APPLICATION OF MULTILAYER OPTICS TO X-RAY DIFFRACTION SYSTEMS

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Introduction

Beam conditioning is one of the most essential parts of an X-ray diffraction system. Typical goals of beam conditioning include increasing flux, improving spectral purity and controlling divergence. In most cases, these three properties can not be independently tuned. Therefore, the optimization of an optical system is a task of getting the best trade-off for an application with currently available optical elements and technology. The most rudimentary optical system is the pinhole or slit system, where one or two pinholes (or slits) control divergence. Such a system offers no intensity enhancement. Based on total external reflection, grazing incident optics are used in many applications to enhance the beam. Total reflection optics' enhancing capability is limited by the low critical angle, typically less than 0.5 degrees for CuK$\alpha$ radiation. Filtration is often used for both pinhole systems and total reflection systems to improve spectral purity. While suppressing the intensity of selected characteristic radiations such as K$\beta$ lines, filtration does not efficiently remove Bremsstrahlung. In addition, flux is further reduced by the filter.

Another category of beam conditioning optics is natural crystal including single crystals and mosaic crystals. Since crystal optics reflect X-rays by diffraction, the spectrum of the beam is nearly perfect. A single crystal optic provides a very narrow bandpass, and is capable of delivering a highly defined beam both spatially and spectrally. However, the narrow bandpass yields a very low throughput. Mosaic crystal optics have a much wider bandpass comparing to single crystal optics. But the beam conditioned by a mosaic crystal is often very divergent due to the nature of the mosaic structure.

The required performance of an optical system for a specific application depends on the nature of the application. There is no single optical system that satisfies the needs of every application. However, multilayer optical systems seem a good candidate for many X-ray diffraction applications, whether used alone or in combination with other optical elements such as slits, pinholes, Soller slits and crystal optics. A multilayer, as its name suggests, is a man-made layer structure. Reflecting X-rays by constructive scattering as a natural crystal does, multilayers also serve as a bandpass filter. Therefore, beams conditioned by multilayer optics are monochromatic. Multilayer optics have a bandpass about two orders of magnitude wider than single crystal optics. Likewise, the Bragg angle is typically two to three times higher than the critical angle of total reflection surfaces. As a result, the flux level delivered by multilayer optics is, in general, higher than both single crystal optics and total reflection optics. Moreover, unlike crystal optics, a multilayer optic's d-spacing can be tailored laterally, satisfying the Bragg condition at each point on a curved optic. These are so called graded d-spacing multilayer optics.

Examples of curved multilayer optics include elliptical optics and parabolic optics. Bandpass can be tuned several ways including varying layer thickness perpendicular to the coating surface (i.e. so called super-mirror), choosing different d-spacings, or application of different material combinations. Furthermore, changing the thickness ratio between the reflecting and spacer layers in a multilayer allows an optic designer to control high-order Bragg peak characteristics. For the last five or six years, multilayers' application in X-ray diffraction has seen an explosive growth. Advances in multilayer coating technology and precision optical construction technology have led to dramatic improvement of many diffraction systems. The remainder of this paper will present the fundamental working principles of multilayer optics and an overall picture of the multilayer optical systems as applied to X-ray diffraction systems.
Multilayer Technique for X-rays

For total external reflection of X-rays at energies used in X-ray diffraction, the typical value of reflectivity at an incident angle beyond the critical angle is only $10^{-5}$ or less. When considering total external reflection, since $\delta$, the real part of the optical index, is much less than 1, grazing incident optics have a very small acceptance angle. The reflectivity of an optical element beyond total reflection can be increased if the reflections from many surfaces can be added coherently \([1, 2]\). Such man-made layer structures were proposed as early as the 1920’s as a solution for achieving high reflectivity of X-rays. The earliest successful attempt to synthesize multilayer or multilayer optics occurred in the late 1930’s, when Dumond and Youutz \([3, 4]\) deposited by evaporation alternate layers of gold and copper with periods of approximately 100Å. The resultant multilayers were found to be metallurgically unstable. The two components diffused into each other over a period of weeks. A poor understanding of the working mechanism combined with technological limitations to slow further research and development until the 1970’s. At that time people realized high reflectivity could be obtained from alternating layers of highly absorbing materials and non-absorbing materials \([5-7]\).

In the last 10 to 20 years, a tremendous amount of effort has been expended in theoretical research, material study, precision coating engineering, optical construction and multilayer application development. These great strides have resulted in the ability to minimize layer roughness at a very low growth rate, to control layer thickness as well as uniformity of layer thickness to very high precision, and to form precision aspherical optical surfaces required by X-ray optics. High performance multilayer optics and new types of multilayer optics have been produced at massive production levels. Today’s multilayer optics have been used in a vast variety of areas, including VUV, soft X-ray, hard X-ray, and neutron applications. Multilayers have been used as both analyzers and beam-conditioning optics. Multilayer optic applications include spectrometry, diffractometry, microscopy, X-ray astronomy, lithography, and neutron analysis. They are used for laboratory sources, synchrotrons, and nuclear reactors.

Theoretical treatment and experimental study of multilayers are complicated matters. However, the aspects of multilayer coating key to various applications can be schematically described in a simplified fashion. A multilayer’s performance is measured by treating reflectivity as a function of incident angle, otherwise known as the rocking curve. From this viewpoint, two parameters can be used to characterize performance: peak reflectivity and full width at half maximum (FWHM) of the rocking curve. A wide rocking curve is the most distinctive characteristic of a multilayer. Figure 1 compares rocking curves for a multilayer and a single crystal (Si 111). The rocking curves are plotted as a function of the angular deviation from peak position. The wide rocking curve of a multilayer can benefit an application in two ways. First, total flux increases when a multilayer is used with a large-size X-ray source. The wider rocking curve of the multilayer yields a larger viewing angle, thus photons from a larger area can be reflected. Second, the increased bandpass of a multilayer is beneficial when used with an X-ray source with wide energy band. Compared to a single crystal, a multilayer typically provides a rocking curve one order of magnitude wider and a bandpass two orders of magnitudes wider.

In the design of an optical system, the FWHM of a multilayer optic should match both the needs of a specific application and the other components of the system, such as the X-ray source. An optic with a wider rocking curve yields larger flux but contributes to poor spatial definition and poor spectral purity. Conversely, a narrower rocking curve yields better spectral purity and better spatial definition. However, depending on the source and system geometrical layout, a narrow rocking curve doesn’t always result in less flux.

In the case of a crystal, the rocking curve depends on the size of the crystal. In other words, the FWHM depends on the volume of the crystal or the number of layers involved in the diffraction. The larger the number of layers, the narrower the angular width is. In the case of a multilayer, the primary beam quickly becomes extinct. Beyond a certain point, additional layers will not further affect the FWHM of the multilayer. The number of layers involved in diffraction is much lower for a multilayer than for a crystal. For this reason, the multilayer has a much wider rocking curve. Figure 2 shows how the rocking curve changes with the number of layers of a multilayer.

Several different approaches can be applied to control the rocking curve width, including changing d-spacing, coating materials, and depth variation of
d-spacing. Figure 3 indicates how changes in d-spacing affect the rocking curve of a multilayer. The smaller the d-spacing, the narrower the rocking curve.
Different coating materials can be used for changing the rocking curve width. Highly absorbing, strong scattering materials yield wider rocking curves since the primary beam will be extinguished faster. Lighter materials lead to narrower rocking curves since more layers involved are in the diffraction. Compared to W/B4C in Figure 2, Figure 4 shows the primary beam of a Ni/C multilayer becomes extinct slower and yields a narrower rocking curve.

Reflectivity of a multilayer is affected by the relative thickness of sub-layers. For a multilayer with two sub-layers, the ratio of the thickness of the heavy material to the thickness of the bilayer is called $\gamma$. The dependence of peak reflectivity on $\gamma$ is shown in Figure 5.

As shown in Figure 5, the reflectivity of a multilayer can be optimised by choosing the appropriate $\gamma$ value. However, reflectivity of higher orders usually yields poor background. For a multilayer tuned to reflect X-rays of a specific energy, the second-order reflection of X-rays with two times higher energy would occur at the same angle. Higher-order diffraction increases background and adds complexity to the diffracted spectrum. For this reason the $\gamma$ value is often chosen to suppress a certain diffraction order. Figure 6 shows that the second order can be suppressed by choosing $\gamma=0.5$.

For a real multilayer, the suppressed order will not disappear completely due to thickness variations within each layer. Second-order reflectivity of less than one percent of the first order is good enough for most applications.

Multilayer coatings have been developed for X-rays with different energies, including Mo K$\alpha$, Cu K$\alpha$, Co K$\alpha$, and Cr K$\alpha$ [8]. Examples of these coatings include W/B4C, W/Si, Ni/C, and Mo/Si. Figure 7 shows some examples of the performance of these coatings. Such information is used as the input parameters for the design of multilayer optical systems.

One-dimensional Multilayer Optical Systems

Depending on the application, a diffractometer used for an application can be either a one-dimensional (1D) system or a two-dimensional (2D) system. One example of 1D system is the powder diffractometer. A great amount of work has been done for parallel beam powder diffractometry. With this method, errors introduced by sample misalignment, transparency and irregular shaped samples in the traditional Bragg-Brentano geometry are all eliminated [9]. For certain configurations with specific resolution requirements, a large flux gain has also been obtained [10]. The simplest 1D multilayer system for powder diffraction is shown in Figure 8, in which only one parabolic multilayer is involved. For the axial plane, a Soller slit is generally used to reduce vertical divergence. On the receiving side, a Soller slit is used in the diffraction plane to provide angular resolution.

A multilayer optic, either flat or parabolic, can be used on the receiving side to provide improved angular resolution. Figure 9 schematically shows the geometry. The resolution and signal-to-noise ratio is greatly improved. Similar geometry is also used for thin film analysis, or reflectometry, in replacing the traditional parallel beam geometry where a slit system is used to collimate the beam [11]. Both flux and resolution of the system have been improved.

Another diffraction method benefiting greatly through the use of a parabolic multilayer optic is the high-resolution diffractometry (Figure 10).

Traditional geometry uses only a channel-cut crystal in the direct beam to control spectral and spatial resolution. Systems where a parabolic multilayer is inserted prior to the channel-cut crystal achieve flux gains close to twenty times [12].

A full line of parabolic multilayer mirrors has been developed for different applications. The variety of the line of optics accommodates the needs of properties such as intensity, spectral purity, divergence, and system geometry. Table 1 lists the ranges of these parameters for X-rays with different energies. The multilayer coatings are W/B4C.

Divergence, throughput and $K\beta$ reduction are determined by both the multilayer properties and the source width. The intensity distribution of the reflected beam is a convolution of source intensity distribution and multilayer rocking curve. The presented data assume a source width of 0.4 mm at 6 degree take-off angle, which is the typical configuration for a fine focus sealed tube. In this case, the viewing angle of the multilayer towards the source is larger than the opening angle of the source. Therefore, divergence is mainly determined by the source. For the case where the source is larger than the viewing angle of the multilayer, divergence will be larger and throughput will be smaller.

The same data for Ni/C coating is given in Table 2. Ni/C is not suitable for Mo K$\alpha$ because the
Fig. 7. Performance of W/B4C and Ni/C.

Fig. 8. Collimating optic used in powder diffractometer.

Fig. 9. Multilayer optic used on the receiving side of the powder diffractometer.
rocking curve is extremely narrow. Ni/C coating has a narrower rocking curve and higher peak reflectivity. Although throughput could be lower than its W/B4C counterpart, beam divergence is smaller and Kβ reduction is better when using Ni/C. For high-resolution diffractometry, since a channel-cut crystal has a much narrower rocking curve, the system throughput can be improved by using a Ni/C coating due to its higher peak reflectivity.

**Two-dimensional Multilayer Optical Systems**

For diffraction studies revealing two-dimensional information, a 2D diffractometer must be used. In a 2D diffractometer, the X-ray source is employed in point projection. For beam conditioning, a pinhole system combined with a graphite monochromator or a filter is still used for some applications such as small angle scattering and small molecule diffraction (with Mo Kα line). Total reflection mirrors (TA) are used for enhancing the beam. In a TA system, two cylindrical mirrors are used for two-dimensional beam conditioning. Each mirror deflects the X-rays in one of the two orthogonal directions. The mirrors can be arranged in a sequential fashion as in Figure 11, an optical arrangement called Kirkpatrick-Baez scheme [13]. At first, spherical mirrors working in grazing incident
condition were used since their nature made for easy engineering of the optics. Spherical mirrors have strong spherical aberration, and were gradually replaced by parabolic and elliptical cylinders.

A focusing beam is preferred since it increases flux and improves resolution if the detector is at the location near the focus. Such an optical path is schematically shown in Figure 12. For a real application, the beam size at the detector will never be zero since the X-ray source has a nonzero size. The focal length, of course, should be determined by the nature of the application under consideration. For protein crystallography, the convergent angle is between 0.15 degrees and 0.25 degrees, depending on the resolution requirement. For small angle scattering, the convergent angle is between zero (parabolic optic) to about 0.15 degrees, depending on the requirement of $Q_{\text{min}}$.

The major problem of Kirkpatrick-Baez system is that the mirror further from the source has a much smaller capture angle. This significantly limits the flux level delivered by the system, especially for a very small source. Another problem is that the magnification is different for the two mirrors. For a parabolic mirror, this leads to different divergences in two directions. For an elliptical system, this leads to different focal sizes in two directions. In addition, the alignment hardware of Kirkpatrick-Baez system is bulky and complicated. The alignment is difficult and time consuming since the mirrors must be aligned to the source and also aligned to each other.

If not for the difficulty of the optical construction the two mirrors can be installed at the same location. This concept was proposed half a century ago [14]. In this system, the two mirrors are arranged in a "side-by-side" configuration as shown in Figure 13. The system overcomes most of the disadvantages inherent in a Kirkpatrick-Baez system. Both mirrors can be installed at the same optimal position in the optical path. The magnification of this system is the same in both directions. The optic is much more compact than that in a Kirkpatrick-Baez system. Both mirrors can be pre-aligned and permanently fixed. The alignment freedoms can be designed to be independent from each other and therefore alignment is much easier.

A long time has passed before the advance of precision optical construction technology made the "side-by-side" scheme possible. The latest 2D multilayer optics developed in Osmic, the Confocal MaX-Flux® (CMF) [15], is based on the "side-by-
side" scheme of a combination of elliptical and parabolic cylinder multilayer mirrors. For most applications, two elliptical mirrors with the same focal distance are used. However, the combination of mirrors with different focal distances, and the combination of one elliptical mirror and one parabolic mirror has also been realized for some special applications.

The CMF optical system has been integrated in diffraction systems for protein crystallography. Different optical systems have been designed for different requirements on resolution. The integration of CMF optics has improved the performance of these diffractometers. For systems with a source of 0.3 mm and 5 kW and configured for unit cells of 250 Å, the flux improvement over the diffractometer with TR systems ranges from 2 to 5 times. For a typical sample of 0.3 mm in size, with the detector arranged at the focus and sample-detector distance of 120 mm, the flux through the sample is more than $3 \times 10^8$ photons per second. For the same geometry, the flux is about $6 \times 10^9$ photons per second for a 0.5 mm sample. As the nature of multilayer can see only the central portion of the source, a smaller source would offer even higher flux and better resolution. Spectral purity is also greatly improved. The Cu Ka component represents more than 98% of the conditioned beam, while the system of TR mirrors with 4 micron of Ni filter has only about 86% Cu Kα. With the improved system, data quality is improved dramatically [16].

The CMF optical system has been integrated into systems for small angle scattering [17]. The focusing optic improves the flux over the graphite-pinhole system by more than one order of magnitude for the $Q_{\min}$ of 0.01 Å$^{-1}$. For $Q_{\min}$ of 0.006 Å$^{-1}$, the flux gain is near 10 times.

The CMF optical system has also been designed and integrated for other applications, such as thin film and stress analysis. With a source of 0.3 mm and 5 kW, the flux is about $1.5 \times 10^9$ photons per second. The size of the beam is 1.5 x 1.5 mm and divergence is about 0.05 degrees (about 1 mrad). Divergence, as discussed before, is determined by the source. With a smaller source, the divergence can be further reduced.

As in the case of single parabolic optics, a full line of CMF optics has also been developed for different needs of various applications. As examples, some of the optics and their major optical parameters are listed in Table 3.

CMF12-38Cu6 is typically applied for protein diffraction, CMF15-165Cu8 is designed for small angle scattering, CMF15-50Mo8 has been used for small molecule diffraction, and CMF12.5INTCu8 has been used for thin film experiment and stress analysis. Table 3 shows the flux for raw beam only. The flux through the sample would depend on the configuration of the diffraction system.

### New Developments

Multilayer optics have caused some serious impact on the performance of diffraction instruments over the past few years. This trend continues. New developments of multilayer-based systems are under way. Some of these development projects revolve around a microfocusing source and CMF optic combination to create new X-ray beam generators, as well as the applications of such beam generators to protein crystallography, small molecule diffraction and small angle scattering.

As discussed in this paper, multilayers have a specific and finite rocking curve. Therefore, only the center portion of the source is effectively reflected. This nature of the multilayer has two consequences: flux is reduced for a large source and the beam has a small angular deviation from its ideal spatial definition, either focusing or collimating. One way to increase flux while maintaining the low angular deviation feature is through the use of a

### Table 3. Examples of CMF optics.

<table>
<thead>
<tr>
<th>CMF Optics</th>
<th>CMF12-38Cu6</th>
<th>CMF15-165Cu8</th>
<th>CMF15-50Mo8</th>
<th>CMF12.5INTCu8</th>
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<tbody>
<tr>
<td>$\lambda$ (Å)</td>
<td>1.54</td>
<td>1.54</td>
<td>0.71</td>
<td>1.54</td>
</tr>
<tr>
<td>Optic type</td>
<td>focusing</td>
<td>focusing</td>
<td>focusing</td>
<td>collimating</td>
</tr>
<tr>
<td>Convergent angle (%)</td>
<td>0.2</td>
<td>0.06</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>Deviation from ideal focusing (%)</td>
<td>~0.05</td>
<td>~0.045</td>
<td>&lt;0.03</td>
<td></td>
</tr>
<tr>
<td>Divergence (°), FWHM</td>
<td></td>
<td></td>
<td>~0.05</td>
<td></td>
</tr>
<tr>
<td>Flux without pinhole (photons/s)</td>
<td>$1.0 \times 10^9$</td>
<td>$1.6 \times 10^9$</td>
<td>$2.3 \times 10^7$</td>
<td>$1.8 \times 10^9$</td>
</tr>
<tr>
<td>Kα suppression (times)</td>
<td>500</td>
<td>500</td>
<td>1000</td>
<td>400</td>
</tr>
</tbody>
</table>
small but bright source. Theoretically, the combination of a microfocusing source and a CMF optic is an ideal system both for flux and for resolution. The development tasks of such a system include developing both a microfocusing source and a special type of CMF optic. Microfocusing sources were traditionally developed for X-ray projection microscopy. In these applications intensity stability and, especially, positional stability are not critical. To couple with a CMF optic and get a reliable performance, both the position stability and the intensity stability has to be improved. Engineering a CMF optic for a microfocusing source has two major difficulties to overcome: the multilayer coating has a much larger gradient in d-spacing and the mirror surface has a much smaller local radius and much larger gradient of radius. In addition, the requirement on d-spacing accuracy and surface figure are much higher compared to that for a rotating anode. Nevertheless, such systems have been developed both for Cu Kα and Mo Kα. The Cu Kα system [18], code named MicroMax, has been engineered for protein diffraction. The microfocusing source has a power loading of 24 W and a 20 micron FWHM. For a 0.3 mm sample, the flux is $2.0 \times 10^8$ photons per second, about two thirds of the flux of a standard 5 kW rotating anode+CMF12-38Cu6. For large unit cells, the MicroMax outperforms the above mentioned rotating anode system with better resolution.

The rocking curve width of a multilayer for Mo Kα is about half of the rocking curve width for Cu Kα. Therefore, the multilayer will see an even smaller portion of the source than in the case of Cu Kα. The concept of microfocusing source+CMF optic is expected to work for Mo Kα [19]. The microfocusing system for small molecule diffraction, code named MolyMax, is also successfully designed, fabricated and tested [20]. The system has a very sharp focus. FWHM is less than 0.1 mm at the focus. With the sample placed at the focus and comparing to a 2 kW sealed tube with a graphite monochromator, the experiment has shown that the flux of the MolyMax is about 6 times for a 0.1 mm sample and 2 times for a 0.2 mm sample. For a 0.3 mm sample, MolyMax delivers roughly the same flux. However, for the samples larger than 0.1 mm, the sample can be positioned before the focus and the detector can be positioned near to the focus. In such a configuration, the system resolution and signal to noise ratio will be greatly improved.

For some applications, the beam width offered by multilayer optics may not be large enough. Increasing the length of the mirror is not an effective method, since the width increased by extending the mirror is inversely proportional to $v x$, where $x$ is the distance between the source and the portion of mirror extended. An optical system such as that shown in Figure 14 can increase the beam a factor of two. Although the dual reflection reduces intensity, it also reduces divergence and improves the spectrum. Based on the same concept, two-dimensional systems can also be realized. This concept will also apply to the focusing case, where two focusing beams can be combined into one beam. Detailed results will be reported in the future.

The application of multilayer optics to diffraction systems has a history of about 6 years. Much work remains to design improvements for existing systems and invent new systems. We look forward to reporting our progress in the future.

References