Periodic and Depth-Graded Cu/Si Multilayer Films for Hard X-Ray Optics

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Abstract

We describe the growth and characterization of periodic and depth-graded Cu/Si multilayer structures for use as coatings in hard X-ray optics. Films have been grown by DC magnetron sputtering, and were characterized by grazing incidence X-ray (8 keV) reflectance analysis. The X-ray reflectance of both periodic and depth-graded structures was found to be high, and stable at room temperature over a period of at least several months. The interface widths determined from fits to the X-ray reflectance data were found to lie in the range 0.23 – 0.3 nm. X-ray diffraction revealed no crystalline phases present in any of the films, only broad peaks indicating either an amorphous Cu or possibly copper-silicide phase. As a result of the small measured interface widths and the low X-ray absorption of Cu just below, and also far above the Cu K-edge (~9 keV,) highly-efficient depth-graded Cu/Si multilayer coatings can now be used for broadband, grazing-incidence X-ray mirrors, for X-ray energies greater than at least 100 keV.

Keywords: thin films; multilayers; X-ray optics

.Depth-graded X-ray multilayer structures are currently being developed to provide broad-band reflectance for grazing incidence, hard X-ray mirrors, for use in a variety of applications including synchrotron and medical optics, and in particular for space-borne astronomical hard X-ray telescopes [1]. In a depth-graded X-ray multilayer, the layer thicknesses vary with depth into the film (in contrast to a periodic X-ray multilayer,) so that different layer pairs are tuned to different X-ray wavelengths, thus increasing the multilayer bandpass. Optically dissimilar materials with low absorption are preferred so that the incident photons penetrate deeply into the stack with minimal loss and reflect efficiently from as many interfaces as possible. Good results above E~10 keV have thus far been obtained with e.g. W/Si [2] and Pt/C [3] depth-graded multilayer structures, but because of large absorption above the W and Pt K edges, these material combinations work best only up to E~70 keV and E~79 keV, respectively. Multilayers using lighter elements such as Ni or Cu are promising candidates for operation at higher energies, because of the lower X-ray absorption of these materials far above their K edges. Indeed Ni/C multilayers have already been developed and have also been shown to be stable up to ~300°C [4]. However, the interface widths in Ni/C multilayers are relatively large, of order 0.4 nm, which greatly reduces the high energy X-ray reflectance of these structures (by removing light from the specular direction.)

We report here on the development of a Cu/Si X-ray multilayer system. These structures are found to have interface widths of order 0.23 – 0.3 nm; the small interface widths, together with the low absorption of both materials at high energies (the K-edge for Cu is near E~9 keV, while that of Si is near E~1.8 keV) means that depth-graded X-ray multilayers are now possible with good broadband response from ~20 keV to well over 100 keV. The Cu/Si system can be used for broadband response below the Cu K-edge as well, where the absorption of Cu is also small. We describe below the growth, X-ray characterization, and stability of both periodic and depth-graded Cu/Si multilayers, and discuss their use in hard X-ray optical elements.

The Cu/Si films described here were grown by DC magnetron sputtering in argon of 99.999% purity, using a deposition system that has been described previously [5]. The system is cryo-pumped, and the argon pressure was maintained at 1.5 mTorr with a closed-loop gas-flow system using a capacitance

manometer and a mass-flow controller. Two 50-cm-long x 9-cm-wide planar magnetron cathodes are used – one for Si (99.9% purity), one for Cu (99.999% purity) – and the individual film thicknesses are adjusted by varying the (computer-controlled) rotational velocity of the substrate (which faces downward) as it travels over the cathodes (which face upward, 10 cm below the plane of the substrate.) The deposition rates were found to scale approximately linearly with power applied to the cathodes: typical rates were 0.6 nm/s for Si with P_{Si}=1000 W, and 1.0 nm/s for Cu with P_{Cu}=300 W. Samples were grown on (unheated) 75-mm-diameter Si wafer substrates having a thin (~2-3 nm) native oxide layer.

X-ray reflectance and diffraction measurements were made in the θ-2θ geometry using a four-circle diffractometer with a rotating anode X-ray source having a Cu target, and a pyrolytic graphite monochromator tuned to the Cu-Kα line near 8 keV (1.54Å.) The angular resolution of the diffractometer is ~0.02°. Fits to the X-ray reflectance data, performed with the IMD software package [6], are used to determine film thicknesses and interface widths (i.e., resulting from interfacial roughness and/or diffuseness.) With this technique, the measured data is compared with a theoretical reflectance curve computed using an algorithm based on recursive application of the Fresnel equations; the formalism described by Stearns [7] is used to account for the effects of interface imperfections, and an error-function interface profile was assumed.

Periodic Cu/Si multilayer structures were grown with bilayer thicknesses ranging from ~2 < d < 16 nm. The as-deposited X-ray reflectance is shown on a log scale in Figure 1(a) for a Cu/Si film having N=40 bilayers with d=3.66 nm, and with approximately equal thickness Cu and Si layers; the X-ray reflectance of films with periods d=2.3 (N=100), 3.0 (N=100), 4.1 (N=100, and 8.0 (N=50) nm are shown on a linear scale in Figure 1(b). Also shown in Fig. 1(a) is the fit to the measured data (dotted line); shown in Fig. 1(b) are the reflectance curves calculated using the layer thicknesses and interface widths determined from the fits to these data, but without including the finite instrumental resolution of the diffractometer, thus illustrating the maximum peak reflectance values that can be obtained with these films. The calculated reflectance for a single-layer Ir film is shown in Fig. 1(b) for comparison: it is clear from the relatively sharp 1st order Bragg peaks in all of these structures that grazing incidence X-ray mirrors coated with Cu/Si periodic multilayers can be used for high reflectance at this wavelength at

incidence angles several times larger than those possible using a mirror coated with a single-layer film (such as iridium.)

Also shown in Fig. 1(a) are the reflectance curves measured for the d=3.66 nm (N=40) Cu/Si film after storage in air at room temperature for periods of one day and ~8 months. Although the small changes in reflectance near the 2nd and 4th order Bragg peaks suggest that minor structural changes have occurred (predominantly during the 1st day,) perhaps as a result of diffusion or compound formation, there are no measurable changes in either the multilayer period or the peak reflectance of the 1st order Bragg peak, indicating good long-term, room-temperature stability.

The interface widths determined from the fit to the measured data in Fig. 1(a) were found to be σ=0.23 nm; the interface widths determined for other films (e.g. as in Fig. 1(b)) were also in the range $0.23 < \sigma < 0.30$ nm. These interface widths are considerably smaller than those reported previously for W/Si (σ=0.35 nm) [2], Pt/C (σ=0.36 nm) [3], and Ni/C (σ=0.40 nm) [4]. This result is significant because smaller interface widths are especially important at high X-ray energies, where the losses in specular reflectance due to interfacial roughness or diffuseness can be severe.

From the specular X-ray reflectance data alone it is not possible to distinguish between interfacial roughness and interfacial diffuseness. However, considering the very large (room temperature) solubility (~75%) [8] and diffusivity (~1.6×10^{-10} cm^2/s) [9] of Cu in Si it seems likely that amorphous interlayers of mixed composition have formed in these structures, similar to the amorphous silicide interlayers observed in Mo/Si [10] and W/Si multilayers [11]. The formation of such amorphous interlayers might present a barrier to further diffusion, which could explain the small observed interface widths as well as the apparent stability of these structures. X-ray diffraction measurements made on as-deposited samples as well as those stored in air for a period of several months revealed no crystalline phases present in any of the films, only broad peaks near $2\theta=45°$, indicating either an amorphous Cu or possibly copper-silicide phase. Further characterization is clearly needed to distinguish between these two possibilities, and to further elucidate the nature of the Cu and Si layers and the Cu-Si interfaces.

Shown in Figure 2(a) is the measured X-ray reflectance of a depth-graded Cu/Si multilayer film containing 300 bilayers, with a power-law thickness distribution [12]; the thickness of the ith bilayer from the bottom of the stack is given by

$$d(i) = \frac{a}{(b+i)^c}, \qquad (1)$$

in this case with a=35.68 nm , b=2.47, c=0.45, and i=1...300; the bilayer thickness thus ranges from $2.73 < d < 20.4$ nm. The reflectance expected from the layer thickness distribution given in eq. (1) is also shown (dotted line) in Fig. 2(a), and the decrease in reflectance with incidence angle is consistent with ~0.28 nm interface widths. As in the case of the periodic Cu/Si film shown in Fig. 1(a), the reflectance of the depth-graded film shown in Fig. 2(a) was found to be stable over a period of several months.

Shown in Fig. 2(b) is the calculated reflectance-vs-energy curve expected for the film shown in Fig. 2(a), for an incidence angle of 1.5 mrad; as can be seen in the figure, this particular film should have reflectance in excess of 45% over the range $20 < E < 100$ keV. Alternative depth-graded Cu/Si multilayer designs can be used, in principle, for high broadband reflectance in other wavelength regions as well: for example, the expected performance of depth-graded Cu/Si multilayers designed for operation below the Cu K-edge, from 3 – 9 keV, is shown in Fig. 3(a), and one designed for use from ~155 – 165 keV in Fig. 3(b). For comparison, the expected response of a depth-graded W/Si film is also shown in Fig. 3(b), illustrating the enhanced performance expected with Cu/Si multilayers.

In summary, periodic and depth-graded Cu/Si X-ray multilayer structures have been grown by magnetron sputtering, and X-ray reflectance measurements reveal small interface widths ($0.23 < \sigma < 0.30$ nm) and consequently high specular reflectance. Depth-graded Cu/Si multilayers can thus be used as coatings for hard X-ray mirrors for broadband reflectance over a wide range of X-ray energies. The reflectance of such structures is expected to be particularly high above ~100 keV (especially as compared to W- or Pt-based multilayer structures) due both to the low absorption of Cu and to the small interface widths that apparently can be achieved in these films. Highly efficient Cu/Si multilayers can also be used in grazing incidence X-ray mirrors operating below the Cu K-edge (9 keV).

Further study is needed to determine the microstructure of the Cu and Si layers in these structures, to further elucidate the nature of the Cu-Si interfaces, and to explain how such small interface widths are obtained considering the large solubility and diffusivity of Cu in Si. It will also be important to measure directly the high-energy reflectance of depth-graded Cu/Si multilayers, and to determine the stability of these films at elevated temperatures.

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Figure Captions

Figure 1. X-ray reflectance (λ=0.154 nm) of periodic Cu/Si multilayer films. A film having a period d=3.6 nm and containing N=40 bilayers is shown in (a). Measurements were made for the as-deposited film, and after storage in air at room temperature for periods of 1 day and ~8 months, as labeled. From the fit to the measured data (dotted line), the interface widths (assuming error-function interface profiles) were determined to be σ~0.23 nm. (b) Measured reflectance curves for films having d=2.3 nm (N=100), d=3.0 nm (N=100), d=4.6 nm (N=100) and d=8.0 nm (N=5) are shown in (b) as solid lines. Also shown are reflectance curves calculated (dotted) for these same structures, using the layer thicknesses and interface widths determined from fits to the measured data, but without including the finite instrumental resolution of the diffractometer. The calculated reflectance for a single-layer Ir film is shown in (b) for reference.

Figure 2. Measured (solid line) X-ray reflectance of a depth-graded Cu/Si multilayer, containing 300 bilayers, and the calculated reflectance (dotted line) assuming 0.28 nm interface widths. (b) The expected reflectance vs. energy response at an incidence angle of 1.5 mrad for the film shown in (a).

Figure 3. Calculated reflectance vs. energy curves for depth-graded Cu/Si multilayers, at the incidence angles indicated, assuming 0.28 nm interface widths. The film shown in (a) contains 600 bilayers, and the depth-grade parameters (eq. (1)) used are a=10.23 nm, b=0.9658, c=0.198, i.e., corresponding to bilayer thicknesses in the range $2.9 < d < 20$ nm; the film in (b) contains 800 bilayers, with a=124.9 nm, b=3582.4, and c=0.50, i.e., corresponding to bilayer thicknesses in the range $1.9 < d < 2.1$ nm. Also shown in (b) is a W/Si film containing 800 bilayers with a=56.46 nm, b=731.11, and c=0.50, i.e., corresponding to bilayer thicknesses in the range $1.4 < d < 2.1$ nm.

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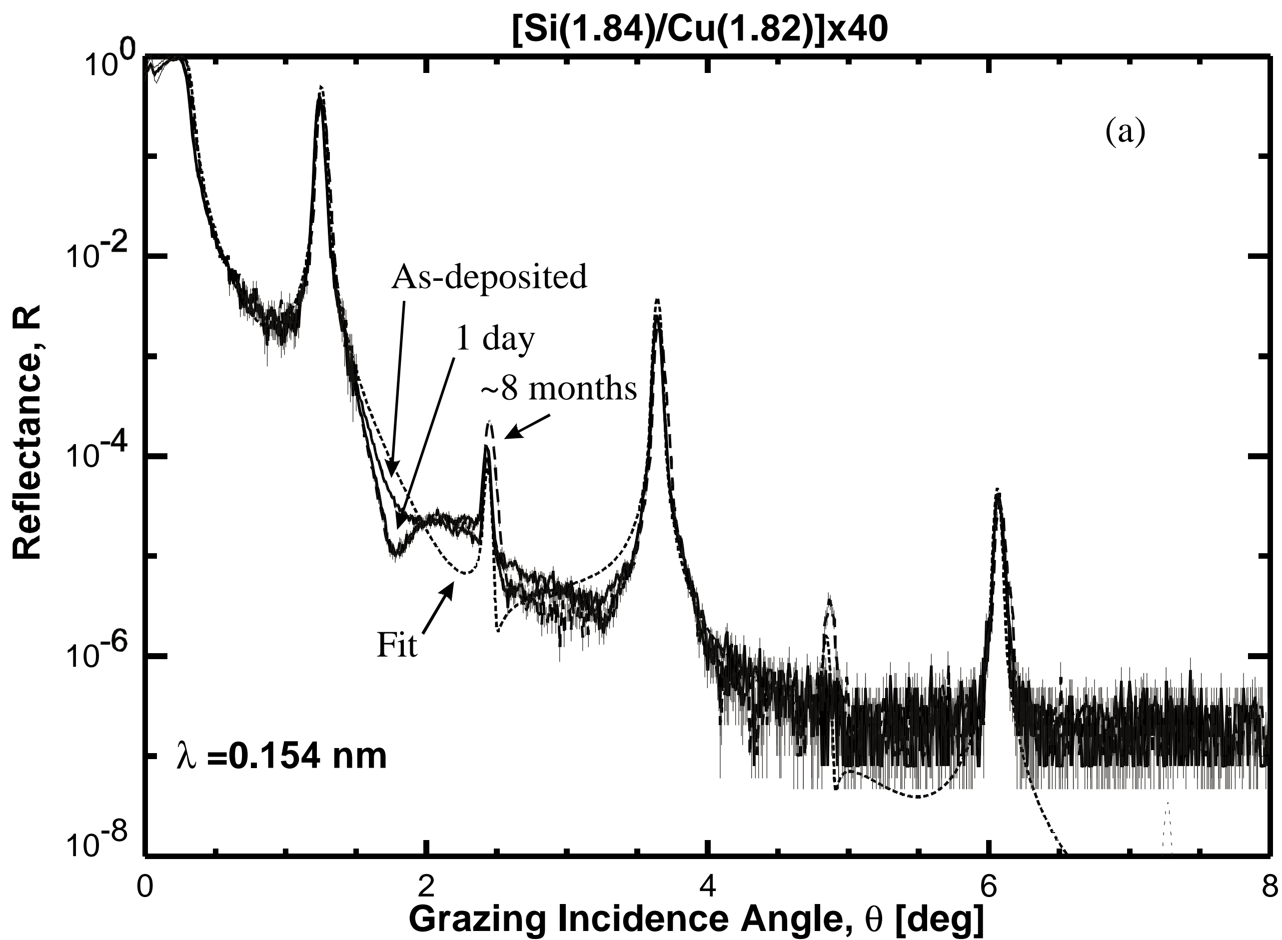


Cu/Si Periodic Multilayers

(b)

Ir Film

d=8.0 nm
N=50

d=4.6 nm
N=100

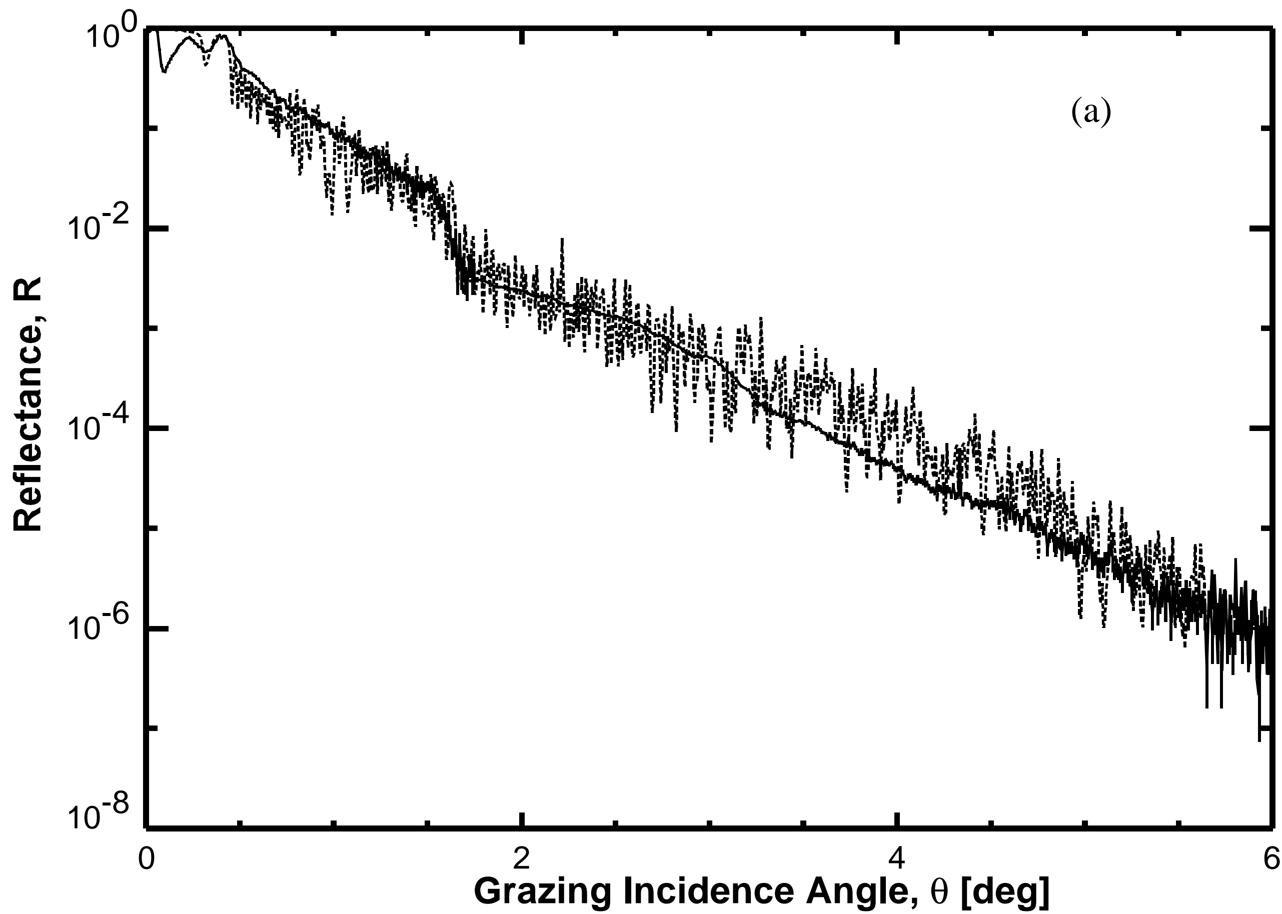
d=3.0 nm
N=100

d=2.3 nm
N=100

λ =0.154 nm

Reflectance, R

Grazing Incidence Angle, θ [deg]



(b)
Reflectance, R
1.0
0.8
0.6
0.4
0.2
0.0
20
40
60
80
100
Energy, E [keV]

(θ=1.50 mrad)

0.40
0.30
0.20
0.10
0.00
Reflectance, R
(a)
2 4 6 8 10
Energy, E [keV]
(θ=1.0 deg)

1.0
0.8
0.6
0.4
0.2
0.0
Reflectance, R
(b)
Cu/Si
W/Si
150 155 160 165 170
Energy, E [keV]
(θ=2.0 mrad)