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Investigation of the properties of multilayer mirrors based on a pair of materials Mo/B_4C

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The properties of Mo/B_4C multilayer X-ray mirrors with periods of 3.74−3.84 nm are studied in this work. The dependences of the transmission band, reflection coefficient and the magnitude of internal stresses in mirrors on the ratio of material thicknesses in the period were investigated. The results of a study of the effect of thermal annealing on the structural parameters and reflective characteristics of mirrors are also presented in the paper.

Keywords: multilayer X-ray mirrors, synchrotron applications, X-ray monochromators.

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Introduction

Multilayer X-ray mirrors (MXRM) are used in various fields of science and technology, such as solar astronomy, X-ray lithography, X-ray monochromatization systems. The main characteristics of mirrors that are of key importance for practical applications are the values of the reflectance R at the operating wavelength λ and the spectral width of the reflection peak at half the height $\Delta\lambda$. The last two values can be combined by the expression $\Delta\lambda/\lambda$, called spectral selectivity and expressed as a percentage. The smaller is this value, the higher is the spectral selectivity.

One of the tasks in which it is required to simultaneously ensure high spectral selectivity and high values of the MXRM reflectance is the creation of optical circuits of monochromators for synchrotron radiation sources. An example of such a source is the synchrotron radiation source „SKIF“ [1], being developed at the Budker Institute of Nuclear Physics, Siberian Branch, Russian Academy of Sciences. The requirements for the monochromator are given in [2]. The required spectral selectivity of a two-mirror monochromator should not exceed 1% for the energy range of 8−14 keV. Therefore, it should be within 1.4% for each of the mirrors.

It is also worth noting that for the use of multilayer mirrors in a number of tasks where samples are exposed to thermal effects, the thermal stability of the reflective characteristics plays an important role. High thermal loads on the MXRM of the monochromator is noted in [2].

A structure based on a pair of materials Mo/B_4C appears to be optimal to meet the above requirements from the point of view of X-ray optical characteristics. At the same time, to ensure a given bandwidth, the problem arises of optimizing the parameter β, which characterizes the ratio of the thickness of the strongly absorbing material in the period (in this case, molybdenum) to the thickness of the structure period d, i.e. $\beta = d(\mathrm{Mo})/d$.

Multilayer B_4C mirrors have previously been widely studied. In particular, MXRM Mo/B_4C with periods in the range $d = 1.22-1.86$ nm were studied in [3]. It was shown that reflectances reached 12.5% in the wavelength range of $0.7-1$ nm. However, Mo/B_4C MXRMs have been the most widely used for solving various problems in the spectral range of $6.7-11$ nm due to the relatively small absorption of boron carbide B_4C and Mo [4–9]. The achieved reflectances in the soft X-ray range are given in these papers. Thermal stability of MXRM with an optimal ratio of layer thickness was studied. The stability of both the reflectances and the position of the Bragg peaks at annealing temperatures up to $600-700^\circ$C is noted. Since the two-mirror monochromator is supposed to use MXRM Mo/B_4C with periods of about 3.8 nm, and the results of the above papers pertain to MXRM with periods of about 3.6 nm, it can be assumed that high stability of X-ray optical characteristics can be expected for monochromator mirrors as well.

However, there is practically no information about the reflective characteristics of the MXRM Mo/B_4C in the hard X-ray range in these papers. The effect of the parameter β, especially in the region of small values, on thermal stability also was not studied. It should also be noted that there are no data on internal stresses S (from English Stress) in the studied structures in all the cited papers. Since the internal stresses in the films strongly affect the shape of the optical elements, it seems important to investigate them too.

The results of the study of the relationship of the reflectance R, spectral selectivity $\Delta\lambda/\lambda$ in the hard X-ray range and internal stresses of S for MXRM Mo/B_4C with periods of about 3.8 nm, as well as the effects of high-temperature annealing on these characteristics are provided in these papers.

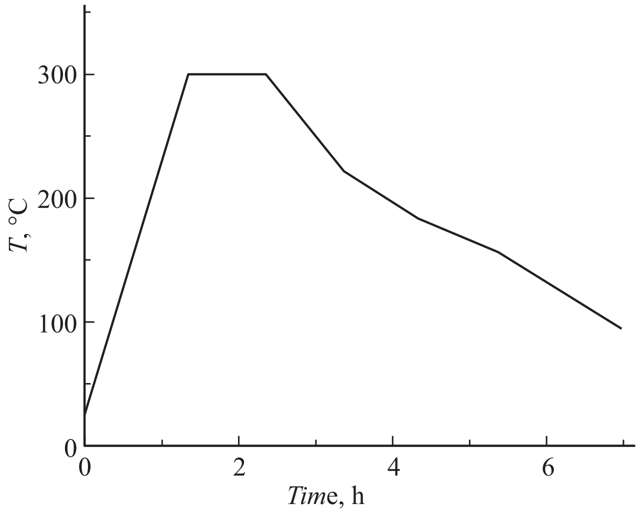

Figure 1. Time relationship of sample temperature and time during annealing for heating to 300°C.

1. Experiment procedure

Multilayer Mo/B_4C-structures were synthesized by magnetron sputtering on the unit described in [10]. Before the technological process, the pressure of residual gases in the chamber was at the level of 10^{-7} mbar. High-purity (99.998%) argon with working pressure of $9 \cdot 10^{-4}$ mbar was used as the working gas. The magnetrons were powered by stabilized current sources developed at the IPM RAS. The voltages were 296 V for Mo and 267 V for B_4C, currents 200 mA for Mo and 1200 mA for B_4C throughout the technological process. Accordingly, the film growth rates: 0.18 nm/s for Mo and 0.56 nm/s for B_4C.

The relationships of the reflectances and the MXRM radiation glancing angle were measured in the hard X-ray range at a wavelength of 0.154 nm using four-crystal diffractometer PANalitycal X'Pert Pro. The parameters of the structures (period, thickness of materials, interlayer roughness) were determined by the method of simultaneous adjustment of reflection curves taken at $\lambda = 0.154$ nm and in the soft X-ray region of the spectrum, using a model for restoring the values of MXRM parameters from X-ray reflection data at several wavelengths and Multifitting software [11,12]. Measurements in the soft X-ray region of the spectrum were carried out using a laboratory reflectometer with a monochromator spectrometer RSM-500 ($\lambda = 1.759$ and 0.989 nm). For more information about the reflectometer refer to [13].

The value of spectral selectivity $\Delta\lambda/\lambda$ was calculated using the results of measuring the angular dependence of the reflectance using the formula

$$\Delta\lambda/\lambda = \Delta\vartheta/\operatorname{tg}(\vartheta), \quad (1)$$

where ϑ is the position of the reflection peak, $\Delta\vartheta$ is the angular width on half the height.

The samples were annealed in a vacuum furnace at a pressure of $6 \cdot 10^{-5}$ Pa. The temperature was controlled by a chromel-alumel thermocouple with an accuracy of ±5°C. The samples were annealed at a temperature of 300°C. The time of one annealing cycle was 1 h. Figure 1 shows the time relationship of the sample temperature and the time for heating to 300°C.

The values of internal stresses in the MXRM were determined using the Stoney formula:

$$S = \frac{E}{6(1-\nu)} \frac{d_{\text{sub}}^2}{d_{\text{ov}}} \left(\frac{1}{R_2} - \frac{1}{R_1} \right), \quad (2)$$

where S — internal stresses, E — Young's modulus of the substrate material, ν — Poisson's ratio of the substrate material, d_{sub} — substrate thickness, d_{ov} — total thickness of MXRM, R_1 — initial radius of curvature of the substrate, R_2 — radius of curvature of the substrate after deposition of MXRM. Plates made of monocrystalline silicon with an orientation of (100) with a diameter of 100 mm were used as substrates. The coefficient is $E/[6(1-\nu)] = 30$ GPa for such a plate. The radius of curvature of the substrate before and after the MXRM was applied to it was measured using a Zygo VeriFire 4 laser interferometer.

2. Experimental findings

As part of the research, 5 structures with periods of 3.74–3.84 nm with different values of the thickness of the strongly absorbing material in the period were synthesized. The total number of periods for each sample is $N = 120$. Reflection curves were measured for each sample and values of internal stresses were determined. The structures and their parameters (period, molybdenum fraction in the period, reflectance in the first Bragg peak, angular width of this peak and spectral selectivity at $\lambda = 0.154$ nm, internal stresses) are given in Table. 1.

The smallest half-width of the first Bragg peak, as expected, is achieved at the lowest value of the parameter $\beta = 0.17$. Spectral selectivity of MXRM, according to the formula (1), 1.68%. In this case, the value of the reflectance is $R = 57\%$. The use of these structures in the two-mirror design of the monochromator will allow obtaining the selectivity of the system at the level of 1.34%. The reflectance of such a setup will be $R = 32.5\%$.

At the next stage of the study, the samples were annealed for 1 h at a temperature of 300°C. The parameters were measured again after annealing to determine the thermal stability of the synthesized structures. Table 2 shows the parameters of MXRM Mo/B_4C after annealing.

The comparison of data in Table 1 and 2 shows that the reflective characteristics of samples with parameter values β in the range 0.22–0.45 change slightly after annealing. Their variations correspond to the measurement error. At the same time, the sample with the thinnest molybdenum layer shows a really noticeable deterioration: R changes from 57 to 50%, $\Delta\lambda/\lambda$ increased from 1.68 to 2.2%. Figure

Table 1. Parameters (period d, molybdenum fraction in period β, reflectance in the first Bragg peak R, angular width of this peak $\Delta\vartheta$, spectral selectivity $\Delta\lambda/\lambda$ at $\lambda = 0.154$ nm and internal stresses of S) MXRM Mo/B_4C before annealing

Sample	d, nm	β	R, %	$\Delta\vartheta$	$\Delta\lambda/\lambda$, %	S, MPa
RS-193	3.74	0.45	62.5	0.039	3.2	−1280
RS-194	3.81	0.34	60.2	0.04	3.3	−1513
RS-197	3.75	0.26	58.6	0.037	3.1	−1623
RS-198	3.84	0.22	57.5	0.027	2.3	−1738
RS-207	3.79	0.17	57	0.02	1.68	−1813

Table 2. Parameters of MXRM Mo/B_4C after annealing

Sample	d, nm	β	R, %	$\Delta\vartheta$	$\Delta\lambda/\lambda$, %	S, MPa
RS-193	3.74	0.45	60.5	0.04	3.4	−395
RS-194	3.81	0.34	61.1	0.04	3.3	−721
RS-197	3.75	0.26	57.5	0.038	3.2	−854
RS-198	3.84	0.22	57.5	0.026	2.2	−1136
RS-207	3.79	0.17	50	0.026	2.2	−1249

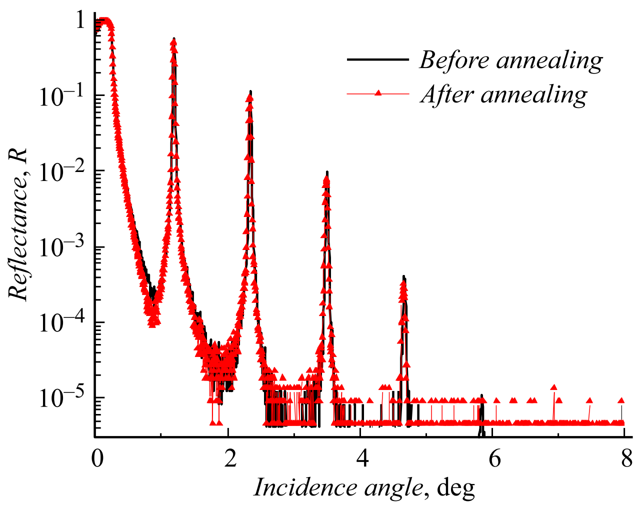

Figure 2. Angular dependences of the RS-207 sample reflectances ($\beta = 0.17$) before (solid curve) and after (symbols) annealing at 300°C. The wavelength is 0.154 nm.

2 shows the angular dependences of the reflectances of the RS-207 sample ($\beta = 0.17$) before and after annealing at 300°C ($\lambda = 0.154$ nm).

It is possible to observe here a slight decrease in the four orders of diffraction after annealing. The fifth order of diffraction is present in the measurements of the reflection of the structure before annealing and there is no fifth order of diffraction after the annealing. These changes correspond to the evolution of the interlayer roughness shown in Table 3.

Table 3. Comparison of interlayer roughness values for RS-207 sample ($\beta = 0.17$) before and after annealing

Process	Mo-on-B_4C, nm	B_4C-on-Mo, nm
Before annealing	0.31	0.22
After annealing	0.33	0.31

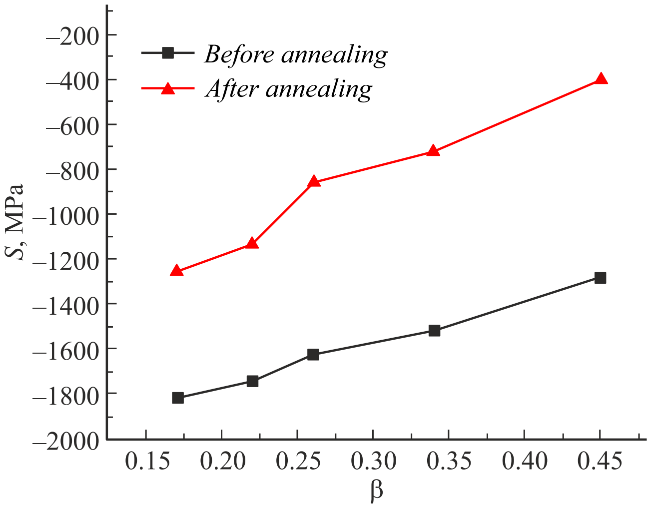

Figure 3. Values of internal stresses depending on the parameter β Mo/B_4C before (square symbols) and after (triangular symbols) annealing for 1 h at a temperature of 300°C.

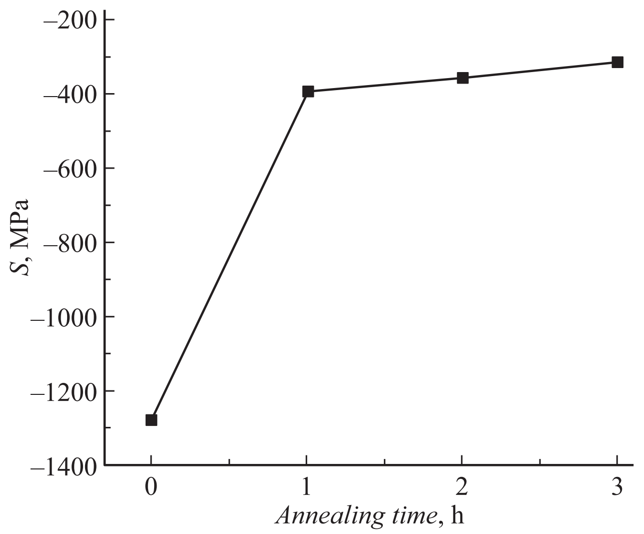

Figure 4. Dependence of internal stresses in the Mo/B_4C structure with the parameter $\beta = 0.45$ on annealing time.

The data listed in Table. 1 and 2 show that the magnitude of compressive stresses in the MXRM Mo/B_4C significantly decreases during annealing. These data are presented graphically in Fig. 3.

Figure 4 shows the dependence of the internal stresses for the RS-193 sample ($\beta = 0.45$) on the annealing time: 1, 2 and 3 h. This sample was successively annealed several times each time for 1 h (the mode of each iteration as in Fig. 1). After each annealing operation, the sample was cooled, removed from the vacuum and underwent the procedure of measuring internal stresses.

If the value of internal stresses significantly decreases from -1280 to -395 MPa after the first hour of annealing, then further repetition of the procedure further significantly reduced this value. After the second and third annealing, the internal stresses were -356 and -314 MPa, respectively.

Nevertheless, a reduction of the magnitude of internal stresses without loss in reflectivity is a positive property of MXRM Mo/B_4C.

Conclusion

The reflective characteristics of multilayer mirrors based on a pair of materials Mo/B_4C with periods $3.74-3.84$ nm were studied in this paper. It is shown that from the point of view of obtaining the lowest bandwidth of the mirror, the optimal ratio of the molybdenum thickness in the period to the thickness of the period is 0.17. At the same time, it was shown that the reduction of the molybdenum thickness in the period leads to an increase in internal stresses in the structure. The annealing samples for 1 h at a temperature of 300°C is one of the methods for reducing the magnitude of internal stresses. At the same time, there was no significant degradation of the reflective characteristics of all samples, except for MXRM with a fraction of molybdenum in 0.17 period.

In general, based on the results of this study, it can be concluded that, despite the use of Mo/B_4C-mirrors for synchrotron applications, for example [14,15], it is not desirable to use them as part of diffraction-quality systems. There are two main reasons. The first is insufficiently high reflectances and spectral selectivity in the hard X-ray range. The second is the presence of strong mechanical stresses, even after thermal annealing, which can distort the shape of the mirror to unacceptable values. It is necessary to look for an alternative for the two-mirror monochromator mentioned above for the spectral range $8-14$ keV, while it is necessary to pay attention not only to the X-ray optical characteristics, but also to mechanical stresses.

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Conflict of interest

The authors declare that they have no conflict of interest.

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