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EFFECT OF ARGON WORKING GAS PRESSURE ON MECHANICAL STRESSES IN Mo/Si MULTILAYER X-RAY MIRRORS

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By the method of X-ray tensometry (λ=0.154 nm), the dependences of residual stresses in Mo/Si multilayer X-ray mirrors (MXMs) obtained by direct-current magnetron sputtering were studied as a function of the sputtering Ar pressure in the range of 1…4 mTorr. It is shown that an increase in pressure is accompanied by an increase in stresses from ~ 0.4 to ~ 0.8 GPa for a group of mirrors with periods near 7 nm and from ~ 0.9 to ~ 1.6 GPa for a group of mirrors with periods near 14 nm. The angles of texture misorientation for Mo crystallites were measured as a function of argon pressure. Mechanisms have been proposed to explain the reasons for the increase in stresses.

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INTRODUCTION

Ion-plasma coating methods facilitate to generating compressive stresses in films due to the high energies of sputtered atoms, which lead to "cold-hardening" of the surface. In many applications they are undesirable and need to be at least weakened. This is especially true for Mo/Si multilayer X-ray mirrors (MXMs), which have high reflectivity in the extreme ultraviolet region (λ>12.3 nm) and are used as the main elements of X-ray optics in X-ray microscopes, telescopes, lithographs, etc. Such mirrors are mainly manufactured by sputtering.

Mechanical stresses that arise during the deposition of Mo/Si MXMs can be significant and reach ~ 1 GPa [1], which inevitably leads to aberrations in devices with multimirror schemes. Therefore, methods are needed to reduce mechanical stress in MXMs without deteriorating their X-ray optical characteristics.

The stress values can be reduced in various ways: by annealing [2, 3]; by depositing layers with a bias potential on the substrate [4]; by applying compensating sublayers [3, 5]; by using barrier layers [6]. Another way to reduce stress can be to lower the energy of the deposited atoms by increasing the pressure of the inert gas in order to thermalize the energy of sputtered atoms. Changing the pressure of the inert gas can reduce the residual stresses in the Mo/Si MXMs, as observed in [7] for a pressure of 6 mTorr. So in this work we study the influence of working gas pressure (Ar) on mechanical stresses in Mo/Si MXMs.

1. METHODS

To deposit the layers, direct-current magnetron sputtering was used in argon. During each experiment, the currents on both magnetrons and the Ar pressure were maintained constant, which ensured constant deposition rates for each specific sample at a certain pressure. However, when the pressure (p_{Ar}) changed from 1 to 4 mTorr, the deposition rates dropped from ~ 0.40 to ~ 0.36 nm/s for Mo and from ~ 0.64 to ~ 0.45 nm/s for Si, since the glow-discharge potentials at the magnetrons decreased. Multilayer mirrors were produced by alternately depositing layers of Mo and Si onto a substrate with the total thickness of ~ 0.4 μm.

The samples were measured using X-ray diffractometer DRON-3M containing a graphite analyzer in CuKα radiation. The X-ray beam divergence did not exceed 0.5°.

The magnitudes of macrostrains and residual macrostresses (σ) in Mo layers were determined by X-ray tensometry ($\sin^2\psi$ method). The smallest errors in determining the lattice parameters are obtained at the largest reflection angles [8]. Therefore, we used the family of {321} planes with diffraction angles of 2θ~134° as reflecting planes. The measurements of multilayer samples was carried out in asymmetric geometry at three different ψ angles (19.1, 40.9, and 55.5°). Based on the angular position of each diffraction maxima, we determined the interplanar distances and lattice parameters and constructed $\sin^2\psi$-graphs. Then we determined the values of the lattice parameter a_o in the unstressed state (at $\sin^2\psi$=0.466), as well as the Mo-lattice parameter in the plane of the sample surface ($a_{||}$ at $\sin^2\psi$=1). Using the obtained values of the lattice parameters a_o in the unstressed state and the lattice parameters $a_{||}$ in the (110) plane, we determined the values of residual macrostrains and then the values of residual macrostresses in the Mo layers.

2. RESULTS AND DISCUSSION

We studied 2 groups of samples. The first group consisted of "short-period" mirrors with periods in the range 5.9…9.1 nm (Mo layer thicknesses: 2.3…3.2 nm); we denote this group with the index "7-nm", and the second group – "long-period" mirrors with periods of 10.7…16.7 nm (Mo layer thicknesses: 4.5…5.9 nm), denoted by "14-nm". The nominal thicknesses of the layers in these groups differed by the factor of 2. Samples from the first group had periods close to those used in X-ray lithography. Since the Mo layer thicknesses in these samples are close to the amorphization boundary of the Mo layers (t_{am}~2 nm), the Mo crystallites have an increased density of structural defects, so we prepared the samples with thicker Mo layers to compare the stresses in both groups.

2.1. DETERMINATION OF MACROSTRESSES IN Mo LAYERS

Residual stresses were determined from the analysis of the $a_o=f(\sin^2\psi)$ dependence. A graphical representation of the dependence for residual macrostresses σ on pressure Ar is shown in Fig. 1. As can be seen from the figure, the resulting macrostresses are tensile (the "+" sign) and increase with pressure. In long-period mirrors, macrostresses vary in the range of σ(p) = 0.93…1.70 GPa with an average value of ~ 1.50 GPa. In short-period mirrors, stresses vary in a narrower range of σ(p) = 0.43…0.81 GPa (average value ~ 0.64 GPa). In samples of the "14-nm" group, the stresses are on average ~ 2.4 times higher than in samples of the "7-nm" group. One of the sources of stress in the Mo/Si MXMs, as indicated in [9], is amorphous Si layers, which are in a compressed state and stretch neighboring Mo layers. The Si layers in the samples of the "14-nm" group is ~ 2 times thicker than in the samples of the "7-nm" group, so the main reason for observing such a difference in tensile stresses for the Mo layers in samples of both groups is the difference in Si layer thickness. We can also see that stresses in samples of the "14-nm" group are more than the doubled stresses in samples of the "7-nm" group. The additional "increase" in stress is associated with the structural features of the MXMs, which will be discussed below.

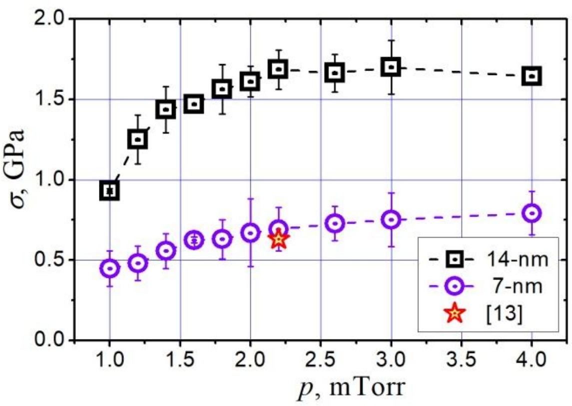

Fig. 1. Dependence of the residual macrostresses, σ, on the pressure, p, of the working gas Ar for two groups of samples

Macrostresses increase noticeably for the first 4 points (p ≤ 1.6 mTorr) for both groups of samples: here the increase in Δσ(p) is more than 40% with a total increase of ~ 60%. At p_{Ar} > 2 mTorr, the stress state stabilizes for samples of both groups. The ratios of the deposition rates of Mo and Si with p_{Ar} change little and do not exceed 5% over the entire range of argon pressures, i.e. there is no noticeable imbalance in the ratio of layer thicknesses in the MXM period. In other words, the increase in the magnitude of macrostresses at low argon pressure cannot be explained by an increase in the fraction of Si layers in the period. The observed increase in stress with pressure can be caused by the following reasons.

Firstly, increasing the Ar pressure, as we established earlier [10], is followed by decreasing the thickness of the mixed zones at the interfaces of Mo and Si layers. It is also known [11] that the formation of zones at Mo-on-Si boundaries is accompanied by a significant relaxation of compressive stresses arised during the deposition of Si layers. In other words, a decrease in the degree of mixing of the Mo and Si layers with increasing Ar pressure can lead to an increase in the level of residual macrostresses in the multilayer coating. A decrease in mixed zones is followed by an increase in the reflectivity of Mo/Si MXMs [10], i.e. there is a positive effect of this phenomenon on their reflectivity, but this occurs at the expense of residual stress growth.

The nominal thicknesses of samples from different groups, manufactured at the same argon pressure, differ by approximately 2 times. At the same time, the macrostresses in the samples of the "14-nm" group differ by more than 2 times compared to the samples of the "7-nm" group. The higher level of stresses exhibited by the samples of the "14-nm" group is due to the fact that, on the one hand, they have thickeer Si layers, and on the other hand, the thickness of the mixed zones in the samples manufactured at the same pressure are identical, i.e. their fraction in the MXM period decreases along with their ability to compensate the stress growth caused by an increase in the Si layer thickness. Assuming that samples of different groups obtained at the same Ar pressure differ only in the thickness of the layers, according to the data shown in Fig. 1, it can be established that in Si layers with a thickness of 3.0…3.5 nm (see the first 2 points in Fig. 1) compressive stresses of ~ 0.9 GPa are created. Deposition of Mo layers in samples of both groups does not affect the level of macro-stresses [11]. Here we took into account that out of 4.5…4.9 nm of deposited silicon, about 1.5 nm is spent on the formation of mixed zones. Using similar reasoning, we established that the relaxing ability of mixed zones, the thickness of which decreases with increasing Ar pressure [10], also decreases, and its dependence on Ar pressure is shown in Fig. 2. From this dependence it can be seen that for p_{Ar} = 1 mTorr, mixed zones may relax up to a half the stresses created by Si layers in samples of the "7-nm" group.

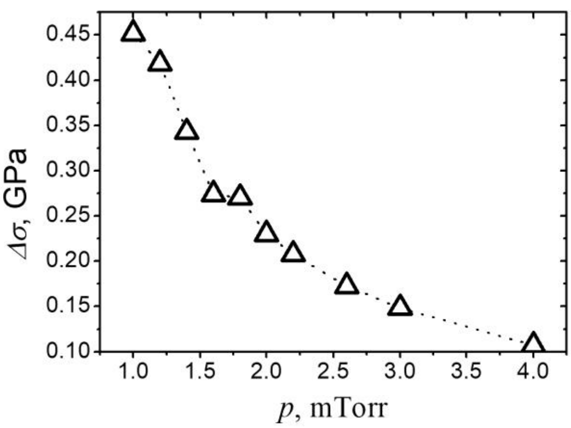

Fig. 2. Estimated value of macrostresses in Mo/Si MXMs relaxed by mixed zones (see the text)

Secondly, at pressures of 1…1.6 mTorr, the glow-discharge potential of the Mo magnetron changes noticeably (> 20%). The nature of its change is similar to that for σ(p): a sharp drop for the first three points and then a slow decline. At thy same time, the decrease in the glow-discharge potential of the Si magnetron with pressure is monotonic over the entire range of Ar pressures. Calculations with SRIM [12] show that in the pressure range p_{Ar} = 1…1.6 mTorr, the energies E_{Mo} of sputtered Mo atoms and the energies E_{Ar} of Ar atoms reflected from the Mo target correlate with the glow-discharge potential of the Mo magnetron. Ar atoms are not reflected from the Si target. Fig. 3 graphically presents the calculated data for E_{Mo} and E_{Ar}. The average energy of Mo atoms (denoted by □) for the first three values decreases by ~ 7%. If we add here the energy of reflected Ar atoms (denoted by Δ), then the total drop in energy transferred to the substrate surface can be more than 11%. Here we took into account that, according to SRIM, ~ 13% of Ar atoms are reflected from the Mo target. In other words, the temperature of the substrate surface at low p_{Ar} can be noticeably higher than that at higher deposition pressures, which can also lead to a stress relaxation.

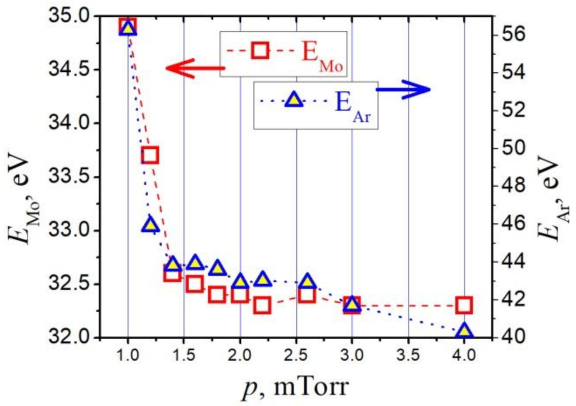

Fig. 3. Change in the energy of sputtered Mo atoms (E_{Mo}) and Ar atoms (E_{Ar}) reflected from the Mo target with Ar pressure, calculated using SRIM program [12]

In addition, the magnetic systems of both magnetrons used may be unbalanced (we did not make special efforts to make them balanced), so at low Ar pressures the magnetron plasma may come into contact with the substrate, because in this case, the density of electrons supporting the glow-discharge in the near-cathode space is low due to the rarefaction of the inert gas. So a negative potential is induced on the substrate surface, that leads to additional irradiation with argon ions from the plasma. All this can be followed by additional heating of the Si layers in particular and the "release" of macrostresses in general at low Ar pressures ($p_{Ar} \leq$ 1.6 mTorr). Since the energy of sputtered Si atoms can only decrease with Ar pressure, i.e. compressive stresses in the Si layers should decrease (due to weakening of the "cold-hardening" effect), the fact itself that stresses in the Mo/Si MXMs increase with pressure indicates that the size of mixed zones can have a significant impact on the stressed state of multilayer mirrors as a whole.

The stress values and sign in the samples of the "7-nm" group are consistent with the data of other authors for MXMs with similar periods. One of these values [13] is shown in Fig. 3 with an asterisk. Although the measured stress levels are generally low, it is necessary to lower the stresses since the stressed multilayer coatings may change the shape of the substrate. Distortion of the mirror shape inevitably leads to aberrations in X-ray optical devices [3], in particular in lithographs, where ~ 9 multilayer mirrors are used in the optical design [14]. The results of these studies show that the manufacture of MXMs at increased p_{Ar} (p_{Ar} < 4 mTorr) is not effective in solving the problems of reducing residual stresses in Mo/Si MXMs.

The results obtained are in contradiction with previously published data [15, 16], according to which it is possible not only to reduce, but even to change the sign of macrostresses in the Mo/Si MXMs. The reason for this discrepancy lies in the difference of deposition methods. Published studies use either RF magnetrons or RF plasma-enhanced magnetrons. In such sources, an increase in the discharge current is achieved both by the RF field and by the imbalance of magnetrons, which leads to an increased level of irradiation of the substrate with inert gas ions [17, 18]. Such bombardment is equivalent to supplying additional energy onto the surface of the growing film and is similar to the annealing effect, which reduces macrostresses in the MXMs [2, 3]. Direct-current magnetron sputtering used in this study provides a "softer" depositing Mo and Si layers without additional bombardment.

2.2. TEXTURE MISORIENTATION ANALYSIS

Molybdenum layers in Mo/Si MXMs grow textured with a (110) Mo being parallel to the substrate plane. In this work, a series of measurements was carried out to estimate the angles, α, of texture misorientation for the Mo crystallites. The peculiarity of recording rocking curves is that only the stage with the sample rotates, and the detector is fixed at the angle corresponding to the reflection from the (110) Mo planes. We took into account the change in the irradiated area of the sample and the reflection intensity, respectively. The width of such a curve at half maximum corresponds to the misorientation angle of the (110) Mo planes. Fig. 4 shows the rocking curve for one of the samples of the "7-nm" group, obtained at a pressure of 2.2 mTorr.

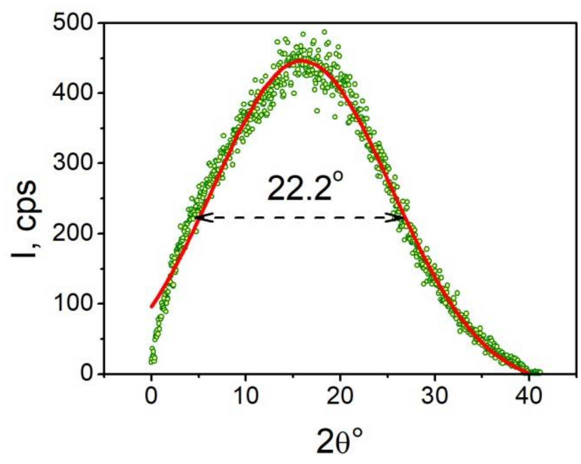

Fig. 4. Rocking curve of the Mo/Si MXM with a period of ~7 nm, manufactured at a pressure p_{Ar}=2.2 mTorr

Fig. 5 shows the dependence of texture misorientation on p_{Ar} for both groups. As can be seen, there is a general tendency for texture misorientation angles to increase for samples with different periods. In short-period samples, the misorientation angles are larger than in long-period ones. Thus, in samples of the "7-nm" group, misorientation increases from ~ 8 to ~ 14°, and for the "14-nm" group – from ~ 7 to ~ 12°. In the samples of the "14-nm" group the actual Mo layer thickness is larger than that in the samples of the "7-nm" group, therefore, a decrease in misorientation angles with p_{Ar} indicates that the process of depositing metal layers occurs dynamically and recrystallization of Mo grains may take place, as was shown earlier [19, 20].

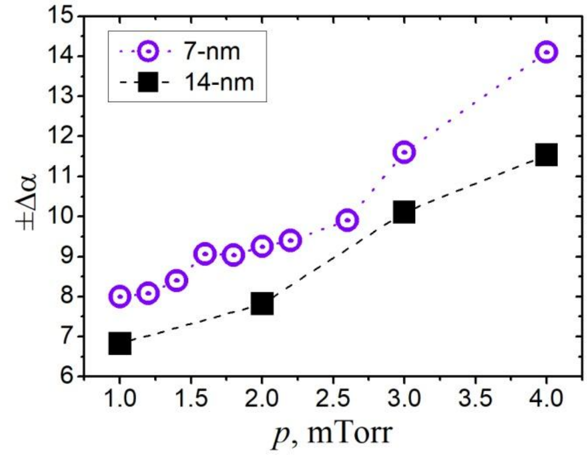

Fig. 5. Dependence of texture misorientation angle on Ar working gas pressure

An increase in the misorientation of Mo grains should be followed by an increase in the interfacial roughness of the MXMs [21], since individual crystallites form differently oriented facets on the Mo layer surface, which determine the interfacial relief. Therefore, according to the trend of increasing texture misorientation angles in Fig. 5, one can expect that the interfacial roughness of the Mo/Si MXMs will also increase with pressure for samples of both groups. For the same reason, one can expect that the roughness of short-period MXMs is greater than that of large-period ones. The increase in texture misorientation angles with pressure indicates that pressure can have a negative effect on the reflectivity of Mo/Si MXMs. Here we also observe that along with macrostresses a development of interface roughness may also play negative role in the efficiency of MXMs despite the fact that Ar pressure growth is followed by reducing the mixed zone thicnesses and increasing efficiency of MXMs [10]. When optimizing the characteristics of Mo/Si MXMs, it is necessary to optimize the influence of all factors.

CONCLUSIONS

Using X-ray tensometry ($\sin^2\psi$-method) at a wavelength of 0.154 nm, residual macrostresses in the Mo layers of Mo/Si MXMs of two groups with periods near 7 and 14 nm, manufactured by magnetron sputtering in the argon pressure range p_{Ar} = 1…4 mTorr, were studied. The results given above allow to draw the following conclusions:

1. Tensile stresses are observed in Mo layers, which increase with Ar pressure. Most (~ 40%) of the increase in stresses in the MXM occurs in the pressure range of 1…2 mTorr, with a general increase in macrostresses by ~ 60% relative to samples manufactured at p_{Ar} = 1 mTorr. The main reason for the increase in stress with pressure is associated with a decrease in the thickness of the mixed zones in the MXM, which compensate the compressive stresses created by the Si layers.

2. A twofold increase in the thickness of the MXM layers leads to an increase in macrostresses by ~ 2.4 times, which is associated with an increase in the thickness of the Si layers, as well as with a decrease in the fraction of mixed zone thickness in the period of multilayer mirrors with large periods.

3. In Si layers with a thickness of 3.0…3.5 nm at p_{Ar} ~ 1 mTorr, compressive stresses of ~ 0.9 GPa are created, half of which are compensated by mixed zones. The dependence for the magnitude of stress relaxation by mixed zones on Ar pressure was obtained, which varies from ~ 0.45 (1 mTorr) to ~ 0.1 GPa (4 mTorr).

4. The misorientation angles of the texture for Mo crystallites were measured, which increase from ~ 8 to ~ 14° (MXMs with periods near "7 nm") and from ~ 7 to ~ 12° (MXMs with periods near "14 nm") with pressure. This indirectly indicates an increase in interlayer roughness with pressure and with a decrease in the mirror period, which negatively affects the efficiency of MXMs.

5. These studies show that it does not seem possible to reduce the amount of residual macrostresses that arise in MXMs during their manufacture by increasing the pressure of the Ar working gas without reflectivity loss in the X-ray wavelength range.

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REFERENCES

1. C. Teyssier, E. Quesnel, V. Muffato, P. Schiavone. Stress characteristics in EUV mask Mo/Si multilayers deposited by Ion Beam Sputtering // *Microelectronic Engineering*. 2002, v. 61-62, p. 241-250.

2. T. Feigl, S.A. Yulin, T. Kuhlmann, N. Kaiser. Damage resistant and low stress Si-based multilayer mirrors // *Proc. SPIE*. 2001, v. 4506, p. 121-126.

3. P.B. Mirkarimi, C. Montcalm. Advances in the reduction and compensation of film stress in high-reflectance multilayer coatings for extreme ultraviolet lithography // *Proc. SPIE*. 1998, v. 3331, p. 133-148.

4. Bo Yu, Chunshui Jin, Shun Yao, Chun Li, Yu Liu, Feng Zhou, Benyin Guo, Hui Wang, Yao Xie, and Liping Wang. Low-stress and high-reflectance Mo/Si multilayers for extreme ultraviolet lithography by magnetron sputtering deposition with bias assistance // *Appl. Opt*. 2017, v. 56, N 26, p. 7462-7468.

5. M. Moss, T. Böttger, S. Braun, T. Foltyn, A. Leson. Stress compensation of a Mo/Si/C highly reflective multilayer by means of an optimised buffer layer and heat treatment // *Thin Solid Films*. 2004, v. 468, p. 322-331.

6. S. Bruijn, R.W.E. van de Kruijs, A.E. Yakshin, E. Zoethout, F. Bijkerk. Thermally induced

decomposition of B_4C barrier layers in Mo/Si multilayer structures // *Surface and Coatings Technology*. 2010, v. 205, p. 2469-2473.

7. J.M. Freitag, B.M. Clemens. Stress development in Mo/Si and Ru/Si multilayers // *Mat. Res. Soc. Symp. Proc.* 1999, v. 562, p. 177-182.

8. Л.И. Гладких, С.В. Малыхин, А.Т. Пугачев. *Дифракционные методы анализа внутренних напряжений. Теория и эксперимент*. Харьков: НТУ «ХПИ», 2006, 304 с.

9. V.V. Kondratenko. Periodic multilayers $MoSi_2$/Si with a large number of periods // *Cryst. Res. Technol*. 1998, v. 33, N 1, p. 71-78.

10. Yu.P. Pershyn, E.M. Gullikson, V.V. Kondratenko, V.V. Mamon, S.A. Reutskaya, D.L. Voronov, E.N. Zubarev, I.A. Artyukov, A.V. Vinogradov. Effect of working gas pressure on interlayer mixing in magnetron-deposited Mo/Si multilayers // *Opt. Eng*. 2013, v. 52, N 9, 095104.

11. J.M. Freitag, B.M. Clemens. Stress evolution in Mo/Si multilayers for high-reflectivity extreme ultraviolet mirrors // *Appl. Phys. Lett*. 1998, v. 73, N 1, p. 43-45.

12. http://www.srim.org/SRIM/SRIM-2013-Std.e

13. V.I. Pinegyn, E.N. Zubarev, V.V. Kondratenko, V.A. Sevryukova, S.A. Yulin, T. Feigl, N. Kaiser. Structure and stressed state of molybdenum layers in Mo/Si multilayers // *Thin Solid Films*. 2008, v. 16, p. 2973-2980.

14. S. Braun, A. Leson. Optical Elements for EUV Lithography and X-ray Optics // *The Nano-Micro Interface: Bridging the Micro and Nano World* / Ed. Marcel Van de Voorde et al. Wiley-VCH Verlag GmbH & Co. KGaA, 2015, 698 p.

15. M. Niibe, A. Miyafuji, H. Kinoshita, T. Watanabe, S. Inoue, K. Koterazawa. Fabrication of an aspherical mirror for Extreme Ultraviolet Lithography (EUVL) optics // *Proc. SPIE*. 1998, v. 3447, p. 32-39.

16. N. Hosokawa, T. Watanabe, N. Sakaya, T. Shoki, K. Hamamoto, H. Kinoshita. Development of beam splitter using multilayer membrane for extreme ultraviolet phase-shift microscope // *Jpn. J. Appl. Phys*. 2005, v. 44, p. 5540-5543.

17. J. Musil, M. Misina, D. Hovorka. Planar magnetron sputtering discharge enhanced with radio frequency or microwave magnetoactive plasma // *J. Vac. Sci. Technol. A*. 1997, v. 15, N 4, p. 1999-2006.

18. M. Yamashita, Y. Setsuhara, S. Miyake, M. Kumagai,T. Shoji, J. Musil. Studies on Magnetron Sputtering Assisted by Inductively Coupled RF Plasma for Enhanced Metal Ionization // *Jpn. J. Appl. Phys*. 1999, v. 38, p. 4291-4295.

19. S. Yulin, T. Feigl, T. Kuhlmann, N. Kaiser, A.I. Fedorenko, V.V. Kondratenko, O.V. Poltseva, V.A. Sevryukova, A.Yu. Zolotaryov, E.N. Zubarev. Interlayer transition zones in Mo/Si superlattices // *J. Appl. Phys*. 2002, v. 92, N 3, p. 1216-1220.

20. E.N. Zubarev, V.V. Kondratenko, Yu.P. Pershyn, V.A. Sevryukova. Growth and crystallization of molybdenum layers on amorphous silicon // *Thin Solid Films*. 2011, v. 520, p. 314-319.

21. M. Shiraishi, N. Kandaka, and K. Murakam. Mo/Si multilayers deposited by low-pressure rotary magnet cathode sputtering for extreme ultraviolet lithography // *Proc. SPIE*. 2003, v. 5037, p. 249-256.

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ВПЛИВ ТИСКУ РОБОЧОГО ГАЗУ АРГОНУ НА МЕХАНІЧНІ НАПРУЖЕННЯ У БАГАТОШАРОВИХ РЕНТГЕНІВСЬКИХ ДЗЕРКАЛАХ Mo/Si

Ю.П. Першин, В.С. Чумак, А.Ю. Девізенко, Є.Н. Зубарєв, В.В. Кондратенко

Методом рентгенівської тензометрії (λ = 0,154 нм) досліджено залежності механічних напружень у багатошарових рентгенівських дзеркалах Mo/Si, які отримані методом магнетронного напилення на постійному струмі, від тиску Ar при напиленні у діапазон 1…4 мТорр. Показано, що збільшення тиску супроводжується збільшенням напружень від ~ 0,4 до ~ 0,8 ГПа для групи зразків з періодами близько 7 нм і від ~ 0,9 до ~ 1,6 ГПа для групи зразків з періодами близько 14 нм. Кути розорієнтації текстури кристалітів Mo були виміряні як функція тиску аргону. Запропоновано механізми, які пояснюють причини зростання напружень.