ISSN 1027-5495. Functional Materials, 28, No.1 (2021), p. 196-201.
doi:https://doi.org/10.15407/fm28.01.196 © 2021 — STC "Institute for Single Crystals"

Characterization of Si/Mg_2Si multilayer mirrors manufactured by sputtering of Mg and Si targets

L.E.Konotopsky, I.A.Kopilets, V.V.Kondratenko, A.V.Fedchenko, S.M.Kosmachev

National Technical University "Kharkiv Polytechnic Institute",
2 Kyrpychov Str., 61002 Kharkiv, Ukraine

Received May 4, 2020

The principal possibility of manufacturing Si/Mg_2Si multilayers by alternately deposited Si and Mg layers is demonstrated. The study of such Si/Mg_2Si multilayer structure in the initial state and after thermal annealing in a temperature range of 100–300°C was made by X-ray diffraction methods. It was shown that a low level of the interface roughness (~ 0.8 nm) can be achieved in the Si/Mg_2Si multilayer manufactured by the proposed method. Such Si/Mg_2Si multilayers are stable up to 300°C.

Keywords: magnetron sputtering, multilayer X-Ray mirror, magnesium silicide, X-ray diffraction, thermal stability.

Дослідження багатошарових рентгенівських дзеркал Si/Mg_2Si, виготовлених методом розпилення мішеней Mg і Si. *Л.Є.Конотопський, І.А.Копилець, В.В.Кондратенко, А.В.Федченко, С.М.Космачов*

Продемонстрована принципова можливість виготовлення багатошарових рентгенівських дзеркал Si/Mg_2Si почерговим нанесенням шарів Si і Mg. Дослідження такої багатошарової структури Si/Mg_2Si у вихідному стані та після термічного відпалу в інтервалі температур 100–300°C проводилося методами рентгенівської дифрактометрії. Показано, що у багатошарових структурах Si/Mg_2Si, виготовлених запропонованим способом, може бути досягнутий низький рівень міжшарової шорсткості (~ 0,8 нм). Такі багатошарові дзеркала Si/Mg_2Si стабільні до 300°C.

Продемонстрирована принципиальная возможность изготовления многослойных рентгеновских зеркал Si/Mg_2Si поочередным нанесением слоев Si и Mg. Исследование такой многослойной структуры Si/Mg_2Si в исходном состоянии и после термического отжига в интервале температур 100–300°C проводилось методами рентгеновской дифрактометрии. Показано, что в многослойных структурах Si/Mg_2Si, изготовленных предложенным способом, может быть достигнут низкий уровень межслоевой шероховатости (~ 0,8 нм). Такие многослойные рентгеновские зеркала Si/Mg_2Si стабильны до 300°C.

1. Introduction

The manufacturing of highly reflective multilayer X-ray mirrors (MXMs) for the 28–33 nm wavelength range is an important problem. Such MXMs are necessary for obtaining images of the Sun with high spatial resolution in the mentioned spectral range [1], as well as for spectral diagnostics of solar plasma and study of the structure of coronal mass ejections.

According to its optical constants [2], Mg is one of the best spacer materials to create MXMs operating at wavelengths greater than 25.1 nm. Magnesium-based MXMs, such as SiC/Mg [3], Y_2O_3/Mg [4], Co/Mg [5], ZrC/Mg [6] are able to provide a reflectivity

of more than 30 % at a wavelength of 30.4 nm. The main disadvantage of these X-ray mirrors is their low thermal stability, which is associated with the high chemical activity of magnesium and its low melting point.

In this paper, we propose to use a magnesium-based compound — magnesium silicide (Mg_2Si) as a spacer layer. It is advantageous to use silicon as the second material in the multilayer. According to the theoretical calculation, Si/Mg_2Si MXMs provide a reflectivity of 42 % at a wavelength of 30.4 nm. The magnesium silicide has a high melting point (1102°C) [7]. Interaction between the layers will be absent, due to the absence of a homogeneity area of Mg_2Si [8]. So, the thermal stability of the Si/Mg_2Si MXMs might be expected to be significantly higher than that of mirrors based on pure magnesium.

Si/Mg_2Si MXMs fabricated by DC magnetron sputtering of Si and Mg_2Si targets have already been studied [9]. A significant disadvantage of these MXMs is that the Mg_2Si layers consist of an amorphous matrix with inclusions of Mg_2Si nanocrystals in the metastable hexagonal modification, which is denser than Mg_2Si in the equilibrium cubic modification. Higher density of h-Mg_2Si leads to a decrease in the reflectivity to 36 %. In addition, annealing at 400°C results in a sharp decrease in the multilayer period (by 0.6 nm). That is associated with the crystallization of the amorphous Mg_2Si in the hexagonal modification which is also accompanied by a reduction in the reflectivity [10].

On the other hand, it is known [11] that upon deposition of a thin Mg film, magnesium reacts with silicon of a bulk substrate to form Mg_2Si in a stable cubic modification. However, such important issues for the manufacture of MXMs as the thickness of the silicide layer, the roughness of the interlayer interfaces, and the possibility of ensuring a strict periodicity of the layers, remain unclear. We are aimed to investigate the possibility of manufacturing Si/Mg_2Si MXMs through the interaction of thin Mg and Si films during their deposition.

2. Experimental

The Si/Mg_2Si multilayers were deposited onto glass (30×20 mm^2) and polished silicon (001) wafers (10×10 mm^2) using alternating DC magnetron sputtering of Mg and Si targets. Before deposition, the residual gas pressure was 10^{-4} Pa and the Ar sputtering gas pressure was 0.2 Pa. Substrates were cleaned by Ar ions before deposition.

The X-ray reflectivity of multilayer structures at grazing incidence was measured in the Θ–2Θ mode. The measurements were performed with a DRON-3M diffractometer using Cu–Kα1 radiation in a two-crystal scheme with a Si (110) monochromator. The periodicity of the multilayers was determined by the full Bragg equation (taking into account refraction). X-Ray diffraction measurements at wide angles were carried out in the Θ–2Θ mode at the same wavelength with the diffractometer equipped with a graphite analyzer.

The numerical parameters of the multilayers, such as the thickness of the layers, their densities and the interlayer roughness were determined by mathematical modeling of grazing incidence X-Ray diffraction patterns using the IMD program [12]. In this program, the calculated diffraction pattern is fitted to the experimental one by changing the parameters of the multilayer (layer thickness, density, roughness).

The calculation of the reflectivity of the multilayers was carried out according to the standard recursive formulas for the reflection by periodic structures [12, 13].

The specimens were annealed in vacuum furnace at 10^{-4} Pa in a temperature range of 100–300°C in steps of 100°C. The time of each annealing was 1 h.

3. Results and discussion

The Mg–Si phase diagram [8] indicates that only one compound (Mg_2Si) can be formed in this system. The reaction of magnesium with silicon to form magnesium silicide is described with the well known formula:

$$Si + 2Mg \rightarrow Mg_2Si. \quad (1)$$

According to theoretical calculations, the maximum reflectivity of Si/Mg_2Si MXM at normal incidence with a wavelength of 30.4 nm can be achieved with layer thicknesses of H_{Si} = 7.3 nm and H_{Mg2Si} = 8.6 nm.

There were two stages in the deposition of each period. At the first stage, thin layers of Mg and Si were deposited to obtain a layer of Mg_2Si. The thicknesses of the Mg and Si layers were chosen on the assumption that they completely interacted with each other. The 6.25 nm of magnesium and 2.69 nm of silicon are needed to form 8.6 nm of magnesium silicide. At the second stage, Si was deposited on the obtained Mg_2Si, as shown in Fig. 1a. The alternation of the steps of layer deposition described

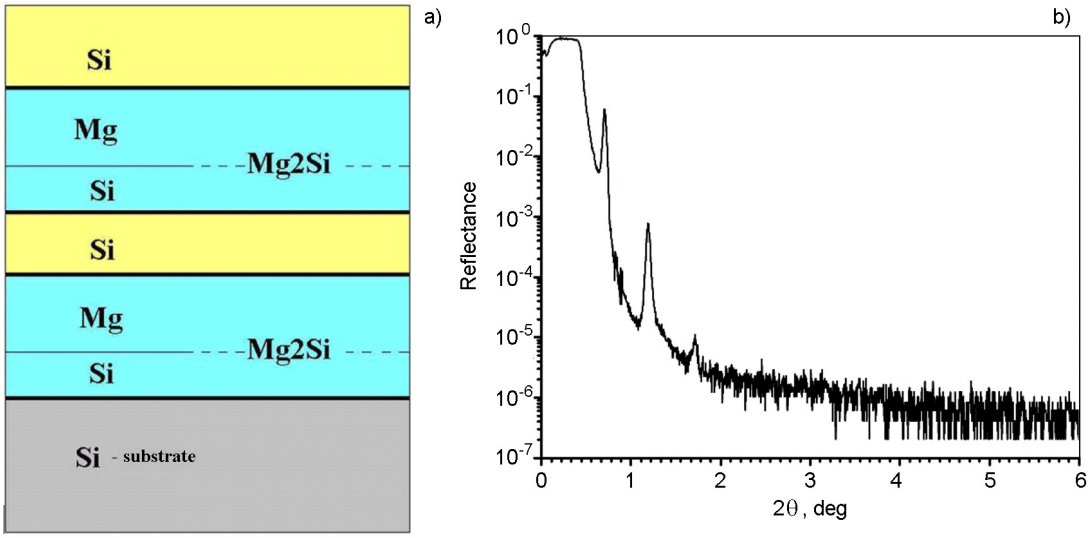

Fig. 1. a) Schematic image of the Si/Mg_2Si MXM construction; b) grazing incidence X-Ray reflectivity pattern for the Si/Mg_2Si MXM ($H_{Mg2}Si$ = 8.6 nm, H_{Si} = 7.3 nm).

above allows one to create Si/Mg_2Si MXM with the required number of periods. Fig. 1b shows the experimental grazing incidence X-Ray reflectivity (GIXRR) scan for such MXM.

In the obtained diffraction pattern, the Bragg maxima are observed only up to 2Θ = 2 deg. This indicates a high interfacial roughness of the X-ray mirror. The results are in agreement with the data on the roughness value obtained by other authors [14] who studied the Si/Mg MXM.

We think that the high level of the interfacial roughness (compared to other Si-based multilayers) is due to the peculiarities of the growth of magnesium layers. To verify this assumption, a relationship was established between the roughness value on the thickness of the magnesium layers (2nd column of Table 1) which further reacts with silicon layers and forms layers of magnesium silicide. For this purpose, a series of X-ray multilayers with parameters presented in Table 1 were made.

Figure 2a shows the experimental and theoretically calculated GIXRR curves corresponding to the Si/Mg_2Si multilayers from Table 1. The values of the interface roughness presented in the last column of Table 1 were obtained from modeling GIXRR spectra. They were used for plotting Fig. 2b. It is important to note that the best agreement between the calculated and experimental spectra was achieved using the density of magnesium silicide of 1.99 g/cm^3, which corresponds to the tabular value of the Mg_2Si density in a stable cubic modification [7]. As follows from Fig. 2b, the roughness decreases with decreasing thickness of the magnesium layers. The less roughness of the thinner magnesium layers is also confirmed by the positions of Bragg maxima on the GIXRR curves (Fig. 2a): they are observed up to 2θ = 5.5 deg for sample 5 (the magnesium thickness is 0.75 nm), while the peaks disappear even before 2θ = 3.5 deg for sample 2 (the magnesium thickness is 2.5 nm). The X-ray mirror with a magnesium layer thickness of 0.75 nm has the most "smooth" interlayer roughness of ~ 0.35 nm.

In order to ensure low roughness of thick Mg_2Si layers, we decided to form Mg_2Si layers by depositing several pairs of thin mag-

Table 1. Parameters of structure of the Si/Mg_2Si multilayers

No.	H_{Mg}, nm	$H_{Mg2}Si$	$d(H_{Si} + H_{Mg2}Si)$, nm	N(number of periods)	σ, nm
1	3.04	4.69	10.3	60	1.2
2	2.32	3.44	10.3	60	1
3	2.3	3.17	11.1	60	0.9
4	0.9	1.24	14.2	60	0.55
5	0.75	1	4.65	60	0.35

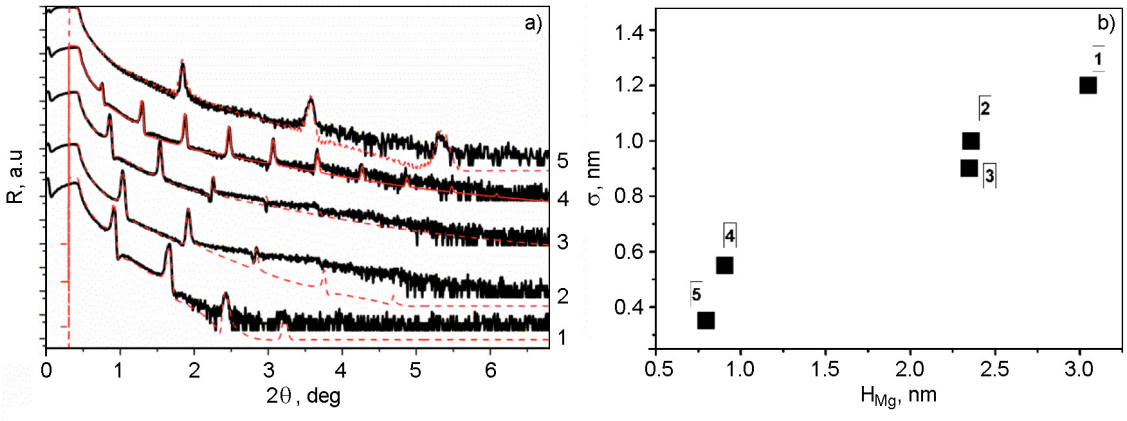

Fig. 2. (a) Experimental (solid line) and theoretical (dash-dotted line) GIXRR patterns of Si/Mg_2Si MXMs. For ease of perception, the diffraction patterns are spaced along the ordinate axis; (b) dependence of the interlayer roughness on the thickness of the magnesium layers in the Si/Mg_2Si

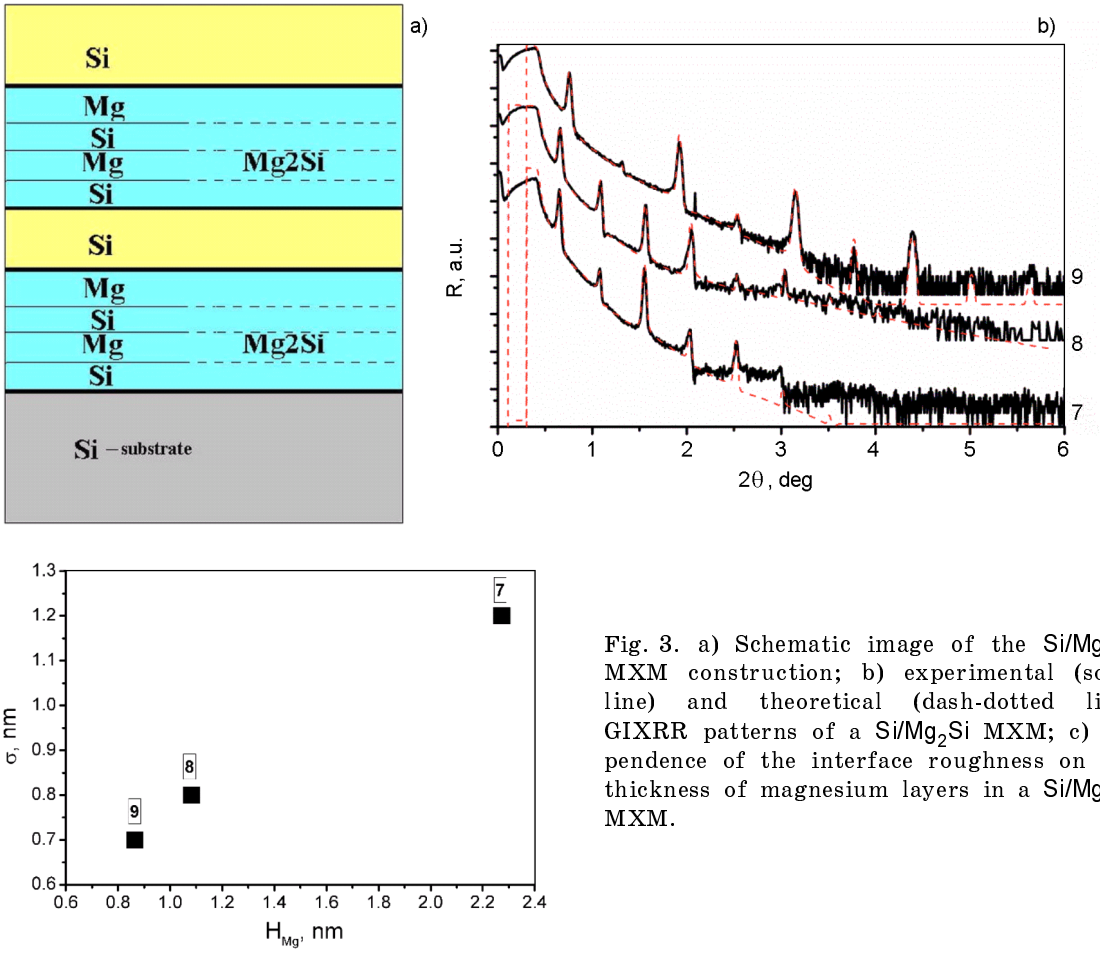

Fig. 3. a) Schematic image of the Si/Mg_2Si MXM construction; b) experimental (solid line) and theoretical (dash-dotted line) GIXRR patterns of a Si/Mg_2Si MXM; c) dependence of the interface roughness on the thickness of magnesium layers in a Si/Mg_2Si MXM.

nesium and silicon layers, as shown schematically in Fig. 3a. The thicknesses of Mg and Si should be chosen so that they fully interact with each other and form Mg_2Si layers of the required thickness. We found out how the proposed X-ray mirror manufacturing technology (Fig. 3a) affected the dependence of the interface roughness on the thickness of the magnesium layers. According to Fig. 3c, in the case of the formation of Mg_2Si layers as a result of the interaction of several pairs of magnesium and silicon layers, the dependence of the inter-

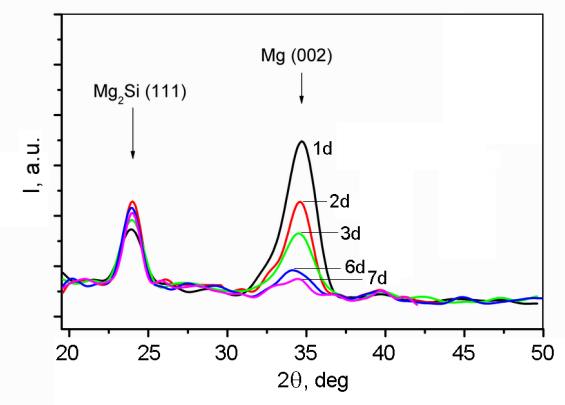

Fig. 4. X-ray diffraction patterns from the Si/Mg_2Si MXM (sample 7) in which Mg_2Si layers are formed from two pairs of Mg and Si layers (the magnesium layer thickness is of 2.27 nm).

face roughness on the thickness of the magnesium layers is the same as in the case of the interaction of one pair of magnesium and silicon layers.

The decrease in the interlayer roughness with a decrease of the thickness of the magnesium layers (Fig. 2b, 3c) is explained as follows. When magnesium is deposited on silicon, the magnesium immediately diffuses into silicon, forming a thin silicide interlayer of Mg_2Si. As the thickness of magnesium silicide increases, diffusion slows down. Starting with a thickness of 1.4 nm [15], Mg_2Si becomes a diffusion barrier for newly arrived Mg atoms. A further increase in the Mg thickness (of more than 1 nm) leads to the growth of a discontinuous magnesium film on the thin layer of magnesium silicide according to the island grows model, as shown in [16]. Subsequent deposition of silicon on a discontinuous magnesium layer leads to the further formation of magnesium silicide. The more the islands of magnesium have grown, the higher the roughness of resulting silicide layer. So, when magnesium is deposited with a thickness of more than 1 nm, a discontinuous (island) film of pure magnesium begins to grow on Mg_2Si. This is confirmed by the presence of the Mg (002) reflection on the X-ray diffraction pattern obtained from sample 7 (Fig. 4). Over time, the formation of silicide continues at room temperature as a result of the interaction of Mg with Si. As it can be seen from Fig. 4, after seven days of storage, the Mg (002) reflection almost completely disappeared, while the intensity of the Mg_2Si (111) reflection slightly increased.

The X-ray diffraction pattern (Fig. 5b) corresponding to the Si/Mg_2Si MXM with Mg layer thickness less than 1 nm (sample 8) shows no reflections related to the crystalline phases of Mg or its silicide. We suppose that amorphous Mg_2Si is formed in this case.

As mentioned above, the low thermal stability of magnesium-based X-ray mirrors is their main drawback. Even at temperatures of about 200°C, the reflectivity of the SiC/Mg, Y_2O_3/Mg, Co/Mg, ZrC/Mg MXMs significantly decreases. In this connection, the issue of the thermal stability of the Si/Mg_2Si MXM is important.

Annealing of the MXM (sample 8) at 200°C for 1 h (Fig. 5b) does not lead to changes in the X-ray pattern. The crystallization of Mg_2Si layers begins only at 300°C which is indicated by the appearance of Mg_2Si (111), Mg_2Si (220) and Mg_2Si (311) reflections. It should be noted that the annealing and crystallization of the silicide layers do not lead to a change in the angu-

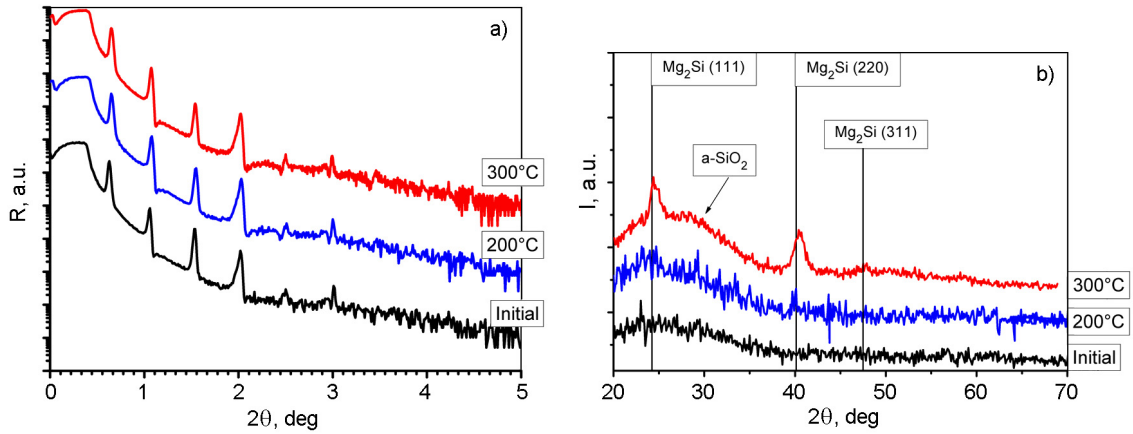

Fig. 5. Experimental GIXRR (a) and wide-angle X-ray diffraction; (b) patterns for the Si/Mg_2Si MXM (sample 8), in which Mg_2Si layers are formed from five pairs of Mg and Si layers.

Table 2. Structure parameters of the Si/Mg_2Si multilayers in which the Mg_2Si layers were formed by depositing several pairs of thin Mg and Si layers

No.	$(H_{Mg} + H_{Si})\times n^*$, nm	H_{Mg2Si}, nm	H_{Si}, nm	$d(H_{Si} = H_{Mg2Si})$, nm	N (number of periods)	σ, nm
7	(2.27 + 0.98)×2	6.2	11.7	17.9	60	1.2
8	(1.08 + 0.47)×5	7.5	10.2	17.7	60	0.8
9	(0.87 + 0.37)×6	7.2	6.9	14.1	60	0.7

*n — the number of pairs of Si and Mg layers in each period of the Si/Mg_2Si multilayers

lar positions of the Bragg maxima on GIXRR patterns (Fig. 5a), which means that the period of the MXM does not change during annealing. This fact demonstrates the advantage of Si/Mg_2Si MXMs manufactured by sputtering Si and Mg targets as opposed to using the Mg_2Si target.

According to Fig. 5a, heating up to 300°C does not lead to a change in the intensity of Bragg peaks. This fact indicates that the ratio of the thicknesses of the layers of magnesium and silicon did not change after annealing. This indirectly confirms the formation of magnesium silicide, rather than a mixture of magnesium and silicon in the initial state. In addition, the angular positions of the peaks on the GIXRR pattern do not change. This allows us to expect that the reflectivity of Si/Mg_2Si X-ray mirrors also does not change under the influence of temperatures up to 300°C inclusive.

4. Conclusions

The principal possibility of manufacturing Si/Mg_2Si MXMs by alternately deposited Si and Mg layers has been demonstrated. Si/Mg_2Si MXMs with a period of $d = 17.7$ nm and with a interface roughness at the level of 0.8 nm can be obtained by forming the 7.5 nm thick Mg_2Si layers as a result of the interaction of six pairs of Si and Mg layers ($H_{Mg} = 1.08$ nm, $H_{Si} = 0.47$ nm) during their deposition. In this case, magnesium silicide is formed in an amorphous state with a density corresponding to the tabular density of Mg_2Si in a cubic modification ($\rho = 1.99$ g/cm^3).

The Mg_2Si layers remain amorphous when heated up to 200°C. Annealing at 300°C leads to crystallization of the Mg_2Si layers. The crystallization of the Mg_2Si layers in the Si/Mg_2Si MXMs does not lead to significant changes in the intensity and angular positions of the low-angle Bragg maxima in GIXRR. This allows us to expect that the EUV reflectivity of these X-ray mirrors after annealing at 300°C will also not change. This fact is an advantage of Si/Mg_2Si MXM manufactured by sputtering Si and Mg targets as opposed to Mg-based mirrors.

References

1. I.A.Zhitnik, S.V.Kuzin, A.M.Urnov et al., *Astron. Lett.*, **31**, 39 (2005).
2. B.L.Henke, E.M.Gullikson, J.C.Davis, *At. Data Nucl. Data Tables.*, **54**, 181 (1993).
3. Hisataka Takenaka, Satoshi Ichimaru, Tadayuki Ohchia, E.M.Gullikson, *J. Electron Spectrosc.*, **144–147**, 1047 (2005).
4. T.Ejima, A.Yamazaki, T.Banse et al., *UVSOR Activity Report*, **44**, 43 (2004).
5. K.Le Guen, M.-H.Hu, J.-M.Andre, P.Jonnard, *J. Phys. Chem. C*, **114**, 6484 (2010).
6. L.E.Konotopskyi, I.A.Kopylets, V.V.Kondratenko, *J. Surf. Phys. Engin.*. **13**, 24 (2015).
7. Haynes, William M., ed. CRC Handbook of Chemistry and Physics (92nd ed.), Boca Raton, FL, CRC Press (2011).
8. Xin-Yan Yan, Y.A.Chang, F.Zhang, *JPE*, **21**, 379 (2000).
9. L.E.Konotopskyi, I.A.Kopylets, V.A.Sevrykova et al., *J. Nano-Electron. Phys.*, **8**, 02021 (2016).
10. L.E.Konotopskyi, I.A.Kopylets, V.A.Sevrykova et al., *Metallofiz. Noveishie Tekhnol.*, **38**, 825 (2016).
11. Haochuan Li, Jingtao Zhu, Zhanshan Wang et al., *Opt. Mater. Express*, **3**, 546 (2013)/
12. D.L.Windt, *Comp. Phys.*, **12**, 360 (1998).
13. C.Montcalm, B.T.Sullivan, H.Pepin et al., *Appl. Opt.*, **33**, 2057 (1994).
14. Jingtao Zhu, Sika Zhou, Haochuan Li et al., *Appl. Opt.*, **49**, 3922 (2010)
15. M.R.J. van Buuren, C.L.Griffiths, H.van Kempen, *Surf. Sci..*, **314**, 172 (1994).
16. L.E.Konotopsky, I.F.Mikhailov, I.A.Kopylets et al., *Metallofiz. Noveishie Tekhnol.*, **39**, 767 (2017).