Contamination experiments for Mo/Si multilayer mirrors with the use of single-bunch synchrotron radiation

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Abstract. An extreme ultraviolet (EUV) irradiation experiment with the use of single-bunch synchrotron radiation (SR) was carried out to evaluate the optics lifetime for EUV lithography due to contaminations. The sequential change in the reflectivity of Ru-capped Mo/Si multilayer mirrors was measured during EUV irradiation in the presence of hydrocarbon gas or water vapor vacuum environment. The EUV dose dependence of decreases in reflectivity for single-bunch SR was almost the same as that for light-attenuated multibunch SR. From the results, there was no marked difference in the dependence of decrease in reflectivity on pulse structure in the frequency range of 2.5 to 500 MHz.

1. Introduction

Reflectivity degradation of Mo/Si multilayer mirrors due to contamination (carbonaceous film growth or surface oxidation) associated with EUV irradiation becomes problematic for EUV lithography (EUVL) optics [1,2]. Therefore, technologies of contamination inhibition and cleaning of contaminated surfaces are extensively studied [3-5]. The specification of optics lifetime for an EUVL system is 30,000 hrs within the 1.6% of decrease in relative reflectivity [3]. Therefore a lifetime scaling experiment is necessary to realize the specification.

It is ideal for the scaling experiment to use a light source of the same means as the real system, such as a pulse laser-produced plasma (LPP) or discharge produced plasma (DPP) source with high power irradiance. However, a synchrotron radiation (SR) source is often used as a simulated source for contamination studies because of its high EUV irradiance and stability. There is a discussion that the reflectivity degrade by a pulse LPP/DPP source (~20 kHz) will be smaller than that by a quasi-continuous SR source (~500 MHz) [6]. On the other hand, recent discussion based on a reaction model reported that there is no difference between the result of pulse source and quasi-continuous source [7].

To obtain basic information for understanding the contamination phenomena, single-bunch (SB) mode SR was employed for measurement of reflectivity change and for quantitative estimation of the optics lifetime. The pulse interval of the SB-SR is only about 200 times longer than that of multibunch (MB) mode SR. However, the pulse duty ratio, which is a very important parameter in examining the reaction model of contaminations, of SB-SR and pulse LPP/DPP sources are almost the same at 1/10,000. Therefore, the single-bunch experiment provides important knowledge for examining the validity of the reaction model [2,7,8]. The contamination mechanism will be discussed with the results of the SB-SR experiment compared to those obtained by MB-SR.

2. Experiments

The experiments were conducted by the contamination evaluation system [9] in the beamline BL9 at the NewSUBARU SR facility at the University of Hyogo. Figure 1 shows the schematic view of the contamination evaluation system. The system can irradiate EUV on Mo/Si multilayer samples having
a 2×2 mm² area by using an undulator light source with a maximum irradiance of about 200 mW/mm². EUV reflectivity and its distribution can be measured in situ by using a 100 μm diameter pinhole and two photodiodes. Contamination growth under various vacuum environment conditions can be observed by introducing hydrocarbon gas or water vapor in the irradiation (main) chamber, which can be differentially pumped out with pressures in five orders of magnitude. The sequential change of multilayer reflectivity and its distribution after irradiation can be obtained in situ. Moreover, an elemental concentration map of atoms at the irradiated surface can be measured in situ by soft X-ray absorption spectrometry [10].

Table 1 shows the pulse structures of the single-bunch and multibunch modes of SR used in this experiment [11] along with a typical pulse plasma source for comparison. As shown in the table, the SB-SR and the pulse source have the same degree of duty ratio. It is also found that the instantaneous intensity value of MB-SR is nearly equal to that of the pulse source.

The EUV irradiation experiments with the use of SB-SR were carried out for carbonaceous film growth and surface oxidation, both of which react to affect the degradation of multilayer reflectivity. Ru-capped Mo/Si multilayer mirrors were used for the samples in the experiment. The base pressure of the main chamber was 2×10⁻⁷ Pa. For the carbon film growth experiment, n-decane (C₁₀H₂₂) was used as a hydrocarbon gas and was introduced into the chamber with the needle valve showing a gas pressure of 1.3 - 5.0×10⁻⁵ Pa. For the surface oxidation experiment, water vapor was introduced at a pressure of 1.3 ×10⁻⁵ - 1.3×10⁻⁴ Pa. For the carbon film growth and surface oxidation experiments, EUV irradiation powers were 12 mW/mm² and 22 mW/mm², respectively, at the irradiation center. For comparison, EUV irradiation using attenuated MB-SR with EUV power comparable to the SB-SR experiment was also carried out by inserting a low reflectivity mirror in the beamline. During EUV irradiation, reflectivity was measured at 20-minute intervals. The measurement error of the reflectivity was ±0.5%. A two-dimensional reflectivity map was obtained after the EUV irradiation. Furthermore, after the irradiation, distribution of elemental concentrations of oxygen (O) and carbon (C) atoms was measured by O-K and C-K edges X-ray absorption intensity.

3. Results and discussion

3.1. Carbonaceous film deposition

Sequential changes in reflectivity of the multilayers during SB and attenuated MB modes of EUV irradiation in the presence of decane gas at P_{decane} = 1.3×10⁻⁵ Pa are shown in Fig. 2. In the SB and MB-SR experiments, the relative reflectivity decreased about 1.7% at the EUV dose of 70 J/mm². In the early stage of EUV irradiation at a dose of 0 – 20 J/mm², the relative reflectivity slightly increased. This could be because the native oxide at the surface of the Ru capping layer was reduced, and the
amount of EUV absorption by oxygen decreased [12]. The EUV dose dependence of change in reflectivity using SB-SR was almost in agreement with that using attenuated MB-SR.

Figure 3 shows the elemental concentration ratio relative to the non-irradiated area of (a):C and (b):O atoms at the irradiated area (x = -1.2 - +1.2 mm in the graphs) after EUV irradiation in the presence of decane gas. These values are almost proportional to the thickness of the carbon or metal oxide layers [10], and the maximum value of the C layer was converted to 2.5 nm. The distribution of grown in the C film was like Gaussian, the shape of which almost agreed with the distribution of the irradiation beam intensity [9]. The shape of the O concentration ratio was different from the intensity distribution of the irradiation beam, taking on a flat-bottomed shape with a 10 – 15% lower value comparing to the non-irradiated area. One possible reason for the distribution is that the native oxide layer at the surface was reduced by active chemical species containing hydrocarbon, and the reduction reached to saturation [13].

The above experiment showed that carbonaceous film grew and reflectivity decreased when EUV was irradiated. There was no remarkable difference in reflectivity change by the contamination on pulse cycles ranging from 2.5 to 500 MHz.

### 3.2. Surface oxidation

Sequential changes in reflectivity of the multilayers during irradiation with SB and attenuated MB mode EUV in the presence of water vapor at $P_{H_2O} = 1.3 \times 10^{-4}$ Pa are shown in Fig. 4. The figure also shows a measurement error indicated by an error bar representative for all the points. The relative reflectivity decreases to about 1.0% from the original at an EUV dose of 130 J/mm² for both SB and attenuated MB experiments. When comparing the SB and the MB experiment results, there is little marked difference in the reflectivity degradation.

![Fig. 2](image-url)  
**Fig. 2** Sequential change in reflectivity of multilayers in the presence of decane gas.

![Fig. 3](image-url)  
**Fig. 3** Elemental concentration ratio of (a): C and (b): O atoms relative to the non-irradiated area after EUV irradiation in the carbonaceous film growth experiment. The legend is common for (a) and (b).

![Fig. 4](image-url)  
**Fig. 4** Sequential change in reflectivity of multilayers in the presence of water vapor.
Figure 5 shows the elemental concentration ratio relative to the non-irradiated area of (a):C and (b):O atoms at the irradiated area (x = -1.2 - +1.2 mm in the graphs) after EUV irradiation in the presence of water vapor. The C thickness decreased in a trapezoidal geometry shape at the irradiated area. It is considered that the native carbon film at the irradiated area was almost uniformly removed by active species containing an oxygen radical that was formed by the EUV irradiation. There is almost no difference in the amount of decrease in the C thickness between SB and MB mode EUV irradiation. There is also little difference between the water vapor pressures of $P_{\text{H}_2\text{O}} = 1.3\times10^{-5}$ Pa and $P_{\text{H}_2\text{O}} = 1.3\times10^{-4}$ Pa.

Oxygen concentration increased about 10% compared to the non-irradiated area. This could be because the surface of the Ru-capping layer was oxidized by the EUV irradiation. The distribution of oxygen concentration was different from the distribution of irradiation beam intensity (Gaussian), and the absorption intensity seemed to saturate the irradiation center. This may be because the oxidation reaction was limited to the supply of water vapor [13].

**Fig. 5** Elemental concentration ratio of C and O atoms relative to the non-irradiated area after EUV irradiation in the surface oxidation experiment.

From the above experiment, the Ru metal surface was oxidized and reflectivity decreased when EUV was irradiated in the presence of water vapor. There was no remarkable difference in reflectivity change by surface oxidation in pulse cycles ranging from 2.5 to 500 MHz. Therefore, the mirror degradation by SB-SR or MB-SR irradiation can be scaled only by the parameter of EUV dose.

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