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Features of Mg_2Si Layer Growth in Si/Mg_2Si Multilayers

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The features of magnesium silicide layer growth in Si/Mg_2Si multilayers in the initial state and after thermal annealing were studied by methods of transmission electron microscopy and X-ray scattering. As-deposited magnesium silicide layers are amorphous with nanocrystalline inclusions of metastable *h*-Mg_2Si. Formation of Mg_2Si in the hexagonal modification occurs under the influence of stresses produced by silicon layers. At $T = 723$ K, Mg_2Si layers finish crystallization in the hexagonal modification with some grain coarsening that is accompanied by 7.3 % reduction in the Si/Mg_2Si multilayer period.

Keywords: X-Ray mirror, Magnesium silicide, X-Ray phase analysis, Electron microdiffraction.

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1. INTRODUCTION

The choice of materials to produce highly reflecting multilayer X-ray mirrors (MXM) is determined by the corresponding values of their optical constants and the technological possibilities of manufacturing on their basis multilayer periodic compositions of alternating nanometer (subnanometer) continuous layers with an acceptable interlayer roughness. According to the rule of the choice of materials to produce MXM [1], which was formulated by E. Spiller, one of the two materials should have a minimum absorption in a specified region of the X-ray spectrum. Si, C, B_4C and Mg belong to such materials. The first three of them are widely used to produce MXM in the wavelength range of 4-14 nm. As for Mg, due to its optical characteristics, it is the most promising for two regions of the X-ray spectrum, namely, 0.989-2.5 nm and 25.1-35 nm. The first region is of interest for X-ray spectral analysis of such chemical elements as Mg, Na, F and O. The second one – for astrophysics, in order to obtain images of the solar corona in the radiation of multiply charged iron ($\lambda = 28.42$ nm) and helium ($\lambda = 30.38$ nm) ions [2].

However, the use of Mg to create MXM is limited by two important properties of this material: low melting point ($T_{melt} = 923$ K) and high chemical activity. A low melting point restricts the possibility of MXM use with magnesian layers at elevated temperatures and makes it difficult to produce continuous ultrathin layers.

As a result of high chemical activity, during manufacture and subsequent operation, there is an interlayer interaction between Mg and most of the materials promising for the production of MXM that is accompanied by a loss of reflectivity. A transition to a chemical compound based on Mg may be a middle course. So, the compound Mg_2Si is more high-melting ($T_{melt} = 1375$ K) than Mg and less chemically active. Mg_2Si is slightly inferior in its optical characteristics to Mg in both the shortwave and longwave spectral regions. Moreover, as the calculations for the shortwave region show, Mg_2Si in combination with tungsten has a higher reflectivity than W/Si MXM, which are traditionally used in X-ray spectral analysis to control the chemical elements Mg, Na, F, O.

The values of the real (n) and imaginary (k) parts of the refraction index of Mg and Mg_2Si for the wavelength of 30.4 nm are close ($n_{Mg} = 0.985$, $k_{Mg} = 0.0028$, $n_{Mg2Si} = 0.965$, $k_{Mg2Si} = 0.0047$), therefore, magnesium silicide can be chosen as a low absorbing layer in the longwave range. The values of n and k were taken from CXRO [3].

Despite the fact that the first proposals on the use of Mg_2Si as a low absorbing layer of X-ray mirrors were made more than 25 years ago [4], at present there is no detailed information on the growth features and structure of nanosized Mg_2Si layers. In this paper we studied the possibility of producing a multilayer Si/Mg_2Si composition with an emphasis on investigating the features of the formation of Mg_2Si layers, as well as their temporal and thermal stability.

The choice of a pair of Si/Mg_2Si materials is caused by prospective application of MXM based on it for the wavelength range of 25.1-35 nm due to, first, the optical constants. Secondly, this eutectic pair of materials allows to avoid interlayer interaction in both the manufacture and subsequent thermal exposure that increases the thermal resistance of MXM on its basis.

Investigation of the structure of magnesium silicide layers in the multilayer Si/Mg_2Si composition allows to obtain important information on the density, thickness and roughness of each layer due to the possibility of modeling the spectra of small-angle X-ray diffraction. It is also necessary to note that the absence of interlayer interaction in this system makes it easier to separate the processes of structural-phase transformations occurring in each MXM layer.

2. EXPERIMENTAL

Si/Mg_2Si samples with a period (the sum of the thicknesses of a pair of alternating layers) $d = 14.7$ nm (Si = 7.7 nm and Mg_2Si = 7 nm) and the number of periods $N = 30$ on glass and single-crystal Si (111) and Si (001) substrates were manufactured by the method of direct-flow magnetron sputtering in an argon atmosphere. The layer thickness was controlled by setting the substrate transport speed over the targets. The deposition rate of the substance from Si and Mg_2Si targets was stable.

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The structure of a multilayer periodic Si/Mg_2Si composition was studied by electron microdiffraction and X-ray diffractometry followed by computer simulation. To obtain images of electron microdiffraction, a transmission electron microscope PEM-U was used. The magnitude of the accelerating voltage was 100 kV. X-ray studies were performed on a X-ray diffractometer DRON-3M in Cu-$K_{\alpha 1}$ radiation ($\lambda = 0.15405$ nm). When imaging small-angle X-ray diffraction patterns, the survey method of (θ-2θ)-scanning was applied. The diffraction patterns for X-ray phase analysis were taken in glancing incidence geometry (GIXRD) at a glancing angle of 2.5° [5, 6]. In this case, the reflections with different $(hkl)_i$ are taken at a fixed position of a polycrystalline sample. Moreover, the diffraction patterns for X-ray phase analysis were taken in (θ-2θ)-geometry. Simulation of the spectra of small-angle X-ray diffraction was conducted in the X-ray Calc program [7] based on the Fresnel formulas taking into account the interlayer roughness.

The measurement of the radius of curvature was performed by the X-ray diffraction method. The survey was carried out on a X-ray diffractometer DRON-3M in Cu-$K_{\alpha 1}$ ($\lambda = 0.15406$ nm) and Cu-$K_{\alpha 2}$ ($\lambda = 0.15444$ nm) radiation. Based on the X-ray diffraction data, the angular distance ω between the maxima of Cu-$K_{\alpha 1}$ and Cu-$K_{\alpha 2}$ was determined. Stresses in silicon films were calculated from the measured values of the radius of curvature of Si (001) single-crystal substrate by the Stoney formula [8].

Annealing of Si/Mg_2Si MXM was performed in a vacuum chamber at a pressure of $P = 10^{-6}$ Pa in the temperature range of 373-723 K.

3. RESULTS AND DISCUSSION

In Fig. 1 we illustrate the experimental small-angle X-ray diffraction pattern from Si/Mg_2Si MXM on a glass substrate.

We should note the low intensity of the Bragg maxima. This is associated with the fact that in the hard X-ray range, the optical contrast is determined by the difference in the densities of the layer composing the MXM. The low oscillation intensity is largely due to the close values of the densities of silicon and magnesium silicide. Indeed, according to the results obtained from the simulation of the experimental spectrum of small-angle X-ray diffraction, the densities of Mg_2Si and Si layers are equal to 2.2 g/cm^3 and 2.23 g/cm^3, respectively (Table 1).

Calculated based on the experimental data obtained from a small-angle X-ray diffraction pattern, the values of the densities of magnesium silicide and silicon differ from the reference values corresponding to bulk materials ($\rho_{c\text{-}Mg_2Si} = 1.99$ g/cm^3, $\rho_{Si} = 2.33$ g/cm^3).

We have already obtained different multilayer compositions with silicon as one of the layers, and its density varied within the range of 2.27-2.33 g/cm^3 [9, 10]. At that, the silicon target was sputtered at a working gas pressure of 0.2 Pa. Due to the sputtering characteristics of the magnesium silicide target, the minimum working gas pressure in the chamber was 0.3 Pa that is the reason for the growth of silicon layers with a density lower than the reference one.

To confirm the effect of the working gas pressure on the silicon layer density, single-layer silicon films were produced on glass substrates obtained at a working gas

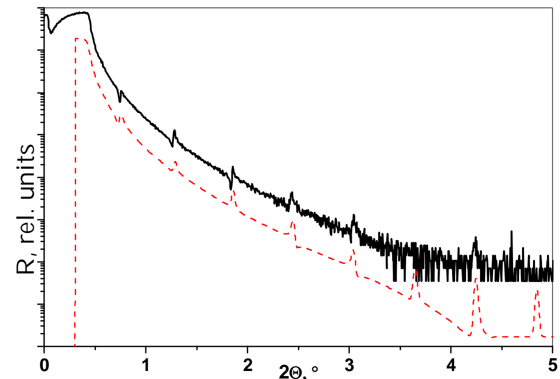


Fig. 1 – Experimental (——) and calculated (-----) small-angle X-ray diffraction patterns in Cu-$K_{\alpha 1}$ radiation from Si/Mg_2Si MXM with a period of 14.7 nm and the number of layer pairs $N = 30$. The calculated and experimental diffraction patterns are spaced along the ordinate axis

Table 1 – The data obtained in the simulation of the mirror reflection curve of Si/Mg_2Si MXM

Number of periods	Material	Layer thickness, nm	ρ, g/cm^3	Interlayer roughness, nm
1	SiO_2	1.5	2.18	0.9
	Si	7.7	2.23	0.3
30	Mg_2Si	7.0	2.2	0.3

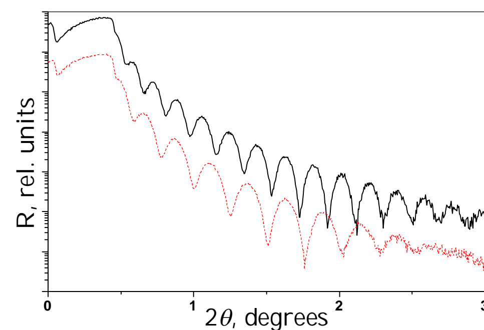


Fig. 2 – Experimental spectra of small-angle X-ray diffractions in Cu-$K_{\alpha 1}$ radiation from the Si films obtained at a working gas pressure in the chamber of 0.16 Pa (——) and 0.3 Pa (-----). The diffraction patterns are spaced along the ordinate axis

pressure of 0.16 and 0.3 Pa. According to the simulation of the experimental spectra of small-angle X-ray diffractions (see Fig. 2), the density of single-layer silicon films obtained at a pressure of 0.16 Pa and 0.3 Pa was equal to 2.33 g/cm^3 and 2.23 g/cm^3, respectively.

The density of magnesium silicide layers calculated from small-angle X-ray diffraction is, on the contrary, larger than the reference density of cubic magnesium silicide produced under standard conditions. The X-ray diffraction pattern of the phase analysis obtained from Si/Mg_2Si MXM ($d = 14.6$ nm, $N = 30$) in the initial state contains only a halo from amorphous silicon layers, and reflexes from the Mg_2Si crystalline phase are absent (see Fig. 3b). At the same time, according to the data obtained from electron microdiffraction of Si/Mg_2Si MXM cross-sections (Fig. 3a), the magnesium silicide layers consist of the amorphous and crystalline phases. At that, magnesium silicide crystallizes in the hexagonal modification, as evidenced by the presence of Mg_2Si (402), Mg_2Si (412), Mg_2Si (621), Mg_2Si (524) reflections. Nevertheless, the density obtained as a result of modeling the experimen-

tal spectra of small-angle X-ray diffraction is less than the density of the hexagonal (2.35 g/cm^3) and is higher than the density of the cubic (1.99 g/cm^3) magnesium silicide. This is explained by the presence in Mg_2Si layers of the amorphous and crystalline hexagonal phases of magnesium silicide, since in the modeling of the small-angle X-ray diffraction spectra, the calculated material density is averaged over the layer thickness.

Thus, based on the results of X-ray phase analysis and electron microscopy of the cross-sections of Si/Mg_2Si MXM, it is established that magnesium silicide layers in the initial state represent the amorphous matrix with inclusions of magnesium silicide nanocrystals in the hexagonal modification. This agrees well with the data on the density of layers obtained from modeling the experimental spectrum of small-angle X-ray diffraction.

It should be noted that the hexagonal modification of magnesium silicide is metastable and certain conditions are necessary for its formation. Thus, Mg_2Si with the hexagonal lattice was obtained in [11] at a pressure of 2.5 GPa and a temperature of 1173 K. In this case, it is noted that this material possess higher resistance to the action of mineral acids and moist air than cubic Mg_2Si. Formation of the hexagonal Mg_2Si modification is possible in Al-Mg-Si alloys [12], while it is reported in [13] that formation of this phase occurs under the influence of stresses, the source of which is aluminum.

We believe that in Si/Mg_2Si MXM, crystallization of magnesium silicide layers in the hexagonal, not in the cubic, modification is associated with the action of compressive stresses, the source of which is the silicon layers. The fact that compressive stresses ($\sigma \approx -1.2$ GPa) are developed in thin silicon films obtained by the method of direct-flow magnetron sputtering is reported in [14]. The stresses measured in the single-layer silicon films of 450 nm thick were approximately equal to 0.7 GPa. The smaller magnitude of the stresses compared with the literature data is caused by the fact that we deposited silicon films in a lower vacuum (P = 0.3 Pa.

To study the effect of temperature on the Mg_2Si layers, we performed a series of annealing of the sample 1, which was the Si/Mg_2Si MXM on the Si (111) substrate with a number of periods of 30 and layer thicknesses of Si = 7.7 nm and Mg_2Si = 7 nm in the temperature range 373-723 K with a step of 50 K. After each annealing, a small-angle X-ray diffraction pattern was taken and the period was measured.

Thermal annealing of Si/Mg_2Si MXM to 573 K does not lead to significant changes in the position and intensity of the maxima on the small-angle X-ray diffraction pattern (see Fig. 4). The subsequent heating of Si/Mg_2Si MXM to 623 K is accompanied by an increase in the intensities of the diffraction maxima. Moreover, there is a sharp decrease in the period by 0.51 nm in the temperature range of 573-673 K (Fig. 5). This behavior of the dependence of the period on the annealing temperature is typical for lots of metal-silicon X-ray mirrors and it is associated, as a rule, with the formation of mixed zones at the MXM interlayer boundaries. Since the Si-Mg_2Si system is eutectic, the possibility of interaction between silicon and magnesium silicide layers is excluded. We believe that the decrease in the Si/Mg_2Si MXM period is associated with processes occurring in the Mg_2Si layers, namely, with crystallization.

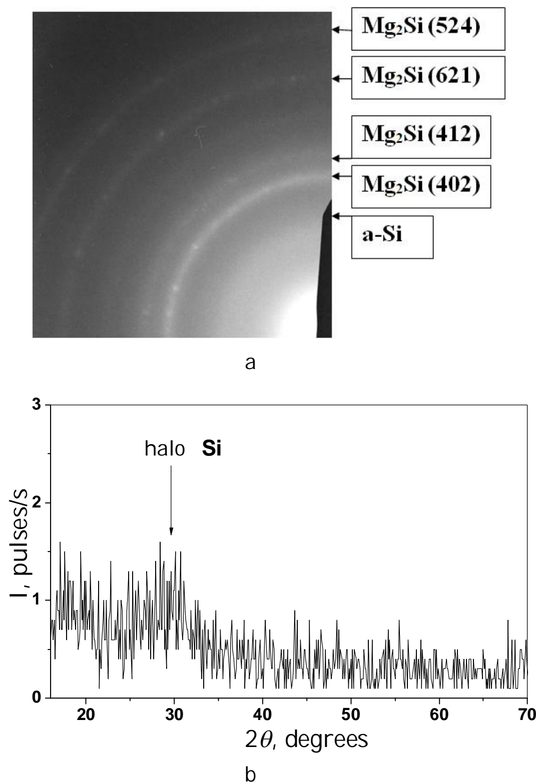


Fig. 3 – Electron microdiffraction of the Si/Mg_2Si MXM cross-section in the initial state (a) and diffraction pattern of Si/Mg_2Si MXM in Cu-K_α radiation (b)

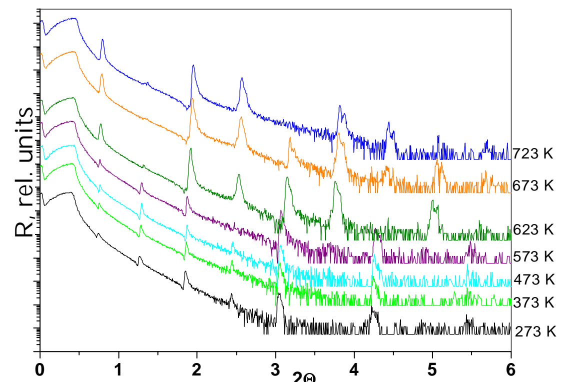


Fig. 4 – Small-angle X-ray diffraction patterns in Cu-$K_{\alpha 1}$ radiation from Si/Mg_2Si MXM in the initial state and after annealing

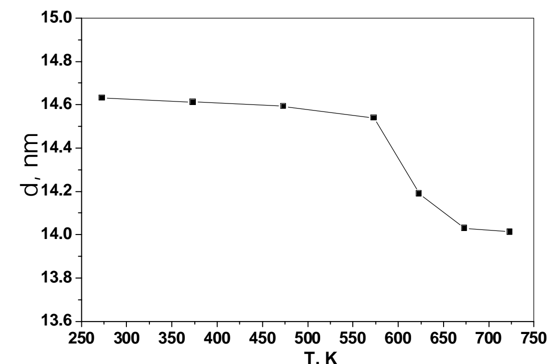


Fig. 5 – Dependence of the period of Si/Mg_2Si MXM on the annealing temperature

To experimentally confirm the relationship between the decrease in the period and the crystallization processes in magnesium silicide layers, sample 2 was prepared with a 30 Si/Mg_2Si periodic coating, in which the Mg_2Si thickness was doubled compared with the Mg_2Si thickness in sample 1. The obtained sample was annealed at a temperature of 673 K. At that, the value of the period of the multilayer periodic Si/Mg_2Si coating in sample 2 decreased by 1.2 nm that is two times greater than in sample 1. Obviously, this is associated with the fact that the magnesium silicide layer thickness in sample 2 was two times larger that confirms the relationship between the decrease in the period in Si/Mg_2Si MXM with processes occurring in magnesium silicide layers. A change in the silicon layer thickness was not observed in this case.

The obtained data on the decrease in the period in samples 1 and 2 confirm the absence of interaction between the layers in Si/Mg_2Si MXM during heating. This is associated with the fact that an increase in the thickness of one of the X-ray mirror layers consisting of materials, which can interact with each other, should not lead to an increase in the period shrinkage as a result of the action of high temperatures on the condition that the MXM layer thicknesses are sufficient to completely form a mixed zone.

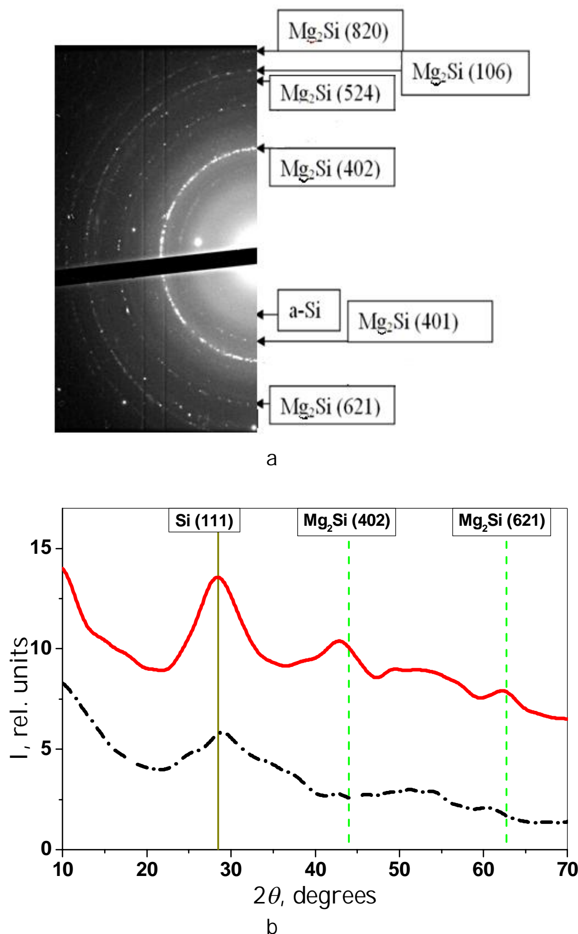
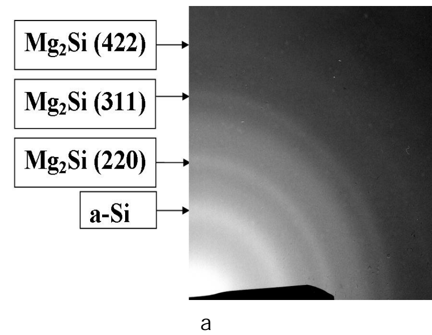


Fig. 6 – Electron microdiffraction of the Si/Mg_2Si MXM cross-section after annealing at a temperature of 723 K (a). Diffraction patterns in Cu-$K_{\alpha 1}$ radiation from Si/Mg_2Si MXM in the initial state (·····) and after annealing at a temperature of 723 K (–––) are obtained in the glancing incidence geometry (b)



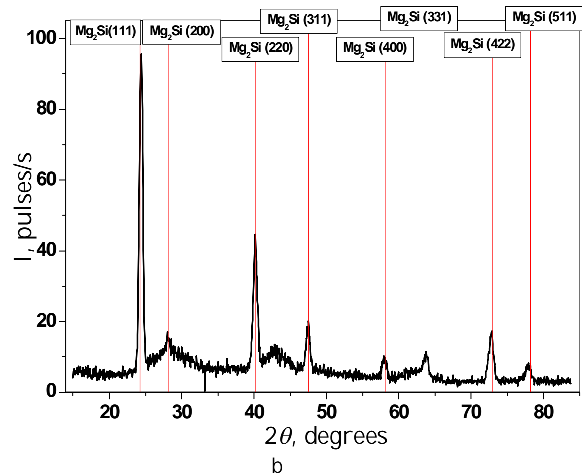


Fig. 7 – Electron microdiffraction of Si/Mg_2Si MXM deposited on a carbon film (a). Diffraction pattern in Cu-$K_{\alpha 1}$ radiation of single-layer Mg_2Si film of 1 μm thick annealed at 723 K (b)

A decrease in the Si/Mg_2Si MXM period is accompanied by the crystallization and recrystallization processes of magnesium silicide layers. This is confirmed by X-ray phase analysis (Fig. 6b) and electron microdiffraction of cross-sections of Si/Mg_2Si MXM annealed at a temperature of 723 K (Fig. 6a). At that, according to the results of modeling the spectra of small-angle X-ray diffraction patterns, the density of magnesium silicide layers increases from 2.2 g/cm^3 in the initial state to 2.35 g/cm^3 after annealing, i.e. to the density of the corresponding hexagonal modification. The increased difference in the density of Si and Mg_2Si layers explains the increase in the intensity of the orders of reflection in the small-angle X-ray diffraction patterns. An increase in the density of Mg_2Si as a result of crystallization makes 6.8 %; and the thickness of magnesium silicide layers in Si/Mg_2Si MXM decreases by 7.3 % during annealing in the temperature range of 573-673 K. The obtained data are close and confirm the relationship between the decrease in the period and the crystallization processes in magnesium silicide layers and also imply that the simulation is performed correctly. The difference of 0.5 % is at the level of error with which the density is determined.

It should be noted that stresses are developed exactly in the film-substrate system, since if the film is separated from the substrate, then the stresses in a "free" film are relaxed. Therefore, to confirm the effect of strained silicon layers on crystallization of magnesium silicide in the hexagonal modification, we performed the following experiment. A carbon film (H = 30 nm) was deposited on NaCl substrate and further separated from the substrate

and placed on a copper mesh, which is applied to obtain electron microscopic images. A Si/Mg_2Si MXM was deposited on the prepared carbon film. Thus, we obtained the Si/Mg_2Si MXM, in which silicon layers are in the unstressed state. The electron microdiffraction was taken after thermal annealing at $T = 723$ K (Fig. 7a). According to the results obtained from microdiffraction, magnesium silicide layers crystallized in the cubic modification that confirms the effect of stresses, the source of which is the silicon layers, on the crystallization of Mg_2Si.

It is important to note that a single-layer Mg_2Si film also crystallizes at $T = 723$ K in the cubic modification (Fig. 7b). This is one more confirmation of the effect of stresses, the source of which is the silicon layers, on the formation of Mg_2Si layers in the hexagonal modification.

It should be noted that magnesium silicide layers have a low level of the root-mean-square roughness $\sigma \approx 0.3$ nm that is less than for such MXM as SiC/Mg, ZrC/Mg, Co/Mg, in which σ exceeds 0.5 nm [15-17]. The theoretically calculated reflection coefficient of the Si/Mg_2Si MXM with a real layer structure was equal to 36 % that indicates the prospects of using this pair of materials to create X-ray mirrors. The period shrinkage, which is observed during annealing up to 673 K, can be removed by performing preliminary heat treatment of X-ray mirrors produced with a pre-calculated long period.

4. CONCLUSIONS

In this paper, the features of the formation of nanosized Mg_2Si layers and the possibility of their use in the Si/Mg_2Si MXM are studied for the first time.

It is established that the densities of silicon and magnesium silicide layer differ from the reference values and are equal to 2.2 g/cm^3 and 2.23 g/cm^3, respectively. The lower silicon density compared to the reference value is caused by the deposition of multilayer Si/Mg_2Si coatings at a relatively high working gas pressure of 0.3 Pa. The larger magnesium silicide density in comparison with the reference value is caused by its structure.

According to the results of X-ray phase analysis and electron microscopy of the Si/Mg_2Si MXM cross-sections, the magnesium silicide layers in the initial state are an amorphous matrix with inclusions of magnesium silicide nanocrystals in the hexagonal modification.

The Si/Mg_2Si MXM structure remains constant during heating to 573 K. As a result of thermal annealing to 673 K, there is a sharp drop of the period associated with magnesium silicide crystallization in the hexagonal modification from the Mg_2Si amorphous phase and, as a consequence, an increase in the density of magnesium silicide layers to 2.35 g/cm^3. At that, a high level of periodicity is preserved in Si/Mg_2Si MXM.

The increase in the Mg_2Si density upon heating leads to a decrease in the reflection coefficient of the Si/Mg_2Si mirrors by 10 relative percentage. Such a reduction is not principal taking into account the possibility of operating mirrors at elevated temperatures.

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