Analysis of Chemical Contents Spatial Distribution in EUV Resist Using Resonant Soft X-ray Scattering Method

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EUV lithography is started to use in high volume manufacturing of 7-nm node semiconductor devices for smart phones. However, a resist development is still remained significant critical issue in EUV lithography. The EUV resist has to be achieved high resolution, high sensitivity, and low line-width roughness (LWR), simultaneously. Especially, the resist is required low LWR performance for a fine patterning. To reduce LWR, it is significant to control and reduce the stochastic behavior of the resist chemical contents such as the functional groups, photo reactive compound (photoacid generators: PAG), additives such as amines and so on. However, there is no method to measure the chemical contents spatial distribution. Therefore, the resonant soft X-ray scattering (RSoXS) method is applied to evaluate the chemical contents spatial distribution. Around the carbon absorption edge, the resonant absorption peaks are specific to the chemical contents of carbon. In RSoXS method, the soft X-ray scattering intensity from the resist is recorded by a CCD camera, which the incident photon energy irradiate to the resist sample is varied around the carbon absorption K-edge of 284 eV. If these chemical contents have large dispersion, the stochastic becomes worth. In this way, the chemical contents spatial distribution in photoresists is measured by RSoXS method, and this method is significant for development of low LWR resist.

Keywords: Resonant soft X-ray scattering, EUV resist, stochastic, small angle X-ray scattering

1. Introduction

EUV lithography is started to use in high volume manufacturing of 7-nm node semiconductor devices for the smart phones. However, significant technical issues of EUV lithography are still remain such as 1) EUV resist development, 2) defect free EUV mask fabrication including defect inspection, 3) EUV light source which has high power at the intermediate focus position and high stability, and 4) EUV pellicle which has high transmittance and high exposure stability. In resist development, it is required to satisfy the specification with high resolution of <10-nm half-pitch (HP), high sensitivity of <15 mJ/cm², low line-width roughness (LWR) of < 1 nm (3σ), and low-outgas property, simultaneously [1]. Then, the most critical issue is to reduce LWR. The origin of LWR is the stochastic phenomena such as 1) the spatial distribution of functional materials in the EUV resist film such as the functional groups, photo reactive compounds (PAGs), additives such as amines and so on [2], 2) the free-volume-spatial distribution by the evaporation of the solvent distribution during prebake process, 3) the EUV photon shot noise [3], 4) the secondary electron blur due to the high energy and low energy electron, 5) the acid diffusion affected by the solvent effect during PEB process, 6) the spatial distribution of developer penetration and development process yield during the development and rinse processes, and 7) the affect by the out of band (OoB) light which has unexpected wavelength generated from the EUV light source such as deep UV light which has a sensitivity in a resist film. In these stochastic origins, the most significant stochastic might be due to the
spatial distribution of functional material in the EUV resist film.

In general, chemical-content-spatial distribution in a resist film is evaluated with the FT-IR and Raman scattering, but in these methods the spatial resolution is more than 1 µm [4]. On the other hands, the small angle X-ray scattering (SAXS) in the hard X-ray energy region is commonly used for the analysis of the material structures, and it has a high resolution of less than 10 nm. However, it cannot evaluate a chemical structure distribution in a resist film because there is no optical contrast (absorption and refractive index difference) of chemical structures in the hard X-ray energy region. On the other hand, the resist material has large absorption in the soft X-ray energy region, especially around the carbon K absorption edge. There are resonant absorption peaks which corresponds to chemical structures. For examples, resonant absorption peaks of 286 eV, 289 eV and 296 eV correspond to the π* bond structure of benzene group, acrylate group, and σ bond structure of carbon, respectively. Therefore, the scattering measurement in soft X-ray region could evaluate the chemical structure distribution. In the resonant soft X-ray scattering (RSoXS) method [6], the incident soft X-ray irradiates to the sample, and the scattering light from the sample is recorded by a CCD camera which is installed in a vacuum chamber. The incident photon energy was varied around the carbon absorption edge of 284 eV. The spatial resolution in this method is approximately 12 nm, and this spatial frequency is enough high to analyze the resist uniformity, which might be affected with the LWR and stochastic.

The RSoXS is commonly used for the characterization of structured soft condensed matter nanomaterials [5], and the tri-block polymer analysis of the patterning formed material in direct-self assembly (DSA) materials [6,7]. In this study, the spatial uniformities of three components in hole pattern structures was evaluated using RSoXS method [8]. Therefore, the RSoXS method is a very useful method for an evaluation of a chemical distribution in a soft material which mainly formed by light elements. In this paper, the RSoXS method evaluated a chemical contents spatial distribution in the resist films in varying the number average molecular weight <Mn> and molecular weight distribution <Mw/Mn>, where <Mw> is weight average molecular weight.

2. Experimental
2.1. Measurement method of RSoXS

Figure 1 shows a schematic drawing the RSoXS system at BL-10 beamline of NewSUBARU [9]. This beamline provides monochromatized energy of the soft X-ray region from 80 to 1000 eV [10]. This beamline has been used for the 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 exposing on a sample is from 60 to 1100 eV. The number of photons estimated by the photodiode current at the focal point was 4 x 10⁹ photons/s at the photon energy of 280 eV. The energy resolution E/ΔE was approximately 2500.

As shown in Fig. 1, the incident soft X-ray 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. A pinhole with 200 µm in diameter employed as an incident aperture to limit the incident beam size to 200 µm. A pinhole with 400 µm in diameter 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 from the resist sample. The center-stop plate with 1 mm in width was located just before the CCD camera, which cut the strong direct beam from the sample.

The 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 mm (H) x 27.6 mm (V). Thus, the acceptance angle of the camera was 11.7°. The camera has 2048 x 2048 pixels and the pixel size is 13.5 µm in square. In the scattering measurement, the 8 x 8 pixels were binned to reduce the readout noise.

Figure 2 shows the scattering image by the CCD camera for a resist sample at photon energy of 280
eV in exposure time of 100 s. The exposure time 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-stop plate, which blocked the extremely bright direct beam to saturate the CCD camera intensity profile. The 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.

Fig. 2. Scattering image of the resist captured by the CCD camera.

Figure 3 shows the schematic image of the scattering from the sample on the image sensor. The scattering vector $q = |\vec{q}|$ can be described by the following equation (1), where $\vec{k}_{in}$, $\vec{k}_{out}$, and $\theta$ are the incident and scattered wave-number vectors, and scattering angle, respectively. And considering the following equation (2), the scattering vector is described as the following equation (3).

$$\vec{q} = \vec{k}_{out} - \vec{k}_{in} \quad (1)$$

$$|\vec{k}_{out}| = |\vec{k}_{in}| = k = \frac{2\pi}{\lambda} \quad (2)$$

$$q = |\vec{q}| = \frac{4\pi}{\lambda} \sin \frac{\theta}{2} \quad (3)$$

Thus, the 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$^{-1}$ corresponded to spatial size of 60 nm. And the maximum scattering vector in this setup was 0.5 nm$^{-1}$, which corresponded to the spatial size of 12 nm, which indicates the spatial resolution in this study.

2.2. Sample

The sample resists were spin coated on the silicon-nitride (Si$_3$N$_4$) membrane substrate. This substrate 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 was 100-nm-thick so a scattering light from the resist can transmit the membrane.

| Sample | Molecular weight ($M_w$) | Molecular weight distribution | Amounts of PAG (wt%) |
|--------|--------------------------|-----------------------------|---------------------|
| 1      | 6000                     | 1.3                         | 30                  |
| 2      | 14000                    | 1.3                         | 30                  |
| 3      | 6000                     | 1.7                         | 30                  |
| 4      | 14000                    | 1.7                         | 30                  |
| 5      | 6000                     | 1.3                         | 15                  |
| 6      | 6000                     | 1.3                         | 0                   |
| 7      | 14000                    | 1.3                         | 0                   |
| 8      | 6000                     | 1.7                         | 0                   |
| 9      | 14000                    | 1.7                         | 0                   |

The samples employed in this study were model components of chemical-amplified resists (CAR), which employed copolymer of polyhydroxy and styrene as a base resin, nonaflate as a PAG. Table 1 shows the composition of the sample. Each sample is dissolved in propylene glycol 1-monoethyl ether.
2-acetate (PGMEA). Sample#6 – 9 were the polymer sample without PAG. Sample#1 – 5 were the base polymer with PAG. The molecular weight, molecular weight distribution, and the PAG contents were varied. In sample fabrication process, Si₃N₄ membrane was attached on a Si wafer by polyimide tape. The liquid was dripped on the membrane using a dropper. The polymer was spin coated and prebaked. The spin-coating speed were 500 rpm or 1500 rpm in 30 s. The prebake condition was at the temperature of 130 °C in 60 s. Thickness of the polymer would be approximately 280 nm and 170 nm when the spin-coating speed of 500 rpm and 1500 rpm, respectively.

Fig. 4. The optical microscope images of the resist coated on the Si₃N₄ membrane at the spin coating speed of (a) 500 rpm and (b) 1500 rpm.

Figures 4(a) and (b) show the optical microscope image of the coated membrane with the spin coating speed of 500 rpm and 1500 rpm, respectively. In Fig. 4(a), the resist film thickness was not uniform. In Fig. 4(b), the resist film thickness was coated with good uniformity.

Figure 5 shows the RSoXS result of sample#9 with the spin coating speed of (a) 500 rpm and (b) 1500 rpm. Scattering images at 4 photon energy were measured, which will be described in section 2.3. The horizontal axis shows the scattering vector $q$. The vertical axis shows scattering signal from the sample, which was normalized at the lowest scattering vector around 0.17 nm⁻¹. For the non-uniform sample, the scattering of each photon energy was quite different with each other in $q > 0.022$ nm⁻¹ region which corresponds to the spatial size of 300 nm.

Fig. 5. RSoXS result of sample 9 on the membrane with the spin coating speed of (a) 500 rpm and (b) 1500 rpm.

The polymer would have large cluster of 300 nm. At 280 eV, the polymer had lower absorption because that is just below the carbon absorption peak of 284 eV. The scattering signal of 280 eV was lower than the scatterings of other photon energies at high
frequency region. If the cluster has uniform chemical structure, the four scatterings would have same profile. Thus, the cluster would have the chemical structure aggregation, which could be caused by hydrophilicity of functional group in the polymer. The dispersion of these scattering signal shows the cluster size and aggregation of the functional group. For the coating condition at 500 rpm, there was many amount of clusters in in the resist films, which was also observed the optical microscope image as shown in Fig. 4(a). Therefore, the coating speed was chosen to 1500 rpm for the RSoXS measurements.

The coating condition affected the cluster size of the polymer, which was detected to the RSoXS result. The coating on the small membrane was hard to obtain uniform coating. Therefore, to evaluate actual resist performance, the sample should be coated on the Si wafer, and measured by the RSoXS in the reflection mode.

2.3. XAS measurement

Around the carbon absorption edge, the resonant absorption peaks are specific to the chemical contents. Then, the scattering at the absorption peaks related to the chemical contents in the resist film. Therefore, the resist samples were measure by XAS with the total electron yield (TEY) method around carbon K edge. After that, the probe photon energies could be determined as the incident photon energy for the small angle scattering. In the XAS measurement, the resist on a Si wafer was measured.

Figure 6 shows the XAS result of the polymer sample #1. The vertical axis shows the absorption amount of the polymer. The horizontal axis shows photon energy of the incident soft x-ray beam. The strong absorption peak at 286 eV was observed, which corresponded to the π* bond structure of benzene group. Absorption peak at 289 eV was corresponded to the bonding structure of acrylate group. The broad absorption peaks around 296 eV correspond to σ bond structure of carbon.

The RSoXS was performed at the photon energies of 280, 286, 289, and 296 eV. The photon energy of 280 eV had just lower than that of the carbon absorption edge. The scattering profile at 280 eV was the base line of the small polymer absorption. Thus, if the spectrum of scattering vector has a similar profile in comparison of that from the base line, the chemical dispersion might be small. Otherwise, if the spectrum of scattering vector has a different profile in comparison of that from the base line, the chemical dispersion might be large.

3. Results and discussion

Figures 7 (a-d) and 8 (a-e) show scattering profiles of the resist samples. The horizontal and vertical axes show the scattering vector and the average scattering intensity in log scale that was normalized around 0.02 nm\(^{-1}\). The scattering intensity with this normalization had large difference each other because of the thickness differences of the resist film. To compare the scattering profile, the signal was normalized around low spatial frequency region of 0.02 nm\(^{-1}\).

1, 2, and 3 in the legend correspond to the molecular weight, molecular weight distribution, and amounts of PAG in the polymer sample, respectively.

Figure 7 shows the scattering spectra of (a) sample#8, (b) sample#9, (c) sample#3 and (d) sample#4 with the molecular weight distribution of 1.7. There was small difference in the spectra with the molecular weight of 6,000 and 14,000 in Figs. 7(a,b) and Figs. 7(c,d). This indicates that there would be small difference of the spatial distribution of the chemical components.

However, the spectra were changed by PAG existence. In Figs. 7(a) and (b) without PAG, the spectra of 4 photon energies were separated from 0.2 nm\(^{-1}\). However, in Figs. 7(c) and (d) with PAG contents of 30 wt%, the profile which becomes separated is at the spatial frequency of at 0.1 nm\(^{-1}\). This difference indicates the cluster size in the polymer was changed by the PAG addition, or the PAG was concentrated to make the cluster. The cluster size was approximately doubled with the PAG addition.

Figure 8 shows the scattering spectra of (a) sample#7, (b) sample#6, (c) sample#5, (d) sample#1
and (e) sample#2 with the molecular weight distribution of 1.3. There was also small difference in the spectra with the molecular weight of 6,000 and 14,000 in Figs. 8(a,b), and Figs. 8(d,e). Thus, the chemical distribution was not affected by the molecular weight difference.

However, the spectra were changed by PAG existence. In Figs. 8(a) and (b) without PAG additive, the spectra of 4 photon energies were separated from 0.1 nm$^{-1}$. However, in Figs. 8(b), (c) and (d) with PAG additive, the separated $q$ was changed to 0.2 nm$^{-1}$. This difference indicates the cluster size in the polymer was changed by the PAG addition. The cluster size became approximately half size by the PAG addition, which was opposite result of that with molecular distribution of 1.7 in Fig. 7.

In addition to the cluster size change, the polymer sample with PAG additive had larger spectra dispersion in the range of $q = 0.03 – 0.2$ nm$^{-1}$ than that without PAG. This separation indicates non-uniformity of chemical structure. Thus, PAG was distributed not uniform in the base polymer. The spatial frequencies of this non-uniformity were in the range of 30 – 200 nm. This non uniformity would cause the LWR and stochastic effect, which should be small for EUV resist.

The RSoXS could detect scattering of chemical structure with high spatial resolution up to 12 nm, which could evaluate the uniformity of PAG, and the concentrated cluster size in the polymer.

4. Conclusion

We have developed the RSoXS method to analyze a chemical contents spatial distribution, which can modulate the absorption contrast of the chemical components by changing the incident photon energy around the carbon absorption $K$-edge. The scattering distributions from the resists were measured at the BL-10 beamline of NewSUBARU synchrotron light facility. The scattering profiles were measured at the
probe-photon-incident energy of 280, 286, 289, and 296 eV. The profiles corresponded to the chemical contents of the spatial distribution in the CARs. Thus, the RSoXS result could show the chemical contents spatial distribution, which was significant to achieve low LWR performance. In the future, we will measure the actual EUV resists using the RSoXS in the reflection mode to measure resist sample on a Si wafer.

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