Deep multilayer gratings with adjustable bandpass for XRF spectroscopy

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ABSTRACT

We propose here a deep multilayer grating with adjustable bandpass as an alternative dispersing element to PET crystal in WDXRF spectroscopy. When making a multilayer grating, we remove part of the reflecting planes of a multilayer, allowing radiation to penetrate deeper. Since the resolution, or the bandpass, is reciprocally proportional to the penetration depth, we improve the resolution and reduce the bandpass of a simple multilayer mirror without affecting the reflectivity. By changing the grating land/period ratio, the amount of the removed material can be continuously varied and, thus, the extinction depth and the bandpass, or resolution, can be continuously varied. In this way we can find an optimum between required resolution and flux for a particular application. Retaining all the advantages of multilayer mirrors, such as stability to moisture and heating, multilayer gratings allow improving resolution of multilayers and making their performance comparable to PET crystals.

Keywords: multilayer gratings, x-rays, XRF spectroscopy

INTRODUCTION

Regular x-ray multilayer mirrors are widely used in wavelength dispersive x-ray fluorescence (WDXRF) spectrometers. More than 10 years ago the multilayers replaced artificial crystals, such as lead stearate, in analysis of light elements from Be to Mg. Employing the multilayers for heavier elements is limited by their relatively low spectral resolution in comparison with crystals, such as PET which are currently used for analysis of elements from Al to Ar. PET crystals, however, are very sensitive to the environment, and degrade fast under the influence of radiation, moisture, etc. Therefore, they don’t last long and usually require temperature stabilization. Multilayer mirrors, on the other hand, are very stable, durable, and easy to use.

An alternative spectral element for analyzing elements from Al to Ar can be a multilayer grating. Multilayer gratings are a new but extensively developing area of research. Many papers have been published on this topic [3 – 10] starting from pioneering works of T.Barbee[1] and W. Warburton [2]. So-called “deep” multilayer gratings have particular interest for XRF spectroscopy. In our previous papers [3-5], we theoretically predicted and comprehensively studied the effect of diffraction orders suppression. A deep multilayer grating works like an ordinary multilayer, but its rocking curve width is adjustable. By taking smaller land/period ratio of the grating (see fig.1), one can make penetration depth bigger. Correspondly the width of the rocking curve will be smaller and spectral resolution higher.

Therefore, the deep multilayer gratings allow enhanced spectral resolution, keeping all other advantages of the multilayer mirrors. Control of the bandpass is very important in many x-ray instruments when an optimum between photon flux and spectral resolution is needed.

In this paper we propose deep multilayer gratings (MG) with adjustable bandpass as alternative dispersing elements for WDXRF spectroscopy. We describe their properties and consider a specific example of application.

FABRICATION OF ION-ETCHED MG

We consider here only ion-etched multilayer gratings, because this technique results in good structures with deep grooves. We need deep grooves, of the order 500 bi-layers of a multilayer to have a narrow bandpass and correspondly high resolution \( \lambda / \Delta \lambda \approx 500 \). In another manufacturing method, where a grating on a substrate is
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fabricated first by ion-etching or mechanical ruling and then a multilayer coating is deposited on it, very high lands of multilayer stack with straight walls can not be achieved with currently existing technology. The multilayer coating on the top of the land looks like a snow roof, if the grating on the substrate has high lands (>> multilayer period). If the grating on the substrate has low lands (~ multilayer period), it splines out when many layers are deposited. Additionally, the surface of the substrate suffers during grating manufacturing so that the following multilayer, deposited on a rough surface, is likely to have low reflectivity and poor adhesion. In contrast, ion-etched multilayer gratings are etched in a high quality multilayer mirror, which is already deposited.

Ion-etched MG can be fabricated by a variety of ways. We consider a typical scheme of the process. The first phase is to prepare a mask for ion etching on top of a multilayer. A layer of electron resist or photoresist on a top of the multilayer mirror is exposed by either direct writing with an electron beam or by photolithography through a mask (step 1 on the fig.1). The thickness of the resist should be more than 0.4 µm, which is enough for the following lift-off process. After exposure and developing of the resist, a grating structure is formed in it. In step 2 on fig.1, Al or Ni of about 0.15 µm is deposited on this structure. The metal lies inside the grooves and on top of lands of the resist and there are open resist arrears on the walls since the resist is thicker than the metal. During the following lift-off process, the dissolvent removes the resist with the metal on top of it. The rest of the metal forms a grating mask on the top of the multilayer for ion etching (step 3 on fig.1). After ion etching through the metal mask a nice multilayer grating with deep straight grooves is formed. It is shown in the step 4 on the fig.1.

An example of a real multilayer grating is shown in fig.2. This is a photograph made in electron microscope of a W/C multilayer grating on a Si substrate. Grating period is 4 µm, land/period ratio is 1:5, multilayer period is 45Å (30Å of C and 15Å of W), and the number of bi-layers is 200. The study of this grating was reported in [5].

Fig. 2 Scanning Electron micrograph of a W/C multilayer grating on a Si substrate.
Grating period is 4µm, land/period ratio is 1:5, multilayer period is 45Å (30Å of C and 15Å of W)
DEEP MULTILAYER GRATINGS

We consider a typical lamellar multilayer grating shown in Fig.3. We will show when the multilayer structure maximizes reflectivity in a particular diffraction order and that this reflectivity rise is especially strong when the grating is deep and diffraction order separation takes place. In Fig.3, $\alpha$ is the incident grazing angle of the incident beam, $\beta$ is the diffracted angle of a particular order, $d$ is the period of the grating, $D$ is the period of the multilayer.

To understand how the multilayer structure increases intensity in a particular order, let us consider the diffraction process in reciprocal space. In Fig.4 four nodes in the reciprocal space are shown. The reciprocal vector responsible for the multilayer structure is $Q_z = \frac{2\pi}{D}$, and the one responsible for the grating structure is $Q_x = \frac{2\pi}{d}$. The wave vector $K_0$ of the incident beam is pointing to the zero node. To find a wave vector of a diffracted beam we draw a circle from the starting point of the vector $K_0$ with the radius equal to the absolute value of the vector $K_0$. When the circle crosses one of the nodes in the reciprocal space, the Bragg condition is fulfilled for that diffraction order $K_{\text{dif}} = K_0$, where $K_{\text{dif}}$ is a wave vector of the diffracted beam. Correspondingly, the diffraction efficiency of this order will be maximized.

So, the multilayer structure adds volume effect to the diffraction on the plane grating. This influence of volume in Z direction leads to Bragg diffraction with maximizing efficiency for a particular grating order at a particular incident angle. When we change the incident angle $\alpha$, the circle on Fig.4 will move striking nodes in the reciprocal space one by one. Every time it strikes the node, the Bragg condition for that grating order is fulfilled, and its efficiency is maximized. The efficiency will be maximized even more if order separation takes place [3-5]. The angular width of the diffraction order reflectivity on the rocking curve is reciprocally proportional to the number of bi-layers where radiation penetrates. This depth is called an extinction depth. The extinction depth is different for a multilayer grating than for a simple multilayer, and has to be calculated from rigorous dynamic theory [4,9].

The finite angular width means uncertainty of the node position in the reciprocal space. In other words $Q_z$ has uncertainty $\Delta Q_z \sim \frac{1}{\Delta N*D}$, where $\Delta N$ is the number of multilayer periods in the effective extinction depth. Clearly, if the angular width of the order is bigger than the angular distance between diffraction orders, then the diffraction order peaks on the rocking curve will overlap, and there will be no order separation. That means that many orders will diffract at the same incidence angle as with an ordinary grating. In the case that the angular width is smaller than the angular distance between peaks, we have order separation. Under this condition, all other orders are completely suppressed except for the one under Bragg conditions. All the reflecting intensity is concentrated in this diffraction order dramatically maximizing its diffraction efficiency.

To obtain order separation, one can do a few things. First, the grating period can be made small. Then, the distance between orders ($Q_x = \frac{2\pi}{d}$) will increase until it is bigger than the angular width (uncertainty $\Delta Q_z$). The exact value of the grating period, when order separation takes place, should be calculated with the rigorous theory of multilayer
grating diffraction [4, 9]. Second, one can make the land/period ratio of the grating small. Then the extinction depth will increase, making the angular width (uncertainty $\Delta Q_z$) of the single order peak smaller until it is smaller than the angular distance between peaks ($Q_x$) on the rocking curve. One also can avoid overlap simply by making a weaker scattering multilayer. This could be done by using lower contrast multilayer materials with low absorption [11], or by making the heavy layer thinner.

The order suppression effect is shown in fig.5. At the incidence angle of 1.45°, only zero order is reflected by the grating. When we rotate the grating to the incidence angle of 1.4°, the zero order gets completely suppressed and only $-1^{\text{st}}$ order is diffracted. The grating in this example has 4µm period, 0.5 land/period ratio, coated with a W/Si multilayer of 3.16nm period and 121 bi-layers [3]. A more advanced grating with higher efficiency and more diffraction orders is described in [5]. The grating was also 4µm period, but the land/period ratio was 1:5, and 200 bi-layers were deposited. The multilayer was W/C of 4.5nm period. The rocking curve of this grating is shown in fig.6. One can see complete order separation and high diffraction efficiency.

Let us now find expressions for angular positions of diffraction orders. From fig.4 we can see:

\[ \vec{K}_d - \vec{K}_0 = p\vec{Q}_x + m\vec{Q}_x \]  \hspace{1cm} (1)

Where $p$ and $m$ is a number of diffraction order due to the multilayer and grating correspondly. Projection of this equation on the X-axis will give us a grating equation:
\[ \cos \beta - \cos \alpha = m \lambda / d \quad (2) \]

Projection of (1) on the z-axis will give us the Bragg condition:

\[ \sin \alpha + \sin \beta = p \lambda / D \quad (3) \]

To maximize efficiency of a particular grating order, we need to satisfy both equation (2) and (3). Equation (2) and (3) don’t account for the effect of refraction. More exact expressions should include optical constants. Due to some finite average value of the refraction index, the angles \( \alpha \) and \( \beta \) will be different inside and outside of the multilayer grating (see fig.7). Again, projection of the wave vectors inside and outside the media will give us the Snell’s law:

\[ n \cos \theta = \cos \theta_0 \quad (4) \]

where \( n \) is an average refractive index. For the multilayer grating it will be:

\[ n = \Gamma \left( \gamma n_v + (1 - \gamma) n_c \right) + (1 - \Gamma) n_v \quad (5) \]

where, \( \Gamma \) is the land/period ratio of the grating, \( \gamma \) is the W/(W+C) ratio of the W/C multilayer, and \( n_v = 1 \) is the refractive index of vacuum. The wave vector in the media is also different from the one in vacuum. Taking into account that \( k = nk \), for (2) and (3) we will have:

\[ \cos \beta - \cos \alpha = m \lambda / nd \quad (6) \]
\[ \sin \alpha + \sin \beta = p \lambda / nD \quad (7) \]

Equations (4) – (7) completely define the angular positions of maximized diffracted orders.

**APPLICATION TO XRF SPECTROSCOPY**

In many cases the resolution of the dispersive element should be adjusted to the experimental requirements. Excessive spectral resolution cuts off useful flux, making measurement time longer. Low resolution does not allow resolving close spectral lines. The bandpass (or resolution) of a multilayer grating can be easily designed according to the requirements. The bandpass, or in other words the angular width of the Bragg peak, is reciprocally proportional to the number of bi-layers in the penetration depth:

\[ \Delta \lambda / \lambda \sim \Delta \theta / \theta \sim 1/N \]

As we saw in the previous section and which is discussed in more details in [5], the penetration depth can be increased by increasing the land/period ratio of the grating. Continuously changing this ratio and depositing a certain number of bi-layers, one can adjust the bandpass of the multilayer grating to the requirements.

Let us consider an example of x-ray fluorescence spectroscopy at SiK\( \alpha \) radiation line with the wavelength of 0.713nm. The required resolution is about \( \lambda / \Delta \lambda \sim 1/500 \). Currently used PET crystals have good reflectivity (~10%) and resolution (~ 1/500), but they are very sensitive to the temperature stability, moisture and don’t last long if special care is not provided.
The alternative spectral element could be a multilayer mirror, which is very stable to the environment. An ordinary multilayer mirror at 0.713nm wavelength has only about 100 bi-layers of penetration depth at grazing incidence of 8 degrees (~2.5nm period). To increase the depth with ordinary multilayer one would need to increase the Bragg angle, or decrease the multilayer period. For small period the roughness significantly degrades the reflectivity. For example, going from 2.5nm to 1.7nm would reduce reflectivity from about 40% to about 6% for Mo/C multilayer with typical roughness about 0.3-0.4nm. In addition, the resolution improves only to ~1/300, which is not enough.

If we now consider a multilayer grating, we can keep the period of the multilayer at 2.5nm, and increase the penetration depth by means of making the right land/period ratio of the grating. That will return good reflectivity of about 40% and will improve the resolution to 1/500. An example grating would be a Mo/C multilayer of 2.5nm period, land/period ratio of 1:3, grating period of 2µm, 500 bi-layers. The comparison of reflectivity of a single Mo/C multilayer and this grating is shown in fig.8.

![Graph showing reflectivity versus wavelength for a single multilayer and a multilayer grating](image)

**Fig. 8** Calculated reflectivity versus wavelength for a single multilayer and a multilayer grating: a) Mo/C multilayer, 2.5 nm period; b) multilayer grating on the same multilayer, 1:3 land/period grating ratio, 500 bi-layers.

**CONCLUSION**

We have shown that deep multilayer gratings can be alternative dispersive elements in XRF spectroscopy of elements from Al to Ar. Retaining all the advantages of simple multilayer mirrors, such as stability to heating and moisture, durability, multilayer gratings provide high reflectivity, of the order of 40%, and resolution $\frac{\lambda}{\Delta\lambda} \approx 500$. This is comparable with the performance of currently used PET crystals, which are, however, very sensitive to heat and moisture, and don’t last long.

The other advantage of the multilayer gratings, adjustability of their bandpass, allows optimizing flux and resolution in accordance with particular requirements. This makes their application unlimited both for spectroscopy and for monochromatization. For example, in XRD measurements, perfect crystal monochromators remove too much useful flux. Multilayer gratings, providing required resolution, can deliver more flux to the sample. Finally, multilayer gratings, in contrast to crystals and multilayers, are truly angular dispersive. There is no other element in the high energy region, below 0.8 nm wavelength, which could spatially disperse light. Therefore, they can be a basis for multi-channel high energy spectroscopy of high efficiency. Multi-channel detection would dramatically reduce time for taking spectra and would allow spectroscopy of fast processes.
REFERENCES: