STRUCTURAL TRANSFORMATION IN Zr/Mg MULTILAYER ON SI SUBSTRATE AFTER ANNEALING

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A Zr/Mg periodic multilayer was deposited onto silicon substrate by DC magnetron sputtering. Study of the Zr/Mg multilayer structure in an initial state and after thermal annealing in a temperature range of 100...600 °C was made by the X-ray diffraction and cross-section transmission electron microscopy methods. It was shown that Zr/Mg multilayers are stable up to 400 °C. Further heating to 500 °C leads to decreasing of the number of the operable periods due to the zirconium and magnesium layers interaction with the silicon substrate. Annealing at 550 °C leads to multilayer periodicity destructing.

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INTRODUCTION

Zirconium and magnesium are one of the most promising pairs of materials for creating multilayer X-ray mirrors (MXM) for the 25…35 nm wavelengths range due to their optical constants [1]. This part of the soft X-ray spectrum contains the emission lines of iron and helium [2]. The registration and analysis of these spectral lines allows us to obtain important information about the processes taking place in the solar corona [3–5].

Previous studies showed that Zr/Mg multilayers deposited by DC magnetron sputtering with a period of 10 nm have a high geometric perfection and an acceptable level of interlayer roughness [6]. These features provided the Zr/Mg multilayer X-Ray mirror reflection coefficient of 30.6 at.% a wavelength of 30.4 nm [7].

Long-term and thermal stability coupled with high reflectance are important requirements for the practical application of multilayers in X-Ray telescopes [4, 8]. It is known that multilayer mirrors based on magnesium, such as SiC/Mg [9], Co/Mg [10], ZrC/Mg [11], and Y_2O_3/Mg [12], lost their reflectivity after heating up to 350 °C. This is due to the fact that magnesium reacts with the second material of the mirror.

The use of non-interacting materials is an effective way to suppress the mixing of layers in a multilayer coating. [13]. The Zr-Mg is one of these pairs of materials. There are no chemical compounds in the Mg-Zr system [14]. But the ultimate answer to about application of Zr/Mg multilayer at high temperature needs experimental verification.

The aim of this work was to study effect of heating in the 100…600 °C temperature range on the structure of Zr/Mg MXM deposited on a silicon substrate.

1. SAMPLES AND INVESTIGATION TECHNIQUE

The Zr/Mg multilayer was deposited onto a polished Si (001) wafer by DC magnetron sputtering by alternate deposition of the Mg and Zr. The residual gas pressure before deposition was 10^{-4} Pa and that of sputtering gas (Ar) was 0.2 Pa. The Si substrates were cleaned by the Ar ions before deposition. The deposition rates for Mg and Zr were 0.45 and 0.08 nm/s, respectively. The number of periods is 40.

Multilayer structures were studied with small-angle X-Ray reflectometry (in the Θ–2Θ mode) using Cu-Kα_1 (8.0 keV) radiation. The measurements were performed with a DRON-3M diffractometer in the two-crystal scheme with a single crystal Si (110) monochromator. A 0.1 mm slit after the monochromator provided selection of the Cu-Kα_1 line. Periodicity of multilayer was defined with the full Bragg equation (taking into account refraction). X-Ray diffraction measurements at large angles was carried out in the Θ–2Θ mode and grazing incidence x-ray diffraction (GIXRD) mode [15] at the same wavelength with the diffractometer equipped with a graphite analyzer.

Cross-sectional TEM images and analysis of the chemical elements along the thickness of the Zr/Mg MXM were obtained using a JEOL JEM-ARM200F electron microscope.

The specimen was annealed in vacuum furnace at 10^{-4} Pa in a temperature range of 100…600 °C in steps of 100 °C. The time of each annealing was 1 hour.

2. RESULTS AND DISCUSSION

Fig. 1 shows measured small-angle X-ray diffraction curves for the Zr/Mg MXM with a period of d = 16.2 nm.

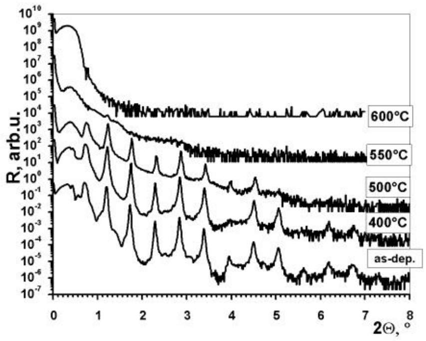
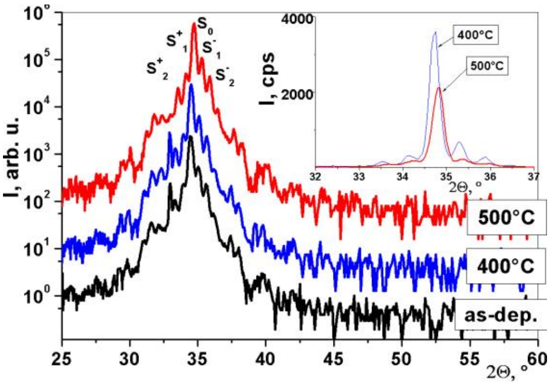


Fig. 1. Measured small-angle X-Ray diffraction curves for the Zr/Mg MXM on a Si (001) substrate in an as-deposited state and after annealing at temperatures of 400, 500, 550, and 600 °C

It should be noted that the Bragg maxima on the diffraction pattern from the Zr/Mg MXM in an as-deposited state are narrow and symmetrical. This indicates a high level of the MXM periodicity.

Fig. 2 shows the X-ray diffraction pattern at large angles for the Zr/Mg MXM. The diffraction for coherent structures [16–18] is observed. Instead of individual peaks from individual phases, there is a peak from the "average lattice" S_0 in the diffraction curve, which is located between the reflections of Mg (002) and Zr (002). On each side of the S_0 the S^+_j and S^-_j superstructural maxima are observed. This phenomenon occurs in layered systems that consist of crystalline layers with the very small lattice mismatch [18, 19]. Analysis of the superstructural maxima intensity ratio provides additional information on the multilayer system structure [19]. This work was done in [6]. It was shown that Zr/Mg multilayers with thicknesses of the magnesium layers more than 5.2 nm can be used for creation of the X-ray mirrors [6]. When thicknesses of the Mg layers less than 5.2 nm they are discontinuous. This is accompanying with decreasing in reflectivity of Zr/Mg MXM. It is important to note that the long-period Zr/Mg multilayers possess a high level of geometric perfection and an acceptable interfaces roughness [6].



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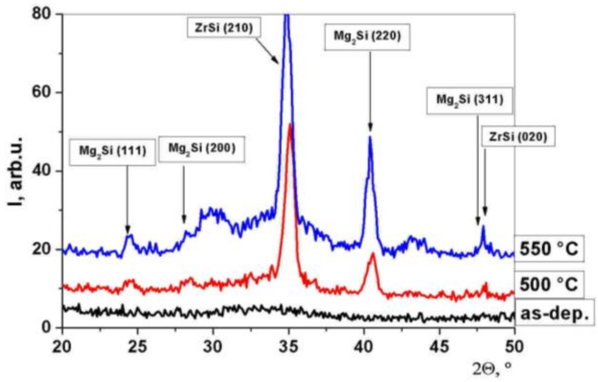

b

Fig. 2. Measured X-Ray diffraction curves for Zr/Mg MXM in Cu–Kα radiation at large angles in an as-deposited state and after annealing at temperatures of 400, 500 °C

Annealing the Zr/Mg multilayer up to 400 °C does not lead to a significant change in the small-angle X-ray diffraction pattern (see Fig. 1). This constitutes evidence that the parameters of the layers remain intact. Hence the mirror is stable up to 400 °C. Further annealing at 500 °C is accompanied by disappearing of the distant Bragg orders of reflection (see Fig. 1). This result differs from one of the authors of [7], where the small-angle x-ray diffraction remains unchanged upon annealing up to 600 °C.

The X-Ray diffraction curves measured at large angles (see Fig. 2,a) also did not change significantly when the Zr/Mg MXM was annealed at 400 °C. Only the displacement of the reflex S_0 toward large angles was observed. It was shown in [7] that compressive stresses are set up in the zirconium layers during the Zr/Mg MXMs manufacturing. Value of the stresses decreases upon the annealing. That leads to a change of the lattice spacing in the zirconium layers. A consequence of this is the displacement of S_0, which position depends on the interplanar distances of the both materials in the multilayer [19].

Further annealing at 500 °C leads to decreasing of the superstructural maxima intensity (see Fig. 2,a). At the same time, peaks corresponding to silicides of the zirconium and magnesium appear on the GIXRD curves (see Fig. 2,b). These reflexes were absent in an initial state of the MXM. We suppose that the silicides are formed by an interaction of the zirconium and magnesium bottom layers with a silicon substrate. This results in a decrease in the number of the MXM periods. As a consequence of this process, the intensity of Bragg reflections on the small-angle X-Ray pattern decreased (see Fig. 1). According to our rough estimate based on the computer modeling of the small-angle pattern, about 20 periods of the Zr/Mg MXM disappeared after annealing at 500 °C. They interacted with the Si substrate. Decreasing of the number of the MXM periods leads to a reducing superstructure maxima intensity too (see Fig. 2,a). In particular, intensity of the S_0 decreased by 1500 cps after annealing at 500 °C in comparison with the intensity of S_0 at 400 °C. It is important to note that periodicity of the top layers remained intact as evidenced by retained Braggs peaks on the small-angle X-ray pattern. Thus the destruction of the Zr/Mg MXM deposited onto a silicon substrate begins from the bottom layers resulting from their interaction with the substrate silicon.

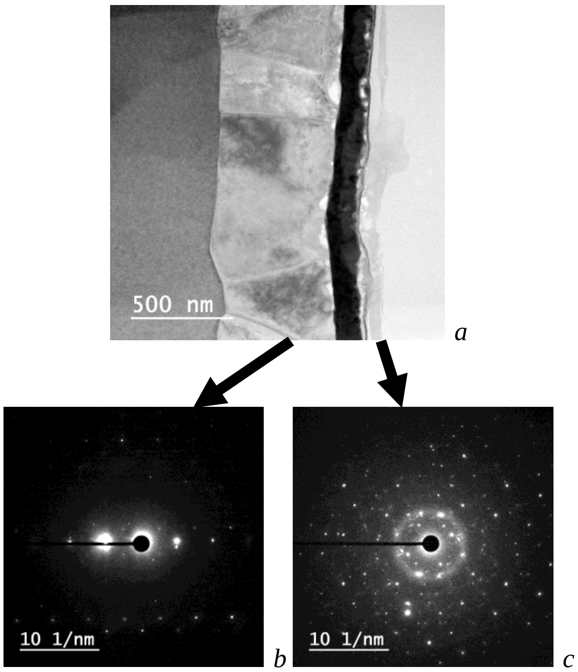

Fig. 3. Cross-sectional TEM images (a) and selected-area electron diffraction patterns for the bottom (b) and top (c) layers for Zr/Mg MXM annealed at 600 °C

Annealing at 550 °C destroys the multilayer periodicity (see Fig. 1). As this takes place, the intensity of peaks corresponding to magnesium and zirconium silicides increases on the X-ray diffraction curves at large angles (see Fig. 2,b). Obtained results on the Zr/Mg MXM destruction after annealing are confirmed by cross section electron microscopy (Fig. 3,a) and electron microanalysis (Fig. 4). As can be seen, the initial multilayer transforms into a two-layer film consisting of magnesium and zirconium silicides separated by silicon oxide. The selected-area electron diffraction patterns indicate the formation of silicides of Mg_2Si (see Fig. 3,b) and ZrSi (see Fig. 3,c).

The formation of zirconium silicide of exactly this composition (ZrSi) is confirmed by a calculation of volume changes in the zirconium after interaction with silicon. Namely, 130 nm thick ZrSi should be formed as a result of reaction of the 82.76-nm thick zirconium (the total thickness of Zr layers in the MXM) with silicon. This is in accordance with the EDS data of the distribution of chemical elements across the Zr/Mg MXM (Fig.4).

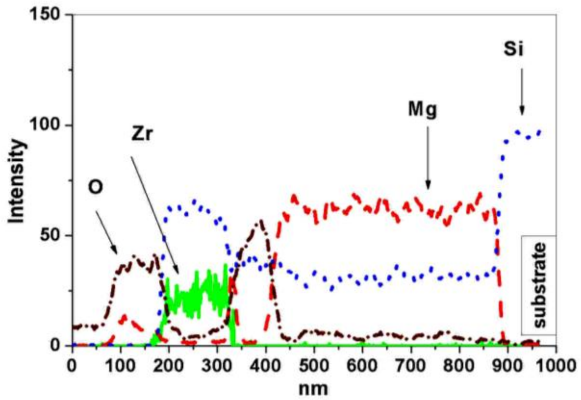

Fig. 4. Distribution of chemical elements along the thickness of Zr/Mg MXM annealed at 600 °C obtained by microanalysis

According to the EDS data in the MXM, both the formation of silicides and an interaction of the mirrors surface with the residual atmosphere occur. In our opinion, these processes of interaction with the atmosphere are most intense at temperatures of 500 °C and above, when a considerable part of the mirror is already destroyed. That is confirmed by significant decreasing (by a factor of 10) of the total external reflection intensity (see Fig. 1).

Thus, according to our results, the mechanism of Zr/Mg X-ray mirror destruction is the interaction of the MXM layers with a silicon substrate The use of substrates of other materials, for example of quartz, can increase a thermal stability of the Zr/Mg MXM. However, this statement invites further investigation.

CONCLUSIONS

The carried out studies show that the main mechanism of destruction of the Zr/Mg MXM deposited on a silicon substrate after annealing is the interaction of the Zr and Mg with the silicon substrate to form ZrSi and Mg_2Si. The interaction process begins from the bottom layers when the MXM heated up to 400 °C. In this case, the “undamaged” top layers retain their periodicity and the initial period value. Further increasing of temperature leads to decreasing of the operable periods amount, and at 550 °C mirror completely destroyed.

It is necessary to use other substrates, for example quartz, for a practical application of the Zr/Mg MXM at elevated temperatures. In addition, it is advisable to use protective coatings on top of the multilayer.

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СТРУКТУРНО-ФАЗОВЫЕ ПРЕВРАЩЕНИЯ В МНОГОСЛОЙНЫХ РЕНТГЕНОВСКИХ ЗЕРКАЛАХ Zr/Mg НА КРЕМНИЕВОЙ ПОДЛОЖКЕ ПРИ ОТЖИГЕ

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Рентгенографическими и электронно-микроскопическими методами исследовано многослойное рентгеновское зеркало (МРЗ) Zr/Mg в исходном состоянии и после отжига (100…600 °С). МРЗ Zr/Mg на кремниевой подложке было изготовлено методом прямоточного магнетронного распыления. Показано, что структура рентгеновского зеркала сохраняется неизменной при отжиге вплоть до 400 °С. Дальнейший нагрев до 500 °С сопровождается снижением числа рабочих периодов за счет взаимодействия слоев циркония и магния с кремниевой подложкой. Отжиг при 550 °С приводит к разрушению периодической структуры в МРЗ.

СТРУКТУРНО-ФАЗОВІ ПЕРЕТВОРЕННЯ У БАГАТОШАРОВИХ РЕНТГЕНІВСЬКИХ ДЗЕРКАЛАХ Zr/Mg НА КРЕМНІЄВІЙ ПІДКЛАДЦІ

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Рентгенографічними і електронно-мікроскопічними методами досліджено багатошарове рентгенівське дзеркало (БПК) Zr/Mg у вихідному стані та після відпалу (100…600 °С). БПК Zr/Mg на кремнієвій підкладці було виготовлено методом прямоточного магнетронного розпилення. Показано, що структура рентгенівського дзеркала зберігається незмінною при відпалі до 400 °С. Подальший нагрів до 500 °С супроводжується зниженням числа робочих періодів за рахунок взаємодії шарів цирконію і магнію з кремнієвої підкладкою. Відпал при 550 °С призводить до руйнування періодичної структури в БПК.