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Stability of Mo/Si Multilayer Structure Used in Bragg-Fresnel Optics *

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The thermal and chemical stabilities of Mo/Si multilayer structure used in Bragg-Fresnel optics were studied to get optimal technological parameters of pattern generation. Mo/Si multilayers were annealed at temperature ranging from 360 to 770 K, treated with acetone and 5‰ NaOH solution, and characterized by small-angle x-ray diffraction technique as well as x-ray photoelectron spectroscopy, and Olympus microscopy.

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A new type of x-ray optical element—Bragg-Fresnel optics[1,2] (BFOs) consisting of patterned multilayer mirrors benefits from the advantages associated with both the layered microstructure of the multilayer structure and the patterned microstructure. The benefits of the multilayer structure are the high reflectivity at nongrazing incidence and the high resistance to temperature and flux. While the benefits of the patterned diffraction microstructure are the high resolution and the possibility used at shorter wavelength region (water window or hard x-ray). The general fabrication process of BFOs consists of multilayer mirror fabrication and diffraction pattern generation in which the multilayer structure will bear heat load and chemical load, and BFOs will also bear heat load when used in x-ray optical systems. So the thermal and chemical stabilities of multilayer structure used in BFOs are very important. In this paper, according to the heat and chemical loads associated with pattern generation and the using situation of BFOs, the multilayers were treated by three kinds of experiments: (1) following real pattern generation process, (2) by heat load only, and (3) by chemical reagent only. Changes of the interface and surface in Mo/Si multilayer structure occurring during thermal annealing and chemical attack were investigated with small-angle x-ray diffraction technique as well as x-ray photoelectron spectroscopy (XPS), and Olympus microscopy. The results showed that the Mo/Si multilayer structure was stable at 570 K in the chemical reagents used in pattern generation process, which will be helpful in working out optimal fabrication parameters in this process.

All the Mo/Si multilayer samples used in the experiment were deposited at the same time on the standard (100) silicon wafers in an ion-beam sputtering system by using a Kaufman type ion gun. Alternating layers of elemental molybdenum and silicon were deposited by Mo and Si targets mounted on the rotatable target holder. The deposition process was *in-situ* monitored by using a quartz crystal vibration monitor which was calibrated before deposition. The multilayer consisted of 15 bilayers with Mo deposited at first and Si deposited at last, and the deposition rates of Mo and Si were 0.53 and 1 nm/min, respectively. The pressure of the argon sputter gas was 4×10^{-2} Pa, and the temperature of the substrate was normally lower than 320 K. The period thicknesses of the multilayer at the center and another at the outlying were both 8.53 nm, as measured by small-angle x-ray diffraction.

Table 1. Period thicknesses of all multilayers in our experiments and the fractional variations in period of post-annealed multilayers comparing with unannealed multilayer.

		Period thickness (nm)	Fractional variation (%)
	Sample#unannealed	8.53	0.0
Pattern generation	Sample#real 1	8.51	−0.2
	Sample#real 2	8.52	−0.1
	Sample#real 3	8.23	−3.5
	Sample#chemical	8.48	−0.6
	Sample#thermal 1	8.47	−0.7
Using condition	Sample#thermal 2	8.38	−1.8
	Sample#thermal 3	8.33	−2.3
	Sample#thermal 4	–	–

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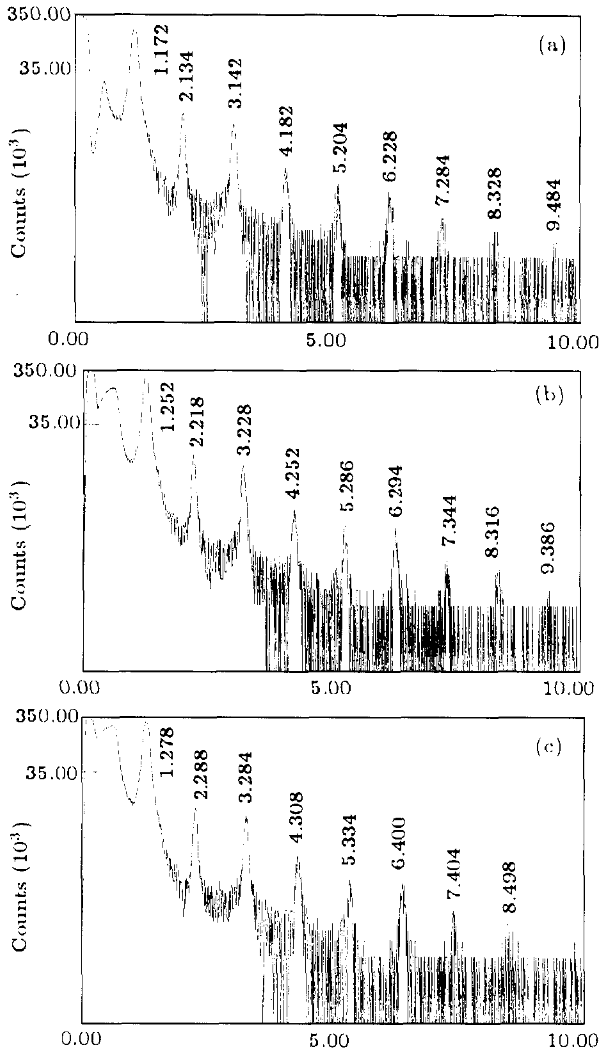

Fig. 1. (a) Small-angle x-ray diffraction pattern showing 9 Bragg peaks from unannealed multilayer sample#unannealed, (b) after treated according to the real pattern generation process (sample#real 1), (c) after thermal annealed for 30 min at 570 K (sample#thermal 3).

The diffraction pattern in BFOs was generated by means of multistep process. First, BP212 resist was spin-coated on Mo/Si multilayers. Then diffraction pattern was generated on resist by UV light, and during resist pattern generation, the multilayer samples were treated through several steps: pre-bake (at 360 K for about 20 min), exposition, development (in a 5‰ NaOH solution for about 90 s), and post-bake (at 400 K for about 30 min). After that a 5 nm thick Cr layer and a 50 nm thick Au layer were evaporated on patterned resist by using an electron gun, and the temperature of the substrate remained unchanged during the evaporation process. Last resist was removed by acetone and diffraction pattern was transfered to Au and Cr layers.

According to the pattern generation described above, the heat and the chemical loads born on multilayers were mainly related to the resist pattern generation. In addition, the BFOs had to be born by heat load in x-ray optical system due to the absorption of x-ray (generally, the temperature was lower than 570 K). Three kinds of experiments were conducted. In experiment (1), sample#reals were spin-coated with BP212 resist, then annealed at 360 K for 17 min, exposed to UV light, and put into a 5‰ NaOH solution for about 90 s. After that, they were annealed at 400 K for 30 min. Finally, resist was removed by acetone. In experiment (2), sample#thermal 1 was annealed at 360 K for 30 min and at 400 K for 30 min, respectively. Sample#thermal 2 and sample#thermal 3 were annealed at 470 and 570 K for 30 min, respectively. Sample#thermal 4 was put into a thermoelectric oven at 550 K, then the oven was continuously heated until the temperature reached to 770 K which was maintained for 30 min, it was taken out when the oven was cooled to room temperature, and the entire annealing time of sample#thermal 4 was about 23 h. In experiment (3), sample#chemical was put into a 5‰ NaOH solution for about 160 s, then cleaned with deionized water, and then put into acetone for about 60 s. In these three experiments, sample#reals, sample#thermal 1, and sample#chemical were treated according to the pattern generation; while sample#thermal 2, sample#thermal 3, and sample#thermal 4 were treated according the using situation of BFOs.

All samples were examined by Rigaku D/MAX-Ⅲ B x-ray (Cu K_α radiation) diffractometer. The measured small-angle diffraction peak intensities were used to evaluate the quality of coatings and interfaces, and the positions of diffraction peaks were applied to check the period thickness. Sample#thermal 4 was measured with VG ESCALAD MK-Ⅱ x-ray photoelectron spectroscope as well as with PM-10AD Olympus microscope. The photoelectron spectroscopy was used to decide what elements were in the sample and whether the element was simple substrate or not. And the information of surface morphology was obtained by Olympus microscopy.

The small-angle x-ray diffraction pattern of unannealed multilayer showed up to 9 Bragg orders. The period thickness calculated from Bragg's law and curve fitting from the measured diffraction angle was 8.53 nm. All the annealed multilayers (except sample#thermal 4) did not show weaker first Bragg peaks, but their period values were decreased in a varying degree. For sample#thermal 4, no Bragg orders were observed at its small-angle x-ray diffraction pattern. The small-angle x-ray diffraction patterns of some pre- and post-annealed samples were shown in Fig. 1, the measured period thickness and the fractional variation in period of every sample were listed in Table 1.

From the measured results of x-ray small-angle diffraction, we found that the fractional variation in period of all the samples (except sample#thermal 4) was less than 5% (generally the x-ray optical system has to be designed to accommodate the shift in period if the fractional variation in period was more than 5%)

and the first Bragg peaks of them did not decrease. So the Mo/Si multilayer structure was stable in pattern generation process when the temperature was below 570 K. For sample#real 3, the fractional variation in period (3.5%) was much larger than that of other four samples (less than 1%) associated with pattern generation process. This was due to that in our experiments, sample#real 3 was a special sample which was treated with different chemicals at different temperature for many times in order to find optimal technological parameters in resist pattern generation process.

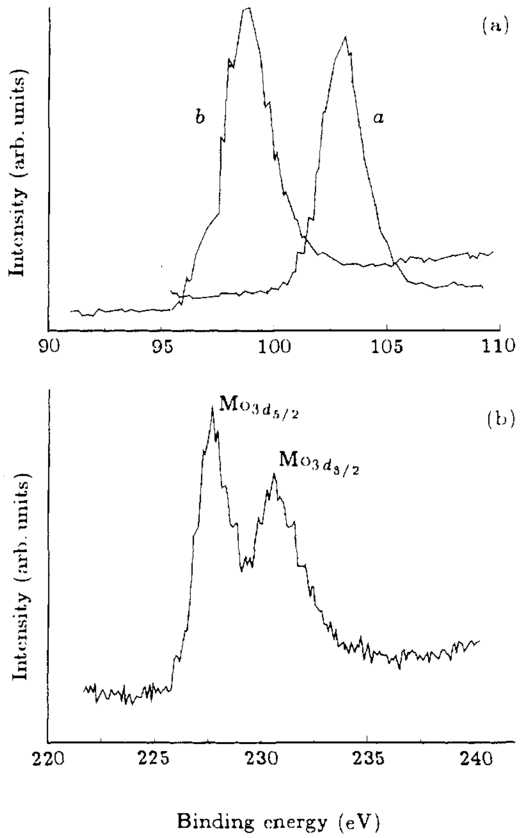

Fig. 2. (a) X-ray photoelectron spectroscopy of Si_{2p} on the surface (curve *a*) and inside (curve *b*) of sample#thermal 4, (b) x-ray photoelectron spectroscopy of Mo_{3d} inside sample#thermal 4.

The thermal stability of Mo/Si multilayers deposited with sputtering was reported in a number of works.[3-6] According to Ref. 6, the reaction temperature for silicide formation was 900 K, but it was reported that for the sputter-deposited samples the interface reaction yielded at temperature around 770 K.[5] In our experiment, the layered structure of Mo/Si multilayer was destroyed (sample#thermal 4) at 770 K. In order to find the reason of the destruction sample#thermal 4 was measured with x-ray photoelectron spectroscopy. At first, the surface of this sample was tested, no element Mo was found, and the binding energy of Si_{2p} was 103.1 eV [Fig. 2(a)]. After etching its surface for about 45 min, elements Mo and Si were both detected. The binding energy of $Mo_{3d_{5/2}}$ was 226.8 eV [Fig. 2(b)], and the binding energy of Si_{2p} was decreased to 98.9 eV [Fig. 2(a)]. So a conclusion was reached that there was compound Si ($Si^{4+}O_2$) on the surface of sample#thermal 4 and simple substrate Si (Si^0) and Mo (Mo^0) inside it, i.e., the oxidation only occurred on the surface and the interface reaction did not occur, but the interdiffusion was very serious. The surfaces of all samples (except sample#thermal 4) were very smooth and very bright when observed by Olympus microscope and there was not any speck on them. But there were many specks in different sizes on the surface of sample#thermal 4, indicating that the thin layers of the multilayer had been peeled off partly and the multilayer structure had been destroyed.

The outcome of the results and discussion described above could be summarized as follows: (1) The thermal and chemical stabilities of Mo/Si multilayer in BFOs were high in the diffraction pattern generation process. (2) The Mo/Si multilayer in BFOs was stable when annealing temperature was lower than 570 K. (3) The layered structure of Mo/Si multilayer was destroyed when annealing temperature was increased to 770 K.

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