination of stable structures. Therefore, measurements need to be done much more quickly, preferably without any motion of the reflectometer, including the sample itself. This points to the necessity of developing a new measurement method as well as new instruments.

In this paper, we will first examine how structural changes to layered thin films have been studied so far, using a conventional X-ray reflectometer. While it is not impossible to observe such changes even through a $\theta/2\theta$ angular scan, experiments have to be carried out very carefully. Then, we will discuss two new methods of performing quick measurements. One measures X-ray reflection spectra of white X-rays, and the other simultaneously measures all angular components of reflected monochromatic X-rays. Finally, we provide an overview of future developments.

2. OBSERVATION OF STRUCTURAL CHANGES BY MEANS OF CONVENTIONAL X-RAY REFLECTIVITY TECHNIQUE

One of the most interesting and significant targets of the quick reflectivity technique would be some kind of phase transitions at surface and buried interfaces. It is extremely difficult to follow the process of the transition by conventional X-ray reflectivity technique based on a $\theta/2\theta$ angular scan. However, it is still possible to obtain the reflectivity curve at each point during the changes by repeating careful *in-situ* measurement as a function of sample environmental parameters.

Peisl and his colleagues in Munich, Germany employed the X-ray reflectivity technique to study surface corrugation during martensitic transformation of polished single crystal $Ni_{62.5}Al_{37.5}$ (001) [17]. As shown in Fig.1, they determined the existence and evolution of a small dip below the critical angle, which indicates the formation of surface relief in mesoscopic scale. This was due to the underlying shear transformation scheme. It was found that a dip appeared at 90K, which was 5K higher than the transformation temperature for the bulk. Furthermore, a large hysteresis of approximately 50 K was observed for the surface, which was considerably larger than any hysteresis that was measured for the bulk transformation. Such very unique properties of surface martensitic transformation were investigated by X-ray reflectivity measurement based on a θ/2θ angular scan at each temperature point. The research was subsequently extended to some other interesting systems, such as Ni_2MnGa single crystal and polycrystalline $Ni_{50.8}Ti_{49.2}$ [18, 19].

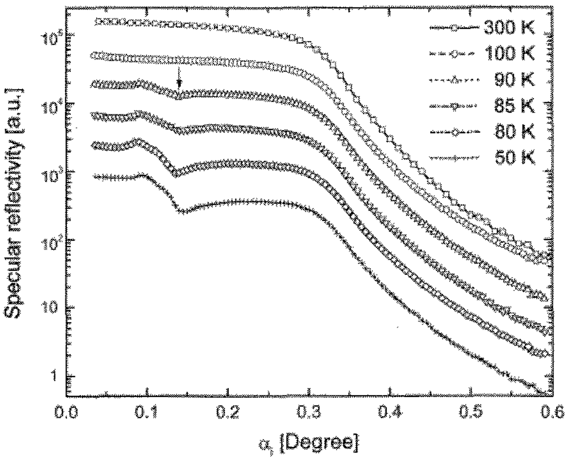

Fig.1 Martensitic transformation of $Ni_{62.5}Al_{37.5}$ (001) surface observed in X-ray reflectivity curve. The energy of X-rays is tuned at 8700 eV, above Ni-K edge (8333 eV). The arrow indicates a dip indicating the formation of surface corrugation. The data correspond to the cooling run. Different temperature dependence was observed for the heating run. (Reproduced with permission from [17], Fig.1.)

Dosch's group in Stuttgart, Germany utilized X-ray reflectivity to explore the interface between ice and silicon wafer in the vicinity of the ice melting point [20]. As indicated in Fig.2, it was discovered that a quasi-liquid layer (QLL) was formed when the temperature came very close to the melting point. The experiments consisted of the repeated recording of the X-ray reflectivity curve as a function of temperature, which was very carefully controlled to a precision of 0.001 K. It was found that the thickness of the QLL depended on the temperature, and became 1.7 nm at 1K below the melting point. The results indicate that the QLL has stronger correlations than ordinary water and a large density close to that of high-density amorphous ice (1.17 g/cm^3). Very recently, the authors applied the same X-ray reflectivity setup to other very interesting topics. This raised the question of what happens when water comes on to a water-repellent surface. It was shown experimentally that a hydrophobic gap exists on an octadecyl-trichlorosilane layer formed on the silicon substrate [21].

We note that the X-ray reflectivity method is really powerful for detecting small changes in a layered structure, by controlling the sample environment parameters. Even a normal θ/2θ angular scan can be employed, when such sample changes are reproducible and are kept fairly stable during scanning for the reflectivity measurement. However, the next step of the research on such structural changes would be so called time-resolved measurement, and this should be done very quickly with fixing the sample completely during the experiment. In the next section, we will look at several different methods for obtaining essentially the same information as via the conventional X-ray reflectivity technique.

3. QUICK X-RAY REFLECTIVITY TECHNIQUES

3.1 The use of high-energy white X-rays

It has been known since the late 1970s [22] that it is possible to carry out almost the same X-ray reflectivity experiment in a different way by measuring the

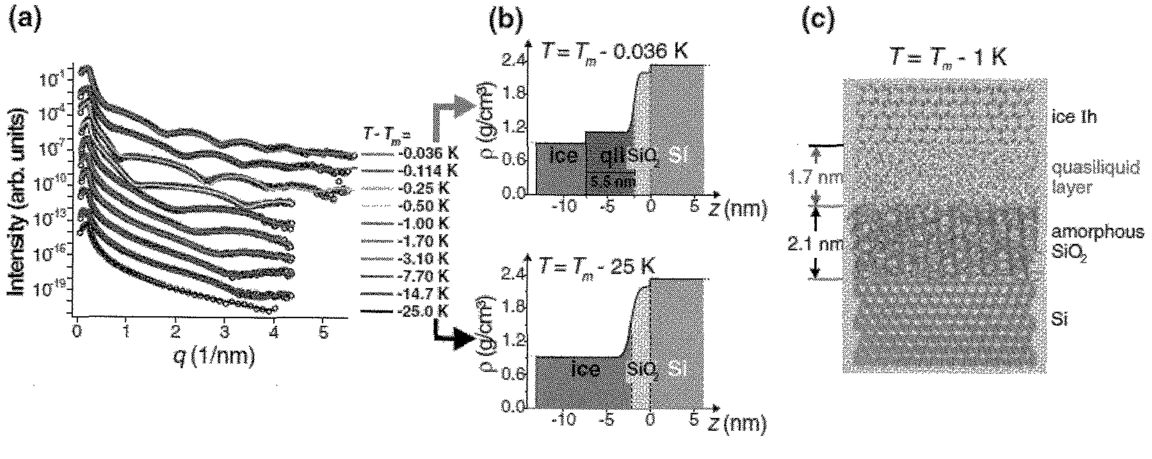

Fig.2 X-ray reflectivity analysis of ice formed on Si substrate. X-ray energy was set as 71.3 keV. (a) Reflectivity curves as a function of temperature. Solid lines show calculations. (b) Density profiles along the depth at 0.036 K and 25K below the melting point of ice. The profiles were obtained from the reflectivity analysis. The QLL was observed only when the temperature was close to the melting point. (c) Real space model of the ice/QLL/SiO_2/Si(substrate) for the temperature 1K below the melting point. (Reproduced with permission from [20], Fig.3. Original figure is given in color print.)

reflection spectra for incident white X-rays. One of the biggest advantages of the energy-dispersive X-ray reflectivity technique is that it can be performed with a completely fixed geometry - the experiments are simply a continuation of counting by an energy-dispersive detector, i.e., a Ge detector, a Si drift chamber etc. [23-26]. So far, the method has not been employed that widely, mainly because of limitations in the quality of the data obtained. Inability to avoid absorption edges due to a narrow X-ray spectral range sometimes degrades the data. However, recent advances in X-ray sources, in particular high-energy synchrotron light sources, could open up new opportunities for quick X-ray reflectivity measurements using high-energy white X-ray spectra [27].

The ordinary reflectivity and energy-dispersive reflectivity techniques are comparable when the data are plotted in terms of the wave vector, q_z ($=4\pi\sin\theta/\lambda$. λ is the X-ray wavelength and can be written as λ=12.3981/E in Å where E is X-ray energy in keV). While ordinary reflectivity uses monochromatic X-rays, of which the energy is E_0, energy-dispersive experiments require a fixed glancing angle θ_0 to be chosen. For small angles, from the simple relation, $E\theta_0 = E_0\theta$, the critical X-ray energy, which corresponds to the critical angle θ_c of the surface, for a certain X-ray energy, E_0, can be expressed as $E_c = E_0\theta_c/\theta_0$. Fig.3 shows an example of X-ray reflection spectra. The sample here is a single crystal molybdenum mirror, which had been previously studied in detail by monochromatic X-rays [28]. As θ_C for 16 keV is 3.7 mrad, E_C for 2.07 and 2.5 mrad are 28.6 and 23.7 keV, respectively. From this, it is readily understood that the energy-dispersive X-ray reflectivity technique needs quite a wide X-ray spectral range. So far, synchrotron radiation sources have not been used so frequently for this type of experiment, because such high energy X-rays are not available at low energy storage ring facilities. As the flux at the sample position is extremely strong and usually even too much for the detector, the technique can deal with extremely small samples (100nm ~ μm), although conventional experiments measure sample sizes of mm ~ cm.

On the other hand, the energy-dispersive X-ray reflectivity technique has an inherent restriction in the

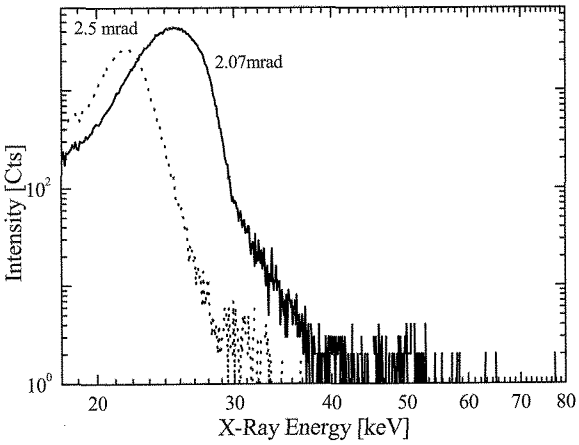

Fig.3 X-ray reflection spectra of single crystal molybdenum mirror, measured at two different glancing angles, 2.07 mrad and 2.5 mrad. The experiments were done at BL28B2, SPring-8 in Japan. The beam size used was 50 μm(H) × 25 μm(V), and the flux was even too much for the detector.

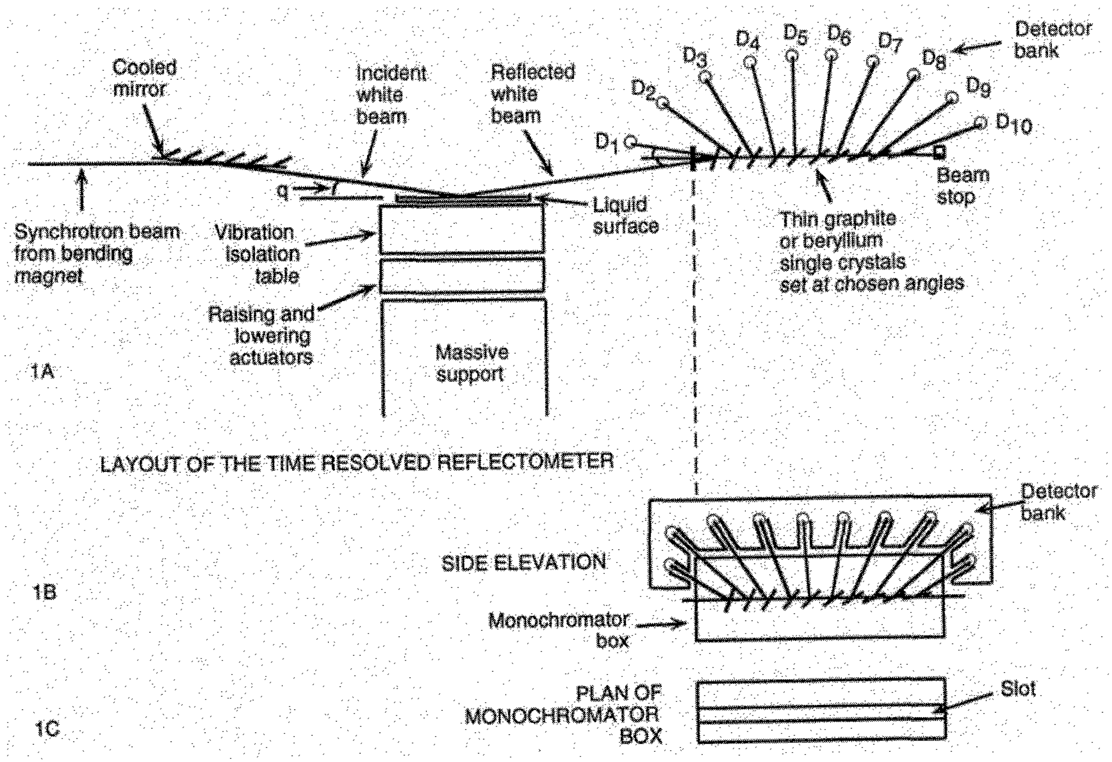

Fig.4 Design of novel wavelength-dispersive X-ray reflectometer for millisecond measurement, proposed by J. W. White. A number of sets of the analyzing crystal and the detector are used simultaneously. (Reproduced with permission from [31], Fig.8.)

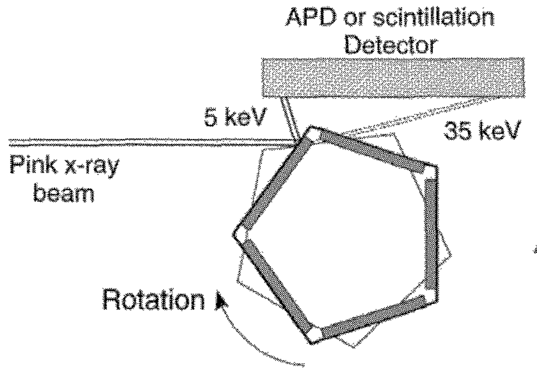

Fig.5 Design of novel wavelength-dispersive X-ray reflectometer for millisecond measurement, proposed by J. W. White's group. A rotator with five analyzing crystals and a single fast detector are used. (Reproduced with permission from [32], Fig.2.)

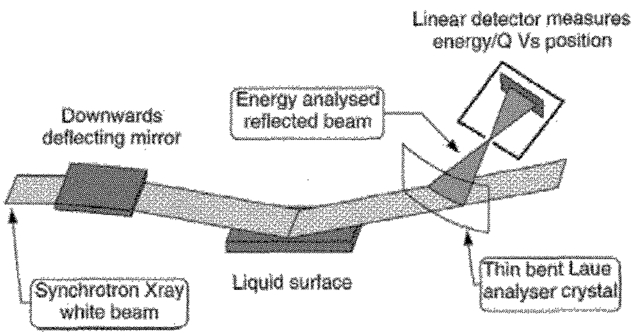

Fig.6 Design of novel wavelength-dispersive X-ray reflectometer for millisecond measurement, proposed by J. W. White's group. A bent Laue-type analyzing crystal and a position-sensitive detector are used. (Reproduced with permission from [32], Fig.3.)

time scale for the measurement, because of the counting rate limit of the detector. The method is suitable for studying reactions in the order of min ~ hour, and in some cases, data collection in sec can make sense. To accelerate X-ray reflectivity measurement further, a much faster detector with a certain energy resolution, e.g., E/ΔE = 10~100, is required. In X-ray fluorescence analysis, or more likely in XAFS in X-ray fluorescence mode, multi-element (e.g., 9~100) Si or Ge detectors have been often employed [29]. One possible way forward would be to use such a detector. For reflectivity applications, the size of each element should be made much smaller than conventional elements [30]. Another important method is wavelength-dispersive detection, i.e., using a crystal analyzer. For a long time, it has been thought that energy-dispersive detection was more or less the only way to cover the wide X-ray energy range. However, as shown in Figs.4, 5 and 6, some special designs are now being considered for the rapid analysis of reflected white X-rays [31, 32]. Note that the performance attributes of the detector system, such as position-sensitive property (area size and resolution), dynamic range, read-out time etc., are crucial here. Recent rapid advances in detector technologies could make possible a time scale of msec or even shorter in the near future. Promising scientific targets would be structural changes of organic thin films at the air–water interface, such as monolayer films of polymeric surfactant on liquid surfaces: bi-layer, tri-layer and multi-layer nucleation, in response to applied mechanical compression [32]. Very recently, another novel design for a wavelength-dispersive X-ray reflectometer using a polychromator has been proposed by T. Matsushita [33].

3.2 The use of large angular dispersion

The X-ray reflectivity technique basically measures the intensity of monochromatic X-rays reflected at an angle equal to the glancing angle, which are scanned from low to high angles (e.g., 0.2 ~ 50 mrad for 8 keV X-rays). Therefore, as shown in Fig.7, which schematically explains Naudon's pioneering concept [34-36], when a divergent beam from a line focus of an X-ray tube is used so that all necessary angular components are included, the position-sensitive detector can record the whole reflectivity curve ranging over 1.6 deg (~30 mrad) simultaneously without moving any part of the reflectometer. One of the biggest advantages is that the concept is a good match with ordinary laboratory instruments. The typical measuring time is 2~10 min, depending on the sample, and it is possible to shorten this by employing a more powerful X-ray source. The main limitation is the detector. A fast detector with a wide dynamic range, large area and good spatial resolution will be crucial for further development.

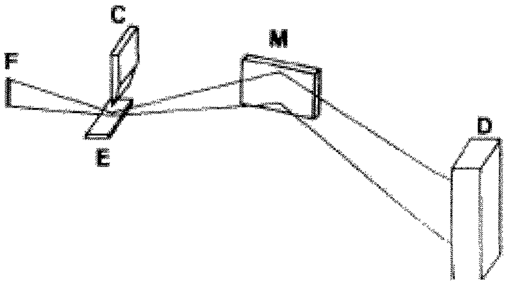

Fig.7 Schematic view of Naudon's method for X-ray reflectivity measurement. F: X-ray line focus (8×0.04mm from 6 deg take off angle), E: sample in a radiation-shielded chamber, C: knife edge made of tantalum, M: Ge(111) curved analyzing crystal in the vacuum housing, D: position-sensitive proportional counter. The distances of F-E and E-M-D are 225mm and 2090mm, respectively. The path M-D is evacuated. (Reproduced with permission from [34], Fig.1.)

Fig.8 shows a similar way of measuring X-ray reflectivity [37]. The main difference is that the sample is in the deposition chamber in order to study the growing process of thin films, while the set-up has several significant instrumental upgrades; including the combination of a point shape of the X-ray source (e.g., looking a line focus along the axis direction) and a Johansson-type monochromator, which had been independently innovated and patented before by another group [38]. The employment of a monochromator reduces not only the background but also unnecessary radiation damage to the sample, when compared with the use of an analyzing crystal downstream from the sample. Such advantages are highly beneficial for materials research [39]. A Johansson-type curved crystal is a somewhat mature technology, and proceeding to an extremely small Rowland radius would be a great challenge. However, H. Okuda et al. have recently reported a novel successful technique for fabricating a variety of curved X-ray monochromators [38]. On the other hand, Naudon's method can be directly improved by placing a flat or curved monochromator between F and E in Fig.7, while keeping the same F-E distance. Employing a high-spatial-resolution detector can reduce the E-D distance, thereby improving efficiency as well.

As clearly shown in Fig.9, in comparison with normal X-ray reflectivity data, the method has the advantage of quickly finding a main feature, such as the positions of the critical angle (5.8 mrad) and the 1st Bragg peak (20.5 mrad). As the method does not require any angular scans, it is possible to find when and how the surface density and/or the periodic length of multilayers change, just by monitoring the reflectivity profile. Another important feature that requires monitoring is the frequency of the interference fringes. Some changes to layer thickness are very likely when controlling the temperature and/or environmental gas, etc. On the other hand, the system counts non-specularly reflected X-rays as well as normal specular reflections. As there are no receiving slits, the data could easily be degraded by the background. Therefore, we view the method as complementing conventional reflectivity techniques and instruments.

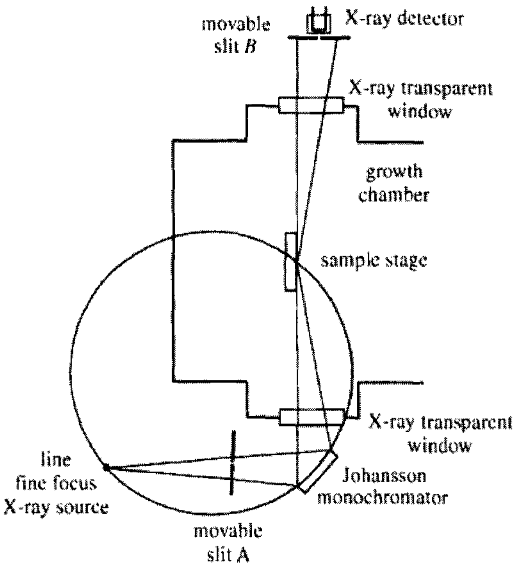

Fig.8 Combination of deposition system and improved Naudon's method with a Johansson-type monochromator, Si(333) Rowland radius 350mm. (Reproduced with permission from [37], Fig.1.)

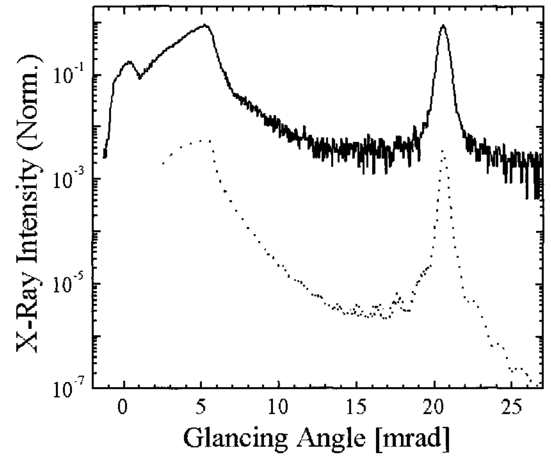

Fig.9 X-ray reflectivity data (λ=1.54Å, Cu Kα_1) for a Ni/C multilayer (2d=77.5Å) obtained from angularly divergent monochromatic X-rays without scan (solid line, measuring time 10 min) and normal parallel X-rays with $\theta/2\theta$ angular scan (dotted line, measuring time 50 min). The instrument was originally developed at NIMS, Tsukuba, Japan [41].

Table 1 Summary of quick X-ray reflectivity techniques - present status and future directions

	Energy (wavelength)-dispersive method (use of white X-rays)	Angular dispersive method (use of large angular dispersion)
Range in q	Depends on the spectral range of X-ray source (typically 7 ~ 70 keV) and the glancing angle. Use of high-energy synchrotron X-rays is promising. Special efforts are necessary for the system using analyzing crystals.	Depends on the angular divergence of incident X-rays (typically 1.5~2 deg for normal X-ray tube system) and the X-ray wavelength. Not easy to extend Naudon's method to experiments with inherent parallel synchrotron X-rays.
Resolution in q	Depends on the energy resolution of the detector (or the crystal spectrometer).	Depends on the spatial resolution of the detector.
Range in intensity	Depends on the dynamic range of the detection system (typically 3~4 decades) and measuring time (or repetition number). Modifying the incident spectral shape widens the effective range.	Depends on the dynamic range of the detection system (typically 3~4 decades) and measuring time (or repetition number).
Measuring time	Depends on the detector system. Measurement in msec ~ sec might become possible using a wavelength-dispersive system with a fast detector.	Depends on incident X-ray intensity and the detector system. Measurement in msec ~ sec might become possible if such experiments can be done with a synchrotron source.
Other remarks	Capable of small area analysis	

4. CONCLUSIONS

As summarized in Table 1, quick X-ray reflectivity techniques are still under development. Measurements in the order of minutes are realistic enough at the present stage, but a much greater scientific impact would be achieved if the time scale were shortened to msec, or at least shorter than 1 sec. Wavelength-dispersive experiments with a high-energy synchrotron source, as well as an efficient and fast spectrometer that covers a wide energy range, are promising. As for the angular-dispersive system, based on Naudon's method, the limiting factor is an X-ray source (or special optics for inherently parallel synchrotron X-rays). There are two ways of overcoming this limitation. One is the further enhancement of intensity or efficiency for a laboratory system, while the other is the development of a focusing optical device with a very large convergent angle. We also note that detector technology is the final key to the future advancement of both the energy (or wavelength) dispersive and the angular dispersive modes.

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