Heat stability of Co/SiO_2 multilayers for use in the soft x-ray region

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Abstract

Heat stability of Co/SiO_2 multilayers was evaluated. Multilayer samples were deposited on the Si substrates by means of the ion beam sputtering method and annealed at temperatures from 100°C to 600°C in a vacuum furnace. For the structural and optical evaluations, small angle x-ray diffraction measurements, soft x-ray reflectivity measurement in a 1 keV energy region, and transmission electron microscopy observations were carried out. As the results, the Co/SiO_2 multilayers annealed up to 400°C maintained the initial multilayer structure and kept the almost same soft x-ray reflectivity as the as-deposited sample. A deterioration of multilayer structure was found on the samples annealed over 500°C, and the soft x-ray reflectivity reduced in accordance with the deterioration of the multilayer structure.

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1. Introduction

In an energy region of 1–10 keV, recently the spectroscopic research based on emission and absorption as well as florescence techniques has been carried out extensively for the various purposes, e.g., the development of new semiconductor material and magnetic devices, and the structural analysis of biological cells. It is because that the emission and absorption phenomena from and to the inner-shell electron states, respectively, of the newly motivated elements are frequently observed in the energy region [1-3].

The great demand for a better monochromator has been arisen the improvements of conventional and multilayer gratings for the 1–10 keV energy range [4-9], which may scan the whole energy region and also endure a high heat load caused by the high brightness sources. They would abolish burdensome conventional crystal and grating monochromators combinations. Recently, a conventional laminar-type holographic grating showed notable high diffraction efficiency [6]. Also the laminar-type gratings coated W/C and Co/SiO_2 multilayers attained high diffraction efficiencies of nearly 0.4 at 8 keV and over 0.4 in an energy range of 4-6 keV, respectively, at moderate grazing incidence angles [9]. Taking advantages of their wide energy scanning range and high diffraction efficiency, a grazing incidence monochromator suitable for SR beamlines consisting of the multilayer gratings and multilayer mirror was proposed [10].

Beside diffraction efficiency, heat load stability is another important requirement for any optical elements applied to high power density beam optics e.g. high brightness SR, FEL, and laser beamlines [11]. Also it is desirable to withstand a baking process required for high vacuum operation.

Original (master) grating made with SiO_2 or SiC have a practical durability against heat load [12-14]. Also W/C multilayers have found to be keeping their structure about up to 400°C and have practical heat stabilities [15-19]. Therefore master gratings with a W/C multilayer are supposed to have a high heat load stability. However, any heat load stability of Co/SiO_2 multilayer has not been evaluated yet.

In this paper, we describe the evaluation of the heat load stability of the Co/SiO_2 multilayer deposited on the silicon substrates for the purpose to estimate the heat load stabilities of Co/SiO_2 multilayer original gratings [9]. The optical performances of the as-deposited and annealed samples were evaluated by means of x-ray diffraction (XRD) measurements and soft x-ray reflectivity measurements quantitatively. The results of comparative studies of these measurements are discussed.

2. Experimental

Seven Co/SiO_2 multilayer samples were fabricated on the Si(*100*) substrates by means of the ion beam sputtering method [9]. The argon-ion gun (hollow cathode type, 5 cm in grid diameter) was operated at an accelerating voltage of 800 V with an ion-beam current of 50 mA. The substrate temperature during deposition was not controlled. The periodic length of the multilayer and ratio of (Mo layer thickness / periodic length) were intended to be 6.5nm and 0.4, respectively. The number of periods was 30 (60 layers) for all multilayer samples.

To evaluate the heat stability of Co/SiO_2 multilayers, the six multilayer samples shown as No. 2 – No. 7 in Table I, except for the as-deposited sample of No. 1, were annealed at temperatures of 100, 200, 300, 400, 500, and 600°C in a vacuum furnace for one hour, respectively. The increasing rate of temperature was 400°C/h. After annealing at each

TABLE 1. Table I. Periodic lengths and the first order Bragg peak reflectivies of the Co/SiO_2 multilayer samples. The measured small angle x-ray diffraction intensities were normalized by the incident x-ray intensity to calculate the reflectivities, and the periodic length was determined by using the Bragg peak positions.

Sample No.		1	2	3	4	5	6	7
Annealing temperature (°C)		As-deposited	100	200	300	400	500	600
Periodic length (nm)	Before annealing	6.50	6.51	6.51	6.55	6.55	6.53	6.53
	After annealing	---	6.51	6.56	6.64	6.70	6.80	(6.92)
1st order Bragg peak reflectivity	Before annealing	0.495	0.484	0.484	0.496	0.496	0.497	0.497
	After annealing	---	0.497	0.505	0.519	0.516	0.357	0.001

temperature, the samples were cooled to room temperature naturally in a vacuum furnace.

The periodic lengths and the first order Bragg peak reflectivities of multilayer samples before and after annealing were calculated from the small angle x-ray diffraction, XRD, measurements with Cu-$K\alpha$ x-rays (E = 8.05 keV) using standard θ-2θ scans. To calculate the x-ray reflectivities, the measured XRD intensities were normalized by the incident x-ray intensity. The periodic length was determined by using the Bragg peak position angles [18,20]. The periodic lengths thus obtained and the first order Bragg peak reflectivies of multilayers before and after annealing are shown in Table I.

For the determination of the initial as-deposited structure of Co/SiO_2 multilayer, the fitting calculation of x-ray reflectivity curve was carried out for the as-deposited multilayer sample (No. 1 in Table I).

An x-ray reflectivity simulation/calculation program (Rigaku, GXRR) [21] was used to estimate the layer thickness, and roughness of the multilayer. For the calculation, it is assumed that each layer has tabulated optical constants [22].

Soft x-ray reflectivity of multilayer samples were measured with an evaluation beamline for soft x-ray optical elements installed on the BL-11 at the Synchrotron Radiation Center of Ritsumeikan University [23,24]. The monochromator system equipped with the evaluation beamline consists of two types of grazing incidence monochromators. One of the monochromators that employs a scanning mechanism based on Surface Normal Rotation (SNR) which provides high throughput at short wavelengths with a simple scanning mechanism by means of grating rotation about grating normal. The use was made of the SNR monochromater for the soft x-ray reflectivity measurements in a wavelength range of 0.7–2.0 nm (about 1.8–0.6 keV).

3. Results and Discussion

To estimate the initial structure of the Co/SiO_2 multilayer, the fitting calculation of x-ray reflectivity curve was carried out. Figure 1 shows the x-ray reflectivity obtained by small angle XRD measurement and the best fitted curve for the as-deposited Co/SiO_2 multilayer sample (No. 1 in Table I). The densities, 8.90 g/cm^3 and 2.20 g/cm^3 for Co and SiO_2, are used for the fitting calculation. The thickness of Co and SiO_2 layers are calculated to be 2.60 nm

and 3.90 nm, respectively. The calculated root mean square (rms) roughness is about 0.8 nm for Co layers, and is about 0.4 nm for SiO_2 layers. Figure 2 shows the measured soft x-ray reflectivity curves and the calculated reflectivities for the as-deposited sample in the 1-2 keV region. The calculations were performed using Fresnel equations [25], Névot-Croce factor, [26] as well as the published optical constants [22]. The thickness of Co and SiO_2 layers derived from the fitting calculation described in Fig. 1 was used. From the calculation, it was found that the as-deposited Co/SiO_2 multilayer should have a rms roughness of about 0.8 nm. This value is consistent with that derived from the structural calculation based on the XRD measurements.

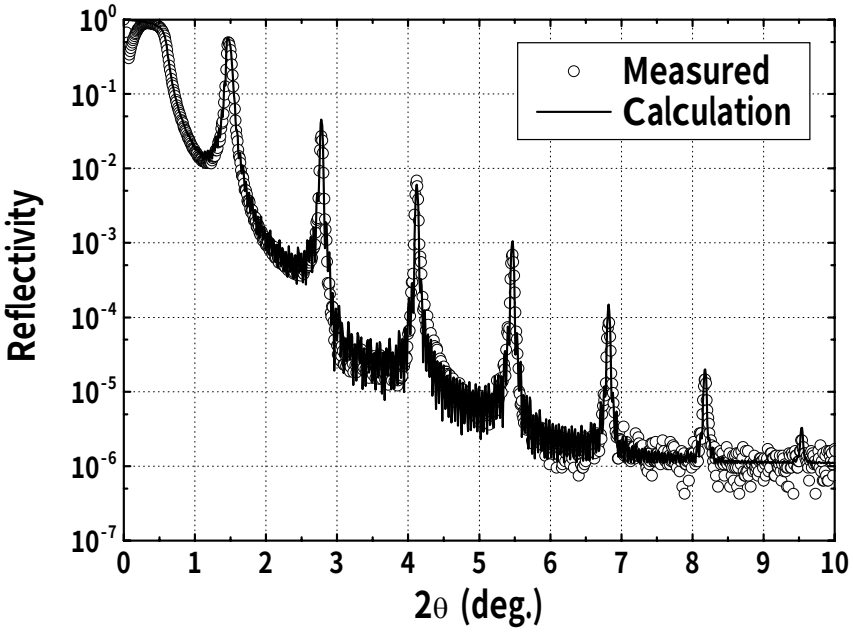

Fig. 1. X-ray reflectivity measurements curve (open circles) of the as-deposited sample (No. 1 in Table I) and the curve obtained by fitting calculation (solid line). For the detail see text.

To evaluate the heat stability of Co/SiO_2 multilayers, the changes in the periodic length and the first Bragg peak reflectivity of the annealed multilayer samples were derived from XRD measurements. Figure 3 shows the relative periodic length and the first order Bragg peak reflectivity as a function of annealing temperature. The periodic length and the x-ray reflectivity of each multilayer sample are normalized by those at the as-deposited conditions. The periodic length of multilayer increases with the annealing temperature slightly (also see Table I). The relative change in the periodic length of multilayer annealed at 400°C is about 2%, and that of annealed at 500°C is about 4%. The change of the periodic length up to 500°C is relatively small, but the reflectivity decreases remarkably after annealing at 500°C. The measured XRD curves of Co/SiO_2 multilayers annealed below 500°C contains as many as 6–7 Bragg peaks. However, for the sample annealed at 600°C only three weak Bragg peaks remain and higher order peaks disappeared completely. Even the periodic length of Co/SiO_2

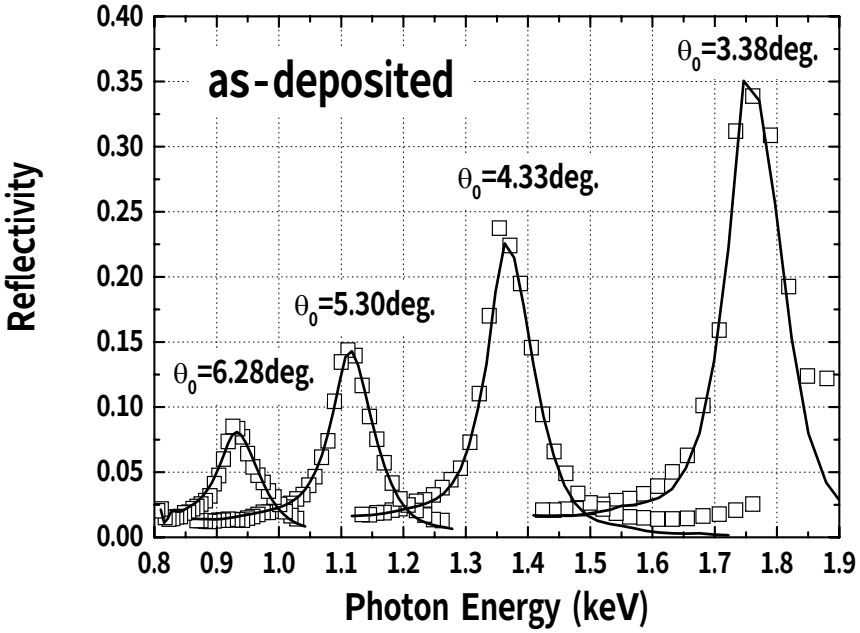

Fig. 2. Measured soft x-ray reflectivity curves for the as-deposited Co/SiO_2 multilayer sample, No. 1 in Table I, (open squares) and the calculated soft x-ray reflectivities (solid line). The calculated grazing incidence angles (θ_0) are indicated in figure. For the parameters of multilayer structure assumed for the calculation, see text.

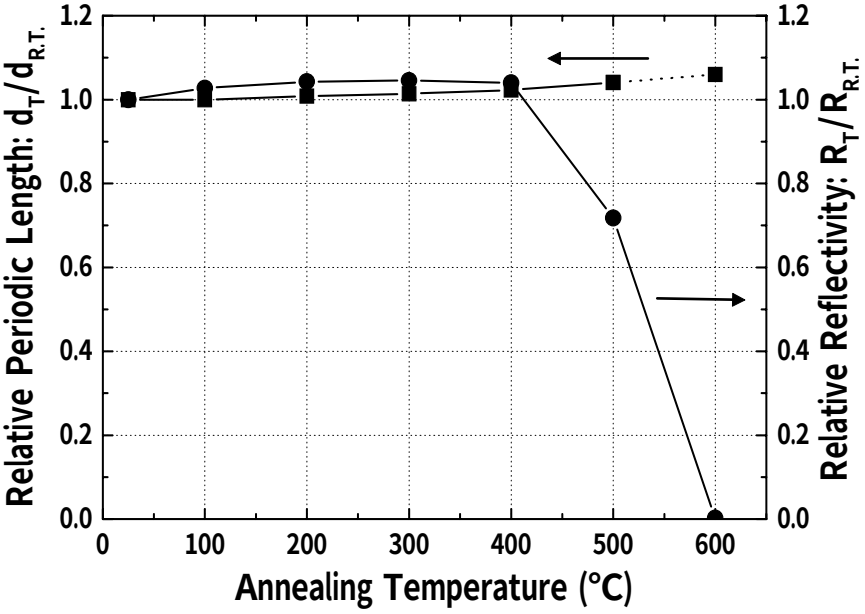

Fig. 3. Relative periodic length and relative first-order Bragg peak reflectivity of the Co/SiO_2 multilayer samples as a function of annealing temperature. The periodic lengths and the reflectivities of the samples were normalized by those of samples before annealing.

multilayer annealed at 600°C increases 6%, the first Bragg peak reflectivity dropped drastically to 0.2% of the initial value.

To investigate the effects of the deteriorations of multilayer structure in the 1–2 keV energy region, a comparative study on reflectivity of the as-deposited and annealed multilayer samples was performed. Figure 4 shows measured soft x-ray reflectivity curves for the as-deposited sample and those for the annealed samples at 400°C and 500°C. The multilayer sample annealed at 400°C keeps almost the same reflectivities as the as-deposited one. On the other hand, the reflectivity curves of the multilayer annealed at 500°C has decreased considerably. It is safely concluded that the results of soft x-ray reflectivity measurements show good agreement with the structural changes of multilayer samples (see Fig. 3).

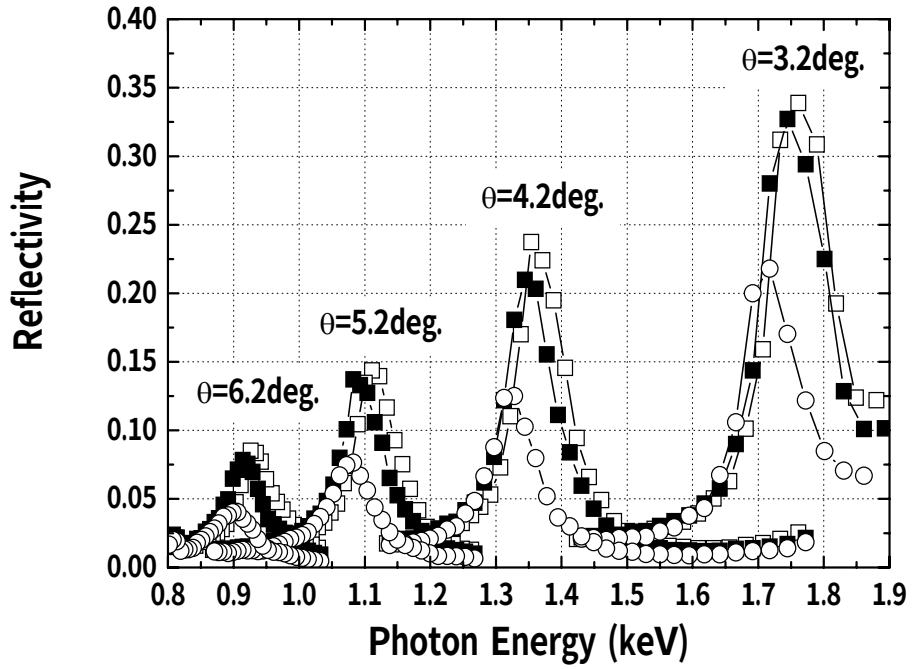

Fig. 4. Measured soft x-ray reflectivity curves for the as-deposited Co/SiO_2 multilayer sample (-□-), the annealed one at 400°C (-■-), and the annealed one at 500°C (-○-) in the energy region around 1 keV. The grazing incidence angles (θ) are indicated in figure.

4. Conclusions

To evaluate the heat stability of Co/SiO_2 multilayer, we have deposited the multilayers on Si substrates by means of an ion beam sputtering methods, and annealed in a vacuum furnace. The multilayer samples annealed up to 400°C maintain the as-deposited structures and have almost the same soft x-ray reflectivities as the as-deposited one. The degradation of multilayer structure was occurred by an annealing at 500°C. The periodic structure of the Co/SiO_2 multilayer annealed at 600°C was destroyed. Therefore, it can be concluded safely that the Co/SiO_2 multilayer has the stable structure and performance up to 400°C which is considered to be enough to practical experimental applications.

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