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New transmission-type X-ray filters consisting of amorphous multilayer films

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New transmission-type X-ray filters have been developed. The filters consist of X-ray-amorphous metal (less than 30 Å)/metalloid (~10 Å) multilayer films sputter-deposited on X-ray-transparent polymer substrates. Such metal/metalloid multilayer films show only very broad diffraction peaks, since the metal and metalloid layers forming the multilayer films are usually X-ray amorphous if the layers are sufficiently thin. The filters use the wavelength-dependent absorption phenomena near absorption edges of elements to reduce the intensity of transmitted X-rays, without generating any crystalline sharp peaks which cause serious problems in experiments such as fluorescence XAFS measurements. The multilayer-film filters were prepared by a multi-target magnetron sputtering deposition technique, paying special attention to the homogeneity of the layer thickness by spinning substrates of the films. The filters are useful in reducing the intensity of undesirable fluorescence emissions and improving the signal-to-background ratios of data acquired in various measurements using a solid-state detector.

Keywords: X-ray amorphous multilayer films; X-ray filters; fluorescence XAFS; absorption edges.

1. Introduction

It is important to improve signal-to-background ratios in order to obtain high-quality X-ray data. Transmission-type X-ray filters which use wavelength-dependent absorption phenomena near absorption edges of elements have been devised and are commonly used (Stern & Heald, 1979).

Such transmission-type X-ray filters have some common problems. If the filters contain crystalline materials, they do not only absorb X-rays of a certain wavelength region and thus reduce background levels, but also generate diffraction X-ray beams which sometimes add an undesirable background to the spectra. This phenomenon causes particularly serious problems when large solid-angle detectors such as large-area/multiple-element solid-state detectors (SSDs) are used for data acquisition. Under a high-flux synchrotron radiation beam, even small portions of crystalline phases in the filters cause unignorable diffraction intensities. X-ray wavelength scanning, which is an indispensable procedure in XAFS experiments, increases the chance of encountering such problems.

To solve these problems, new transmission-type X-ray filters consisting of X-ray-amorphous multilayer films, from which no sharp crystalline diffraction peaks are observed, have been developed and applied to fluorescence XAFS measurements.

2. General concept of X-ray-amorphous multilayer filters

The X-ray-amorphous multilayer-film filters can be prepared on polymeric film substrates which are almost transparent in the hard X-ray region (5–20 keV). Polyimide films are the most suitable, because of their thermal stability and mechanical toughness (Seymour & Carraher, 1981). Such multilayer films for X-ray optics are usually prepared by a multi-target sputtering deposition technique.

Generally, sputter-deposited multilayer films show only broad diffraction peaks, if the constituent layers are sufficiently thin, since a new layer starts to deposit onto an older one before the original layer grows thick enough to crystallize (Takagi *et al.*, 1985). Although the maximum layer thicknesses in which elements can remain in amorphous states depend on the elements, their chemical states and the deposition conditions, the maximum thickness of metal layers is ~30 Å, while that of metalloids (C, B or Si) is ~100 Å. Therefore, by inserting a light-element metalloid such as C or Si, which is transparent to hard X-rays, between thin metal layers, we can obtain a multilayer-film filter consisting of X-ray-amorphous layers. A typical transmission diffraction image from an X-ray-amorphous multilayer film, a Co(18 Å)/C(20 Å) multilayer film, taken by an image plate, is shown in Fig. 1. Only one broad peak, attributable to the first-order peak of the amorphous structure of the metal and metalloid layers, was observed. Another advantage in using transmission-type filters is that any sharp diffraction peaks from the layer structures in the low-angle region, which appear in the reflection geometry, do not appear in the transmission geometry.

The absorption mechanism of incident X-rays by X-ray-amorphous multilayer filters is no different to that of the traditional crystalline transmission filters. Absorption efficiency per thickness of the metal layers in the filter will not be much different from that of the traditional crystalline filters, since the densities of the amorphous phases are only slightly lower than those of the crystalline phases of the metals commonly used in the filters.

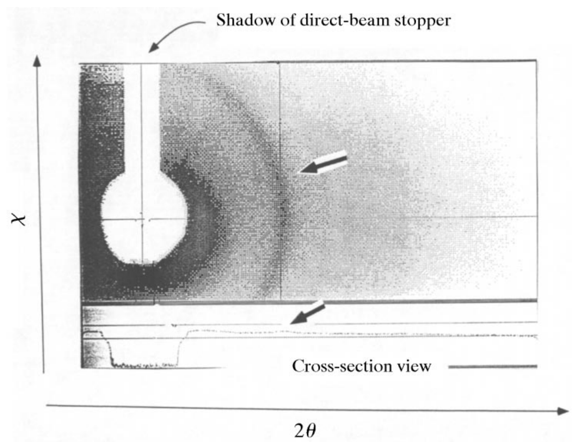

Figure 1
Typical transmission image-plate diffraction image of the X-ray-amorphous multilayer-film deposited on a polyimide film substrate, Co(18 Å)/C(20 Å) – (1100 + 1100 layers on both sides of the substrate) analysed by BAS 2000 (Fuji Film Co. Ltd) at λ = 1.7 Å.

3. Fabrication technique of X-ray amorphous multilayer-film filters

The desired multilayer films can most easily be prepared by using a multi-target magnetron sputtering deposition technique. However, special attention must be paid to obtaining homogeneous layer thicknesses in order to achieve uniform filter absorption characteristics. The film substrates were spun in the substrate plane at an appropriate spinning rate to compensate for the slow shutter speed, as shown schematically in Fig. 2 (Takagi *et al.*, 1995). The improvement in the layer homogeneity using this method is shown in Fig. 3. A similar technique has been developed by Kortright *et al.* (1993).

The multilayer films were deposited a few hundred layers at a time alternately on both sides of the polyimide films, in order to avoid warping and peeling of the films due to internal stress during the deposition.

4. Application of the filters in fluorescence XAFS experiments

X-ray-amorphous multilayer-film filters were prepared for use in improving the signal-to-background ratio and decreasing the dead-time of multi-element SSDs in fluorescence XAFS experiments.

The prepared filter was mounted on an acrylic holder in order to fit in front of the aperture of the multi-element SSD used in various types of fluorescence XAFS experiments at PF-BL3A (Mizutani *et al.*, 1994).

The wavelengths and energies of the absorption edges and the fluorescence transitions referred to in the following sections are listed in Table 1.

4.1. *Example 1: Cr/C multilayer-film filters to reduce the intensity of Fe K-edge-related fluorescence in Cu Kα fluorescence XAFS measurements*

Cu $K\alpha$ fluorescence XAFS measurements are very useful in clarifying the crystal structures of Cu precipitates (~1 at.%) in Cu-added steels (Takagi, Okitsu *et al.*, 1993; Imafuku *et al.*, 1996). In such an experiment, it is important to reduce the intensity of Fe K-edge-related fluorescence transitions from the matrix Fe phase, while keeping the weak Cu $K\alpha$ fluorescence intensity from the precipitates intact, in order to obtain data with a high signal-to-background ratio. A Cr(15 Å)/C(10 Å) (200 layers) multilayer-film filter was prepared on a polyimide film substrate for this purpose. Energy spectra obtained using the multi-element SSD with and without the filters are shown in Fig. 4. The Cr/C multilayer film absorbs Fe $K\alpha$ and $K\beta$ fluorescence photons while the intensities of Cu $K\alpha$ and $K\beta$ fluorescence photons are little changed, since the energy of the Cr K-edge is much closer to the energies of the Fe K-edge-related fluorescence photons than the corresponding Cu K-edge fluorescence photons.

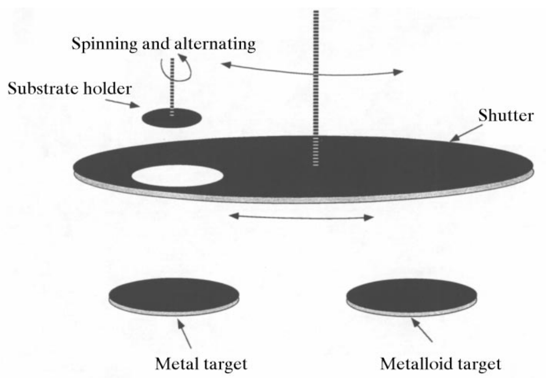

Figure 2
Substrate-spinning mechanism for homogenizing the layer thickness of the multilayer filter (Takagi *et al.*, 1995).

Table 1
Wavelengths and energies of the absorption edges and fluorescence transitions related to the present study (Weast, 1984).

Wavelength (Å)	Element	Designation	Energy (keV)
1.0723	Pt L_{III}	Absorption edge	11.562
1.31304	Pt $L\alpha_1$	$L_{III}M_V$	9.4423
1.32432	Pt $L\alpha_2$	$L_{III}M_{IV}$	9.3618
1.38059	Cu K	Absorption edge	8.9803
1.38109	Cu $K\beta_2$	$KM_{IV,V}$	8.9770
1.392218	Cu $K\beta_{1,3}$	$KM_{II,III}$	8.90529
1.48807	Ni K	Absorption edge	8.33165
1.540562	Cu $K\alpha_1$	KL_{III}	8.04778
1.544390	Cu $K\alpha_2$	KL_{II}	8.02783
1.60815	Co K	Absorption edge	7.70954
1.74346	Fe K	Absorption edge	7.11120
1.7442	Fe $K\beta_5$	$KM_{IV,V}$	7.1081
1.75661	Fe $K\beta_{1,3}$	$KM_{II,III}$	7.05798
1.936042	Fe $K\alpha_1$	KL_{III}	6.40384
1.939980	Fe $K\alpha_2$	KL_{II}	6.39084
2.07020	Cr K	Absorption edge	5.9888
43.68	C K	Absorption edge	0.28383

4.2. *Example 2: Co/C multilayer-film filters to reduce the intensity of Cu K-edge-related fluorescence in Pt Lα fluorescence XAFS measurements*

Pt L_{III}-edge fluorescence XAFS measurements are very useful in the clarification of the states of Pt included in the quench-and-melt-growth Y–Ba–Cu oxide superconductors (Takagi, Tanaka *et al.*, 1993; Tanaka *et al.*, 1995). In this experiment, it is very important to reduce Cu $K\alpha$ fluorescence intensity from the $YBa_2Cu_3O_7$ and Y_2BaCuO_5 matrix phases to avoid an increase in the SSD dead-time, while keeping intact the Pt L_{III}-edge-related fluorescence intensity from the minor phases. For this purpose, a Co(18 Å)/C(20 Å) (200 layers) multilayer-film filter was prepared.

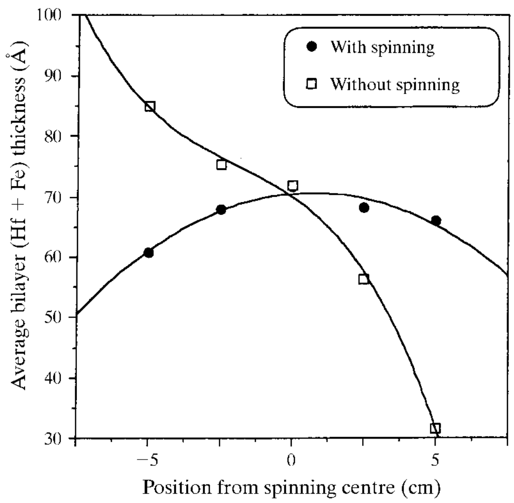

Figure 3
Dependence of the layer thickness in an Hf/Fe multilayer film on the position from the spinning centre of the substrate, with and without spinning (10 turns s^{-1}). The bilayer thicknesses of Hf and Fe were estimated from the low-angle diffraction peaks from X-ray diffraction of the layer structure (Takagi *et al.*, 1995).

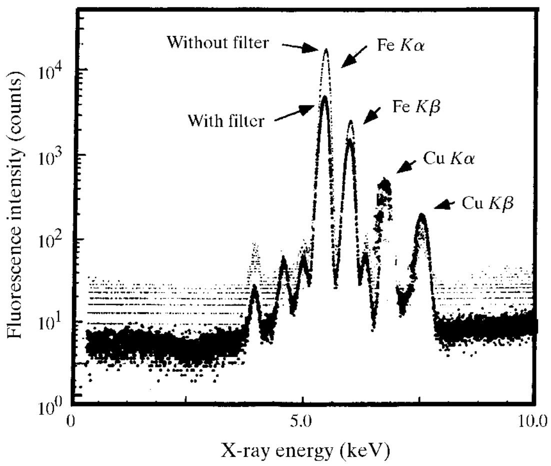

Figure 4
Fluorescence energy spectra from the Cu-added steel taken by the multi-element SSD system, with and without the Cr/C multilayer filter, at PF-BL3A.

Cu $K\alpha$ fluorescence photons are absorbed by the Co/C multilayer filter to a much greater extent than Pt $L\alpha$ photons, since the photon energies of Cu $K\alpha$ and $K\beta$ fluorescence are only a little larger than that of the Co K-edge, while the energy of Pt $L\alpha$ is much greater. The dependence of the filter performance on thickness was examined by changing the number of layers of the filter inserted in front of the SSD. The results are summarized in Fig. 5. The intensity ratio of Cu $K\alpha$ to Pt $L\alpha$ was reduced more than that of Cu $K\beta$ to Pt $L\alpha$, as the wavelength of Cu $K\alpha$ is closer than that of Cu $K\beta$ to the Co K-edge. Good linearity of the intensity ratios (especially that of Cu $K\alpha$ to Pt $L\alpha$) *versus* the number of layers verifies our assumption that the C layers are almost transparent for all fluorescence photons in this X-ray wavelength region. This is due to the low energy of the C K-edge compared with the energies of both the Cu K- and Pt $L_{\rm III}$-edges. The dead-time was improved by more than 20% compared with an unfiltered case.

5. Conclusions

Although systematic studies of the performance of the transmission-type X-ray-amorphous multilayer-film filters must be carried out, it is clear that the filters are very effective tools in improving the signal-to-background ratios in various X-ray experiments by reducing undesirable background intensity. The easy preparation method and broad range of applicable elements also give powerful advantages over other types of filters. The combination of multiple metal elements as constituent layers will also enable the preparation of band-pass-type amorphous filters.

The filters will also be useful in the detection of very weak diffraction arcs taken by image plates, since an amorphous filter can improve the signal-to-background ratio without adding new diffraction arcs.

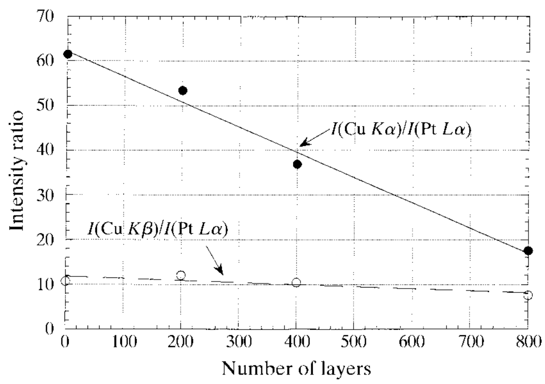

Figure 5
Dependence of fluorescence intensity ratios I(Cu $K\alpha$)/I(Pt $L\alpha$) and I(Cu $K\beta$)/I(Pt $L\alpha$) on the number of layers of the Co/C multilayer filter.

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References

Imafuku, M., Mizutani, T., Takagi, Y. & Okitsu, Y. (1996). *Proceedings of the International Conference on Microstructures and Functions of Materials (ICMFM 96)*, edited by N. Igata, Y. Hiki, I. Yoshida & S. Sato, pp. 25–28. Department of Materials Science and Technology, Science University of Tokyo, 2641 Yamazak, Noda 278, Japan.

Kortright, J. B., Gullikson, E. M. & Denham, P. E. (1993). *Appl. Opt.* **32**, 6961–6968.

Mizutani, T., Imafuku, M., Kikuchi, T. & Takagi, Y. (1994). *Photon Factory Activity Report* 12, p. 28. Photon Factory, Tsukuba 305, Japan.

Seymour, R. B. & Carraher, C. E. (1981). *Polymer Chemistry*, p. 451. New York: Marcel Dekker.

Stern, E. A. & Heald, S. M. (1979). *Rev. Sci. Instrum.* **50**, 1579–1582.

Takagi, Y., Flessa, S. A., Hart, K. L., Pawlik, D. A., Kadin, A. M., Wood, J. L., Keem, J. E. & Tyler, J. E. (1985). *Proc. SPIE*, **563**, 66–69.

Takagi, Y., Iijima, I., Akiyama, N. & Yamada, H. (1995). Jpn Patent P01972555. (In Japanese).

Takagi, Y., Okitsu, Y., Mizutani, T. & Imafuku, M. (1993). *Photon Factory Activity Report* 11, p. 35. Photon Factory, Tsukuba 305, Japan.

Takagi, Y., Tanaka, M., Mizutani, T., Takebayashi, S. & Imafuku, M. (1993). *Photon Factory Activity Report* 11, p. 34. Photon Factory, Tsukuba 305, Japan.

Tanaka, M., Morita, M., Takebayashi, S., Hayashi, S., Takagi, Y. & Hashimoto, M. (1995). *Proceedings of the 7th International Symposium on Superconductivity (ISS 94)*, edited by K. Yamafuji & T. Morishima, pp. 693–696. Berlin: Springer-Verlag.

Weast, R. C. (1984). Editor. *Handbook of Chemistry and Physics*, 64th ed., pp. E133–E180. Florida: CRC.