Multilayer optics for X-ray analysis

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1. Introduction

1.1. History of the development of multilayers

Since W. von Laue discovered X-ray diffraction using a zinc sulfide single crystal in 1912, single crystals including Si, Ge, LiF, etc. have been used as analyzing crystals for X-ray analysis. However, as the research and applications of X-rays advanced, the wavelength region also extended significantly. Analyzing crystals made of single crystals can no longer cover all X-ray analysis requirements. A new type of analyzing crystals is each made of a periodic layer structure with a period longer than the wavelength of X-rays. For example, if two different kinds of thin layers are overlaid alternately to form a periodic multilayer structure, the multilayer can be used as an analyzing crystal for X-ray analysis. In fact, such a structure was proposed a long time ago after the discovery of X-ray diffraction. However, it was not until the 1970s that scientists were able to make multilayer devices because of the advances of sophisticated ultra thin-film deposition techniques such as electron-beam evaporation, sputtering deposition, etc. The development of multilayer X-ray optical devices has advanced rapidly since the 1970s. In 1980s, the Osmic, Inc. (now Rigaku Innovative Technologies, RIT) in the US commercialized multilayer devices for X-ray fluorescence analysis under the brand name of "Ovonyx". The multilayer optical devices have now been widely used in X-ray diffraction, X-ray fluorescence, and X-ray projection/imaging technologies.

A multilayer optical device is also called "artificial lattice," "artificial multilayer film", or "artificial stacked film". In this article, we call it "multilayer optics," or simply, "multilayer."

1.2. X-ray fluorescence analysis

The X-ray fluorescence technique can be used for elemental identification and concentration determination of materials by irradiating primary X-ray beam onto the materials to excite their constituent elements, and measuring the fluorescent characteristic X-ray intensities from the elements. In X-ray fluorescence analysis, an X-ray fluorescence system basically consists of an X-ray source, an analyzing crystal and a detector. These three major components are important for the performance of a high-sensitivity and high-precision X-ray fluorescence analysis.

Four important properties for a modern X-ray fluorescence system are:

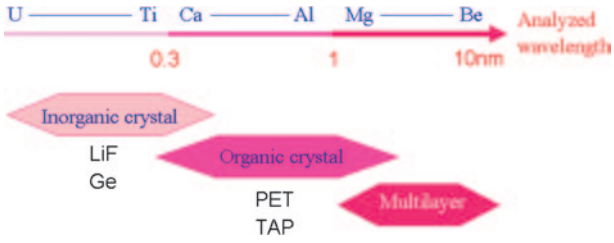

Fig. 1. Analyzing crystals for X-ray fluorescence analysis.

- High intensities for high-precision and high-sensitivity analysis.
- High wavelength resolution to minimizing overlapping effects by adjacent X-ray fluorescent lines.
- High signal to noise (S/N) ratios for trace-element analysis.
- Long-term stability for reproducible results.

It can be very difficult to use just one analyzing crystal to measure fluorescent X-rays emitted by all elements presented in materials. The entire X-ray wavelength region can normally be divided into three wavelength regions, and a best-suited analyzing crystal can be used for each wavelength region (see Fig. 1). For the wavelength region of heavy elements heavier than or equal to Ti, a lithium fluoride (LiF) or a germanium (Ge) single crystal is commonly used. For the wavelength region of elements from Ca to Mg, an organic single crystal such as pentaerythritol (PET) or thallium acid phthalate (TAP) can be used. TAP ($2d$=2.57 nm, where d is lattice spacing), which has the longest lattice spacing among all analyzing single crystals, is unsuitable for analyzing ultra light elements lighter than or equal to N. For light elements in this long wavelength region, a total reflection mirror or a LB (Langmuir–Blodgett) film, in which soap films are multiply overlaid, can be used[2]. However, LB films give low S/N ratios and are relatively unstable. In the early 1980s, Spiller[3] and Barbee[4] reported that light elements with soft wavelengths can be successfully analyzed using multilayer optics. This development opened a new possibility for X-ray fluorescence analysis of light elements. Since then, the developments of multilayers have advanced significantly. Multilayers are now being used widely as standard analyzing optics for ultra light element analysis.

1.3. X-ray diffraction analysis

In X-ray diffraction, the X-ray wavelengths commonly used are in the range from 0.05 to 0.2 nm. Such as Si and Ge having perfect crystal lattices, or graphite crystal

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having high integral intensities are used as a collimator and/or monochromator. In the mid 1990s, multilayers attracted many attentions in X-ray diffraction applications when the Osmic, Inc. (now RIT) and the Fraunhofer Gesellshaft in Germany had successfully manufactured parabolic graded multilayers which convert a divergent incident X-ray beam from an source into a parallel (or collimated) X-ray beam[5]. In a graded multilayer, the value of layer spacing or period d is gradually changed along its parabolic surface so that the Bragg condition can be satisfied by the divergent incident X-ray beam. In this way, divergent X-rays generated from a source can be monochromatized and collimated by reflections from the parabolic surface.

In 1998, Osmic, Inc.[6] developed a confocal mirror (CMF) that focuses two dimensionally from a point source. In a confocal mirror, two perpendicular multilayers with the same focal length are bounded together. In the past, it was said that there were no lens (or crystals) that can focus X-rays effectively. For example, it is necessary to use a very long total-reflection mirror because the incident X-ray angles are very small from 0.2° to 0.3°. This type of long mirror is rarely used except in special cases such as for synchrotron radiation. A confocal mirror is a revolutionary device because it can use divergent X-rays effectively at one order of magnitude larger than those of a total-reflection mirror.

Moreover, a graded multilayer makes possible to obtain either a parallel X-ray beam reflected from a paraboloidal surface or a focusing X-ray beam from an ellipsoidal surface. With these innovative developments, the use of multilayers in an X-ray diffractometer has advanced rapidly. First, parabolic-surface graded multilayers are well suited to be used with a line source to collimate and monochromatize an incident X-ray beam for X-ray powder diffraction, thin-film diffraction and reflectivity measurements. The gains in Cu-Kα (λ= 0.15 nm) intensities are about an order of magnitude higher than those using a conventional crystal.

Furthermore, with the development of a confocal mirror, the range of applications has expanded drastically. A noticeable application of it is for protein crystal-structure analysis, in which it replaces two total-reflection mirrors arranged perpendicularly to focus X-rays in small spot. An order of magnitude higher in intensities, depending on the combination of the mirrors in a CMF, can be obtained.

When the size of X-ray source exceeds the width of a diffraction width of a multilayer, exceeded X-rays will not be reflected by the multilayer and do not contribute to the X-ray analysis at all. Therefore, the brightness of a source (small source size) becomes more important than the total power of that. New rotating-anode X-ray sources such as FR-E SuperBright and RA-Micro7 have recently been developed. The new Rigaku FR-E+ SuperBright and RA-Micro7HF X-ray generators, each featuring a true 70-μm diameter source size and an extreme bright incident X-ray beam, are two of the most intense laboratory X-ray sources available today. These X-ray sources in combination with CMF provide brightness exceeding those of some second generation bending magnet synchrotron beam lines. In addition, a new sealed X-ray tube with a source size of 50 μm or less is also extremely effective to limit an incident X-ray beam onto a micro-size spot on a patterned wafer. It becomes obvious that the development of a new system with a combination of a high brightness and micro-focus X-ray source and a multilayer can significantly enhances the performances and greatly expands the application range of an X-ray diffractometer system for the characterization of materials.

2. X-ray reflection by a multilayer and the optimization of its structure

A multilayer for dispersing X-rays is normally formed by alternately stacking of two different kinds of thin layers. The material used in one kind of layer normally consists of a heavy element with a high X-ray refractive index, and the material in the second kind of layer consists of a light element with a low refractive index. The former layer is called “reflection layer”, and the latter is called “spacer layer”. As shown in Fig. 2, when an X-ray beam impinges onto a multilayer, X-rays are reflected by each of the reflection layers due to the differences in refractive indexes between the reflection and the spacer layers. When these reflected X-ray beams satisfy the interference condition (or Bragg condition), strong reflected intensities are obtained similar to those of a diffraction peak when the Bragg condition is satisfied:

$$n \cdot \lambda = 2d \cdot \sin\theta$$

where n is positive integer; λ wave length, d period of the multilayer or layer spacing, θ incidence angle of the X-ray beam.

When the reflection process by a multilayer with that by a single crystal composed of actual atoms is compared, there are the following differences. In X-ray reflection by a single crystal, in which atoms are arranged in a perfect array, a series of lattice planes (or atomic planes) serve a reflection plane for the incident X-ray beam. On the other hand, in the case of a multilayer, each interface between a heavy-element layer and a light-element layer with significant difference in refractive indexes forms a reflection plane. A major advantage of a multilayer is that it can be made with desired layer materials and layer spacing, d.

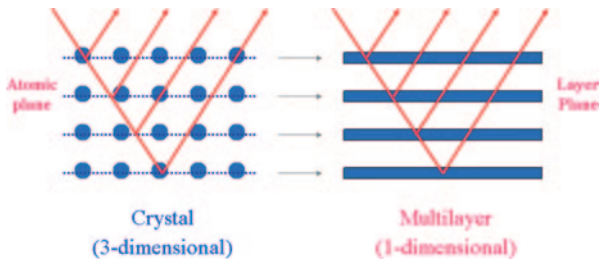

Fig. 2. Reflection of X-rays by a single crystal (left) and by a multilayer (right).

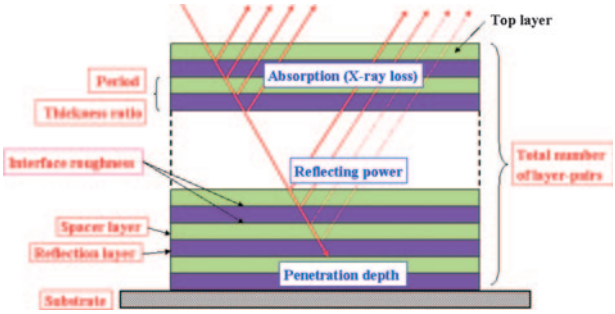

Fig. 3. Structure of a multilayer.

The structure of a multilayer is shown in Fig. 3.

Parameters characterizing the multilayer structure are discussed in the following paragraphs.

2.1. Components of a multilayer: reflection layer and spacer layer

The reflective performance of a multilayer mainly depends on the kinds of materials used for the reflection and the spacer layers. Normally, the reflection layers are made of a heavy-element substance and the spacer layers consist of a light-element material.

2.2. Period

The period (also called periodic length or *d*-spacing) of a multilayer determines the reflection (or Bragg) angle for the incident X-ray beam. The smaller the value of period (or *d*-spacing), the lower the reflective efficiency and also the background intensities caused by total reflection, and this leads to higher S/N ratios. The angular distance between adjacent peaks increases with decreasing *d*-spacing and with increasing wavelength selection (i.e., resolution). Therefore, if high intensities are not required, the use of a smaller period (or *d*-spacing) can result in a better reflective performance, especially in XRF applications. However, it must be noted that too small lattice spacing might cause an abrupt decrease of reflectivity because the multilayer cannot hold a regular layer structure. Therefore, value of period (or *d*-spacing) must be selected properly by taking into account of the lower limit of *d*-spacing.

2.3. Total number of layer pairs

Normally, the larger the number of layer pairs in a multilayer, the higher the reflection intensities and the narrower the reflection peaks (i.e., the better the wavelength resolution). However, the interfaces in the bottom region of a multilayer may not be able to contribute to the reflection process, because of X-ray absorption and/or multiple internal X-ray reflections inside the multilayer. In practice, it is enough to stack a limit number of pairs, normally from 10 to a few hundred, which can actually contribute to the reflection process. There is no use to make a multilayer with its number of layers beyond the layer limit. To improve resolution (narrower diffraction width), a multilayer with a large number of layer pairs participating in the reflection process is required. This can be achieved by selecting proper layer materials to increase X-ray penetration depth so that large number of layer pairs can participate to the X-ray reflection process.

2.4. Thickness ratio between reflection and spacer layers

As shown in Fig. 3, there are two kinds of layer interfaces (e.g., upper and lower interfaces of a reflection layer) exist within each pair of layers in a multilayer. The degree of X-ray interference among all the reflected beams from all interfaces varies depending on the thickness ratio of the reflection and the spacer layers. If the thickness ratio of the reflection layer and the spacer layer is expressed by a simple integer ratio of $H:L$, related $n\cdot(H+L)^{\text{th}}$ order reflections are suppressed (n is a positive integer). Another thickness ratio of H: d (where $d=H+L$), also called "Γ(gamma) value", is another important factor for the reflection by a multilayer. It is found that both reflectivity and peak width vary systematically with Γ. Value of reflectivity increases initially with Γ, and reflectivity reaches a maximum at around $\Gamma=0.4$, then the reflectivity decreases slowly with increasing Γ. On the other hand, the value of the peak width increases monotonically with Γ.

2.5. Interfacial state (roughness) in each interlayer

Usually the reflection and spacer layers are amorphous and/or polycrystalline. Geometrical irregularity (shape roughness) causes an unnecessary scattering loss of incident X-rays. In addition, blurring of reflection plane caused by intermixing and/or diffusion (diffusion roughness) of atoms from adjacent layers reduce reflection efficiency. Reflection intensity decreases exponentially with increasing roughness. For a high-reflection performance, it is useful to have smooth and sharp interfaces.

2.6. Surface roughness of the substrate

In analogy with the interface roughness discussed above, the surface status of a substrate is another important parameter in X-ray reflection. If a multilayer is formed on a rough surface, the rough status is propagated into the multilayer, disturbing the formation of a smooth interface. Since the surface roughness of a Si wafer can be controlled within one or more atomic levels using modern semiconductor technology, Si wafers are one of most frequently used substrates. For a curved-surface multilayer optic, finely polished glass substrates have also been used.

In order to select the most appropriated parameters for the deposition of a multilayer, theoretical X-ray reflectivity intensities are usually first calculated. Computer simulation has been found to be very helpful for optimal selections of multilayer's parameters. Test depositions are performed to evaluate their reflective performances. A final multilayer structure can eventually be obtained.

A multilayer structure has basically different reflective features from those of a single crystal as mentioned earlier. Therefore, these two types of reflection devices

Table 1. Advantages and disadvantages of a multilayer.

Advantages	Disadvantages
High reflectivities (Constituent substances are optimized for each wavelength range.)	Low wavelength resolution (One to two orders of magnitude lower than a single crystal)
Values of Layer thickness and the length of the period of a multilayer can be selected	Background intensities are high and S/N ratios are low.
Suppression of specified high-order reflections is possible.	Fluorescent X-rays from the multilayer may cause a problem.
Lengths of the period in the in-plain and depth directions of a multilayer can be changed	The periodic lengths may vary for each film-formation lot.

should be used differently according to the purposes of their applications. Table 1 summarizes the advantages and disadvantages of a multilayer.

3. Applications to X-ray fluorescence analysis

3.1. Optimization for light-element analysis

With the recent advances and developments in the areas of new materials (or compounds) and deposition techniques, researches on new multilayer structures continues to move forward rapidly. In this section, a new development in multilayer optics for B (boron) analysis is described below.

One of the typical applications in which the B analysis becomes very important is the analysis of BPSG (boro phospho silicate glass) thin films. BPSG is widely used as an interlayer insulation film in semiconductor devices. Since physical properties of BPSG are extremely sensitive to the concentration of B, a high-precision and high-throughput analysis in a manufacturing process is required. X-ray fluorescence analysis has been utilized as one of the analytical methods, which can meet these requirements. Since the efficiency of generating B-Kα X-rays is extremely low, it has long been a challenge to find an efficient X-ray analyzer for measuring the fluorescent B-Kα line.

In order to enhance the reflection efficiency of a multilayer for measuring B-Kα, the layer-material combination in the multilayer structure needs to be carefully considered. Reflection efficiency is dominated by both the optical contrast (difference in refractive indices) at the layer interfaces and X-ray loss in the multilayer. One of the most convenient methods for obtaining an optimal selection is to construct a map of complex refractive indices of possible materials for B-Kα X-rays. Fig. 4 shows such a map, in which values of the real part of the complex refractive indices for various materials are plotted in the horizontal axis and values of the imaginary parts in the vertical axis. To find out the optimum combination from this map, materials that exist at as low positions as possible in the vertical axis (low absorption) and as far as possible from each other in the horizontal axis (high contrast) should be considered. Fig. 4 shows that B and La are most suitable to be used as the spacer and the reflection layers in a multilayer for analyzing B-Kα X-rays. However, La is well known to be a highly reactive and unstable substance. In addition, B is known as a substance having difficulty to form a continuous thin layer of a few nm thick. Therefore, in the case of this new multilayer structure, the optimization of deposition conditions becomes a challenge for obtaining a stable and ideal layer structure.

Figures 5 (a) and (b) show the qualitative and quantitative results on B using the newly developed multilayer and a traditional analyzer, respectively. The analyzed sample is a BPSG thin film deposited on a Si wafer. It can be seen that both the B-Kα peak intensity (see Fig. 5a) and the slope (sensitivity) of the calibration curve for the B-Kα radiation are enhanced to about two times or more than those obtained by the traditional analyzer, in which Mo and B_4C are used in the reflection and the spacer layers, respectively. The intensity enhancements agree with those predicted by theoretical simulation.

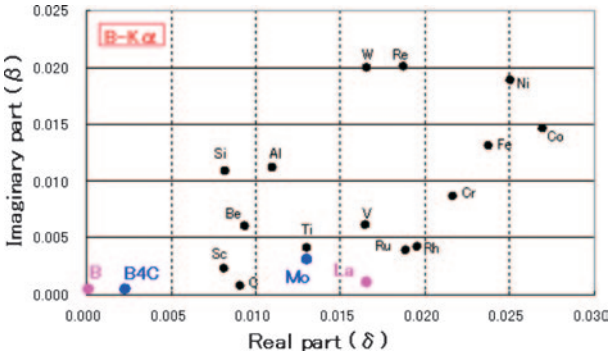

Fig. 4. Complex refractive-index map for B-Kα

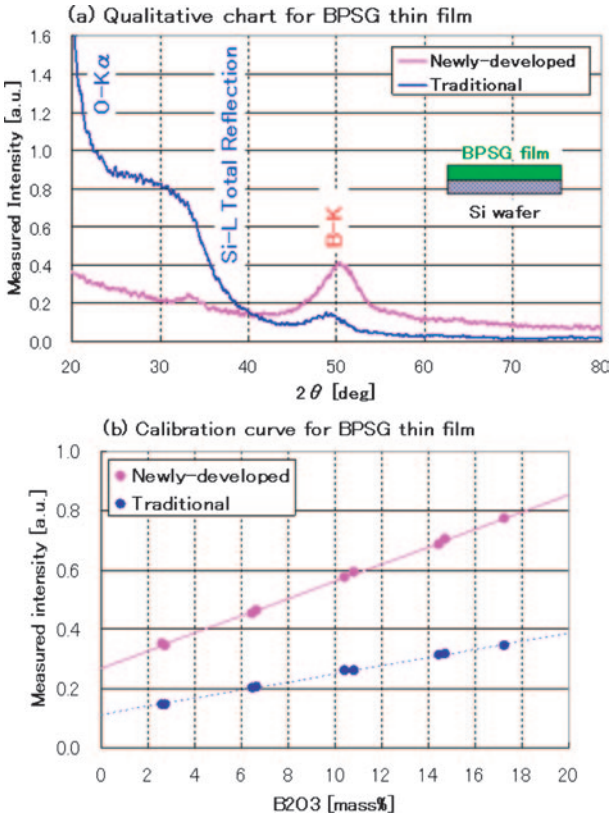

Fig. 5. Analysis results for a BPSG thin film by a newly developed multilayer.

Table 2. Multilayer analyzers for X-ray fluorescence analysis of ultra-light elements.

Product name	2d value [Å]	Analysis elements	Features
RX25	30±1	F to Mg	Ultra short period, high resolution, substitute for TlAP
RX35	55±2	O to Mg	High intensities. For O-Kα to Mg-Kα
RX40	80±2	N and O	Very high intensities for N-Kα and O-Kα
RX45	110±3	N only	Highest intensity for N-Kα (about 5 times of RX40)
RX61	160±5	C, (B)	Suppressed O-Kα. Also usable for B -Kα
RX75	160±5	B only	High intensity for B-Kα (about 2 times of improvement).
RX80	200±8	Be only	Effective for X-ray wavelengths of 10 nm or longer

Moreover, secondary effects such as a reduction of total-reflection tailing of the Si-L line and a suppression of the interference by the O-Kα peak are also observed. The above example is just one of recently achieved optimization cases. Other new multilayers have also been developed in the past few years. One of the new multilayers is an ultra short-period multilayer, which can be used as an alternative to TlAP. Another new multilayer is a C analyzer, which has the abilities to suppress the interfering O-Kα line and to be usable also as a B analyzer. Table 2 listed the summary of the latest multilayer analyzers for X-ray fluorescence analysis manufactured by Rigaku.

3.2. Other comments on XRF analysis

Results on a similar XRF analysis of a PSG (phosphor silicate glass) thin film are shown in Fig. 6. It shows that a small B-Kα peak appears from the PSG film containing no B. This kind of peak is known as "pseudo peak" and can be observed when the multilayer, which is optimized for a specified element such as B or C, contains the same specified element. One of the possible reasons for the presence of a pseudo peak is that a part of incident X-rays excited and caused secondary fluorescence by the constituent element (such as B or C) in the multilayer. The fluorescent X-ray is then reflected by the multilayer itself (7). Another possible reason is that the optical contrast of multilayer structure changes abruptly at X-ray absorption edge of the constituent element, and the reflection efficiency also changes greatly at the same time. This behavior can be observed as an intensity change having a peak shape at the angle of absorption

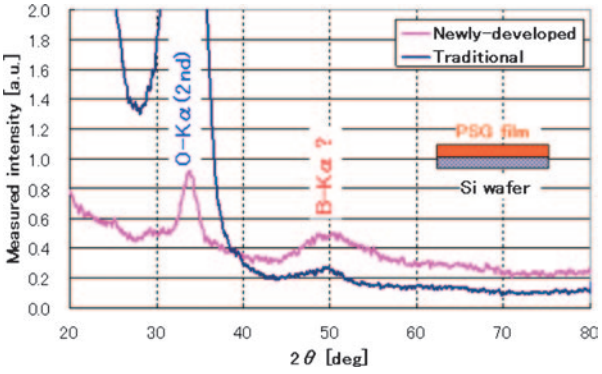

Fig. 6. Qualitative analysis chart of a PSG thin film.

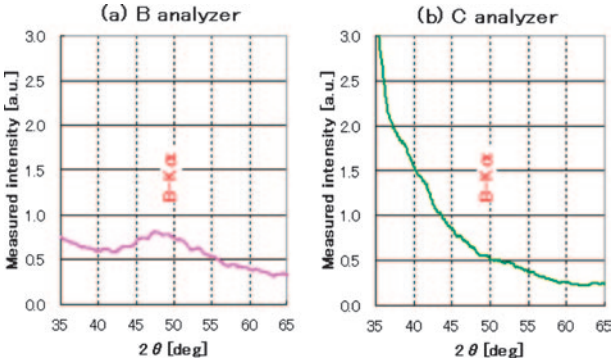

Fig. 7. Analysis of fused quartz using (a) B and (b) C analyzers.

edge, such as the B-K edge or the C-K edge.

The presence of a pseudo peak can be a nuisance in an actual XRF analysis. For a quantitative XRF analysis, a calibration curve is normally used and the observed intensity of the pseudo peak is treated as one of the background-intensity components. Therefore, the pseudo peak does not produce a problem in an actual quantitative analysis. On the other hand, in the case of a qualitative analysis, the constituent elements are identified directly on a qualitative chart such Fig. 6, and pseudo peaks may lead to a false conclusion. One way to prevent such a misleading situation is to use an alternative multilayer, which does not contain the analyzed element(s). For example, when a qualitative analysis is required for identifying the presence of B in a sample, it is better to use a C analyzer containing no B, in place of a B analyzer containing B. The recently developed multilayer analyzer for C has almost the same reflective efficiency for the B-Kα line obtained by a traditional analyzer for B. Figures 7 (a) and (b) show qualitative charts measured for a fused quartz (SiO_2) sample by using a B and a C analyzers, respectively.

It can be clearly seen from Fig. 7 that no pseudo peak appears at the B-Kα reflection angle when using a C analyzer. It is also possible to use a N analyzer for the qualitative analysis of C.

4. Multilayer optics in X-ray diffraction

4.1. Structure of multilayer

In X-ray diffractometry, multilayers are used to control an incident X-ray beam from a divergent X-ray source in an effective way for performing diffraction and scattering measurements. For example, A graded parabolic multilayer is used to monochromatize incident X-rays by means of Bragg diffraction from the multilayer and to collimate the incident X-ray beam by reflection from its parabolic surface. As shown in Fig. 8, a graded multilayer with a parabolic surface can diffract a divergent incident X-ray beam into a monochromatized and collimated (or parallel) X-ray beam. Figure 9 shows the Cu-Kα peaks diffracted from different positions on the surface of a W/Si multilayer. The peak actually shifts gradually and systematically when diffracted from different positions on the parabolic surface of the multi-

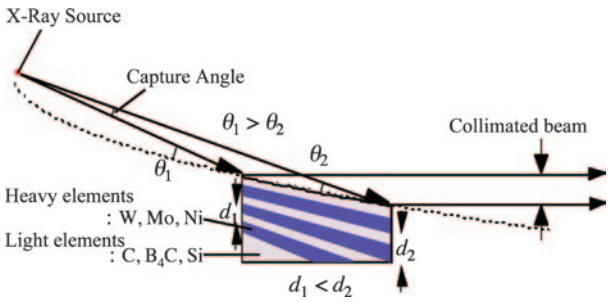

Fig. 8. Schematic structure of a graded parabolic multilayer. Monochromatized and collimated X-rays are obtained by making the multilayer on a parabolic surface with the X-ray source at the focus.

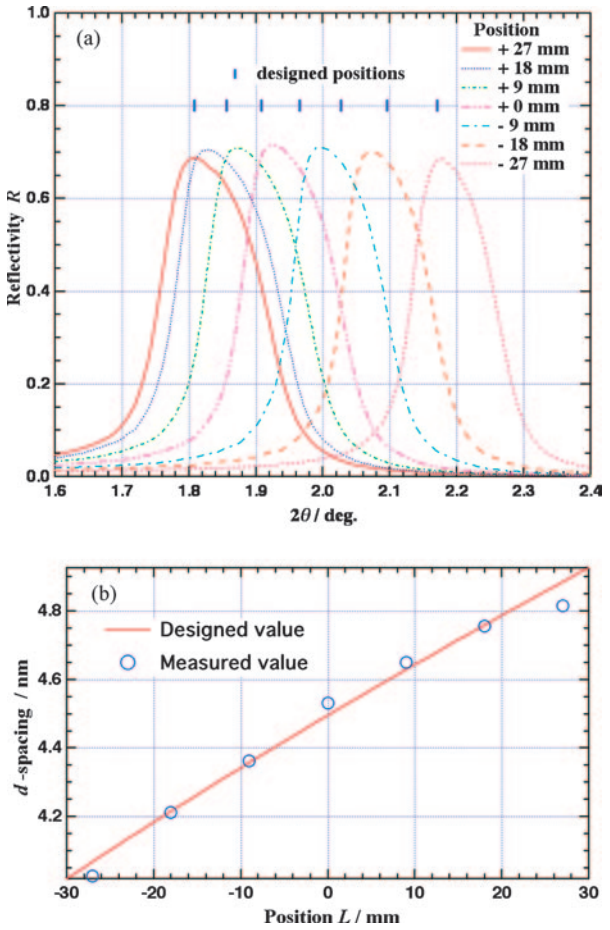

Fig. 9. (a) Diffraction curves from various positions on the surface of a W/Si multilayer. As the position moves away from the X-ray source (i.e., the+direction), the diffraction angle moves to lower angles. (b) The designed and measured positions of the lattice spacing match within errors of 0.1 nm or less.

layer. The d values calculated from the observed peak positions are very close to that of the designed values.

Figure 10 shows the result of analyzing the collimated and monochromatized X-ray beam. From this figure, it is found that the divergent angle of the parallel (or collimated) beam is about 0.04°, and the Kβ peak intensity was suppressed to about 0.5% of the intensity of the Kα_1 peak. When a multilayer is used for X-ray diffraction, it is important to know the basic properties of a multilayer. The basic features of a multilayer are the same when its surface shape is elliptical. However, in this case, its performance is not evaluated by the divergence of the collimated beam but by the size of the focused X-ray spot.

The factors that determine these basic performances include not only the properties of the multilayer itself characterized by its interface spacing and roughness, but also by a possible deviation (figure error) from an ideal parabolic or elliptical surface, the size of the X-ray source, etc. Therefore, when an X-ray optical system is designed, all factors should be evaluated and optimized. When a multilayer is used in X-ray diffraction, it plays the role of a reflecting mirror for characteristic X-ray lines rather than analyzing an X-ray spectrum, so it can simply be called as a "mirror." In the rest of this article, we shall use this expression.

A special kind of mirror shown in Fig. 11 is called "confocal mirror," which is obtained together by bonding two perpendicular multilayer mirrors made in such a way that their focal positions coincides with each other. X-rays are reflected once by each mirror, and then focused in the direction perpendicular to each mirror surface. Therefore, a confocal mirror can be used to control an X-ray beam two-dimensionally. The confocal mirror is specially designed so that when one multilayer is aligned with the X-ray source, the other multilayer will be automatically aligned.

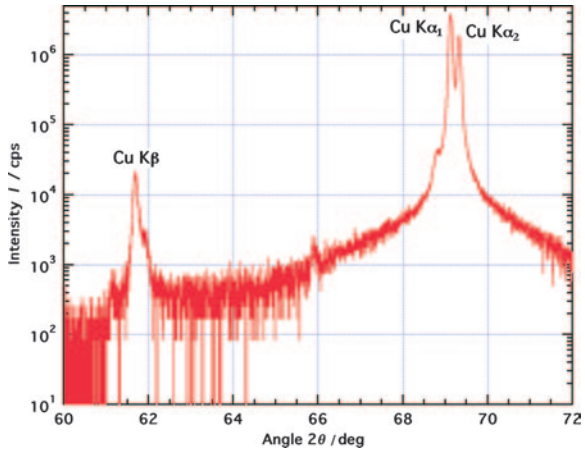

Fig. 10. X-ray spectrum from a W/Si parabolic multilayer analyzed by a Si (400) crystal. The Kβ X-ray peak intensity is about 0.5% of the main Cu-Kα_1 peak. The divergence of the collimated beam is estimated to be about 0.04°.

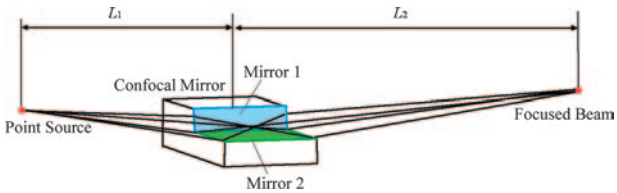

Fig. 11. Schematic diagram of a confocal mirror. X-rays from a point source are focused to a spot. (It is also possible to obtain a parallel beam according to the surface shape of the multilayer mirror.)

For a one-dimensional parabolic (elliptic) mirror as shown in Fig. 8, an X-ray line source is generally used for powder diffraction. On the other hand, a confocal mirror described above can only be used with an X-ray point source. Therefore, the developments of new high brightness X-ray point sources have rapidly attracted a great deal of attention. Newly developed X-ray sources include: an unprecedented rotating anode and high-brightness X-ray source, a fixed target micro-focus tube with a focal spot size of about 50 μm, etc.

4.2. Applications to X-ray diffraction analysis

The advent of multilayers revolutionized the X-ray optical systems used in X-ray diffractometry. Some of the major applications are as follows:

4.2.1. Polycrystalline (or powder) diffraction

The para-focusing method has been the most commonly used technique to measure X-ray diffraction using a powder diffractometer since the 1940s, when the first X-ray powder diffractometer was developed. When the sample surface is not flat and/or the absorption is small, X-rays can penetrate deep into the sample. These will cause diffraction peaks appear/displace to higher 2θ angles than their correct angles. When the parallel-beam method with a multilayer mirror is used, correct diffraction angles free of sample's displacement and/or transparency errors can be obtained. In a high-temperature diffraction measurement, the surface of a sample expanded during X-ray measurements at high temperatures. The parallel-beam method can give correct 2θ angles, and this will make easy for precise measurements of lattice constant(s), thermal expansion coefficient(s), etc.

The grazing incidence X-ray diffraction method (GIXD), in which the incident X-ray beam is impinged at grazing angles onto the surface of a sample, is a relatively new and powerful technique for measurements of thin films. In the case of using a divergent incident X-ray beam in GIXD, the beam usually spreads over on the entire sample and spills over the sample onto other parts of a diffractometer. This can generate unwanted background intensities. Using a parallel beam from a graded multilayer and to set a grazing incident angle of the parallel beam to less than or equal to the critical angle for total reflection (i.e., about 0.2 to 0.5° depending on the density of a sample), the top surface (a few nm) of a thin film can be characterized with extremely high sensitivities. Furthermore, the "in-plane diffraction," in which the diffracted X-rays exit the surface of a sample at the same grazing angle, X-rays diffracted from crystal planes which are perpendicular to the film surface can be measured. A diffractometer system ATX-G, developed for precise measurements of in-plane diffraction, came to market for the first time worldwide in 1998[8]. Figure 12 shows the ATX-G results on measuring in-plane diffraction for a mono-layer organic $CH_3(CH_2)_{17}SiCl_3$ (OTS) film formed on a Si substrate by using the Langmuir method[9],[10]. From the in-plane diffraction measurements, it became clear that the molecules are

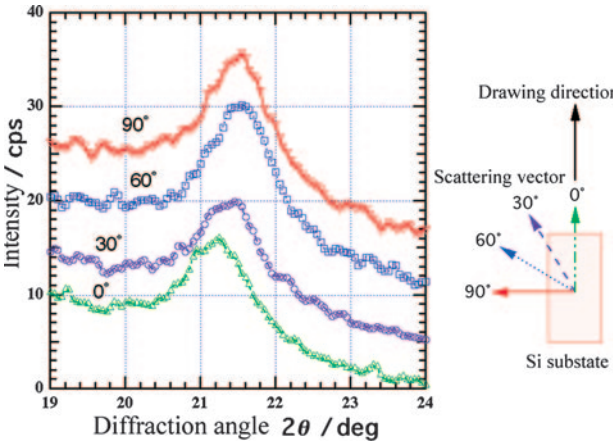

Fig. 12. In-plane diffraction measurement results on a mono-layer OTS film. Anisotropy along the direction which the substrate is drawn from the water surface was observed.

tilted by about 10° in the direction along which the substrate was drawn from the water surface of a Langmuir trough. The thickness of this single-molecule film determined to be 2.35 nm by X-ray reflectivity.

Figure 12 shows that X-ray diffraction profiles from the periodic lateral structure of an organic mono-layer film with a very weak scattering ability can successfully be measured using an ATX-G. In recent years, various ultra thin films are used as functional devices, and in-plane diffraction using a multilayer mirror is extremely effective to characterize crystalline structures of these ultra thin films[11],[12].

In-plane diffraction measurements can also be enhanced using the new SmartLab high-resolution diffractometer system for thin films and also the Ultima IV multi-purpose diffractometer system. In-plane diffraction has now become one of the most popular techniques for characterizing thin films.

4.2.2. Crystal structure of proteins

The growth of a protein single crystal of about 1 mm in size used for X-ray crystal-structure determination can be difficult. In X-ray diffraction, overlaps of adjacent diffraction peaks of a protein crystal are common, because of its relatively large lattice constants. A diffractometer system with a high-intensity X-ray source, which can focus incident X-rays to a spot of about 0.1 mm^2 at the sample position, is needed. To achieve a small X-ray spot at the sample position, an incidence optical system with two total reflection mirrors combined has been used. However, because the incidence angles for total reflection are low and their footprints large on the reflection mirrors, an adjustment and alignment of the optical system can be complicated. Furthermore, because in total reflection, the reflected X-rays are not monochromatized. This leads to the problem of a streak appearing on a diffraction spot. However, by using a point-focus confocal mirror, this problem can be drastically reduced.

There are a broader range of choices of confocal mir-

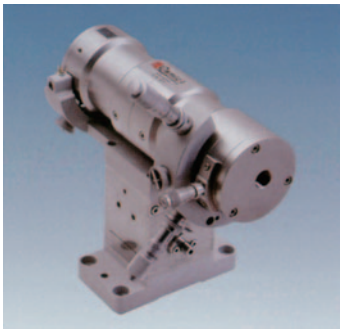

Fig. 13. Confocal mirror VariMax for crystal-structure analysis of proteins.

rors depending on high intensities and/or high resolution. For example, one of the choices is the use of a mirror which has a large divergent angle of 0.6° and also 15-time intensities higher than those of a conventional total reflection mirror. Another choice is the use of a mirror with a small divergent angle of 0.1° to provide both sufficient high intensities and with high resolution (see Fig. 13).

4.2.3. Small-angle scattering

A multilayer mirror is very useful for measuring small-angle X-ray scattering intensities. Since small-angle scattering measurements are commonly performed using only a Kβ filter because small-angle scattering results are insensitive to the monochromaticity of the incident X-rays. However, short-wavelength continuous X-rays can cause problems. The use of a multilayer mirror in the incident X-ray beam can effectively reduced the Kβ and the short-wavelength continuous X-rays to 0.5% and less of the Kα X-rays (see Fig. 10). Therefore, multilayer mirrors are ideal for measurements of small-angle scattering. For example, if we use a general-purpose X-ray diffractometer equipped with a parabolic mirror in the incident beam as discussed previously, it becomes possible to perform an X-ray measurement with minimum 2θ values of about 0.1 to 0.2° by using proper slit widths in the incident and the scattered beams of a conventional diffractometer.

A conventional point-focus small-angle scattering apparatus, which is not commonly used because of its low intensities, can become extremely useful and effective when the apparatus is equipped with a confocal mirror. Such a point-focus small-angle scattering apparatus is, of course, indispensable for the characterization of a sample with strong preferred orientation such as muscular substance and polymer fiber. In addition, it is also useful for a non-oriented sample such as a liquid sample, because vertical divergence of the beam can be neglected and it is needless to correct slit length effects. A special-purpose apparatus for small-angle scattering, namely NANO-Viewer, uses a specially designed confocal mirror. Two orders of magnitudes in intensity gains over those obtained by a conventional pin-hole collimator and a graphite monochromator can be obtained (see Fig. 14). A sample holder to control the temperature and humidity on the instrument can also be used to characterize phase transition and reaction process in a sample.

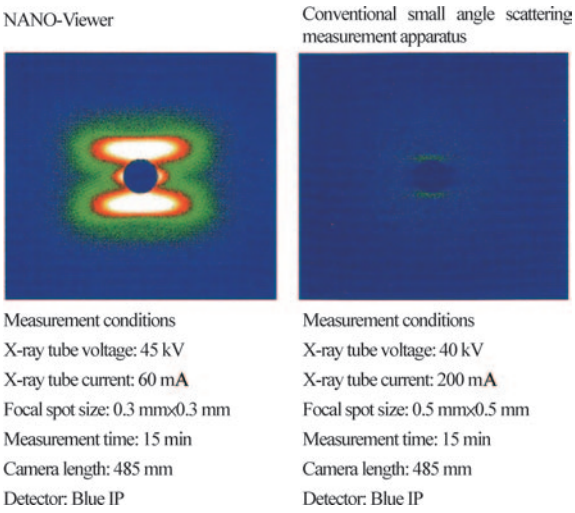

Fig. 14. Comparison of small angle scattering apparatuses.

4.2.4. Other applications

A multilayer can also be used effective for X-ray reflectivity measurements and the characterization of a thin-film deposited on a single-crystal substrate, in which a highly collimated parallel X-ray beam is required. In addition, in a semiconductor inline monitoring apparatus, e.g. MFM series, the incident X-ray beam needs to be focused on a micro spot in a semiconductor chip. This can be done by using a micro-focus X-ray source with a focal spot size of 50 μm or less to measure the thickness and the composition of a thin film.

In summary, a multilayer mirror integrated with an X-ray source is indispensable to be used in a diffraction system to create an incident X-ray beam tailoring to the purpose of an X-ray analysis.

5. Future prospects

Major disadvantages of using a multilayer instead of a single crystal for X-ray fluorescence analysis include that wavelength resolution of a multilayer is about one to two orders of magnitudes lower than that of a single crystal, and that the S/N ratios are also lower because of higher background intensities. One of the new possibilities is to use a “multilayer grating”. This is done by creating a fine groove structure machined to a regular multilayer to make it looks like a grating, and its purpose is to reduce the apparent density of the multilayer structure. With the grating sctucture, the incident X-rays can penetrate deeper into the multilayer. In this case, the number of interfaces contributing to X-ray reflections is increased, and an enhancement of wavelength resolution can be obtained. By reducing the density of a multilayer structure, the component of the total reflection from the surface of the multilayer decreases, thus leads to improvements in S/N ratios. However, in order to achieve high improvements in S/N ratios, while keeping high reflection intensities as previously obtained, the groove structure must be formed perfectly. At the present time, it is difficult to accomplish this even using the state-of-the-art technologies such as lithography technology and

ion beam etching[13].

Presently, the structure of each layer in a multilayer is polycrystalline or amorphous. The practical periodic layer thickness in a multilayer is limited to 1 nm or more. In the future, however, the attainment of a more ultra short periodic multilayer structure is desired. One of the possible ways to achieve this is to make every layer single crystal, and each layer is laminated and stacked with high precision. Molecular beam epitaxy, atomic layer deposition and other similar methods are some of the commonly used singe-crystal thin-film deposition techniques. In order to secure consistence atomic arrangements, the number of possible combinations of materials is rather limited. There are also many problems to overcome such as crystallinity was reported to collapse at the halfway of a film deposition[14].

Many problems in further enhancing the performance of a multilayer as a device for X-ray diffraction are common to those for X-ray fluorescence. If a multilayer with small roughness and a small d (or period) value can be obtained, divergent X-rays from an X-ray source with a larger solid angle can be obtained. This will make possible to obtain drastic enhancements in X-ray intensities. In addition, in order to focus a high-intensity X-ray beam onto a micro area, it is important to make the surface of the multilayer to be smooth like a mirror and as close as possible to an ideal parabolic or elliptical surface (to reduce figure error). For example, if the defocus at the 200-mm focusing position from the mirror is to be reduced to 3 μm or less, the figure error must be suppressed to 0.05 arc min or less. This corresponds to about one order of magnitude higher in precision than the present state of precision that can be achieved. Presently, reflections from two flat mirrors are used to focus X-rays two-dimensionally. If a high-precision toroidal mirror can be made, X-rays can be focused with a single reflection from the surface of the toroidal mirror. In this way, the capture solid angle is large and the focus X-ray intensities are high. Continued efforts are needed to achieve these goals.

Technical breakthroughs in the fields of film deposition technology and ultra precision machining technology can also play an important role in the developments of new multilayers.

6. Concluding Remarks

A multilayer, in which two different layers are alternatively stacked repeatedly to realize an analyzing property like a crystal from its periodic layer structure, becomes indispensable to both X-ray fluorescence analysis and X-ray diffraction analysis. Advances in X-ray optical systems together with X-ray sources have made tremendous progresses. It can be expected that the developments of new X-ray optical devices and X-ray sources will continue to advance and to make significant progresses.

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