Resonant Soft X-ray Scattering for the Stochastic Origin Analysis in EUV Resist

Jun Tanaka*, Takuma Ishiguro, Tetsuo Harada, and Takeo Watanabe

Center for EUV Lithography, Laboratory of Advanced Science and Technology for Industry, University of Hyogo, 1-1-2 NewSUBARU, Kouto, Kamigori, Ako-gun, Hyogo 678-1205, Japan
*jtanaka@lasti.u-hyogo.ac.jp

The resist development is a critical issue in EUV lithography for high volume manufacturing of semiconductor devices. Especially, the resist should have low line-width roughness (LWR) performance in fine patterning. To reduce the LWR, it is significant to control and reduce the stochastic behavior in the resist material. We employed the resonant soft X-ray scattering (RSoXS) method to evaluate the non-uniformity of the resist material components such as base polymer, functional group, and photo-acid generator and so on. In RSoXS method, the soft X-ray scattering intensity from the resist is recorded by a CCD camera, which the incident photon energy irradiated to the resist sample was varied around the carbon absorption K-edge of 284 eV. Around the carbon absorption edge, the absorption spectrum had resonant absorption peaks that depended on the chemical bonding structure of carbon. The scattering signal profile of a commercial chemical-amplified resist was different at each absorption peaks, which indicated non-uniformity of resist material. Thus, the non-uniformity of the resist material was measured by RSoXS method, which was important for development of low LWR resist.

Keywords: Resonant soft X-ray scattering, EUV resist, Resist material stochastic

1. Introduction

EUV lithography are going to use in high volume manufacturing of semiconductor devices in the second half of 2019 [1], which is a major candidate for 10-nm half pitch (HP) patterning after 2020. For the 10-nm HP patterning, the critical issue is to develop a resist which satisfy the specification such as high resolution of <10-nm HP, high sensitivity of <15 mJ/cm², low line-width roughness (LWR) of < 1 nm (3σ), and low-outgas property, simultaneously [2].

In these requirements, the most important issue is to achieve low LWR property. To reduce the LWR, it is significant to reduce the stochastic behavior in the resist process. For example, the photon shot noise is well known to cause the stochastic [3]. Recently, Zeiss research group reported the stochastic behavior was not caused only by the photon shot noise, but also resist material non-uniformity based from a base polymer, functional groups, and a photo-acid generator and so on [4].

It is required ultra-uniform distribution of a resist material for the 10-nm patterning to reduce the stochastic. Therefore, spatial uniformity of the resist material should be evaluated. In general, FT-IR and Raman scattering methods evaluate chemical structure distribution of the resist. The spatial resolution of FT-IR and Raman methods were not high and exceeds more than 1 μm [5]. On the other hands, the X-ray microscope, X-ray scattering, and electron microscope have high resolution of less than 10 nm. However, these cannot evaluate the chemical structure distributions.

The resonant soft X-ray scattering (RSoXS) [6] at BL-10 beamline of NewSUBARU synchrotron light facility [7] was developed. In the RSoXS method, soft X-ray scattered image of a resist material was recorded on a CCD camera inside the vacuum chamber, which energy was varied around carbon absorption edge of 284 eV. Around carbon absorption edge, absorption spectrum has resonant absorption peaks that depend on chemical bonding...
structure of the carbon. The scattering at the absorption peaks would indicate the distribution of each chemical bonding structure. The spatial resolution was 30 nm in this paper, which depended on the exposure wavelength of soft X-ray and numerical aperture of the detector.

RSoXS was widely used for the characterization of structured soft condensed matter nanomaterials [8], and the tri-block polymer analysis of the patterning formed material in direct-self assembly (DSA) [6,9]. The polymer contrasts were changed by the photon energy selection around the resonant absorption of carbon. In addition, each chemical structures had an individual absorption around its resonant-absorption peak. Thus, the RSoXS method is a useful method for the evaluation of the soft material uniformity which mainly formed by the carbons. In this paper, resist material uniformity of three resists were evaluated by the RSoXS method.

2. Experimental

2.1. Measurement method of RSoXS

Figure 1 shows the schematic drawing of the RSoXS system at BL-10 beamline of NewSUBARU. This beamline provides monochromatized energy of the soft X-ray region from 80 to 1000 eV [10]. This beamline has been used for EUV reflectometry to measure the reflectance of EUV optics [11] and the X-ray absorption spectroscopy (XAS) for the chemical reaction analysis of EUV resist materials [12]. The photon energy range to expose on a sample is from 60 to 1100 eV. The number of photons estimated by the photodiode current at the focal point was $4 \times 10^9$ photons/s at the photon energy of 280 eV. The energy resolution $E/\Delta E$ was approximately 2500.

![Fig. 1. Schematic drawing of RSoXS measurement of the sample resist [6].](image)

As shown in Fig. 1, the incident soft X-ray beam was irradiated from the right side to the left side, which formulated almost in parallel beam. The focusing point of the incident beam was located at 2.1 m upstream from the sample. The $\phi 200 \mu m$ pinhole employed as an incident aperture to limit the incident beam size to $\phi 200 \mu m$ in diameter. The $\phi 400 \mu m$ pinhole employed as a scattering cut was located just before the sample to cut the direct-back-scattering light from the incident aperture. And then the sample was exposed by the soft X-ray beam and scattered light was led to the in-vacuum CCD camera (MTE-2048B, Roper Scientific) to measure the scattered image of a resist sample. The center-stop block with 1 mm in height was located just before the CCD camera, which cut the strong direct beam from the sample.

Distance from the incident pinhole to the sample was 75 mm, and that from the sample to the CCD camera was 57 mm. The sensing area size of the CCD camera was $27.6 \times 27.6 \text{ mm}^2$. Thus, the acceptance angle of the CCD camera was 11.7°. The CCD camera has 2048 × 2048 pixels and the pixel size is 13.5 µm in square. At measurement, the 8 × 8 pixels were binned to reduce readout noise.

2.2. Sample

The sample resist was spin coated on the silicon-nitride (Si$_3$N$_4$) membrane substrate, which had the membrane thickness of 100 nm, and the membrane window size of 2 mm in square. The membrane frame was silicon wafer with 200-µm-thick and 5-mm-square-size. The membrane film of 100-nm-thick was enough thin to measure the transmittance scattering from a resist film. The resists which employed in this study were polymethyl methacrylate (PMMA), ZEP520A (Zeon) resist, and a commercially available chemical-amplified resists (CAR). PMMA and ZEP520A resists are widely used for electron beam lithography. Chemical structure of PMMA and ZEP520A resists are shown in Fig. 2.

PMMA resist is homo-polymer structure and has a high resolution of 10 nm HP [13]. ZEP520A resist is copolymer and has a high resolution of 12.5 nm HP [14]. Because of these high resolution with low LWR, PMMA and ZEP520A resists were expected to have a uniform distribution of the resist material component as mention before. On the other hand, the resolution of the CAR was not high and was more than 100 nm. The CAR had complex structure that includes photo-acid generator (PAG), deprotection group, and amine additive. Thus, chemical structure distribution of the CAR was expected to be non-uniform in comparison to PMMA and ZEP520A resists.
The Si$_3$N$_4$ membrane was fabricated on a Si wafer by spin-coating and prebake. The resist coating condition was same for the three resist samples with the spin-coating speed of 500 rpm in 30 s. The prebake conditions of PMMA resist, ZEP520A resist, and CAR were at the temperature of 90 °C in 90 s, that of 180 °C in 180 s, and that of 90 °C in 90 s, respectively. Thickness of resist on other Si wafer substrate with same coating condition of the membrane substrate was approximately 200 nm.

Figure 3 shows the optical microscope image of the coated membrane with the PMMA resist. There are some particles attached on the resist surface and the resist film thickness non-uniformity on the membrane. The uniform region was measured by the RSoXS method, which had small beam diameter of 200 µm.

2.3. XAS measurement

In the RSoXS method, scattering is measured at the resonant absorption energy of each chemical bonding structure of the resist component materials. Thus, before the RSoXS measurement, the resist samples were measure by XAS with total electron yield (TEY) method around carbon K edge. In the XAS measurement, the resist on the membrane was measured. Figure 4 shows the XAS result of the three resists. The vertical axis shows the TEY current intensity, which corresponded to the absorption amount of the resist. The large TEY current indicates large absorption. The horizontal axis shows photon energy of the incident soft X-ray beam. For ZEP520A resist and CAR, the strong absorption peaks at 286 eV were observed, which corresponded to the π* bond structure of benzene group. PMMA resist and CAR had absorption peak at 289 eV of the bonding structure of acrylate group. The broad absorption peaks around 294 eV correspond to σ bond structure of carbon.

The RSoXS was performed at the photon energy of 280, 286, 289, and 294 eV for CAR and ZEP520A resists, and 280, 286, 289 eV for PMMA resist. The photon energy of 280 eV was just lower than that of the carbon absorption edge. At this energy, carbon had small absorption, which did not depend on the chemical structure. Thus, the scattering profile corresponded to total structure of the resist material.

Figure 5 shows the scattering image by the CCD camera for the CAR at the photon energy of 280 eV in 200 s exposure time, which was determined not to saturate the scattering signal.

The strong scattering signal was observed at the center position. The black rectangle at the center region indicates shadow of the center block plate, which blocked the extremely bright direct beam to saturate the CCD camera intensity profile. Circular-arc shaped signals around right side were stray light. Averaged scattering intensity on each pixel was counted as the distance from the center position, which did not include the shadow and stray light signal. As the result, the intensity was scattering.
intensity at each radial position. This distance indicated angle $\theta$ from the optical axis, which converted to the scattering vector $q$. The scattering vector is shown in Eq. (1), which is normalized by the wavelength $\lambda$.

$$q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right)$$

Thus, a spatial frequency of the sample corresponds to a scattering vector even if the incident photon energy is varied. For example, the scattering vector of 0.1 nm$^{-1}$ and 0.05 nm$^{-1}$ corresponded to spatial frequency of 60 nm and 120 nm, respectively.

Fig. 5. Scattering image of the resist captured by the CCD camera.

### 3. Results and discussion

Figures 6 (a)-(c) show scattering profiles of the three resist samples. The horizontal and vertical axes show the scattering vector and the averaged scattering intensity in log scale that was normalized around 0.02 nm$^{-1}$, respectively. The scattering intensity with this normalization had huge difference each other due to the transmittance and thickness difference of the resists. To compare the scattering profile, the signal was normalized around low spatial frequency region of 0.02 nm$^{-1}$.

Figure 6(a) shows the scattering spectra of PMMA resist. The scattering signal difference of varied photon energy was small. Thus, the acrylate group might be uniformly distributed in the PMMA resist polymer. Since the main-chain scission occurs inside PMMA resist under the EUV exposure, the high resolution and low LWR performance would be based on this good uniformity.

Fig. 6. The soft X-ray scattering distribution (a) PMMA, (b) CAR, and (c) ZEP520A in the four conditions of the photon energy.
Figure 6(b) shows the scattering spectra of CAR. The scattering signals from the photon energy of 286 and 294 eV to 280 and 289 eV have a difference property. This difference was caused by the absorption difference of the functional groups, and it indicated that CAR had non-uniform distributions of the resist chemical components. The absorption peaks at the photon energy of 286 and 289 eV related to the benzene ring and acrylate group, respectively. And the absorption peak at the photon energy of 280 eV related whole carbon distribution. Since the scattering distributions at the photon energy of 286 and 294 eV were similar, the benzene ring distribution would be non-uniform. In addition, because of same scattering distribution at the photon energy of 280 and 289 eV, the acrylate group would be uniformly distributed in the CAR.

It is considered to suggest that in the case of CAR having a small molecular weight dispersion, even if the molecular weight dispersion of the polymer is small, the size of the polymer in the resist is not uniform due to aggregation of the polymer. Moreover, since the molecular weight of the acrylate group is overwhelmingly small compared to the polymer molecular weight, the aggregation is present in the resist film without aggregation. Thus, it is considered that the variation of the normalized scattering intensity is reduced.

Figure 6(c) shows the scattering distribution with ZEP520A resist. The scattering distribution of ZEP520A was smaller than that of CAR. However, the scattering distribution of ZEP520A was larger than that of PMMA. The cause of this may be local deviation of the rate of copolymer polymerization of ZEP520A. To clear the origin of the distribution, it is necessary to measure a more accurate scattering profile with the high noise to signal ratio in the RSoXR method.

4. Conclusion

We have developed RSoXS method to evaluate uniformity of resist material distribution, which can modulate absorption contrast of functional group by changing the incident photon energy around carbon absorption edge. The scattering distributions from three types of the resist were measured at the BL-10 beamline of NewSUBARU synchrotron light facility. The scattering profiles were measured at the 280, 286, 289, and 294 eV. The scattering profiles of the CAR at 286 and 294 eV were different from that of 280 and 289 eV, which indicated the non-uniformity of the resist material. Since these of PMMA resist had unity scattering profile, the PMMA resist had uniform distribution of acrylate structure in resist. Thus, the RSoXS result could show uniformity of resist material structure, which was important to achieve high resolution and low LWR performance. In future, we will measure actual EUV resists using RSoXS with quantitative uniformity evaluation and with higher signal-to-noise ratio condition.

References
1. E. S. Jung, "4th Industrial Revolution and Foundry: Challenges and Opportunities," IEDM2018 Plenary talk (2018).
2. K. Ronse, International Symposium on Extreme Ultraviolet Lithography, (2018) Closing remarks.
3. D. D. Simone, Y. Vesters, and G. Vandenberghe, J. Photopolym. Sci. Technol., 31 (2018) 651.
4. B. Geh, SPIE Advanced Lithography 2019 EUV Lithography X, Plenary talk (2019) 10957-1.
5. H. Ishida, Panasonic Tech. J., 59 (2013) 45 (in Japanese).
6. Y. Nakatani, T. Harada, A. Takano, M. Yamada, and T. Watanabe, J. Photopolym. Sci. Technol., 30 (2017) 77.
7. Web site of NewSUBARU Synchrotron facility, http://www.lasti.u-hyogo.ac.jp/NS/
8. T. Araki, H. Ade, J. M. Stubbs, D. C. Sundberg, G. E. Mitchell, J. B. Kortright, and A. L. D. Kilcoyne, Appl. Phys. Lett., 89 (2006) 124106.
9. C. Wang, D. H. Lee, A. Hexemer, M. I. Kim, W. Zhao, H. Hasegawa, H. Ade, and T. P. Russell, Nano Lett., 11 (2011) 3906.
10. M. Kuki, T. Uemura, M. Yagamuchi, T. Harada, T. Watanabe, Y. Muramatsu, and H. Kinoshita, J. Photopolym. Sci. Technol., 28 (2015) 531.
11. Y. Fukushima, N. Sakagami, T. Kimura, Y. Kamaji, T. Iguchi, Y. Yamaguchi, M. Tada, T. Harada, T. Watanabe, and H. Kinoshita, Jpn. J. Appl. Phys., 49 (2010) 06GD06.
12. K. Emura, T. Watanabe, M. Yagamuchi, H. Tanino, T. Fukui, D. Shiono, Y. Haruyama, Y. Muramatsu, K. Ohmori, K. Sato, T. Harada, and H. Kinoshita, J. Photopolym. Sci. Technol., 27 (2014) 631.
13. H. Duan, D. Winston, J. K. W. Yang, B. M. Cord, V. R. Manfrinato, and K. K. Berggen, J. Vac. Sci. Technol. B, 28 (2010) C6C58.
14. H. Kobayashi, H. Iyama, T. Kagatsume, and T. Watanabe, Proc. SPIE, 8522 (2012) 852208.