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Influence of background pressure on the microstructure and optical properties of Mo/Si multilayers fabricated by magnetron sputtering

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Mo/Si multilayers were fabricated by using magnetron sputtering method at different background pressures: 6×10^{-5} Torr, 3×10^{-5} Torr, and 3×10^{-6} Torr. The reflectivity of the Mo/Si multilayers increased from 1.93% to 16.63%, and the center wavelength revealed a blue shift to 0.12 nm with the decrease of background pressure. Grazing incident X-ray diffraction (GIXRD) indicated that multilayers fabricated at high background pressure possessed better periodic structure and thinner Mo-on-Si interlayers. Low crystallization degree in (110) preferred the orientation of Mo layers and serious interdiffusion in the Mo/Si multilayers fabricated at low background pressure were observed by transmission electron microscopy (TEM). According to quantitative analysis of microstructural parameters, the Mo layers thickness and thickness ratio Γ of Mo/Si multilayers both decreased and approached the design value gradually by the decrease of background pressure. In addition, the thicknesses of Mo-on-Si and Si-on-Mo interlayers were 1.17 nm and 0.85 nm respectively. It is suggested that the influence of background pressures on the microstructure has a critical role in determining the optical properties of Mo/Si multilayers.

background pressure effects, optical properties, multilayer, microstructure, crystalline orientation

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1 Introduction

Mo/Si multilayers are widely used in X-ray astrophysics, synchrotron radiation applications and extreme ultraviolet (EUV) lithography [1–3]. This is primarily because of the high stability and fairly high reflectivity in the EUV spectral region [4]. Particularly, for high-resolution solar EUV images, the Mo/Si multilayers mirror has important application in the optical system of space EUV normal incidence telescopes [5–9]. The optical properties of Mo/Si multilayers composed of alternating Mo and Si layers depend highly on structural stability.

Successful fabrication of high reflectivity Mo/Si multilayers has already been demonstrated by magnetron sputtering [10,11], ion-beam sputtering [12] and electron beam evaporation techniques [13]. Magnetron sputtering is the preferred fabrication method because of the room-temperature operation and ease of control for deposition parameters, such as radio frequency (RF) power, electric current,

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working pressure and substrate temperature [14–16]. The control of deposition parameters is the most critical factor the fabrication of Mo/Si multilayers with desired properties as reported by several researchers [11,14]. Among those, however, the effect of background pressure on the microstructure and optical properties of Mo/Si multilayers has recieved less research focus. In practice, tiny gas leaking, which is difficult to be detected, result in the reduction of background pressure. In this case, the impurity gas (such as H_2 and O_2) enter into the vacuum chamber and affect the nucleation of the Si and/or Mo atoms, which leads to the uneven growth of film and coarsening of Mo/Si interlayers [17]. Therefore, it is necessary to understand the relationships between the optical properties and microstructures of Mo/Si multilayers under different background pressures. It is useful to understand the intrinsic characteristic regarding the effect of tiny impure gas on Mo/Si multilayers growth.

In this paper, the influence of background pressure, which is caused by gas leakage, on the microstructure and optical properties of Mo/Si multilayers fabricated by magnetron sputtering were investigated. The detailed information about the microstructure of Mo/Si multilayers and the influence on the optical properties has been investigated by using Grazing incident X-ray diffraction (GIXRD) and transmission electron microscope (TEM). The study focuses on the microstructural evolution of Mo layer and the interlayer in Mo/Si multilayers with the variation of background pressures.

2 Experimental

Mo/Si multilayers were fabricated by magnetron sputtering onto 10×10 (mm^2) superpolished single silicon (100) wafer substrate in Ar (99.99%). The flow rate of Ar gas is 15 sccm, and the operating pressure is 0.75 mTorr. Depositions were performed at room temperature, with the substrate temperature retaining at less than 373 K during deposition. Two RF targets (300 W) and two direct currency (DC) targets (300 mA) were used to deposit Si (99.999%) and Mo (99.95%), the deposition rates being 0.131 nm/s and 0.134 nm/s respectively. The sputtering power was kept constant. According to various diameters of the mirror, the angle of sputtering guns could be altered from 0° to 25° for better uniformity. A detailed description of the magnetron deposition system is given elsewhere [10]. Various vacuum pressure of the vacuum chamber was achieved by two methods. Firstly, under a state of tiny gas leaking (3.1×10^{-6} Torr L/s), background pressure was controled as 3×10^{-5} Torr and 6×10^{-5} Torr with pumping time, respectively. Secondly, higher background pressure of 3×10^{-6} Torr was obtained when no gas leaking was detected. The parameters of multilayer structure were designated as: period d=16.35 nm, the number of periods N=30, and the thickness ratio $\Gamma=d_{Mo}/d\approx 0.25$.

The structural parameters of Mo/Si multilayers were characterized by GIXRD with a rotating-anode Cu K_α source (λ=0.154 nm) and the angle resolution of XRD is 0.005°. The GIXRD operated over the angular range of 2θ= 0–6°.

Measurements of the EUV reflectivity of multilayers were carried out by using a EUV/soft X-ray reflectometer (EXRR) near the normal incidence (2°). The measured reflectance repeatability and wavelength repeatability of EXRR are ±1% and ±0.04 nm, respectively [18,19].

The cross-sectional TEM investigations were performed by aid of JEM-2010 type TEM, which operated at 200 kV acceleration voltage. Ultrathin cross sections of the selected multilayer samples were prepared by mechanical polishing (~50 μm) followed by careful Ar ion beam milling in Gatan model 691 precision ion polishing system.

Digital micrograph (DM) software was used to measure the thickness of period, Mo layers and interlayers. Such a procedure was repeated five times for every TEM image, the typical average value was chosen as the thickness. The accuracy of thickness measurements was at the level of $\Delta t\approx\pm0.02$ nm [20].

3 Results and discussion

The center wavelength and reflectivity of Mo/Si multilayers at various background pressures are shown in Figure 1. The reflectivity of Mo/Si multilayers fabricated at 3×10^{-6} Torr (16.63%) is much higher than others (3.31% at 3×10^{-5} Torr and 1.93% at 6×10^{-5} Torr). Moreover, the center wavelength of multilayers reveals a blue shift of 0.12 nm which was fabricated at 6×10^{-5} Torr. The EXRR result shows that the optical properties of Mo/Si multilayers are significantly affected by background pressure.

Figure 2 shows the GIXRD curves of multilayer films fabricated at different background pressures. The definite diffraction peaks for the Mo/Si multilayers indicate a re-

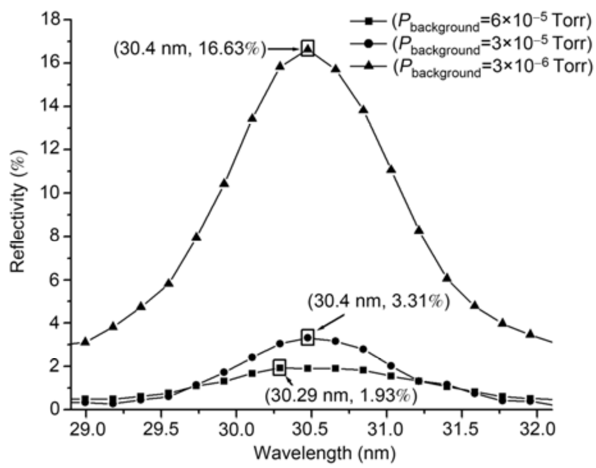

Figure 1 Reflectivity of Mo/Si multilayers fabricated at different background pressures.

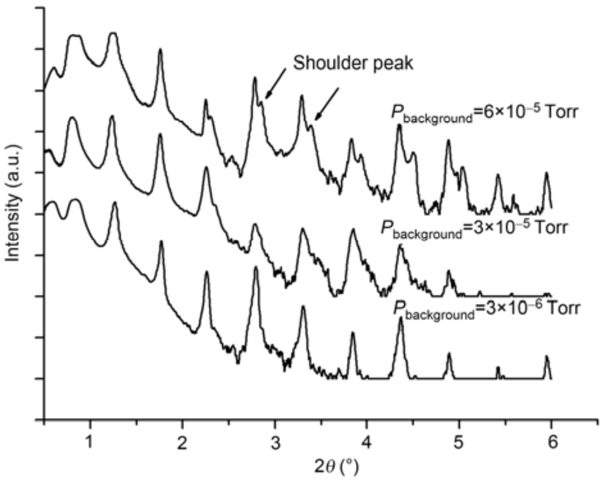

Figure 2 GIXRD curves of Mo/Si multilayers fabricated at different background pressures.

producibility of stacking along direction normal to the silicon (100) substrate. As presented in Figure 2, some diffraction peaks in curve *a* have a lower shoulder peak. Based on work reported by Liu et al. [10], this shoulder peak was caused by thicker interlayers between Mo layers and Si layers. The Bragg reflection angle (2θ) in Figure 2 is only determined by the period thickness of Mo/Si multilayers. Therefore, shoulder peak in curve *a* could be attributed to the uneven period thickness (*d*) of Mo/Si multilayers prepared at background pressure of 6×10^{-5} Torr. There is no shoulder peak in curve *b* and curve *c*, and the peaks in curve *c* are sharper and smoother than curve *b* and curve *a*. It can be deduced that Mo/Si multilayers fabricated at 3×10^{-5} and 3×10^{-6} Torr had better periodic structure and thinner Mo-on-Si interlayers. The GIXRD results show that the background pressure has a decisive role in Mo/Si multilayers period structure.

In order to obtain more information on microstructure in Mo/Si multilayers, a number of TEM images from multilayers fabricated at different background pressures were observed. Figure 3 shows the cross-section bright field TEM images taken from Mo/Si multilayers, which represents the bilayer periodicity of Mo/Si multilayers. The bright regions correspond to amorphous Si and the dark regions correspond to crystalline Mo. Some layers near the substrate were bended and fractured as in Figure 3(a). The adverse effects of impurity gas atoms (H, O) on the substrate of these sputtered films were anticipated at low background pressure because of tiny gas leakage [21]. Based on our previous report, the reason for the bending and fracturing was that Mo and Si layers absorbed hydrogen atoms [22]. Figure 3(b) shows the TEM images of Mo/Si multilayers fabricated at 3×10^{-5} Torr. A better bilayer periodicity of Mo/Si multilayers was obtained under this condition, however, the boundaries of both Mo and Si layers display a somewhat wavy nature. This phenomenon indicates that there are rough interlayers between Mo and Si layers in Mo/Si multilayers which were fabricated at the background pressure of 3×10^{-5} Torr. A perfect structure is observed from Figure 3(c), which shows the TEM images of Mo/Si multilayers fabricated at 3×10^{-6} Torr. It can be clearly seen that both Mo layers and Si layers are well distributed, both straight and smooth. Therefore, it has been clearly shown that the background pressure has great influence on the microstructural homogeneity of Mo/Si multilayers.

Figure 4 shows the magnified cross-section bright field TEM images of Mo/Si multilayers fabricated at different background pressures, in which the microstructures of the interlayers in Mo/Si multilayers can be observed directly. TEM images of the multilayers fabricated at 6×10^{-5} Torr and 3×10^{-5} Torr (background pressure in 10^{-5} Torr order) shown in Figure 4(a) and (b) demonstrate the presence of thicker Mo layers (~6 nm) and interlayers (Mo-on-Si and Si-on-Mo). Moreover, the interlayers are rougher and bended. When the background pressure decreases to 3×10^{-6} Torr, the boundaries of interlayer become smoother, and the thicknesses of both Mo layer and interlayers decrease, as shown in Figure 4(c). It can be deduced reasonably based on the observed results that background pressures have influence on the roughness and thickness of interlayers, which directly leads to the deterioration of the optical properties of Mo/Si multilayers.

In order to quantitatively analyze the influence of background pressure on the microstructure of Mo/Si multilayers, the thicknesses of period, Mo layers and interlayers were accurately measured by using DM software. Table 1 shows that Mo layers thickness and Γ of Mo/Si multilayers decrease and approach the design value gradually with the decrease of background pressure from 6×10^{-5} Torr to 3×10^{-6} Torr. Specifically, the thicknesses of Mo-on-Si and Si-on-Mo interlayers reduce to 1.17 nm and 0.85 nm, respectively, which are almost half of interlayer thicknesses fabricated at 6×10^{-5} Torr.

The typical HRTEM images of Mo/Si multilayer fabricated at different background pressures are shown in Figure 5. It is remarkable that Mo/Si multilayers are composed of polycrystalline Mo layers and amorphous Si layers, being separated by thinner interlayers. At higher background pressure (10^{-6} Torr order), the body centered cubic (bcc) type of Mo crystallites show a preferred (110) orientation, which places the most densely populated planes parallel to the Si substrate, as shown in Figure 5(a). Figure 5(b) shows the typical HRTEM image of Mo/Si multilayer fabricated at lower background pressure (10^{-5} Torr order). It can be observed that there is no crystallographic preferential growth orientation in Mo layers, whereas a random crystallographic orientation is present within the Mo layers. Moreover, it can be seen that the Mo layers are much thicker than Si layers from Figure 5(b), which result in the structure of Mo/Si multilayers not been accorded to the design value. As a re-

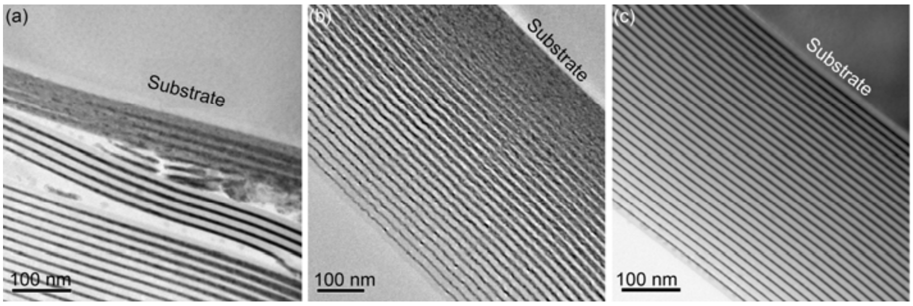

Figure 3 TEM images of Mo/Si multilayer samples fabricated at different background pressures: (a) 6×10^{-5} Torr; (b) 3×10^{-5} Torr; (c) 3×10^{-6} Torr.

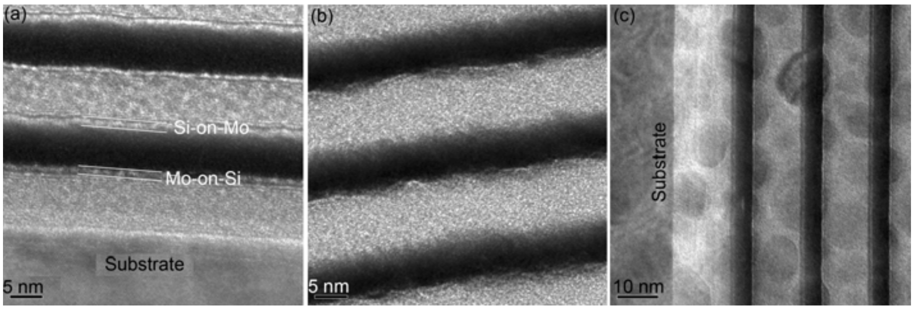

Figure 4 TEM images of Mo/Si multilayer samples fabricated at different background pressures: (a) 6×10^{-5} Torr; (b) 3×10^{-5} Torr; (c) 3×10^{-6} Torr.

Table 1 Microstructural parameters of Mo/Si multilayers fabricated at different background pressures

	6×10^{-5} Torr	3×10^{-5} Torr	3×10^{-6} Torr	Design value
Period (nm)	16.41	16.37	16.33	16.35
Mo (nm)	5.47	5.13	4.28	4.10
Γ	0.33	0.31	0.26	0.25
Mo-on-Si (nm)	2.11	1.49	1.17	–
Si-on-Mo (nm)	1.34	1.27	0.85	–

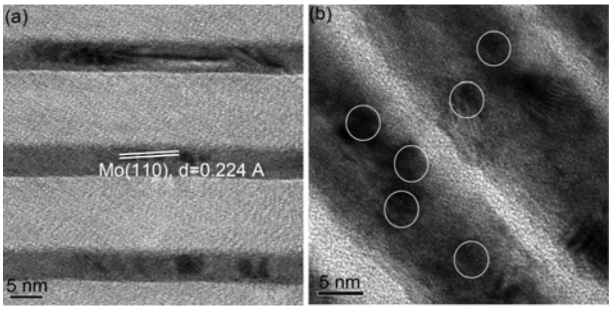

Figure 5 HRTEM images of Mo/Si multilayer samples fabricated at different background pressures: (a) 3×10^{-6} Torr and (b) 6×10^{-5} Torr.

sult, a decrease of the reflectivity of Mo/Si multilayers fabricated at lower background pressures would be expected, as shown in Figure 1. It is suggested that the low background pressure seriously affect the crystallization degree of Mo and interdiffusion behavior between Mo atoms and Si atoms.

Low content of impurity introduced by tiny gas leaking was obtained during the fabrication of Mo/Si multilayers which is not possible to effectively control by practical experiment. The content of impurity gas can be estimated using the formulas

$$C = F / L, \tag{1}$$

where F is the flow rate of Ar gas, the L is the rate of gas leaking. The value of 3.6 ppm of impurity gas is obtained. The experimental results mentioned above suggest that such a low content of impurity gas introduced by tiny gas leaking in the vacuum chamber (at the background pressure of 10^{-5} order Torr.) could seemingly influence the growth and nucleation behavior of Mo/Si multilayers. Apparently, the results in this paper are useful in understanding the interaction mechanism between the impurity gas and microstructure and optical properties of Mo/Si multilayers. It is also significative for the fabrication of Mo/Si multilayers in practical usage.

The introduction of tiny impurity gas may cause density changes, the formation of voids, bending and even fracturing in Mo and Si layers [23,24]. As an important reflecting layer in Mo/Si multilayers, crystalline Mo layer has a decisive role in optical properties. The reduction of sputtering rate and surface mobility of Mo adatoms, which is induced by impurity gas, resulted in serious diffusion and the formation of thick-roughed interlayers. At the background pressure of 10^{-6} order Torrr, the surface mobility of Mo adatoms increased because of increased collisions with energetic particles striking the film, as well as arriving adatoms having larger initial kinetic energies. With greater adatom mobility, voids collapse to dimensions comparable to the range of interatomic distance and thus crystallization degree in (110) of the preferred orientation increases [25]. The crystallization of Mo layer effectively reduced the interdiffusion between Mo and Si layers, which decrease the roughness of interlayers. Therefore it can be reasonably deduced that the influence of background pressure on the crystallization degree and diffusion determines the optical properties of Mo/Si multilayers.

4 Conclusions

Herein we investigated the influence of background pressure with respect to the optical properties and microstructure of Mo/Si multilayers in magnetron sputtering. The experimental results demonstrate that the decrease of background pressure leads to higher crystallization degree in (110) preferred orientation of Mo layer with a decrease of interlayer thickness, which finally results in greater optical properties of Mo/Si multilayers. For the higher-resolution solar EUV images, it is critical to increase stability of microstructure of the Mo/Si multilayers by applying lower background pressure range as well as controlling the magnetron sputtering system.

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1 Windt D L, Donguy S, Seely J. EUV multilayers for solar physics. Proc SPIE, 2004, 5168: 1–11
2 Attwood D. Soft X-rays and Extreme Ultraviolet Radiation: Principles and Applications. Cambridge: Cambridge University Press, 1999
3 Montcalmc G R F, Hudyma R M. Atomic-precision multilayer coating of the first set of optics for an extreme-ultraviolet lithography prototype system. Appl Opt, 2002, 41: 3262–3269
4 Takahashi S, Kitamoto S, Takahama S. Characterization of multilayer reflectors and position sensitive detectors in the 45–300 Å region. Rev Sci Instrum, 1992, 63: 1513–1515
5 Chen B, Gong Y, Ni Q L. A complex solar X-ray and EUV imaging telescope design. Proc SPIE, 2004, 5171: 155–159
6 Wilhelm K, Lemaire P, Curdt W. First results of the summer telescope and spectrometer on SOHO-I, Spectra and spectroradiometry. Solar Phys, 1997, 170: 75–104
7 Delaboudiniere J P, Artzner G E, Brunaud J. Eit: Extremeultraviolet imaging telescope for the soho mission. 1995, 162: 291–312
8 Tsuneta S, Ichimoto K, Katsukawa Y. The solar optical telescope for the Hinode mission: An overview. Solar Phys, 2008, 249: 167–196
9 Gussenhoven M S, Mullon E G. Space radiation effects program: An overview. IEEE Trans Nucl Sci, 1993, 40: 221–227
10 Liu Z, Yang L, Chen B. Mo/Si multilayers used for the EUV normal incidence solar telescope. Sci China-Phys Mech Astron, 2011, 50: 406–410
11 Andreev S S, Gaponov S V, Guesv S A. The microstructure and X-ray reflectivity of Mo/Si multilayers. Thin Solid Films, 2002, 415: 123–132
12 Bajt S, Stearns D G, Kearney P A. Investigation of the amorphous-to-crystalline transition in Mo/Si multilayers. J Appl Phys, 2001, 90: 1017–1025
13 Bruijn S, van de Kruijs R W E, Yakshin A E. The effect of Mo crystallinity on diffusion through the Si-on-Mo in EUV multilayer systems. Defect Diffus Forum, 2009, 283–286: 657–661
14 Guen K L, Maury H, Andre J M. X-ray interface analysis of aperiodic Mo/Si multilayers. Appl Surf Sci, 2007, 253: 8443–8446
15 Tseng C H, Wang W H, Chang H C. Effects of sputtering pressure and Al buffer layer thickness on properties of AZO films grown by rf magnetron sputtering. Vacuum, 2010, 85(2): 263–267
16 Wen R, Wang L, Wang X. Influence of substrate temperature on mechanical, optical and electrical properties of ZnO: Al films. J Alloys Compd, 2010, 508(2): 370–374
17 Xu X M, Wang J, An J. Effect of modulation structure on the growth behavior and mechanical properties of TiN/ZrN multilayers. Surf Coat Technol, 2007, 201: 5582–5586
18 Dong N N, Li M, Liu Z. Wavelength calibration of extreme ultraviolet monochromator (in Chinese). Opt Precis Eng, 2008, 16(9): 1660–1665
19 Zubarev E N, Zhurba A V, Kondratenko V V. The structure, diffusion and phase formation in Mo/Si multilayers with stressed Mo layers. Thin Solid Films, 2007, 515: 7011–7019
20 Lv P, Wang X D, Liu H. Microstructures of the interlayer in Mo/Si multilayers induced by proton irradiation. Sci China-Phys Mech Astron, 2012, 55: 2194–2198
21 Zhu J T, Huang Q S, Bai L. Manufacture and measurement of SiC/Mg EUV multilayer mirrors in different base pressures (in Chinese). Optics Precis Eng, 2009, 12(17): 2946–2951
22 Guan Q F, Lv P, Wang X D. Microstructures of Mo/Si multilayer mirror after proton irradiation (in Chinese). Acta Phys Sin, 2012, 61: 016107
23 Windt D L, Christensen F E, Craig W W. Growth, structure, and performance of depth-graded W/Si multilayers for hard X-ray optics. J Appl Phys, 2000, 88(1): 460–470
24 Pinegyn V I, Zubarev E N, Kondratenko V V. Structure and stressed state of molybdenum layers in Mo/Si multilayers. Thin Solid films, 2009, 516: 2973–2980
25 Windt D L, Brown W L, Volkert C A. Variation in stress with background pressure in sputtered Mo/Si multilayer films. J Appl Phys, 1995, 78(4): 2423–2430