Functional Materials 14, No.4 (2007)

Nanoscale Co/C multilayers for "carbon window" Schwarzschild objective

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Received July 3, 2007

The formation features of the Co/C multilayer with ≈2.3 nm period have been studied with the aim to form a Schwarzschild objective on a "carbon window" for medical and biological investigations. A sequence of multilayer deposition on curved substrates has been proposed that provides the matched functioning of both objective mirrors. The interaction features of the Co and C layers during deposition, period and reflectivity changes under heating have been considered.

Изучены особенности формирования многослойных пленочных композиций Co/C с периодом ≈2,3 нм с целью создания объектива Шварцшильда на "углеродное окно" для биологических и медицинских исследований. Предложена последовательность нанесения многослойных покрытий на криволинейные подложки, обеспечивающая согласованную работу двух зеркал объектива. Рассмотрены особенности взаимодействия слоев Co и C в процессе выращивания, изменения периода и отражательной способности при нагреве.

One of the tasks is the development of X-ray microscopy being an important analytical instrument for studying biological and medical objects [1, 2]. The encouraging results in development of imaging systems obtained up to now are generally related to the long-wave part of the soft X-rays (λ = 13.4, 18.0, 46.9 nm) where X-ray mirrors have the high reflectivity (up to 70 %) [3–5]. Several attempts to move the imaging forward to the shorter wavelength have been undertaken as well [6], but they are not so successful. In many respects, it is caused by difficulties in developing high-performance X-ray mirrors with short periods (less than 2.5 nm). Increase of X-ray penetration into the mirror that entails decrease of bandwidth and reflectivity decrease due to interface roughness makes additional considerable demands in technology and design of a nanoscale multilayer. It is important to provide a multilayer period value at a high accuracy not only in multilayer depth but also within the working area of a curved substrate with the necessary law of period distribution to work coatings in a multimirror optical system. Those imperfections, such as interlayer roughness and interlayer interaction, have to be studied in detail since they are of a great importance in the reflectivity decrease [2]. The aim of this work is to study the formation features of a nanoscale Co/C X-ray multilayer coating to develop Schwarzschild objective (Fig. 1) for "carbon window" ($4.36 \le \lambda \le 5$ nm), the wavelength range which follows the jump in carbon absorption edge. Unlike the "water window" ($2.36 \le \lambda \le 4.43$ nm), where the maximum contrast of proteins and other hydrocarbons may be achieved in comparison with water [7], the "carbon window" range is a very convenient for absorption microscopy of thick biological objects (up to 30 μm). The highest penetration of soft X-rays ($1.5 < \lambda < 100$ nm) into organic objects is just in "carbon window" spectral range. More-over, the absorbance difference of cellular structures is 5–6 times higher than in "water window" range, thus provides enabling the differential contrast of DNA, proteins, fat, and other materials for the sample support (e.g., paraffin).

The Co/C multilayers were prepared by dc-magnetron sputtering of Co and C targets under low Ar pressure (10^{-2} Pa) onto a substrate at 50°C. The deposition rate of both materials was about 0.1 nm/s. The flat Si wafers and the curved (concave and convex) finish-ground blanks of quartz (the Schwarzschild objective components) were used as the substrates. The substrates were axially rotated (about the objective optical axis) during deposition that provided centrally symmetric distribution of the layer thicknesses. An Ar ion gun was used to clean the substrates prior to deposition. The number of periods in the multilayers was varied from 100 to 200 and made 100 in the objective coatings.

To analyse the multilayer quality and to obtaining quantitative characteristic, the small angle (0–5°) diffraction curves were taken using a DRON-3M general-purpose diffractometer in Cu Êα_1 radiation in the Θ–2Θ geometry. Theoretical simulation of experimental diffraction curves basing on the Fresnel formulas [8] and Henke atomic scattering factors [9] enables calculating the multilayer period, thickness of individual layers, and estimating layer density and interface roughness across a multilayer. Because of shadowing primary beam at small angle X-ray scattering, the radial period distribution for concave mirror was determined from a series of multilayers deposited onto 4×6 mm^2 silicon wafers. The wafers were mounted on the arch holder located at the same place as the concave mirror, so their surfaces were tangent to spherical one. The structure of layers and interfaces in Co/C multilayers was studied by high resolution TEM of cross-sectional view using a PEM-U microscope operated at 100 kV. The sample preparation included both mechanical and ion thinning.

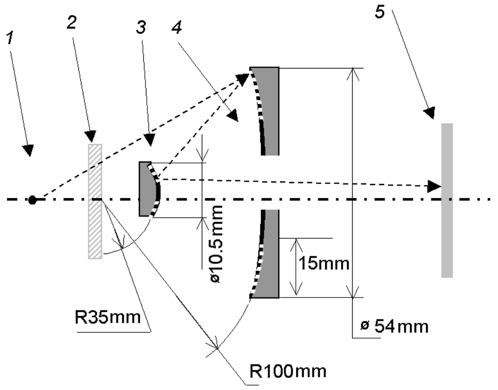

Fig. 1. A draft of Schwarzschild objective (*1* — X-ray source; *2* — analyzing object; *3* — multilayer coating on convex mirror; *4* — multilayer coating on concave mirror; *5* — film or X-ray sensitive matrix). The working mirror range is marked by white points.

The maximum reflectivity of X-ray mirrors composed of the best material pairs in terms of optical indices has been calculated in [10]. The normal incidence Co/C mirror has the peak reflectivity about 64 % near the carbon absorption edge, conceding only Th/C and U/C mirrors having reflectivity 72 and 82 %, respectively. It should be noted that Cr/C mirror has the same reflectivity as Co/C, however, the integral reflectivity of Co/C mirrors is one third higher.

Our experimental study of the Co/C mirrors with 2.3 nm period [11] has shown that the observed reflectivity is several times lower than theoretically predicted value and accounts for 10–15 % (Table). This is connected with a substantial difference between the real multilayer structure and its ideal model used in the reflectivity calculations. The interlayer roughness and the layer mixing are the main imperfections that cause the decreased mirror reflectivity. According

Table. Parameters of Co/C X-ray mirrors experimentally observed in "carbon window"

Specimen	No.1	No.2	No.3 annealed at 200°C
Period: d, nm	2.275	2.245	2.29
Number of periods: N	100	200	200
Normal incident reflectivity: R, %	9.7	14.3	14.8
Bandwidth: $\Delta\lambda$, nm	0.044	0.026	0.028
Wavelength: λ_{peak}, nm	4.522	4.466	4.555

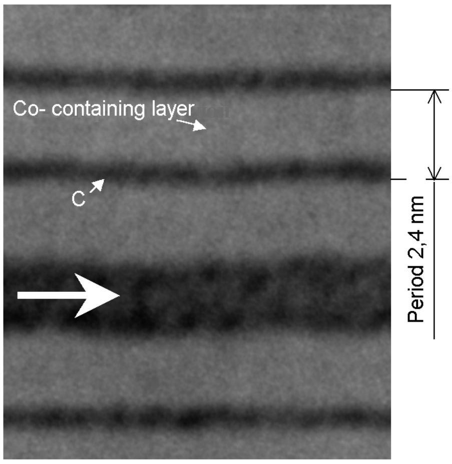

Fig. 2. Cross-section electron microscopy image of Co/C multilayer with period 2.4 nm. The horizontal arrow indicates where the Co layer has been omitted.

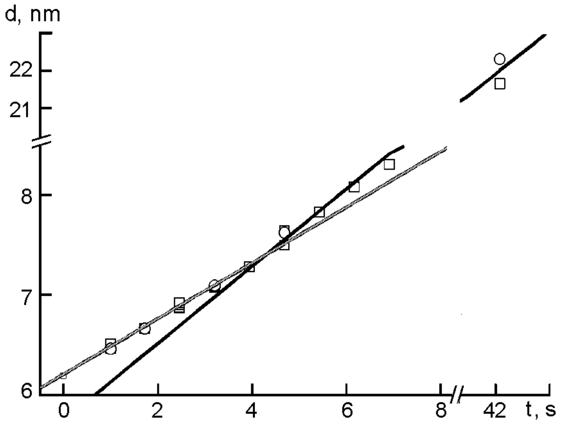

Fig. 3. Dependence of Co/C multilayer period from the time of Co deposition.

to simulation of small angle X-ray spectra and diffraction curves at normal incidence, the interface roughness in the Co/C multilayer is about 0.3–0.35 nm. The roughness level is due mainly to features of the Co/C multilayer growth and not to the substrate roughness replication, since the substrate surface was finished down to 0.1–0.15 nm. The layer intermixing discovered in the Co/C system (see below) decreases the reflectivity as well due to smoothed optical contrast of the layers and increased fraction of the absorbing layer in the multilayer period. Nevertheless, the achieved reflectivity of the Co/C two-hundred-period mirrors up to 14–15 % provides a Schwarzschild objective with total reflectivity exceeding 2 % that is enough for practical purposes. However, the large number of the bi-layers ($N \geq 200$) results in extremely narrow spectral bandwidth of the reflective coating down to $\Delta\lambda < 0.025$ nm ($\Delta\lambda/\lambda \sim 1/N$). The additional requirement of a good period matching and setting across the working surface of the mirrors demands an engineering solution in developing lateral-graded X-ray mirrors. Although the optimal number of periods is 200 and higher, the number of bi-layers was limited by 100 to meet the requirements of large aperture optics as the first step towards the high-throughput Schwarzschild objective.

Cobalt and carbon do not form stable chemical compounds according to the phase diagram, but may form metastable Co_3C and Co_2C carbides [12]. These carbides have been found in a thin film Co–C system as well because of layer interaction between Co and C under heating and further crystallization of the reaction products [13, 14]. Investigation of layer interaction processes in a Co/C multilayer in as-deposited state by diffraction methods is hampered by low crystal perfection and small thickness of layers. Consideration of electron microscopy images does not reveal directly the mixed zones as the product of Co and C interaction (Fig. 2). At the same time, the mixed zones may be seen well in Mo/Si and Sc/Si multilayers [15, 16]. A high-quality imaging of the mixed zones in these multilayers as compared to Co/C ones is provided by distinction in the kind of contrast. A diffraction contrast prevails in polycrystalline metal layers while the absorption and phase one dominates in the adjacent mixed zones. However, there are numerous experimental results indicative of the interaction between Co and C. First, the varying thickness ratio of the constituent layers testifies a mixing Co and C. The electron microscopy images show that the metal-to-carbon layer thickness ratio is 4.3/1, while the deposition time derived from Co and C rates was set to provide said ratio 1/1.7 (Fig. 2). Therefore, it has been observed the increase of Co containing layer thickness and the decrease of the C one. Second, when the only cobalt layer has been skipped (Fig. 2), the thickness of carbon layer increases not by a factor 2 as should be expected for unmixed system but by a factor 4 to the thickness of carbon in the regular stack. The excess of the carbon layer results from the "disappearance" of two C–Co and Co–C boundaries, where carbon is consumed by metal-containing layer due to mixing. In the third

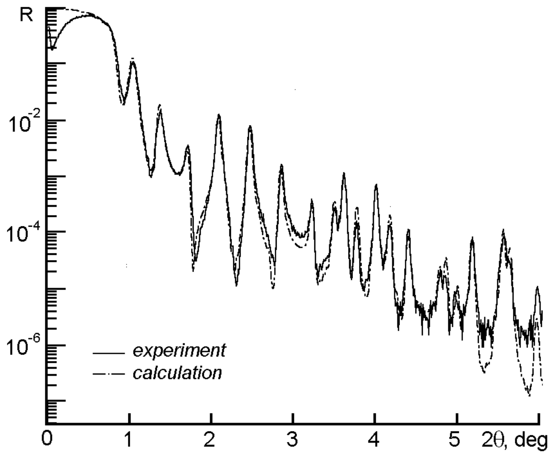

Fig. 4. Angular dependence of the reflectivity (λ = 0.154 nm) of Co/C multistack coating consisted from 5 regular stacks each of N bi-layers numbered from multilayer surface: (d = 22.32 nm, N = 9; d = 12.8 nm, 15; d = 9.4 nm, N = 21; d = 7.1 nm, N = 28; d = 6.5 nm, N = 30).

place, the multilayer period shrinks down by 8 % in comparison with the predicted value apparently as a result of an alloy formation with a more compact structure than the simple mixture of Co and C. Taking into account the degree of the layer thickness change, we expect the alloy density to be around 6–6.5 g/cm^3.

To detail the process of the Co/C multilayer formation, a series of multilayers with fixed carbon thickness was deposited and the multilayer period was plotted as a function of cobalt deposition time (Fig. 3). Each multilayer consisted of several unique regular stacks. In spite of the complex diffraction pattern, the coincidence between experimental and calculated curves was acceptable (Fig. 4). In Fig. 3, two linear sections are seen with different slopes that correspond to different Co/C multilayer growth rates. This dependence is representative for a multilayer where a mixed zone is formed [17, 18]. The smaller rate in the first stage of multilayer growth is caused by the layer interaction. The rate increase in the second section is connected with period increase due to formation of non-interacting cobalt and carbon layers. A model of the multilayer structure has been derived from simulation of the X-ray spectra. According to it, cobalt containing layer has a thickness up to 1.6 nm and the reduced density of about 6 g/cm^3 that is correlated with estimations for Co–C alloy mentioned above. At the same time, the density of about 50 nm and more thick cobalt layer is about 8 g/cm^3 that nevertheless is lower than 8.9 g/cm^3 of bulk cobalt.

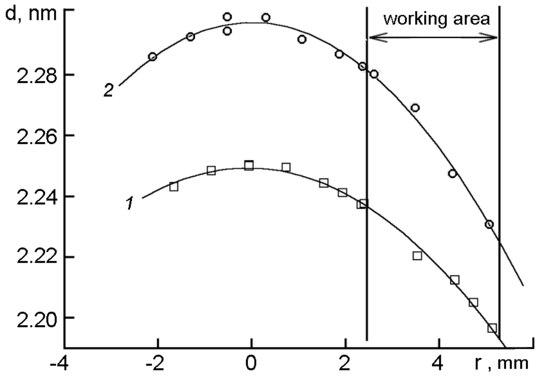

Fig. 5. Period distribution along a convex mirror surface in as-deposited state (*1*) and after annealing at 220°C (*2*).

The Co/C multilayer deposition technique on the Schwarzschild substrates proposed here expects that X-ray source in the image experiments will have continuous or quasi-continuous spectrum around the absorption edge of carbon. This makes it possible, first, to extend somewhat the working wavelength range and not to be referred to the fixed spectral line (e.g. C–Ê$_{\alpha}$) that in turn moderates the requirements for the period value accuracy under multilayer deposition. Second, the distribution of multilayer period over the mirror surface may be relatively arbitrary, providing that it is smooth and symmetrical with respect to the mirror center and changes within to several per cent. A simple rotation of convex mirror about its axis under the targets has met the requirements without applying any shadow mask between the targets and the substrate (Fig. 5). The multilayer period starts from ≈2.3 nm at the mirror center and varies domically down to about 2.24 nm at the mirror edge having the variation about 2.6 %.

To reach the highest objective throughput, the X-ray wavelength, the incidence angle and period have to satisfy the Bragg's law in every point. The experimentally measured period distribution across the convex mirror allows computing the multilayer period distribution for a concave mirror basing on the Bragg's law with correction for the refraction [19]. The calculation result is shown in Fig. 6 (triangles). The period change within the objective aperture (working area from 11 to 26 mm of the

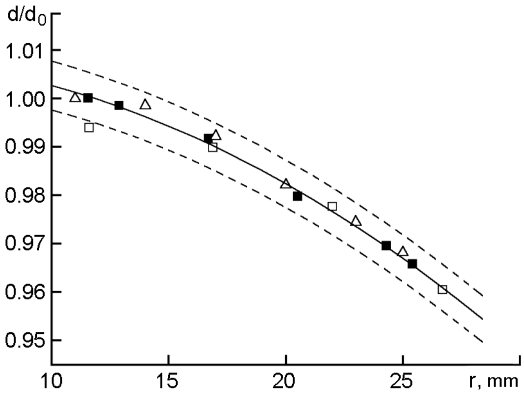

Fig. 6. The calculation (solid squares) and experimental (triangles and open squares) normalized period distribution along the concave mirror surface.

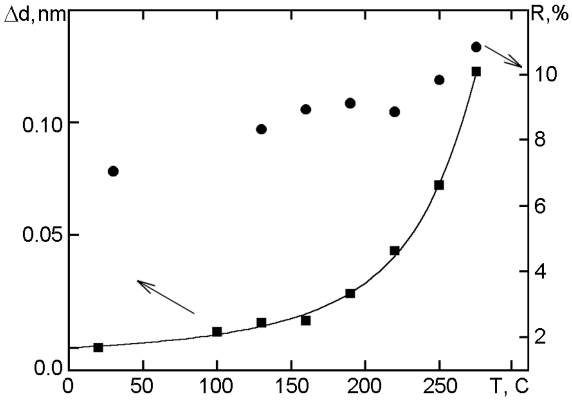

Fig. 7. Dependence of period increase (squares) and reflectivity circles from annealing temperature.

mirror radius) is about 3 %. The dashed lines indicate a zone outside which the double mirror optics reflectivity is halved.

To obtain the required period distribution across a concave mirror, two techniques of shadow mask deposition have been applied. In the former, axially rotated substrate was translated under the masked targets at variable velocity. The shadow mask was designed to get uniform coating onto a flat substrate being translated with constant velocity [20]. The substrate traveling law was fitted using deposition process computer simulation for both cobalt and carbon separately. The results of applying this technique are represented in Fig. 6 by solid squares. The measured period distribution is very close to the design chart (triangles) and deviation is less than 0.23 %, accordingly, the reflectance loss at a specified point of the concave mirror should not exceed 20 %.

In the second case, the axially rotated substrate was exposed for appropriate time under open Co target and C target covered by a mask of another design. Exposition of the concave substrate under the open cobalt target brings the thickness distribution of Co very close to the calculated law at corresponding choice of the substrate distance. The carbon target was covered by a shadow mask that corrected the exposition time for specific substrate points and required thickness distribution was obtained by several refinements of its shape. The open squares in Fig. 6 show the obtained period distribution with desired accuracy, a central part excepted, within the whole working range. The additional experiments have to be performed to define the mask shape and placement more exactly.

It is well known that the period and reflectivity of metal/carbon X-ray mirrors vary during heating [21, 22]. As it has been shown for Ni/C, Cr/C, Cr_3C_2/C, and CrB_2/C mirrors, both the period and reflectivity increase at the initial stage of annealing. This feature of the carbon-based mirrors is very important for period correction in the case of a somewhat shorter multilayer period than needed was obtained. The absolute variation of the period and reflectivity depends on the nature of materials, the period value, and the thickness ratio of the components. In this connection, the influence of heat treatment on the period and reflectivity change in the Co/C mirrors with periods around 2.3 nm has been studied. The data obtained from the small angle diffraction (Cu Kα) are presented in Fig. 7. It is seen that the multilayer period increases from 0.01 to 0.125 nm when the temperature rises from 100 to 275°C. The reflectivity increases as well that is in agreement with the soft X-ray data (see Table 1). The annealing temperature elevation above 275° Co results in the mirror failure and, as a consequence, in the reflectivity dropping. The period dependence on the annealing temperature provide the correction of the coating period towards the design value for both objective mirrors. Meanwhile, the period distribution law does not undergo significant changes. A little deviation of the period from the initial distribution on convex mirror after annealing has been included in calculation of the period distribution law for matched concave mirror.

The obtained results of the study of the X-ray Co/C mirrors with period 2.3 nm substantiate an optimistic forecast for Schwarzschild objective development. The proposed and realized technique of mirror coating is: (i) covering a convex mirror; (ii) determination of the period distribution law; (iii) period calculation for a concave mirror; (iv) covering a concave mirror; (v) period adjusting annealing. The experimental data suggest that this is the technique of very good prospects in case of quasicontinuous X-ray source. The achieved correspondence of calculated and experimentally observed period distribution laws for a concave mirror implies an opportunity to deposit 200 Co and C layer pairs and, in spite of narrowing bandwidth to $\Delta\lambda \approx 0.025$ nm in "carbon window", to increase the objective throughput twice in comparison with one-hundred-period mirrors. However, extension of the multilayer to 300 bi-layers requires additional efforts for decreasing thickness errors in the course of deposition, investigation of roughness evolution across the multilayer stack, etc. The interaction between Co and C under deposition is accompanied by the multilayer contraction, changing the layer thickness ratio, and density reduction of cobalt-containing layer in comparison with the density of a single Co layer. These features will be taken into consideration to carry out optimal design of the Schwarzschild mirrors. The results of the study demand the next step in objective development, namely, the soft X-ray test in "carbon window": point-to-point reflectivity measurements as a function of wavelength under the normal incidence angles in the working range of matched mirrors.

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Нанорозмірні багатошарові плівкові композиції Co/C для об'єктива Шварцшильда на "вуглецеве вікно"

Є.А.Бугаєв, О.Ю.Девізенко, Є.Ь.Зубарєв, В.В.Кондратенко

Досліджено особливості формування багатошарових плівкових композицій Co/C з періодом ≈2,3 нм з метою створення об'єктива Шварцшильда на "вуглецеве вікно" для біологічних і медичних досліджень. Запропоновано послідовність нанесення багатошарових покриттів на криволінійні підкладки, що забезпечує узгоджену роботу двох дзеркал об'єктива. Розглянуто особливості взаємодії шарів Co і C у процесі вирощування, зміни періоду і відбивної здатності при нагріванні.