Resonant Soft X-ray Reflectivity for the Chemical Analysis in Thickness Direction of EUV Resist

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In the advanced lithography, the pattern collapse is significant issue. Since the resist pattern collapse origin to the surface force of the rinse solvent such as ultra-pure deionized water, pattern strip and pattern collapse occur easily when the resist aspect ratio exceeds two. The pattern strip and pattern collapse occur near or at the bottom layer and of a resist inside the resist film, respectively. Thus, the layer analysis inside the resist is significant. The layer separation analysis inside the resist film is very difficult by the X-ray reflectivity method because the layer separation contrast is very small using hard X-ray. Therefore, the resonant soft X-ray reflectivity (RSoXR) method was utilized for the layer separation of the resist film. A commercial chemical-amplifier resist was employed as a sample to in this study. Around carbon absorption edge region of 284 eV, optical index will depend on chemical-bonding structure of the resist strongly. The separated-layer structure was clearly analyzed at 287.1 eV. The resist had 5 nm and 6 nm separated layer at the top and the bottom position.

Keywords: Photoresist, Resonant soft X-ray reflectivity, Chemical structure separation

1. Introduction

EUV lithography will be used for high volume manufacturing of semiconductor devices around second half of 2019 [1], which is a major candidate for 10-nm half pitch (HP) patterning after 2020 [2]. Since the resist-aspect ratio should be less than two to prevent the resist collapse, the resist thickness should be less than 20 nm in the case of 10-nm half pitch patterning. Nakagawa et al. reported that a resist had separated layer around top and bottom in the resist [3,4], which had a different mechanical property in nanoimprint lithography.

The thinner the resist film thickness, the higher the proportion of the layer separation in the vicinity of the surface layer or in the vicinity of the substrate interface, and the properties of the layer separation greatly affect the resist pattern collapse or stripping. This kind of layer separation would degrade the resist performance, because the resist should be quite uniform to prevent stochastic effect [5].

Especially, the bottom-layer separation would influence the adhesion property to the substrate. The adhesion strength of resist to the substrate should be high, not to cause the pattern collapse. And the substrate material and roughness would also influence the bottom-layer separation. Since the pattern collapse is critical for lithography, the under-layer [6] the surfactance [7] have been developed. Thus, the bottom- and surface- layers separation should be evaluated to fabricate fine resist patterns. The thickness of these layers is thin and these layers have almost same chemical composition in comparison to the main body of resist. The separated surface layer is detectable by surface sensitive methods of atomic force microscopy and Raman scattering. However, it is difficult to detect the separated layer structure by such surface-sensitive-analysis method.

Therefore, the soft X-ray reflectivity (RSoXR) method was developed to evaluate the layer separation inside the resist film. In this paper, more detail of RSoXR method and layer separation results is described and discussed, respectively.

In the RSoXR method, the reflectance angle from
the resist was recorded with soft X-ray, of which energy was varied around carbon absorption edge of 284 eV. The instrumentation setup in RSoXR is almost as same as the common instrumentation setup of $\theta$-2$\theta$ measurement in X-ray reflectivity (XRR). The film density, thickness, layer structure, and roughness can be obtained from the reflectance spectrum by fitting calculation algorism in similar using that in XRR analysis. In XRR the incident photon energy is usually 8 keV of hard X-ray region, and the optical index of the film corresponds to the density in hard X-ray region. However, since density difference of typical carbon films such as resist films is small, it is difficult to analyze the stacked-layer structure and its interfacial roughness by XRR. Especially, the optical contrast between the separated and the body layer would be very small to indicate.

On the other hand, around carbon absorption edge in soft X-ray region, there are resonant peaks that depend on chemical bonding structure in the resist material. These resonant absorption peaks are generally measured by X-ray absorption spectroscopy (XAS) to evaluate chemical structure of the carbon material. [9,10]. The optical index of the resist will be dramatically different near these peaks. Thus, the optical contrast between the separated and the body layers can be optimized to analyze the chemical-layer structure, phase separation, and interfacial roughness by RSoXR. The RSoXR was used to analyze the interfacial roughness of the stacked polymer film [11,12].

2. Experimental
2.1. RSoXR setup

The RSoXR measurements were performed at the vacuum chamber of the reflectometer of BL-10 beamline at the NewSUBARU synchrotron light facility. This beamline provides monochromatized soft X-ray energy range from 60 to 1,000 eV [13]. This beamline has been used for EUV reflectometry to measure the reflectance of the EUV optics [14] and XAS for the chemical analysis of EUV resist materials [15-17].

The number of photons estimated by photodiode current was $4 \times 10^9$ photons/s at the photon energy of 280 eV. The energy resolution E/ΔE was approximately 2500. The beam size on the sample stage was 0.1 × 0.8 mm² in full width at half maximum. The sample stage is rotated as $\theta$ axis from 0 to 90 degrees, and the detector arm is rotated as 2$\theta$ axis from 0 to 180 degrees. The sample holder was insulated to measure the sample-surface current at XAS measurement. The detector was SXUV-100 photodiode (Optodiode, Inc.) was employed as a detector, and this sensor has 10 mm-squared sensing area, which has high quantum efficiency and durability for X-ray irradiation.

2.2. Sample resist

Sample resist which was employed in this study was a commercially available chemical amplifier resist (CAR), which was usually used in electron beam lithography. The patterning resolution of this resist was approximately 100-nm HP. This CAR was spin coated on a silicon wafer. Before the resist coating, Hexamethyldisilazane was coated on the wafer to improve the adhesion between the bottom surface of a resist and the surface of a wafer. Rotation speed of the spin coat was 3,000 rpm in 30 s. The baking condition was 90 °C in 90 s. The resist thickness of CAR was measured to be 75.3 nm by the optical interference type film thickness measurement tool (NanoSpec6100, NANO metrics Inc.).

3. Results and discussion

3.1. XAS measurement result

XAS spectrum of the CAR around carbon $K$ edge was measured using the total electron yield method (TEY) as shown in Fig. 1. The horizontal axis shows the incident photon energy. The vertical axis shows TEY current intensity, which was normalized around 280 eV at which it had no absorption signal.

![Fig. 1. XAS spectrum of the CAR C$_K$ bonding.](image_url)

The TEY current intensity related to the absorption amount of the resist. At 285.9 eV, the CAR had strong absorption peak, which corresponded to the $\pi^*$ bonding structure of benzene ring. And, there were three absorption peaks around 290 eV, which would correspond mainly to the functional group such as protection group of the CAR. The broad absorption around 294 eV corresponded to the $\sigma^*$ bonding structure. We
selected 280 eV, 287.1 eV, and 310 eV for RSoXR measurement.

Since the photon energy of 280 eV is smaller than the energy of the carbon absorption edge, it means that the optical-index did not depend on the chemical-bonding structure at the photon energy of 280 eV. Thus, the optical index would mainly depend on the layer density. At the photon energy at 285.9 eV, since the absorption of the resist was the highest, it was difficult to evaluate the surface and bottom structure. Thus, we did not perform the RSoXR measurement at the photon energy of 285.9 eV as an incident photo energy. At the photon energy of 287.1 eV, the absorption was weak enough to detect surface layer information. Since absorption tails from the 285.9 to 290 eV peaks were covered this energy, the optical index would depend on the chemical bonding structure. Thus, the layer separation of the surface and bottom was expected to be evaluated at the photon energy of 287.1 eV. At the photon energy of 310 eV, the σ* bonding structure of carbon had too high absorption.

Figure 2 shows the reflection spectra measured in RSoXR method. The horizontal axis shows scattering vector. The scattering vector \( q \) is shown in Eq. (1), which is normalized by the wavelength \( \lambda \).

\[
q = \frac{4\pi}{\lambda} \sin \left( \frac{\theta}{2} \right) \quad (1)
\]

Thus, the fringe pitch will not change with varied photon energy if the optical index does not depend on the photon energy.

The measurement range of the stage angle \( \theta \) was varied from 0 to 30 degrees in grazing angle of incidence. The reflectance spectra depended on the photon energy strongly.

Fig. 2. RSoXR measurement result of the CAR at the incident photon energy of 280.0, 287.1, and 310.0 eV.

Figure 3 shows a fitting calculation result of the reflection spectrum at the photon energy of 280 eV. There is no carbon group dependency at the photon energy of 280 eV, the incident photon energy was fixed to 280 eV in the layer separation evaluation. The fitting calculation to the measured scattering spectrum was performed by IMD software program. [18] The fitting calculation applied by the single layer model with 80.15 nm in thickness, 0.9992 in refractive index \( n \) and 0.000113 in extinction coefficient \( k \). The \( \chi^2 \) value in this fitting calculation was small enough to be 0.0036.

Where the \( \chi^2 \) value is the square of the residual divided by the standard deviation, which indicates the fitting calculation certainty. Thus, the CAR could not have density separated layer at the surface and the bottom.

Fig. 3. Fitting result of RSoXR spectrum at the incident photon energy of 280 eV with the single layer model.

Figure 4 shows the fitting results of the reflection spectrum at the incident photon energy of 287.1 eV. We tried to fit the spectrum by the following four fitting models such as (a) single-layer model, (b) two models of bi-layer (surface-separation and bottom-separation), and (c) tri-layer model. The \( \chi^2 \) values for the single- and the bi-layer models were large, and that of the tri-layer was small as 0.000689. The fitting result of the tri-layer model was shown in Table 1.

As the results, the CAR might have thin surface layer and thin bottom layer with a thickness of 5.0 and 6.2 nm, respectively. In addition, the refraction index \( n \) was slightly changed at each layer, and the interlayer surface roughness of (surface layer)/(main body) and (main body)/(bottom layer) are 5.4 and 5.6 nm, respectively. Since the roughness was not smooth, the separation did not have clear interface but also had mixed or diffused interfaces.

The extinction coefficients \( k \) was almost same at the surface and the main body layers. However, the extinction coefficient of the bottom layer had about 3 times higher than other layers. These results indicated the chemical structure of the bottom layer was quite different from the other two layers. This
bottom separation might cause poor adhesion and pattern collapse.

![Diagram](image)

Fig. 4. The fitting result of RSoXR measurement at the incident photon energy of 287.1 eV with (a) single-layer model, (b) two-layer models (surface separation), (c) two-layer models (bottom separation), (d) tri-layer model.

### Table 1. Fitting result by the tri-layer model.

| Type of layer | Thickness (nm) | Refraction coefficient | Extinction coefficient | Roughness (nm) |
|---------------|---------------|------------------------|-----------------------|----------------|
| Top           | 5.02          | 0.9991                 | 0.00036               | 0.17 (vacuum/top) |
| Main body     | 68.45         | 0.9995                 | 0.00039               | 5.40 (top/middle) |
| Bottom        | 6.19          | 0.9997                 | 0.00116               | 5.63 (top/bottom) |
| Si sub.       | --            | 0.9951                 | 0.00281               | 0.10 (bottom/Si wafer) |

The RSoXR method is sensitive to the chemical-structure separation of the resist. In near future, we would expose EUV to a resist with a grazing angle, and evaluate distributions of generated acid and chemical structure modification.

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