Recent Developments of Multilayer Mirror Optics for Laboratory X-ray Fluorescence Spectrometers

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This paper presents various improvements we made in the development of multilayer mirror optics for the detection of carbon with home-lab x-ray fluorescence spectroscopy (XRF) equipment. In order to detect of light elements using XRF, we developed a number of new multilayers with improved detection limits for boron and aluminium on silicon [1-3]. To detect of carbon, TiO2/C multilayers improve the detection limit by 29 % compared to the V/C multilayers previously used.

The multilayers were deposited by magnetron sputtering in vacuum systems with base pressures below 10^-5 Pa, using Ar of purity 6.0 or better as sputtering ambient at pressures of typically 0.2 Pa. The structure of the films was investigated using x-ray reflectometry. Plan-view and cross-sectional transmission electron microscopy (XTEM) were performed using a Philips CM30 microscope at an operating voltage of 300 kV. The soft x-ray characterization was performed with s-polarized radiation at the synchrotron reflectometer G1 at HASYLAB/DESY. Laboratory soft x-ray measurements were carried out in wavelength-dispersive XRF spectrometers of type Bruker AXS S303 or S4. Experimental details can be found in previous publications [1-3].

Although multilayers have been used as optical elements in XRF instruments for more than 20 years, improvements are still possible. This is due to progress made in deposition techniques which make more exotic thin film material available. In addition, not only the peak intensity but also background suppression is of importance in XRF applications, so that matrix effects that result from unwanted signals from other elements in the sample must be taken into account. Therefore optimization of a multilayer depends on the overall sample composition, making the identification of the best multilayer analyzer a complex task. Here we have shown how advanced multilayer material combinations can lead to lower detection limits of the low-Z element carbon.

We carried out research for better multilayer mirrors to detect carbon (277 eV). Previously, V/C and Ti/C had been considered the best multilayers for this energy. We discovered that replacing elemental V or Ti by particular alloys of V and Ti improves the theoretical reflectivity. Tab. 1 shows that oxides or nitrides give the best results. The origin of this improvement is the favorable position of the N and O absorption edges, close but not too close to the C edge, and the reduced density of the alloys, both together promising an improved absorption-to-dispersion ratio.

<table>
<thead>
<tr>
<th>Material</th>
<th>V/C</th>
<th>VC/C</th>
<th>VN/C</th>
<th>VO/C</th>
<th>Ti/C</th>
<th>TiC/C</th>
<th>TiN/C</th>
<th>TiO2/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reflectivity (%)</td>
<td>41.3</td>
<td>40.6</td>
<td>48.7</td>
<td>48.5</td>
<td>39.2</td>
<td>39.8</td>
<td>49.4</td>
<td>51.2</td>
</tr>
</tbody>
</table>

Table 1: Calculated reflectivities of a number of ideal multilayers with a d-spacing of 6 nm and a l/g ratio of 0.4 at a photon energy of 277 eV.

Some of the multilayers shown in Tab. 1 were deposited by magnetron sputtering, and examined by synchrotron radiation (Fig. 1). The peak reflectivities at 277 eV are 29.4 % and 37.1 % for the V/C and the TiO2/C multilayers, respectively. Although these reflectivities are lower than those calculated for ideal multilayers, the expected trend shown in Tab. 1 is confirmed experimentally. The energy scans in Fig. 1 also reveal the different behaviour of the two multilayers at energies in the range 450 – 525 eV. The V/C multilayer has an enhanced reflectivity at around 525 eV that is due to the V L edge. This higher reflectivity is unwanted because it can produce unwanted background in samples containing oxygen (525 eV). It can therefore be concluded from Fig. 1 that V as a multilayer material is disadvantageous if the sample contains significant amounts of oxygen. The Ti L edge is located at about 450 eV, sufficiently far away from the O K emission line at 525 eV. Note that the difference in reflectivity between both multilayers at 525 eV is more than the
factor of 10. Therefore we expect a lower background when the Ti based multilayers are used. A second effect that leads to improved background is the reduced density and absorption of the oxide or nitride multilayers. This has been confirmed experimentally in Fig. 2, which shows the best background suppression for the TiO_2/C multilayer. The carbon detection limits derived from Fig. 2 are 181 ppm for V/C, 146 ppm for TiN/C (19 % improvement), and 128 ppm for the TiO_2/C multilayer (29 % improvement).

![Figure 1: Experimental reflectivities of V/C and TiO_2/C multilayers as a function of the photon energy.](image1)

![Figure 2: XRF spectra of a graphite sample using V/C, TiN/C and TiO_2/C multilayers as analyzers](image2)

Twenty years after the introduction of multilayer mirrors in laboratory x-ray analytical equipment, these multilayer mirrors have become an essential element in these instruments. The detection of light elements has become routine with multilayers, with detection limits being further reduced by improvements on optical elements.

We thank M. Störmer at GKSS for experimental support.

**References**

