Synthesis and structure evaluation of Mo/B periodical nano-layered coatings for beyond EUV optics

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ABSTRACT. The structure of Mo/B periodical multilayer coatings for beyond extreme ultraviolet (BEUV) optics was investigated. The coatings were deposited by a combination of Pulse DC/RF magnetron sputtering and investigated by HRTEM, XPS, and grazing incidence X-ray reflectometry. It was shown that the formation of thin interlayers occurred at Mo/B interfaces. The thickness of interlayers was around 0.4 nm, and they consisted of a mixture of molybdenum borides. A low interface roughness of 0.3-0.4 nm was reported. Theoretical calculation based on the real structure predicted two times higher reflectivity at the wavelength of 6.7 nm compared with conventional BEUV mirrors based on B\textsubscript{4}C.
1. Introduction

In the computer industry, there is a continuous trend towards a reduction in process scale to raise operation frequency and lower the power consumption of microprocessors. To follow this trend, it is required to improve the resolution of the lithography equipment correspondingly through the reduction of the working wavelength[1]. Recently, the resolution was enhanced by the replacement of so-called Deep ultraviolet (DUV) wafer scanners by the new generation of devices using Extreme Ultraviolet (EUV) irradiation with the wavelength of 13.5 nm. The next step would be the further reduction of the wavelength down to 6.7 nm and moving to beyond extreme ultraviolet (BEUV)[2].

Due to the extremely high absorption of EUV and BEUV radiation in materials, advanced reflective optical devices such as periodical multilayer x-ray mirrors (PMMs) should be used. PMMs are artificial Bragg crystals consisted of alternated layers of “light” and “heavy” materials and having a periodicity of the half of the working wavelength [3, 4] For the wavelength of 13.5 nm, the combination of Mo and Si is mostly used, but they are not suitable for shorter wavelengths.

Mo/B PMMs have one of the best reflectivity in the wavelength of 6.6 – 11.5 nm[5]. Nonetheless, despite the theoretical supremacy of Mo/B PMMs, the vast majority of researches was dedicated to the investigation of its less effective competitors such as Mo/B₄C, Pd/B₄C, and La/B₄C PMMs [6-10] Researchers focused on the less effective PMMs since the deposition of high-quality Mo/B PMMs was quite complicated. The complexity is caused by the dielectric nature of boron, which leads to instability of the magnetron sputtering, which was generally used for the synthesis of PMMs. That is why boron was replaced with less effective but more predictable boron carbide (B₄C).
In general, the manufacturing of first-class PMM is far beyond just alternating stacking of two materials. It requires control of the structure and composition of layers, interface roughness, spatial uniformity, and time stability of the deposition rate. The structure of the PMMs is the crucial factor that defines the optical properties. For instance, the intense investigation of the structure and interlayer mixing in La/B PMM allowed significant improvement of their reflectivity[11]. Regarding Mo/B PMMs, their structure remained almost unknown due to the complexity of the synthesis mentioned above. The several existing publications were dedicated to the investigation of the optical properties of Mo/B PMM without profound structural analysis[5].

In this work, the synthesis of high-quality Mo/B PMMs was reported, and their structure was investigated in detail. The knowledge about the structure was used for the theoretical prediction of reflectance of Mo/B BEUV mirrors at the wavelength of 6.7 nm.

2. Experimental details

Different types of Mo/B PMMs were deposited onto polished Si wafers by magnetron sputtering in a custom-built deposition system with a base pressure of $10^{-6}$ Torr[12]. Each type of PMM has a different thickness of Mo and B layers. The thickness of the B layers was varied in the range of 1.5-1.8 nm. The thickness of the Mo layers was 1-8 nm. A number of periods was ranged from 16 to 300 to maintain the same total thickness of PMMs. In all PMMs, the bottom layer was 5 nm thick Mo, and the top layer was 14 nm thick B. Pulsed DC power source was used for sputtering of the Mo target (40 kHz, 50 mA). RF power source (300 W) was used for the B target. The same deposition rates of Mo and B were used for all PMMs; the deposition rates were preliminarily calibrated. The thickness of Mo and B layers was controlled by adjusting the deposition time. Sputtering was performed in the Ar atmosphere under the pressure of 2.5 mTorr. The substrate
temperature was monitored during the deposition process by a thermosensitive sensor; it did not exceed 100°C.

A DRON-3M X-ray diffractometer (Cu-Ka radiation, 0.154nm) was used in the Θ–2Θ geometry to measure grazing incidence X-ray reflectometry (GIXR). A Si(110) single-crystal monochromator was used to separate the Cu-K_α_1 line and collimate a primary beam with a divergence of 0.015°. GIXR, in combination with the computer simulation, was used for evaluation of thickness, density, and the interface roughness of individual layers in PMMs. The computer simulation of GIXR was performed by the X-Ray Calc code[13]. The calculated GIXR curves were fitted to measured ones by adjusting parameters of the computer model. The computer model was described by the chemical composition, thickness, density, and interface roughness of each layer. The example of measured and calculated GIXR curves is shown in Figure 1.

The structure of PMMs was also investigated by cross-sectional high-resolution transmission electron microscopy (HRTEM, JEOL JEM-ARM200F). The cross-sections for the HRTEM were manufactured by a focused ion beam (FIB, JEOL JIB-4601F). The chemical composition was evaluated by X-ray photoelectron spectroscopy (XPS, Thermo Scientific Mono). Residual stress was calculated based on the substrate curvature using the modified Stoney’s equation[14]. Substrate curvature was measured using a 3D stylus profilometer (Dektak, Bruker).
Figure 1. GIXR fitting. An example of the measured and two best fitted calculated GIXR curves for Mo/B PMM having thicknesses of Mo and B layers of 2.2 and 1.1 nm, respectively. The total number of Mo/B pairs was 300. The simple model consisted only of Mo and B layers. The realistic model included MoB\(_2\) 0.4 nm thick interlayers. The inset shows 3-d and 4-th diffraction orders on a linear scale.

3. Results and discussion

For evaluation of the deposition process, a series of coatings were prepared with various deposition times and fixed deposition rates. The exact thickness of Mo and B layers was obtained from GIXR data and plotted as functions of the deposition time (Figure 2). The thickness of individual layers linearly increased with increasing deposition time. The linear approximation of growth curves in Figure 2 demonstrated that the y-intercept of the Mo growth curve lay above zero rather than going to zero. In the case of the B growth curve, the y-intercept was below zero. In other words, both growth curves were shifted regarding the natural position. The behavior exhibited the formation of interlayers during the deposition. The similar behavior of the growth
curves was observed in other layered structures such as Sc/Si, Mo/Si, and W/B₄C [15-17] The negative shift of the B growth curve indicated that boron diffused into Mo layer casing formation of the interlayers at the interface. In other words, “consumption” of boron occurred. The creation of the boron-molybdenum compounds caused the “swelling” of the Mo layer and the positive shift of the Mo growth curve.

To confirm the existence of interlayers and further evaluate the structure of PMMs, cross-sectional HRTEM was used. An example of a Mo/B PMMs structure is shown in the HRTEM image (Figure 3a). The dark strips corresponded to Mo layers, the bright ones – to B layers. The thickness of Mo and B layers was ~5 and ~11 nm, respectively. The microdiffraction (Figure 3a inset) revealed the amorphous structure of the coating. The amorphous structure of Mo layers could be explained by the solid-state amorphization mechanism [18-20]

Symmetrical interlayers between Mo and B are clearly visible in the form of gray strips (Figure 3b). According to the HRTEM, the thickness of the interlayers was around 0.5 nm. The interlayers

![Figure 2. Growth curves. Thickness of (a) boron and (b) Mo layers as functions of the deposition time.](image-url)
were further investigated by GIXR. The model parameters are summarized in Table 1. The acceptable matching between theoretical and experimental GIXR curves was achieved only when interlayers with thickness around 0.4 nm were introduced into the model (Figure 1). The best matching was obtained for the MoB\textsubscript{2} interlayers having a density of 7.1 g/cm\textsuperscript{3}. In the opposite, using of 2-layer model (Table 2) and reducing the density of the Mo layers did not allow to match of calculated and measured curves.

The larger thickness of interlayers given by HRTEM was attributed to possible slight tilt of the cross-section specimen during measurement. Because the thickness of layers was much smaller compared with the total thickness of the specimen in the projection direction, a little tilt caused extension of shadows on the image. Thus, the GIXR data were considered as more trustworthy. The similar phenomena were observed in other studies were HRTEM and FIXR were used together[21]. Besides, the measurement of interlayer’s thickness was also complicated due to interface roughness.

**Table 1.** Parameters of the realistic model with interlayers for GIXR simulation.

| Stacks   | N  | Layers          | Thickness, nm | Roughness, nm | Density, g/cm\textsuperscript{3} |
|----------|----|-----------------|---------------|---------------|----------------------------------|
| Top      | 1  | Boron           | 8             | 0.8           | 2.37                             |
|          |    | MoB\textsubscript{2} | 0.4          | 0.3           | 7.1                              |
|          |    | Molybdenum      | 0.4           | 0.4           | 10.2                             |
|          |    | MoB\textsubscript{2} | 0.4          | 0.3           | 7.1                              |
|          |    | Boron           | 2.1           | 0.24          | 2.37                             |
| Main     | 300| Molybdenum      | 5             | 0.5           | 10.2                             |
| Sublayer | 1  | Silicon         | $\infty$      | 0.5           | 3.2                              |
| Substrate| -  |                 |               |               |                                  |
Table 2. Parameters of two-layer model for GIXR simulation.

| Stacks     | N  | Layers         | Thickness, nm | Roughness, nm | Density, g/cm³ |
|------------|----|----------------|---------------|---------------|---------------|
| Top        | 1  | Boron          | 8             | 0.8           | 2.37          |
| Main       | 300| Molybdenum     | 1.2           | 0.44          | 8.5           |
|            |    | Boron          | 2.1           | 0.24          | 2.37          |
| Sublayer   | 1  | Molybdenum     | 5             | 0.5           | 10.2          |
| Substrate  | -  | Silicon        | ∞             | 0.5           | 3.2           |

The chemical composition of the PMMs was also evaluated by XPS. Before the acquisition of XPS spectra, the surface of the specimen was etched by a 500 eV Ar ion beam for 20 mins. Thus, the XPS data represent the chemical composition inside the PMM rather than on its surface. XPS spectra (Figure 4) indicated the presence of pure B and Mo alongside with their compounds. The spectra (Figure 4a) shows the primary Mo 3d₅/₂ and Mo 3d₃/₂ peaks located at 228.5 and 231.9 eV. Besides peaks of pure Mo, several fewer intensive secondary peaks located at 229.3, 230.36, 232.4, and 233.9 eV were found. The presence of the secondary peaks indicated chemical bonding between Mo and B [22, 23, 24]. The B 1s peak was also deconvoluted to the main peak located at 188.2 eV and several secondary peaks (Figure 4b). The main peak corresponded to pure boron. The secondary peaks attributed to chemical bonding between Mo and B. The presence of XPS peaks associated with pure boron, molybdenum, and molybdenum borides additionally proved the existence of interlayers between layers of pure Mo and B.
According to the curvature measurements, PMMs exhibited compressive residual stress of 0.8-0.9 GPa. Formation of compressive stress is quite general for coatings deposited at low temperatures and having an amorphous structure, but the observed values of stress are relatively small. For instance, several times higher compressive stress was observed in Mo/B₄C and Pd/B₄C PMMs [6, 10]. The reduction of mechanical stress minimizes the risk of delamination of the PMMs or deformation of thin substrates.

As it was mentioned in the Introduction section, the ideal periodical structure consisted of Mo and B layers, and having sharp interfaces should have the highest reflectivity at the wavelength of 6.7 nm. According to the simulation results, the peak reflectivity of such a mirror was 60% (Figure 5). The reflectivity of the real BEUV mirrors significantly affected interface roughness. According to HRTEM and GIXR, the real Mo/B PMMs had relatively smooth interfaces; the interface roughness was around 0.3 nm. Introducing such interface roughness into the ideal model reduced...
the reflectivity to 52%. The presence of interlayers blurred the interfaces and caused the further reduction of the reflectivity compared with the ideal model. Nonetheless, according to the simulation results, the real Mo/B PMMs having 0.4 nm thick interlayers and roughens of 0.3 nm, would have reflectivity around 47%. This was approx. 2 times higher than the reflectivity of Mo/B4C or Sb/B4C PMMs [6, 13].

![Figure 4. XPS Data. Deconvolution of (a) Mo 3d and (b) B 1s XPS peaks for Mo/B PMM having thicknesses of Mo and B layers of 2.2 and 1.1 nm, respectively.](image)

4. Conclusions

The deposition of Mo/B PMMs by magnetron sputtering was demonstrated, and the structure of PMMs was evaluated. Mo/B PMMs consisted of smooth amorphous Mo and B layers separated by ~0.4 nm thick interlayers with the chemical composition and density close to MoB$_2$. According to the simulation results, such PMM should have a reflectivity of 47% at a wavelength of 6.7 nm.
Figure 5. Calculated BEUV reflectivity. Comparison of the calculated peak reflectivity at the wavelength of 6.7 for different PMM models: an ideal Mo/B; Mo/B with the interface roughness; real Mo/B with interlayers; real Mo/B$_4$C. The angle of incidence was $5^\circ$ off normal.

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ABBREVIATIONS

BEUV, beyond extreme ultraviolet; PMM, periodical multilayer x-ray mirror; GIXR, grazing incidence X-ray reflectometry.
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