Development of High-Reflective W/Si-multilayer Diffraction Grating for the Analysis of Fluorine Materials

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For the analysis of fluorine materials and 3d transition metals by soft-x-ray absorption spectroscopy, a new diffraction grating with multilayer coating was installed at the BL-10 beamline of the NewSUBARU synchrotron light source. The target photon energy range of this grating is from 500 eV to 1,000 eV, which includes absorption edges of fluorine and 3d transition metals. The beam intensity of BL-10 in this range was very low due to low reflectance of the diffraction grating for the usage of monochromator. In order to obtain high reflectance, we developed wideband W/Si multilayer and this multilayer was coated on a new diffraction grating. The reflectance of this multilayer was approximately 13-times higher than that of previous Ni single layer at the fluorine absorption energy edge of 697 eV. The beam intensity at the energy of 697 eV using the new diffraction grating was over 40 times stronger than that using the previous Ni-coated diffraction grating. As the result, using the new diffraction grating, it can be observed that the high-quality absorption spectrum of EUV resist at the absorption edge of fluorine and standard materials of 3d transition metals. The results show that the W/Si multilayer coating significantly improved the performance of the grating at the target energy range.

Keywords: W/Si multilayer, wideband multilayer grating, synchrotron light, soft x-ray absorption spectroscopy

1. Introduction

Soft-x-ray absorption spectroscopy (XAS) is widely used for the analysis of light element materials, which measures absorption spectrum near the absorption edges. The XAS system at BL10 beamline of NewSUBARU synchrotron light source [1-4]. For example, deterioration mechanism of tire rubber and engine oil were analyzed [2, 3]. In addition, we analyzed the chemical reaction of the extreme ultraviolet (EUV) chemically amplified (CA) resist using BL-7 XAS system [5]. We measured XAS spectrum around the fluorine absorption energy edge of 697 eV to evaluate the decomposition reaction of photoacid generator (PAG) of CA EUV resist during EUV exposure. However, this previous result had large noise due to low photon intensity in this energy region. In order to develop of high-sensitive EUV resist, it is necessary to measure the fluorine energy regions with low noise in and sufficient energy resolution. The main reason of the poor intensity own to the low reflectance of the diffraction grating in BL-7 and BL-10 beamlines, which had a small deviation angle of 168° for the diffraction grating.

Since in general, a CA resist is easy to deteriorate, it is important to analyze the resist by XAS near the resist process equipment for resist coating, baking, developing spin coater, developer, and hot plate in the clean room. Thus a new diffraction grating which had high reflectance on 697 eV for the usage of XAS at BL-10 beamline of NewSUBARU should be installed. For considering general usage of BL-10, target energy of the new grating was set from 500 eV to 1,000 eV, which includes absorption
edges of fluorine and 3d transition materials. High reflectance of the new grating is essential for the precise reaction mechanism analysis of the resist for the semiconductor devices.

The platinum coated grating would have not enough reflectance due to the small deviation angle of the grating for BL-10. For example in the soft-x-ray emission spectroscopy, wideband multilayer coating significantly improved reflectance of a grating [6]. Thus, we developed a multilayer coating and it was coated on the grating in this study to enhance the reflectance in the target energy region. The beam intensity and XAS spectrum were evaluated with the new multilayer-coated grating.

2. Experimental
2.1 Design of beamline BL-10

The optical layout of BL-10 of NewSUBARU is shown in Fig. 1. This beamline was originally designed for reflectometry of EUV optics, where a reflectometer is located at the end of the beamline. The vacuum chamber for the reflectometer was used for the XAS measurement. The entrance slit design is slitless. The M0 mirror is a concave mirror with a grazing angle of incidence (GAOI) of 3°, which horizontally focuses on the sample which was settled in the XAS chamber with magnification of three. The acceptance angle of the M0 is 5 mrad in the horizontal direction. The monochromator type which was utilized for BL-10 beamline is the plane varied line-space grating (VLSG), and it was described the paper written by Hettrick and Underwood [7]. The reflected light by the spherical concave M0 mirror focused on the exit slit in the vertical direction by M1 concave mirror and diffraction grating. Two gratings were installed in the monochromator, which had groove densities of 600 mm\(^{-1}\) (G1) and 1,800 mm\(^{-1}\) (G2). The deviation angle of the grating is small as 168°, because BL-10 was originally designed for low-energy use of the research for EUVL energy region. The G1 grating was originally installed for the EUV research. The G2 grating was installed for XAS measurement in 2009. In this study, a new grating with groove density of 2400 mm\(^{-1}\) (G3) was installed. The exit slit is relayed up to 5.2 m downstream at unity magnification by a vertical refocusing mirror, where the focusing size is approximately 0.05 × 0.8 mm\(^2\) on a sample. The all GAOI of the three glancing spherical mirrors such as M0, M1, and M2 is 3°. The mirrors were coated with single layer of platinum with the thickness of 50 nm. The deviation angle of the grating is 168°, and was corresponded to GAOI of 6° with specular-reflection condition. The G2 grating was coated with single layer of Ni with the thickness of 100 nm. The calculated reflectance of the glancing mirrors and G2 grating are shown in Fig. 2. These two data were calculated value using the IMD software [8] in this paper. The surface roughness was assumed to be 1 nm. Since the reflectance of the glancing mirrors was approximately 30% at the photon energy of 697 eV, the reflectance of the grating requires higher than 10% in the target energy region. However, since the reflectance of the G2 grating was less than 1% in the
energy range higher 700 eV, the beam intensity becomes very low at the sample surface for XAS experiment. Thus, the high reflective coating is needed to increase the light intensity. And, the groove height of 4.2 nm for the G3 grating was optimized to achieve high diffraction efficiency at the photo energy of 697 eV.

2.2. Design of multilayer coating

In this study, a W/Si-multilayer coating was developed for the G3 grating to enhance the reflectance in the target photo energy region. The material pair of the multilayer was chosen to W/Si because of high optical contrast and low absorption to achieve high reflectance. Figure 3 shows the calculated reflectance of aperiodic W/Si multilayer, periodic W/Si multilayer, Pt single layer, and Ni single layer, with GAOI of 6°. Platinum is generally used for mirror coating of glancing mirrors for the beamline of the synchrotron. Surface roughness of the single layer was assumed to be 1 nm with the thickness of 50 nm. Roughness of the multilayer interface was assumed to 0.5 nm. The periodic W/Si multilayer film had 10 periods of 3.0-nm-thick W layer and 7.0-nm-thick Si layer. Reflectance of this periodic W/Si multilayer was approximately 30% at the photon energy of 697 eV, and has more than 20% in the target photo energy region. As a results, an aperiodic design had wideband reflectance as shown in Fig. 3, and the structural design of the W/Si multilayer is shown in Fig. 4.

As a results, it was achieved that high reflectance the diffraction grating of over 10% in the whole target energy region by coating an aperiodic-designed W/Si multilayer.

The multilayer had aperiodic structure which consisted of one periodic multilayer coated on ten periodic multilayer. And the multilayer thickness was optimized to obtain the high reflectance in the photon energy target region. The periodic structure reflects well in energy region from 800 to 1,000 eV, where the period thickness was optimized to reflect this region. And, the top two layers widely reflects low-energy beam below 800 eV, because reflectance of tungsten single layer was enough high in this low energy region. Thicknesses of the two top layers were optimized to make positive interference of the reflections from the top surfaces (vacuum/W, W/Si, Si/W and W/Si). Further, the thickness of this multilayer was easy to control in deposition because the thickness of the period structure was able to measure with high accuracy by x-ray reflectivity (XRR) measurement.
2.3 Deposition system

The W/Si multilayers were prepared by a magnetron-sputtering deposition system as shown in Fig. 5. A 6-inch RF cathode was used for Si layer deposition, and a 6-inch DC cathode was used for W layer deposition. Twelve samples of 6-inch Si wafer were usually settled by a large holding plate with 830 mm in diameter. Each 6-inch-wafer sample was settled at the distance of 300 mm from the rotation center on the holding plate. For each deposition layer, the deposition layer thickness was controlled by the rotation speed of the holding plate. The deposition system was pumped down to the vacuum pressure higher than 1.5 × 10⁻⁴ Pa, and typically the deposition was carried out at the Ar pressure of 1.7 Pa. When W/Si multilayer was deposited on a Si wafer at the Ar pressure of 0.17 Pa, the film was peeled off due to high film stress. The Ar gas pressure was chosen to 1.7 Pa to reduce the film stress. At this Ar pressure condition, the deposited multilayer did not peel off.

For the development of the multilayer, a Si wafer was used as a substrate. The grating substrate is 150 mm in length, 30 mm in width, and 25 mm in thickness. And the groves were patterned in the region of 130 mm (L) × 22 mm (W). In deposition, the grating substrate was set the groove region parallel to the rotation direction of the holding plate.

2.4. Measurement condition of reflectance

Reflectance of W/Si multilayer on a Si wafer was measured at the reflectometer of BL-10. Reflectance of a 76.5-nm-thick Ni and 52.9-nm-thick Pt single layers were also measured. The G2 grating was chosen. When the width of the exit slit was set to be 50 μm, the monochromated photon energy resolution of 600 can be achieved around the photon energy of 700 eV. A photodiode (IRD SXUV-100) was used as a detector to measure the beam intensity. GAOI was 6°. A 1-μm-thick Cu filter was installed to cut the high order light from the grating. The reflectance in photon energy range from 500 to 930 eV, because absorption edge of the Cu filter was around 930 eV.

2.5. XAS measurement of EUV resist

The sample was poly hydroxyl styrene-co-tert-butylacrylate (PHS-TBA) resist with a phot-acid generator of tri-phenyl sulfonium nonaflate (TPS-nonaflate), which measured in previous paper [5]. The resist film thickness of 50 nm was spin-coated on a wafer. EUV light of 91.8 eV with the G1 grating was exposed on the sample with seven exposure dose condition from 0 to 98 mJ/cm². XAS spectrum was measured by total electron yield (TEY) method. The seven exposed position was measured around fluorine absorption edge of 650 to 730 eV with the G3 grating. The exit-slit width was 20 μm, where the energy resolution was 1,300 around 700 eV.

3. Results and discussions

Figure 6 shows the measurement result of the reflectance. At the photon energy of 697 eV for the fluorine 1s core level absorption edge, the reflectance of the Ni single layer, the Pt single layer and the wideband W/Si multilayer were about 0.7%, 2.7% and 13.4%, respectively. The reflectance of the W/Si multilayer is 13 times higher than that of Ni single layer. And since the W/Si multilayer had high reflectance of more than 10% for the photon energy region from 500 to 930 eV, this multilayer was coated on the G3 grating substrate and it was installed in BL-10 for the soft x-ray absorption spectroscopy.

Figure 7 shows the beam intensity measured by the photodiode with the G2 and the G3 grating without filters. The exit-slit width was 10 μm. The electron current measured by the photodiode with the G3 diffraction grating at the photon energy of 697 eV was 69 nA and the photodiode current was 40 times larger than that with the G2 diffraction grating. In addition, the photon energy region from 500 to 1,000 eV, the photodiode current was
significantly improved and was more than 50 nA. This result shows the largest photon number can be obtained using the G3 diffraction grating in the target photon energy region.

Figure 8 shows the result of TEY-XAS measurement of the EUV CA resist material. The absorption structure of fluorine 1s core level was measured with a high signal-to-noise ratio. We successfully observed the peak height of the absorption spectra decreased slightly with increasing the EUV exposure dose. This is indicated that the fluorine 1s core level of the anion of photo acid generator in the EUV CA resist decomposed during EUV exposure. Figure 9 shows the 1s core level absorption spectra measured by TEY-XAS method for the fluorine of the anion of PAG in the EUV resist and 3d-transition-metal compounds. All the spectra were measured with a high signal-to-noise ratio. The monochromator had enough energy resolution to evaluate the chemical bonding for the compounds. In addition to the target energy region, the absorption spectrum of Zn 1s core level around the photo energy of 1,020 eV was clearly resolved. The TEY-XAS method using BL-10 beamline has a good capability to measure the absorption spectra to evaluate chemical bonding in the photon energy region from 500 to 1100 eV.

4. Conclusions
We developed high reflective and wideband multilayer coating for the photon energy from 500 to 1,100 eV. This coating had aperiodic structure of W/Si with 11 periods. The reflectance of this coating was 13 times higher than the previous Ni single
layer coating, and was over 10% in the target photon energy region. We deposited the wideband multilayer on the grating substrate of G3, which was employed as a monochromator of BL-10 beamline for the TEY-XAS measurement method. The beam intensity was significantly improved more than 40 times at the absorption edge energy of fluorine 1s core level. And, high photon intensity can be achieved in the target photon energy region. We measured the resist sample using TEY-XAS method. The fluorine decomposition reaction of the resist was clearly measured with good signal-to-noise ratio. And, the absorption structures of standard 3d transition metal compounds were also resolved clearly. This result shows BL-10 beamline had high capability of XAS measurement in the photon energy region from 500 to 1100 eV with a sufficient energy resolution and high beam intensity. In addition, the reflectometer of BL-10 can measure the reflectance of the metal coatings on an optical element in this photon energy region, and it can be strongly contributed the development of soft x-ray optics. The well-developed W/Si aperiodic multilayer diffraction grating can provide significant improvement of beamline performance for the high energy photon region.

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