Studies on the stress and thermal properties of Mo/B₄C and MoₓC₁₋ₓ/B₄C multilayers

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Abstract

A comparative study of Mo/B₄C and MoₓC₁₋ₓ/B₄C multilayers deposited by DC magnetron sputtering technology was presented in this paper. Using a homemade real-time stress measure instrument, the stress of two kinds of multilayers was investigated. Characterizations of the multilayers before and after annealing were performed by grazing incident and at-wavelength near-normal incident x-ray reflectivity. Experimental results show that after replacing Mo by MoₓC₁₋ₓ, MoₓC₁₋ₓ/B₄C multilayers obtain relatively smaller compressive stress compared with Mo/B₄C multilayers. The corresponding stress value changes from −0.99 GPa to −0.36 Gpa. MoₓC₁₋ₓ/B₄C multilayers have also proven to have better thermal stability up to 600 °C. After repeatedly annealing from 100 °C to 600 °C, Mo/B₄C multilayers had a ~2% decrease in near-normal incident reflectivity, while MoₓC₁₋ₓ/B₄C multilayers had a smaller 1.4% loss of reflectivity and a higher stability temperature.

1. Introduction

Multilayers were successfully used for focusing [1–3], reflecting, and filtering [4, 5] beams from various x-ray sources [6]. Multilayers also allowed the use of normal incidence optics in the soft x-ray regime and substantially enhance the x-ray reflectivity of the optical substrates [7]. Particularly, when multilayers were used under intense x-ray beams, their stability was found even more important than initial high reflectivity [8, 9]. In some experiments, the multilayer-based optics were subject to strong heat loads without cooling system, thermal load may lead to interdiffusion of atoms and subsequent compound formation at the interfaces of multilayers, consequently reducing optical contrast and causing a lower reflectivity [10].

Normal-incidence multilayers operating at 6.6–7 nm wavelength range require a period thickness around 3.5 nm. The interfaces in these short-period multilayers constitute a larger fraction of the multilayer period, thus the interface imperfections, such as interfacial roughness and interdiffusion, play a bigger role in the multilayer performance [11]. High reflectivity was demonstrated with multilayer pairs with B₄C used as a spacer layer and La, Ru, Mo or W used as an absorber layer [12, 13]. Theoretically, La/B₄C and Ru/B₄C give the higher normal incidence reflectivity. However, some disadvantages result in lower experimental value. Previous studies conducted investigations on at-wavelength performances of B₄C-based multilayer systems. The La/B₄C multilayer structures give the highest reflectivity (40% with 250 bilayers) as compared to other material combinations. However, the active chemical properties of La make it difficult to preserve the high reflectivity of La/B₄C multilayers. After annealing at 250 °C, a maximum relative reflectivity loss of 13.4% was found in La/B₄C multilayers [13]. After annealing, the serious interdiffusions between Ru and B₄C layers make multilayer unsuitable for some applications with high thermal load. For soft x-ray free electron laser, the reflectivity dropped from 20% to 10% after annealing at 500 °C for 1 h [14]. W/B₄C multilayers can form smooth interfaces and prove to be thermally stable. Reflectivity of 8% was obtained using W/B₄C multilayer...
Consisting of 50 bilayers at the 15° off normal incidence, while the measured reflectivity dropped 1% after 500 °C annealing [15]. We have chosen the Mo/B₄C multilayer bilayers in this study because B₄C can form relatively smooth interfaces with Mo [16], and Mo/B₄C has higher theoretical reflectivity compared to W/B₄C multilayers within 6.6–7 nm wavelength range.

Mo/B₄C, as a promising material pair of multilayer for the 6.6–7 nm wavelength range, the thermal stabilities of its stress and interface have been extensively studied [17, 18]. Based on the previous results, the main shortcomings of Mo/B₄C multilayers are high intrinsic stress and serious interfacial roughness [19], in which the interfacial roughness was the primary cause of low reflectivity. Similarly, a Ru/B₄C multilayer with 4 nm period thickness was found to be characterized by a compressive stress of −1.5 GPa [20]. A W/B₄C multilayer was reported to have a stress value of −1.51 Gpa, after introduction of reactive sputtering, the stress value is reduced to −0.42 Gpa [21].

It has been observed that serious interdiffusion expansion occurred in Mo/B₄C multilayers upon annealing. The phenomenon of both period expansion and compaction were observed during annealing, depending on the thickness of the B₄C layers, annealing temperature and annealing time [22]. An increase in multilayer period thickness was observed for annealed La/B₄C multilayers. After annealing at 250 °C, a period expansion of 0.6% was found [13]. Similar trend has been found in the W/B₄C multilayers. The W/B₄C multilayers experience an expansion of 1% after annealing at 500 °C, the period thickness remains the same after annealing at 700 °C and above [15].

Note that while reducing the stress, the introduction of roughness should be avoided especially for multilayers with short period. As a substitute for Mo, Mo₂C can effectively optimize the multilayer interface characteristics while reducing the multilayer film stress [23]. In this paper, we fabricated the co-sputtering MoₓC₁₋ₓ/B₄C multilayer and compared their stress and thermal performances with the conventional Mo/B₄C multilayers.

2. Experiments details

A direct current (DC) magnetron sputtering deposition system was used to fabricate Mo/B₄C and MoₓC₁₋ₓ/B₄C multilayers on silicon substrates. The machine has 3 targets: Mo target, C target and B₄C target. All the Mo/B₄C and the MoₓC₁₋ₓ/B₄C multilayers used in this study consisted of 100 bilayers. The multilayer period thickness was 3.6 nm and the thickness ratio of Mo (MoₓC₁₋ₓ) layer to the period, \( \Gamma = d_{Mo}/(MoₓC₁₋ₓ/B₄C) \), was 0.4. The sputtering was performed with the argon gas pressure of 2 mTorr. While depositing the MoₓC₁₋ₓ layers, Mo and C targets were adjusted at an included angle in order to achieve Mo and C co-sputtering. The power of C target was changed as the period increased in order to control the carbon concentration in Mo and C co-deposited layer. The powers of C were 0 W, 20 W, 40 W, 60 W, 80 W, and 100 W, where 0 W of C power corresponds to a Mo/B₄C multilayer bilayer was deposited on the substrate.

The curvature of each substrate was measured after each Mo (MoₓC₁₋ₓ) or B₄C layer was deposited on the substrate. The measurement was performed using a homemade real-time stress measure instrument. This system mapped the curvature of the substrate related to the stress of the multilayers by a laser matrix with a wavelength of 694.3 nm. The differences in the reflectivity measurements were performed at the BL08B beamline of the NSRL at 10° off normal incidence. Table 1 shows the group name of prepared multilayer samples and the corresponding annealing methods and test methods, each group included two samples: Mo/B₄C and MoₓC₁₋ₓ/B₄C multilayers.
3. Results and discussion

3.1. Stress measurement

Measurements of the curvature obtained from one sample for 6 different C powers are shown in figure 1(a). Figure 1(b) shows the corresponding stress values of each Mo$_{x}$C$_{1-x}$/B$_4$C layer in the multilayer. The layer thickness was calculated from the GIXRR measured data. Measured results of the curvatures, the stress value of the entire Mo$_{x}$C$_{1-x}$/B$_4$C multilayers that correspond with each individual C power, and the standard deviation of the stress values and curvatures are shown in table 2.

Although the data contained a high level of noise, it was clear that curvature decreased more for Mo/B$_4$C multilayer structure with C power of 0 when compared with other Mo$_{x}$C$_{1-x}$/B$_4$C multilayer structures. When the C power of co-sputtering was 40 W, the Mo$_{x}$C$_{1-x}$/B$_4$C multilayers reached the lowest stress value of $-0.36$ GPa.

Residual stress has proved to be related to microstructure in a multilayer system [25, 26]. In [21], the reduction of stress value is mainly caused by the crystalline-to-amorphous of W layer after the introduction of reactive sputtering. However, multilayers with period thickness of 3.6 nm and $\Gamma = d_{Mo/(MoC_{1-x})}/D$ of 0.4, contain Mo layers that are much thinner than 2 nm, which is smaller than the critical thickness of the amorphous-to-crystalline transition of molybdenum [27, 28]. This means that the Mo layers in the multilayer are amorphous. The high compressive stress is suggested to mainly come from the stress of the interlayers, not from the polycrystalline structure of Mo layers. It is well known that at low plasma pressures, as used in this study, the material is deposited with a high packing density due to the large energy input by a high number of

![Figure 1.](image-url) Curvature and stress data as a function of multilayer thickness. Compressive stress is negative and tensile stress is positive.

| Power of C (W) | 0    | 20   | 40   | 60   | 80   | 100  |
|---------------|------|------|------|------|------|------|
| Curvature/m$^{-1}$ | $-0.10 \pm 0.010$ | $-0.05 \pm 0.009$ | $-0.04 \pm 0.012$ | $-0.05 \pm 0.008$ | $-0.05 \pm 0.013$ | $-0.06 \pm 0.011$ |
| Stress/GPa     | $-0.99 \pm 0.10$ | $-0.43 \pm 0.08$  | $-0.36 \pm 0.11$  | $-0.46 \pm 0.08$  | $-0.51 \pm 0.13$  | $-0.62 \pm 0.11$  |

Table 2. Measured curvatures and stresses for sputtering under 5 different C powers.
collisions with energetic Ar ions. This results in high compressive stress which is attributed to the peening-effect [28]. The interfaces are not perfect and the presence of interdiffusion cause the high stress. After the introduction of Mo$_x$C$_{1-x}$ layer, the interdiffusion improved significantly, which in turn reduced the stress of the multilayers. Based on above discussions, the thickness changes of the interlayers can effectively modulate the overall stress of the multilayers. Thickness changes of interlayers in the Mo$_x$C$_{1-x}$/B$_4$C multilayers, versus different C sputtering power, can partly explain the observed changes in stress with sputtering power of C in the Mo$_x$C$_{1-x}$/B$_4$C multilayers.

3.2. GIXRR measurement
The GIXRR measured data of Mo/B$_4$C and Mo$_x$C$_{1-x}$/B$_4$C multilayers in group A before and after annealing from 100 °C to 600 °C are shown in figure 2. After fitting the GIXRR data [20], the change of the period thickness can be found in figure 3.
As depicted in figure 2, peak drift and broadening were observed, especially for Mo/B₄C multilayers after annealing, which reveals that the period expansion and interfacial roughness/diffusion of Mo/B₄C multilayers were more serious than that of MoₓC₁₋ₓ/B₄C multilayers.

The period expansion can be explained by the relaxation of packing density as well as the growth of interlayers. The rich B and C elements in the interfaces result in the formation of relatively low-density compounds and the period expansion [29]. MoₓC₁₋ₓ is already a low-density molybdenum carbides compound which also reduces the growth of interlayers, and therefore reduces the period expansion. Results in the layer expansion can be observed here. A MoₓC₁₋ₓ/B₄C multilayers expansion of <1% and Mo/B₄C multilayers expansion of <2% were measured for annealing temperatures up to 600 °C.

Based on the GIXRR fitting results, after annealing for 6 h, the Mo-on-B₄C interfacial roughness/diffusion of Mo/B₄C multilayers increased from 0.3 nm to 0.7 nm, while that of the MoₓC₁₋ₓ-on-B₄C interface increased from 0.2 nm to 0.4 nm. The B₄C-on-Mo interfacial roughness/diffusion of the Mo/B₄C multilayers increased from 0.6 nm to 1.5 while the B₄C-on-MoₓC₁₋ₓ interfacial roughness/diffusion increased from 0.3 nm to 0.8 nm. The results in [29, 30] show that after annealing, the increase of interfacial roughness was negligible compared to that of the interdiffusion. So the broadening of Bragg peaks in the kinds of multilayers can be attributed to the fact that the increase of interdiffusion in Mo/B₄C multilayers is much more serious than that in MoₓC₁₋ₓ/B₄C multilayers.

The fitting results indicated the asymmetry of this multilayer system with a sharper Mo(MoₓC₁₋ₓ)-on-B₄C interface and a more diffuse B₄C-on-Mo(MoₓC₁₋ₓ) interface. After annealing, the B₄C-on-Mo interfaces experience greater expansion than the B₄C-on-MoₓC₁₋ₓ interfaces. The expansion of B₄C-on-Mo(MoₓC₁₋ₓ) interfaces is more severe than that of the Mo(MoₓC₁₋ₓ)-on-B₄C interfaces. After annealing, the difference in roughness/diffusion of the two interlayers changes from 0.3 to 0.8 in Mo/B₄C multilayers, from 0.1 to 0.4 in MoₓC₁₋ₓ/B₄C multilayers.

The fitting results also indicated that MoₓC₁₋ₓ/B₄C multilayers have better thermal stability compared to La/B₄C [13] and W/B₄C [15] multilayers.

### 3.3. At-wavelength reflectivity measurement

All three groups of samples were measured by at-wavelength near-normal incident reflectivity at the BL08B beamline of the NSRL. The experimental and fitting results are shown in figures 4 to 6. Table 3 compares the changes of the reflectivity, peak wavelength and the corresponding period fitting from the reflectivity measured data for two different multilayer pairs.

The results presented in table 3 show good agreement with the results calculated from the GIXRR data. Near-normal incident measurements with a synchrotron reflectometer are more sensitive to small changes in the multilayer period and reflectivity than grazing incidence measurements done with the Cu Kα-line. After annealing, the shift in peak wavelength and the decrease in reflectivity were obvious.
Figure 5. Reflectivity measurements (solid line) and fitting results (dotted lines) at 10° off normal incidence of the samples in group B before and after annealing at 400 °C.

Figure 6. Reflectivity measurements (solid line) and fitting results (dotted lines) at 10° off normal incidence of samples in group C before and after annealing at 500 °C.

Table 3. Changes of reflectivity, peak wavelength and the corresponding period thickness of three groups of samples before and after annealing process.

| Material combination | ΔR  | Δλ   | ΔD   |
|----------------------|-----|------|------|
| Group A              |     |      |      |
| Mo₅Cₓₓ₋ₓ/B₄C         | −1.4% | 0.070 nm | 0.041 nm |
| Mo/B₄C               | −2.0% | 0.120 nm | 0.071 nm |
| Group B              |     |      |      |
| Moₓₓ₋ₓ/Cₓₓ₋ₓ/B₄C     | −0.4% | 0.035 nm | 0.021 nm |
| Mo/B₄C               | −0.9% | 0.055 nm | 0.033 nm |
| Group C              |     |      |      |
| Moₓₓ₋ₓ/Cₓₓ₋ₓ/B₄C     | −0.8% | 0.050 nm | 0.029 nm |
| Mo/B₄C               | −1.3% | 0.085 nm | 0.048 nm |
It has been reported that the annealing process leads to the broader interlayer and a negligible increase in interfacial roughness in Mo/B₄C multilayers [31]. The reduction in peak reflectivity after annealing is due to the increase of interdiffusion, which reduces the optical contrast between two layers. Results of three annealing processes reveal the similar patterns, both Mo/B₄C and MoₓC₁₋ₓ/B₄C multilayers experienced a peak wavelength shift and a decrease in near-normal incident reflectivity, but the changes were more serious for Mo/B₄C multilayers. The difference in the changes of two material combinations indicated that MoₓC₁₋ₓ/B₄C multilayers had better thermal stability than Mo/B₄C multilayers.

4. Conclusion

Experimental results show that, under 2 mTorr plasma pressures, with C power increased from 0 W to 100 W, MoₓC₁₋ₓ/B₄C multilayers stress changes from −0.99 GPa to −0.36 GPa. The data for 40 W C power reveal the lowest stress. After annealing, both MoₓC₁₋ₓ/B₄C and Mo/B₄C multilayers experience peak shift toward a longer wavelength and a decrease in reflectivity. The shift in the peak wavelength and the decrease in reflectivity were more serious in Mo/B₄C multilayers.

All the results show that stress property and thermal stability of MoₓC₁₋ₓ/B₄C multilayers are much better than that of the Mo/B₄C and other B₄C-based multilayers. Therefore, the replacement of Mo layers by co-sputtering MoₓC₁₋ₓ layers can significantly improve the thermal stability and stress property of the multilayers.

Acknowledgments

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