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Thermal stability of Mo/Si multilayers

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ABSTRACT

The thermal stability of Mo/Si multilayers for x-ray mirror applications was investigated by annealing studies at relatively low temperatures for various times. The as-deposited and annealed multilayers were examined using conventional small and large angle x-ray diffraction, normal incidence x-ray reflectance measurements using a synchrotron source, selected area electron diffraction, and high-resolution electron microscopy. The as-deposited structure consists of pure layers of crystalline Mo and amorphous Si separated by thin regions of amorphous Mo-Si. At temperatures between 200–400 °C, the amorphous Mo-Si interlayers grow and hexagonal MoSi₂ forms by a thermally activated process(es), and the bilayer spacing and x-ray reflectivity decrease. A determination of the effective activation energy of the process(es) suggests long-term stability at the mirror operating temperature, although additional low temperature testing is warranted.

1. INTRODUCTION

Mo/Si multilayers are attractive as x-ray mirrors due to the relatively high associated reflectivity. Consequently, it is believed important to assess the structural stability of these mirrors. Relatively recent work by the authors and other investigators assessed the stability of Mo/Si multilayers [1–5]. Most of these works emphasized temperatures above 400 °C and relatively short annealing times. The remaining work examined the thermal stability at temperatures nearly as low as 200 °C. However, operating temperatures may approach ambient temperature and the assessment of the long-term structural stability of the multilayers by extrapolation from higher temperatures may not be reliable. The rate-controlling mechanism for a thermally activated process may change significantly with modest changes in temperature. It is the objective of this (and subsequent) work to perform a series of near ambient-temperature annealing treatments of Mo/Si multilayers over relatively long time periods to allow a reliable assessment of stability during mirror service at ambient and near ambient temperatures.

2. EXPERIMENTAL PROCEDURE

The multilayers in this study consisted of 40 bilayers of Mo and Si deposited onto a 75 mm polished single crystal (100) Si wafer covered with approximately 2 nm of native oxide. The nominal bilayer spacing was 7.0 nm and the ratio of the Mo layer thickness to the bilayer thickness was ~0.43. The multilayers were deposited using d.c. magnetron sputtering in an Ar plasma. A detailed description of the vacuum system and deposition procedures is presented elsewhere [6]. The 75 mm specimens were then cleaved into 10 (12 mm x 24 mm) specimens, which were encapsulated into glass tubes at a pressure of less than 10⁻⁵ Torr. All but one of the specimens were annealed at temperatures ranging from 127 °C to

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394 °C for times from 1 to 100 hours; the remaining specimen was retained as a control (unannealed) to determine if any changes to the multilayer structure resulted from the encapsulation procedure.

The thermal stability was assessed by reflectivity measurements using conventional small angle x-ray diffraction (SAXS) and normal incidence x-ray reflectance (NIR) measurements using a beamline of the VUV Radiometric Laboratory at the BESSY synchrotron facility. The formation of new phases was examined by conventional large angle x-ray diffraction (LAXS) and selected area electron diffraction (SAED) at the Center for Solid State Sciences at Arizona State University. The structure of the control specimen and some of the annealed multilayers was further examined by high resolution electron microscopy (HREM) of ion-milled foils using a JEM 4000 at the Facility for Electron Microscopy at Arizona State University.

3. RESULTS AND DISCUSSION

The as-deposited multilayer consists of amorphous Si layers and crystalline Mo layers [(110) planes parallel to interfaces]. The amorphous Si and crystalline Mo layers are separated by thin amorphous Mo-Si interlayer regions. This is consistent with earlier characterization of the microstructure by the authors and coworkers [7]. Table 1 indicates the effect of the annealing temperature on the bilayer spacing (Λ), as measured by SAXS. Table 1 also indicates the normal incidence peak reflectivities (R_p) and wavelengths (λ_p) which will be discussed in a later section of this manuscript. The control specimen values (unchanged by the encapsulation procedure) are $\Lambda = 6.97$ nm and $R_p = 57\%$ at $\lambda_p = 13.6$ nm. The SAXS data suggests that microstructural alterations and/or reflectivity is affected by thermal exposure to 227 °C (100 h), 298 °C (1 and 100 h) and 394 °C [1 h (and presumably longer)]. The fractional change in bilayer spacing is graphically illustrated in Fig. 1 along with the data of Stearns et al. [1] and Holloway et al. [2]. The contraction trends of this study are qualitatively consistent with those of the earlier work.

Table 1. Effect of annealing on x-ray properties of Mo/Si multilayers.

Annealing Temperature (°C)	Decrease in SAXS Bilayer Spacing (%)		Normal Incidence Peak Reflectivity (%)		Normal Incidence Peak X-Ray Wavelength (nm)	
	1 h	100 h	1 h	100 h	1 h	100 h
127	<1	<1	56	55	13.5	13.4
171	<1	<1	56	56	13.5	13.4
227	<1	3	54	56	13.4	13.2
298	1	17	54	1.2	13.1	11.3
394	18	—	0.6	—	11.2	—

The microstructural details of the changes suggested by the SAXS was investigated by HREM, SAED, and LAXS. Figure 2 shows an electron diffraction pattern of a Mo-Si multilayer, annealed 1 h at 394 °C. The figure shows a diffuse ring which was confirmed as corresponding to the [111] reflection of hexagonal MoSi₂. This identification was further confirmed by LAXS. Figure 3 shows the (110) Mo diffraction peak ($2\theta = 40.0^\circ$) from the unannealed specimen. With annealing and the formation of h-MoSi₂, we expect a (111) h-MoSi₂ ($2\theta = 41.6^\circ$) peak in close proximity to the (110) Mo peak. This is consistent with the apparent small shift of a "single" peak with annealing. The specimen annealed 100 h at 298 °C exhibited SAED and LAXS data nearly identical to those of Figs. 2 and 3. The HREM of Fig. 4, shows that after annealing 1 h at 298 °C, the substantially amorphous Mo-Si interlayer region grows thicker on both sides of the Mo layer. Holloway et al. [2] observed that the amorphous Mo-Si interlayer regions formed by deposition of Mo on Si thicken at a greater rate than those formed by deposition of Si on Mo. We do not observe this disparity. Once the reaction is complete, as shown in the specimen annealed 1 h at 394 °C, relatively thick layers of MoSi₂ are separated by thin layers of "unreacted" crystalline Mo. The pure Si layers have been completely consumed by the formation of MoSi₂. The HREM of the specimen annealed 100 h at 298 °C appears similar to that of Fig. 4c.

Figure 1. The fractional change in Mo/Si bilayer spacing with annealing at various temperatures and annealing times, as measured from SAXS.

Figure 2. An electron diffraction pattern of a Mo/Si multilayer on a Si single-crystal substrate. The diffuse ring corresponds to (111) h-MoSi₂.

Figure 3. LAXS results from unannealed and annealed (1 h at 394 °C) Mo/Si multilayers. The single diffraction peak shifts slightly with the formation of h-MoSi₂.

Figure 4. HREM micrographs of (a) a control and (b, c) annealed (1 h at 298 °C and 1 h at 394 °C) Mo/Si multilayers. These micrographs suggest the sequence of expansion of the (substantially) amorphous Mo-Si interlayer regions followed by crystallization and growth of the h-MoSi₂ phase. Eventually, the pure Si layer is completely consumed by the formation of MoSi₂, as shown in (c).

Normal incidence reflectance measurements were also performed, as these are relevant to the expected soft x-ray projection lithography (SXPL) application. The fundamental requirements for precision imaging multilayer mirrors in SXPL include high reflectivity and long-term stability at the operating temperature, estimated to be at or very near ambient temperature. These mirrors would be utilized as normal incidence reflective optics for soft x-rays of ~ 13 nm. The reflectance measurements were performed on a beamline of the VUV Radiometric Laboratory at the BESSY synchrotron facility. In a typical measurement, the angle of incidence of the x-rays was fixed at 0.8° from the normal, and the x-ray wavelength was scanned between 10 and 15 nm. On each sample, the reflectance was measured at several different positions across the surface (beam diameter ~ 200 μm) and was found to be uniform to within 5%. A detailed description of the x-ray beamline and reflectometer is presented elsewhere in this proceedings [8].

The measured reflectance of the multilayer mirror was compared with the theoretical reflectance that was calculated using a matrix method modified to incorporate nonideal interfaces [9]. This model allows for a determination of the chemical composition and composition profile of the interlayer regions if the thicknesses of these regions, as well as those of the pure interlayers, are known. Estimates of these thicknesses were obtained from HREM measurements and are listed in Table 2. Theoretical fits of the experimental normal incidence x-ray diffraction (NIR) data were obtained using interlayer regions of uniform MoSi_2 stoichiometry, and by assuming abrupt interfaces (no roughness).

Table 2. Effect of annealing on Mo/Si interlayer thicknesses, as measured from HREM data.

Annealing Time at Temperature	Bilayer Spacing (nm)	Thickness of Mo Layer (nm)	Thickness of Mo-Si on Mo (nm)	Thickness of Si Layer (nm)	Thickness of Mo-Si on Si (nm)
Control	7.0	2.6	0.4	3.0	1.0
1 h at 298 $^\circ\text{C}$	6.9	2.5	0.6	2.3	1.5
100 h at 298 $^\circ\text{C}$	5.7	1.5	4.2	—	—

Figure 5 (a-c) shows the theoretical and experimental NIR first order peaks for the control, annealed 1 h at 298 $^\circ\text{C}$, and annealed 100 h at 298 $^\circ\text{C}$ specimens, respectively. These best-fit models were calculated using optical constants determined by Windt [10]. The slight drop and shifting of the peak reflectivity for the specimen annealed 1 h at 298 $^\circ\text{C}$ compared to that of the control specimen is consistent with the slight contraction of the bilayer spacing as measured by SAXS. The specimen annealed 100 h at 298 $^\circ\text{C}$ exhibits only 1% reflectivity at a peak wavelength of 11.2 nm (well below the Si_L absorption edge of 12.4 nm) consistent with the bilayer contraction to 5.76 nm as measured by SAXS.

It should be mentioned that although the various measurement techniques suggest thermal stability at the lower temperatures (see Tables 1 and 2), it was observed that the higher order peaks in the SAXS spectra were modified at these temperatures. This may be a consequence of atomic arrangements very near the interface that were not obvious with HREM.

The thermal stability of these multilayers at ambient temperature is estimated by calculating the interdiffusion coefficient D of the Mo/Si couple as a function of temperature, described by a pre-exponential coefficient D_0 , which is temperature independent, and an effective activation energy of interdiffusion E_a :

$$D = D_0 \exp(-E_a/kT). \quad (1)$$

The growth kinetics of the Mo-Si interlayer is determined by assuming that the interlayer growth is diffusion limited with constant concentrations at the interfaces between the Mo-Si interlayer and elemental layers, and that the concentration gradient dc/dx across the interlayer width w is given by [11]

$$dc/dx = (-1/w). \quad (2)$$

Figure 5. Normal incidence reflectivity of (a) control, annealed (b) 1 hour and (c) 100 h at 298 °C.

The interdiffusion coefficient is related to the rate of change in interlayer width by substituting Eq. (2) into Fick's first law:

$$D = w(dw/dt). \quad (3)$$

For a multilayer with a Mo-Si interlayer width $w(t)$ after annealing time t , the interdiffusion coefficient is then given by

$$D = [w^2(t) - w^2(0)]/2t, \quad (4)$$

where $w(0)$ is the initial width. Because there are two Mo-Si interlayer regions per bilayer period Λ , the interdiffusion coefficient can be evaluated based on the growth of either one of these regions directly from HREM data. For the case where post-anneal HREM data is not available, the individual Mo-Si interlayer thicknesses $w_1(t)$ and $w_2(t)$ on either side of the pure interlayer material can be determined from the SAXS bilayer contraction data if the unannealed interlayer thicknesses $w_1(0)$ and $w_2(0)$ are known. Using bulk densities values for Mo, Si, and MoSi_2 , the total increased thickness of the Mo-Si (represented by uniform MoSi_2 stoichiometry) interlayer region(s) per bilayer period is related to the bilayer contraction $\Delta\Lambda$ by

$$w(t) - w(0) = 2.5\Delta\Lambda. \quad (5)$$

Therefore, the individual Mo-Si interlayer thicknesses, given by combining Equations 2 and 3, are

$$w_1(t) = [\alpha^2 + w_1^2(0) + w_2^2(0)]/2\alpha \quad (6)$$

and

$$w_2(t) = \alpha - w_1(t), \quad (7)$$

where

$$\alpha = w_1(0) + w_2(0) + 2.5\Delta\Lambda. \quad (8)$$

Fig. 6 is an Arrhenius plot of $\log D$ versus $1/T$. The interdiffusion data of this study (calculated from SAXS data using Eqs. 6–8) is plotted with that of Stearns et al. [1], Holloway et al. [2] [(calculated directly from HREM data using Eq. 4), Sloof et al. [3], and Nakajima et al. [4]. Interdiffusivities reported by Sloof et al. and Nakajima et al. were evaluated from the relative decrease in SAXS first order intensity $I(t)$ using the relationship

$$D = (\Lambda^2/8\pi^2t)\ln[I(0)/I(t)], \quad (9)$$

where $I(0)$ is the initial intensity. Our interdiffusivities calculated from annealing experiments performed over the temperature range of ~ 225 – 400 °C are in close agreement with those reported by Stearns et al. and Sloof et al. However, our interdiffusion coefficient results at 400 °C are midway between those of Holloway et al. and Nakajima et al., with D varying by nearly five orders of magnitude. Whether the large differences in interdiffusion coefficients are indicative of the different methods used to calculate D , or to structural features associated with multilayers fabricated in different sputtering systems is not clear. In spite of these differences in D , the effective activation energy for all three sets of data is equal to ~ 1 eV. The data from Sloof et al. suggests a slightly lower E_a than those of the other studies. This may be the result of a decrease in E_a below about 300 °C, due to the possibility of lower activation energy mechanisms becoming rate-controlling at decreased temperatures. This emphasizes the importance of performing long-term annealing experiments at lower (100 – 200 °C) temperatures.

Figure 6. Arrhenius plot of the interdiffusion coefficient in Mo/Si multilayers as a function of temperature, based on Mo-Si interlayer growth determined from HREM data, SAXS bilayer contraction data, or relative decreases in SAXS first order intensity, observed in this and other studies.

Assuming a constant E_a of ~ 1 eV at temperatures below 200 °C, our data suggests that changes in reflectivity of Mo/Si multilayer mirrors at ambient temperature are negligible over the time-scale relevant to SXPL. This is based on modeling the interlayer widths required to reduce the reflectivity, using Eqs. (4–8) to calculate the interlayer growth. The data of Sloof et al. [3] would, however, suggest degradation in less time due to the lower effective activation energy and (slightly) higher interdiffusion coefficients. For example, critical degradation (normal incidence reflectivity reduced by 10 relative percent) at ambient temperature could occur within several years if $E_a \sim 0.7$ eV and the interdiffusion coefficient is ~ 3 orders of magnitude higher. This uncertainty, in addition to the higher order peak changes with low-temperature annealing observed in SAXS, emphasize the importance of determining realistic values for E_a and D_0 at low temperatures.

4. CONCLUSIONS

- 1) Annealing Mo/Si optical multilayers for 1–100 h at temperatures between 200–400 °C can result in decreased multilayer performance.
- 2) This loss of reflectivity may be the result of interdiffusion of Si and/or Mo in the (principally) amorphous Mo-Si interlayer region, causing growth of this interlayer region that eventually crystallizes to h-MoSi₂. The MoSi₂ appears to continue to grow until all of the Si is consumed.
- 3) An effective activation energy for interdiffusion, E_a , was calculated, assuming Arrhenius behavior, and our values are consistent with other investigations. Our extrapolations of the reaction process(es) to ambient (operating) temperature indicate that sufficient thermal stability may be expected, although, additional, lower-temperature annealing studies are warranted.

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