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Fabrication and characterization of Sb/B_4C multilayer mirrors for soft X-rays

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Abstract

Structure characterization of Sb/B_4C multilayers for soft X-ray optics with a layers thickness from 0.5 nm to 7 nm is reported for the first time. Sb/B_4C coatings were manufactured via magnetron sputtering. Amorphous and crystalline phases of the layers and the multilayer structure parameters were characterized with the X-ray diffraction data and the TEM data. The Sb/B_4C multilayers demonstrated long term stability of their parameters and performances. The reached value of the reflectance of the Sb/B_4C multilayers is 19–28% measured at the near-normal incidence in the wavelength range of 6.64–8.5 nm. The influence of reduced Sb density on the reflectivity is discussed.

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1. Introduction

Multilayer optics for Extreme Ultraviolet (EUV) wavelength range from 12.5 nm to 19 nm has been extensively investigated in recent few decades, driven by EUV lithography, astrophysics, and plasma diagnostics applications. In recent years a shorter soft X-ray wavelengths around 6.7 nm attracted great attention as the next milestone for next generation of EUV/soft X-ray lithography [1] and [2]. Also reflective optics and instrumentation for wavelengths of 6.7–12 nm are highly required for comprehensive characterization of astrophysical objects, variety of plasma sources, high harmonic generation [3] and pulse compression applications.

A number of multilayer mirrors, such as Mo/B_4C, Ru/B_4C, FeNiCr/B_4C, La/B_4C, Mo/Y, have been tried so far for wavelengths of 6.7–11 nm [4], [5] and [6]. However, the reflectance achieved is not high enough for lithography and other applications, and researches continue to search for new prospecting multilayer systems. Sb/B_4C multilayer is one of the most promising systems due to very favorable combination of optical properties of the materials. Low absorption of EUV radiation in both materials and relatively high refraction in antimony [7] are expected to result in high reflectance of the multilayer in the wavelength range of 6.7–12 nm.

Maximum possible theoretical reflectivity of Sb/B_4C and other promising periodic multilayers versus wavelength is shown in Fig. 1. La/B_4C multilayer has the highest theoretical reflectance in the range of 6.7–8.5 nm [6]. However, strong intermixing of the La and B_4C layers prevents formation of sharp interfaces and causes reduction of the reflectance by a factor of 1.5–2 as compared to the theoretical value [8]. Sb/B_4C multilayers also have one of the highest theoretical reflectances (Fig. 1). At the same time, intermixing is not expected for the Sb/B_4C multilayers since they consist of non-interacting materials: Sb does not form compounds with carbon and boron and is marginally soluble in both of them [9] and [10]. This is expected to result in sharp interfaces and hence high reflectivity. Moreover, as it can be seen in Fig. 1, these multilayers can potentially provide high reflectance over the whole range of the wavelengths under interest (6.7–10.5 nm) which is very important for design of wideband multilayer mirrors for this part of the spectrum [11].

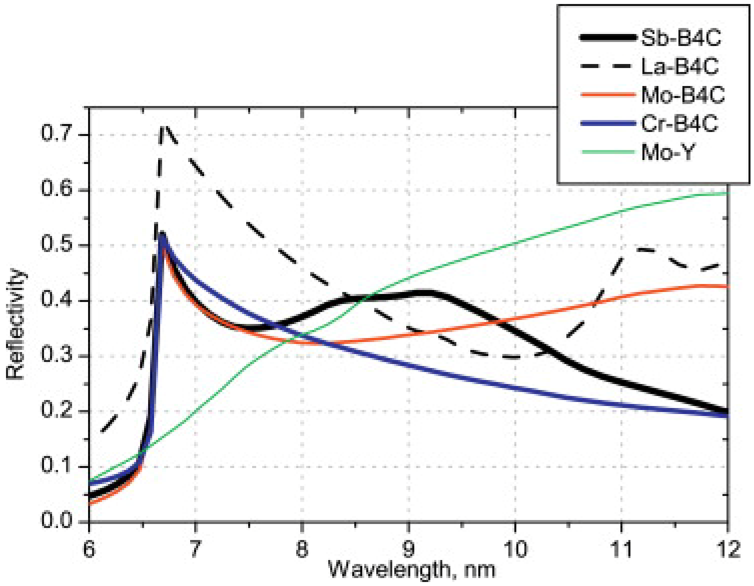

Fig. 1.

The theoretical maximum achievable normal incidence peak reflectance of ideal periodic Sb/B_4C, Mo/B_4C, Cr/B_4C, La/B_4C, Mo/Y multilayers, calculated using Henke's optical constants [7] and assuming the tabulated crystalline densities and absolutely sharp and smooth interfaces.

However, at present Sb/B_4C coatings are poorly investigated experimentally. To our best knowledge, no attempts in making X-ray optical elements based on Sb/B_4C multilayers have been reported so far. In [12] we reported on manufacturing of Sb/B_4C multilayer mirrors for the first time, results of the first measuring of their reflectance, some performance data for aperiodic Sb/B_4C multilayers. In this paper, most attention is given to characterization of structure and reflectance of real Sb/B_4C multilayers, covering both hard and soft X-ray measurements.

2. Experimental

The periodic Sb/B_4C multilayer coatings were deposited on glass and single-crystal silicon substrates using dc magnetron sputtering. No noticeable difference was observed between the structures and functional properties of the Sb/B_4C multilayers fabricated using one substrate material or the other. Surface roughness of the substrates was as small as 0.3 nm. The targets of Sb and B_4C were sputtered in an Ar medium at the pressure of 2×10^{-3} Torr. The top and bottom layers of the coatings were of B_4C for all the multilayers. Thicknesses of the layers varied from 0.5 nm to 7 nm. The number of layer pairs (N) was from 10 to 500 depending on the thickness of the layers. The ratios of Sb layer thickness to bilayer period (Γ) were in the region of 0.3–0.5.

Parameters of the multilayers such as thickness, density, and an interface roughness were determined with small-angle X-ray diffraction (SAXD) measurements and simulations. The method is also known as X-ray reflectometry. The measurements were performed with a DRON-3M diffractometer in the Θ–2Θ mode using Cu-K_α (8.0 keV) radiation. A Si (1 1 0) crystal monochromator was used to separate the Cu-$K_{\alpha 1}$ line and collimate a primary beam with residual divergence of 0.015°. SAXD scans were modeled using XRayCalc code [13] and Henke's atomic scattering factors [7]. The simulated reflectivity curves were fitted to the experimental ones by adjusting thickness, density, and interface roughness of the layers of the model multilayers.

Characterization of crystallinity of the materials of the layers was performed with a large angle X-ray diffraction (XRD) tool equipped with a secondary beam graphite monochromator.

Structure of the multilayer stacks was investigated with a cross-sectional transmission electron microscopy (TEM) using a Selmi PEM-U microscope.

Reflectivity measurements in the soft X-ray wavelength region between 6.6 nm and 6.9 nm were made at Beamline 6.3.2 at the Advanced Light Source at LBNL. The glancing angle was Θ = 73–88°. The details of the ALS beamline instrumentation are given in [14].

3. Results and discussion

A typical SAXD scan for an as-deposited Sb/B_4C multilayer is shown in Fig. 2 with a black line. The sharp Bragg peaks up to an angle of 9.5° (2Θ) point to a highly periodic layer structure with smooth and sharp interfaces. This proves that Sb/B_4C periodic multilayers composed of nanoscale layers can be fabricated by magnetron sputtering.

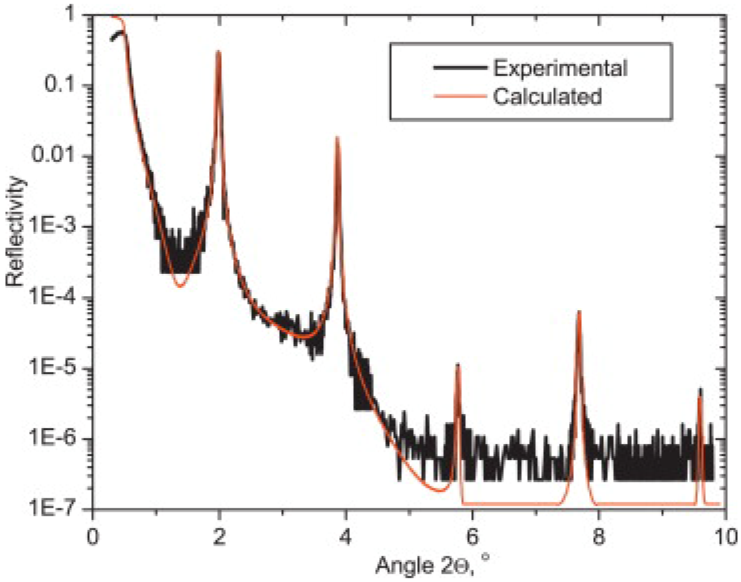

Fig. 2.

Measured and calculated small-angle X-ray diffraction $\Theta/2\Theta$ scans for Cu-$K_{\alpha1}$ for a Sb/B_4C multilayer consisting of 60 layer pairs, with a period of 4.61 nm and $\Gamma = 0.33$.

Simulation of SAXD data of the Sb/B_4C multilayers with Sb thicknesses in the range of 1–7 nm provided a quantitative characterization of the multilayer structure. The interface roughness which might include some intermixing was found to be of 0.32–0.4 nm rms. The obtained value of the roughness is somewhat higher as compared to W/B_4C and Mo/B_4C multilayers, but it is close to the roughness measured for Cr/B_4C, Co/C, Ni/C multilayers [15] and [16]. Thus, Sb/B_4C multilayers fabricated with dc-magnetron sputtering have fairly smooth interfaces with roughness as low as the one for X-ray multilayers made of other materials. Cross-section TEM confirms smooth interfaces of the Sb/B_4C multilayer stack (Fig. 3). In spite of the low melting point of antimony (631 °C), the Sb layers with a thickness of 1.5 nm are continuous with no evidence of 3D island growth.

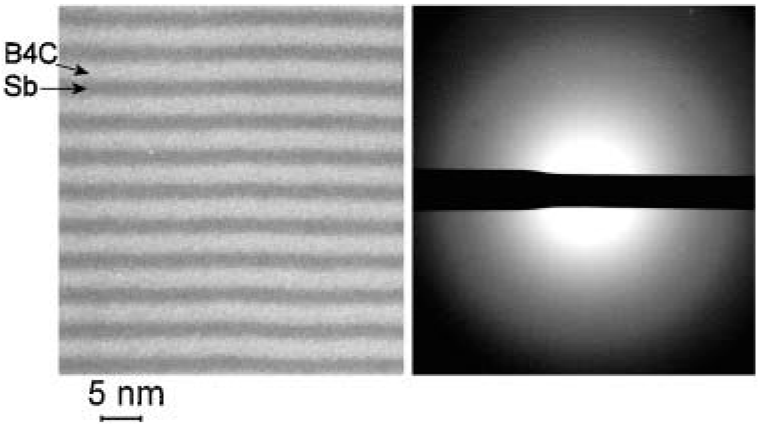

Fig. 3.

Cross-section TEM image and selected area electron-diffraction pattern of the Sb/B_4C multilayer with a period of 4.4 nm.

The simulation of the SAXD revealed a low density of 5.3 g/cm^3 of the Sb layers with thicknesses under 4.6 nm. This is significantly less than the value of 6.7 g/cm^3 tabulated for crystalline antimony. The low density can be explained assuming amorphous structure of the Sb layers since a density value of 5.3 g/cm^3 for amorphous antimony has been reported [17]. There is no clear Bragg peaks in the XRD from the Sb/B_4C multilayers with small periods (Fig. 4). The electron diffraction pattern also shows only amorphous rings for the multilayer (Fig. 3), and signs of crystallinity are not visible in the TEM images. It counts in favor of the amorphous structure of the thin Sb layers.

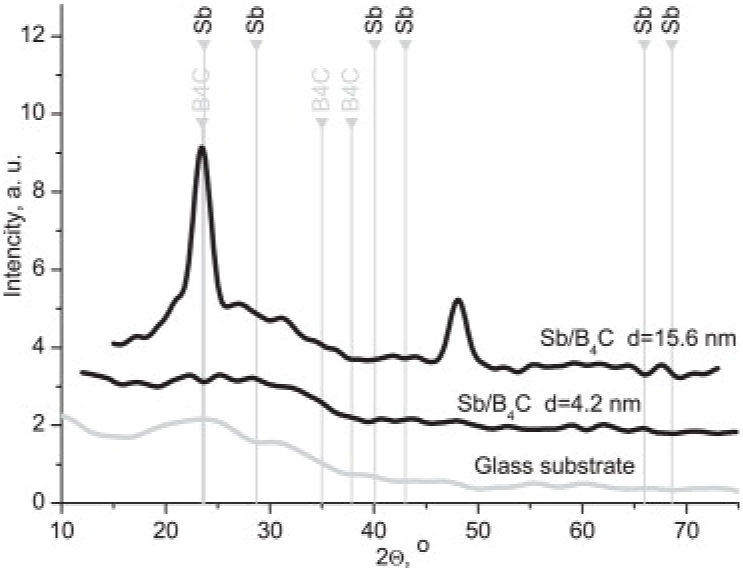

Fig. 4.

Large-angle X-ray $\Theta/2\Theta$ scans for Cu-K_α for the Sb/B_4C multilayer with a period of 4.2 nm and an uncoated glass substrate. The potential peak positions from crystalline Sb and B_4C are marked according to the ICDD Powder Diffraction File. It is seen that any sharp peak is absent and the amorphous “halo” from the glass substrate make a determining contribution to the diffraction pattern of the multilayer.

For the Sb/B_4C multilayers with Sb layers of 5.6 nm and thicker, the best fit between simulated and measured SAXD curves was obtained when the crystalline Sb density of 6.7 g/cm^3 was assumed. That is consistent with the high-angle X-ray results which showed some crystalline Sb peaks for these multilayers (Fig. 4).

Growth of amorphous Sb thin films deposited with high-temperature vacuum evaporation [18] and pulsed laser deposition [19] was previously reported. Sb layers formed by thermal vacuum evaporation can stay amorphous up to the thickness of 100 nm, which can vary depending on a growth rate, temperature, and a substrate. For pulsed laser deposition, crystallization of an amorphous Sb layer occurs at the thickness of 6–10 nm. We found that the amorphous-to-crystalline transition of Sb layers in the Sb/B_4C multilayers occurs in the thickness range from 4.6 nm to 5.6 nm. SAXD simulations and AFM measurements show that the interface roughness did not increase after the transition. Some reduction of the roughness with increase of the thickness was even observed.

A dependence of hard X-ray peak reflectivity at the first Bragg peak for Sb/B_4C multilayers versus the multilayer period is shown in Fig. 5. Reflectivity of multilayer mirrors typically reduces slightly as the period decreases down to a threshold value of 2.5–6 nm (depending on the multilayer materials) and then drops steeply [15] and [20]. For the Sb/B_4C multilayers, this sharp reflectivity fall occurs at the period less than 4 nm. The graph in Fig. 5 indicates that the Sb/B_4C pair of materials allows fabrication of efficient X-ray multilayer mirrors with a period of 3 nm or greater. SAXD scans show some Bragg reflections from the Sb/B_4C multilayers with a period as small as 1.2 nm. This indicates presence of a layered and periodic structure, and the fact that 0.6 nm thick layers of Sb and B_4C deposited with magnetron sputtering are not intermixed completely.

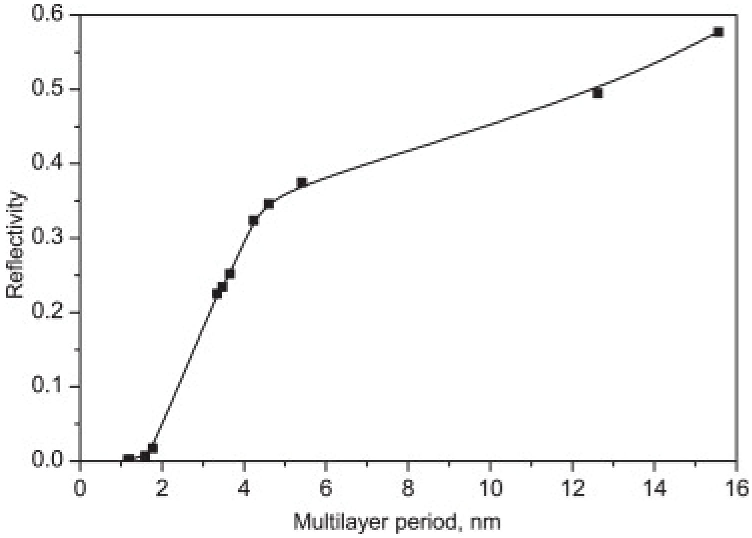

Fig. 5.

Peak reflectivities measured at $\lambda = 0.154$ nm (Cu-Kα_1) for Sb/B_4C multilayers against the multilayer period. The ratios of Sb layer thickness to bilayer period are in the region of 0.45–0.5.

A soft X-ray reflectivity of Sb/B_4C multilayers measured at near-normal incidence in a wavelength range of 6.6–9 nm is shown in Fig. 6 and Fig. 7. Reflectivity of the Sb/B_4C X-ray multilayer mirror with a period of 3.48 nm was measured as high as 28.5% at the wavelength of 6.63 nm (near the B-Kα absorption edge) at the glancing angle of 73°. The same multilayer demonstrated a reflectance of 19.9% at a wavelength of 6.77 nm (the B-Kα characteristic line) at the angle of 78°. The achieved peak reflectance of the Sb/B_4C coating (28.5%) surpasses those of FeCrNi/B_4C (16%), Rh/B_4C (20%) [4] and Mo/B_4C (25%) [21] multilayers optimized for the same wavelengths, and today it is second only to the La/B_4C (48.9%) [6] and LaN/B (57.3%) multilayer mirrors [22].

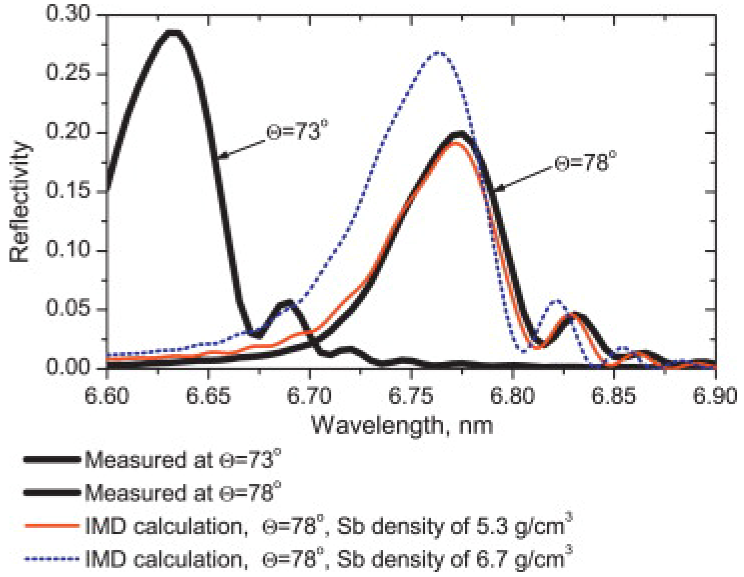

Fig. 6.

Experimental (at $\Theta = 73°$ and $\Theta = 78°$) and calculated (at $\Theta = 78°$) reflectivity dependences on wavelength for a Sb/B$_4$C multilayer with a period of 3.48 nm ($N = 250$ periods). The black lines show the experimentally measured data and the red and blue lines show calculation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

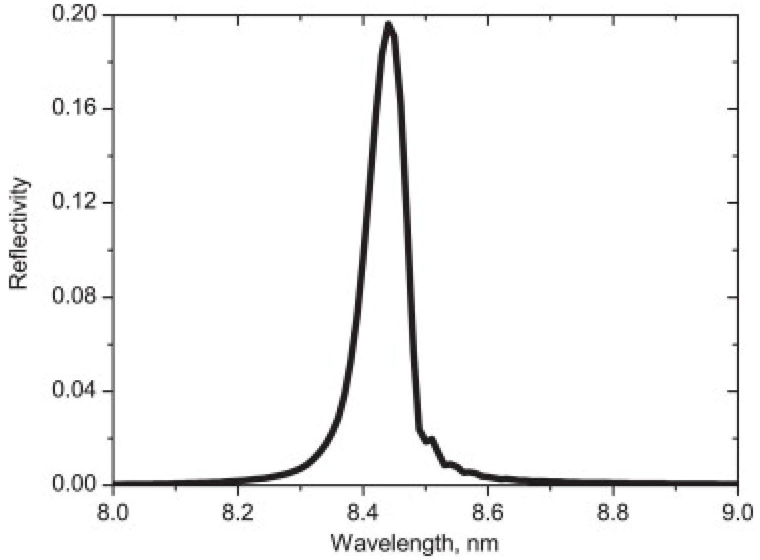

Fig. 7.

Measured reflectivity dependence on wavelength for a Sb/B$_4$C multilayer with a period of 4.29 nm ($N = 300$ periods). The angle of incidence was 2° off normal.

A reflectivity of 19.6% of the Sb/B$_4$C multilayer with a 4.29 nm period was measured at wavelengths of 8.4–8.5 nm (Fig. 7). The full width at half-maximum (FWHM) of the peak at $\lambda = 8.5$ nm is 0.070 nm. One can see, both the measurements performed at different wavelengths (Fig. 6 and Fig. 7) yield similar values of the reflectance. This confirms that the reflectivity of Sb/B$_4$C multilayers changes slightly in the wavelength range from 6.7 nm to 8.5 nm, as it was predicted by calculations (Fig. 1).

The experimental soft X-ray reflectivity of the multilayers is significantly less than the theoretical values calculated for ideal multilayer structures (see Fig. 1). The discrepancy is caused by imperfections of real multilayers, revealed by SAXD. Use of parameters of the multilayers obtained by fitting SAXD data (Sb density of 5.3 g/cm^3, the interface roughness of 0.4 nm, and some drift of the period) results in a realistic soft X-ray reflectance (a red dash line in Fig. 6) which is in a good agreement with the experiment (a black curve in Fig. 6). A blue dot curve in Fig. 6 depicts reflectance of a multilayer calculated using the same parameters but a tabulated value of a Sb density of 6.69 g/cm^3 instead of 5.3 g/cm^3. It is seen that a low density of the amorphous Sb layers has a severe impact on reflectivity of Sb/B_4C multilayers. Increase of the density to the value which corresponds to crystalline antimony would provide a significant improvement of the reflectivity. The relative rise of the reflectivity is more than 30%.

Since amorphous materials are metastable, stability of amorphous low-melting antimony layers might be an issue. Long-term temporal stability of performance of Sb/B_4C multilayers was verified against possible degradation. SAXD measurements were performed for the Sb/B_4C multilayer in the as-deposited state (black curve in Fig. 8) and after 21 months of storage in air at the room temperature (red curve in Fig. 8). It is seen from Fig. 8 that neither the angular position, nor the height of the Bragg peaks changed. Therefore, the thicknesses of the layers remained constant over the time, no intermixing of the layers and no roughness build-up occurred. Some change in the background line (in between the peaks) is probably related to formation of a thin oxide film on the top of the coating. The soft X-ray reflectivity was found almost unchanged as well. A marginal reduction of the reflectance from 28.5% to 28.3% (at $\lambda = 6.64$ nm) and from 19.9% to 19.3% (at $\lambda = 6.77$ nm) after a year-long storage in air was observed. The Sb/B_4C multilayers proved to be stable under the laboratory conditions.

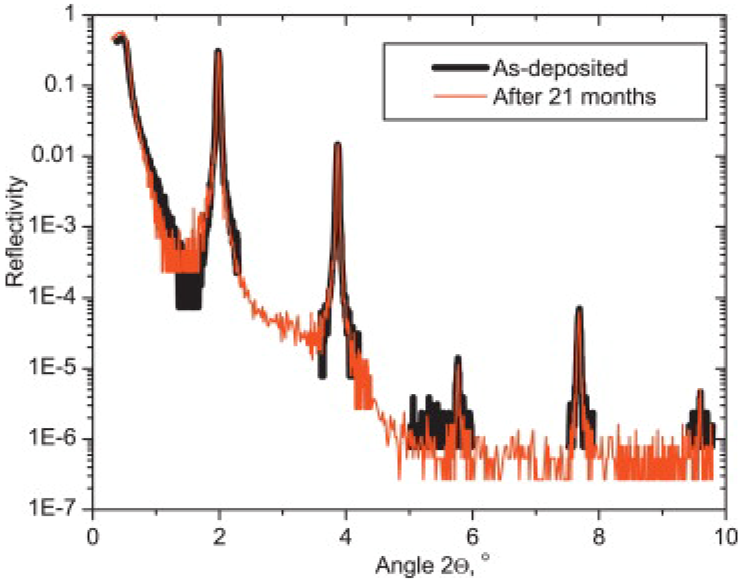

Fig. 8.

Small-angle X-ray diffraction $\Theta/2\Theta$ scans for Cu-$K_{\alpha 1}$ for a Sb/B_4C multilayer with the 4.61 nm period taken in as-deposited state and after 21 months.

4. Conclusions

We demonstrated for the first time that the Sb/B_4C X-ray multilayer mirrors can be manufactured via magnetron sputtering technique.

The short period Sb/B_4C multilayers consist of amorphous layers with smooth interfaces. Density of amorphous Sb estimated as low as 5.3 g/cm^3 is substantially reduced as compared to the tabulated value.

The Sb/B_4C multilayers demonstrated long term stability of their parameters and performances. No volume changes occurred, the period remained constant, the reflectivity did not degrade at least over a year.

Fabricated Sb/B$_4$C multilayers demonstrated reflectance of 19–28% measured at near-normal incidence in a wavelength range of 6.64–8.5 nm. The measured peak reflectance of Sb/B$_4$C multilayers proved to be greater than that of multilayers based on many conventional materials pairs optimized for the wavelengths of 6.6–9 nm. But it did not reach the reflectance level of La/B$_4$C multilayer. The low density of amorphous Sb layers is one of main factors which reduce the reflectivity of Sb/B$_4$C as compared to the theory predictions. Control of structure of the thin Sb layers in order to achieve a crystalline state with a high antimony density could become an effective way to improve reflectance of Sb/B$_4$C multilayers.

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DISCLAIMER

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