A Study of Acid Diffusion Behaviors of PAG by using Top Coat Method for EUVL

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Semiconductor microfabrication technologies for the 22-nm generation require high-performance resists with superb exposure characteristics. Specifically, this means resolution, exposure sensitivity, and edge roughness values not exceeding 18 nm, 10 mJ/cm², and 2 nm (3σ), respectively. Resist exposure characteristics must be evaluated using actual exposure spectra. Since six-mirror exposure optics now represents the mainstream, we installed a resist evaluation system[1] capable of obtaining reflectance spectra of these exposure optics at the BL3 beamline in the NewSUBARU[2] synchrotron radiation facility and performed resist evaluations. The system allows evaluations of various parameters for lithography simulations, including exposure sensitivity,[3] acid diffusion length,[4] light desorption characteristics,[5] Dill's ABC parameters,[6] and quenching rate parameters.[7] Using the top coat method, we examined the diffusion behavior of the acid generated by the PAG. This paper reports the results of our study.

Keywords: Chemically amplified resist, Photo-acid generator, Acid diffusion length, Acid diffusion coefficient, EUV Lithography

1. Introduction

The top coat method has been proposed as a method for measuring the distance of diffusion (diffusion length) of acid, which is generated from PAG due to the exposure, during the PEB process and for calculating the diffusion coefficient[8]-[9]. We applied a top coat material ("TC" hereinafter) containing PAG (second layer) to a PAG-free EUV resist (first layer), then performed the exposure and PEB processes. The acid generated in the TC (second layer) during the exposure diffused into the EUV resist in the lower layer (first layer) when the PEB was performed. The process of developing this sample removed the TC and the parts of the first layer into which the acid had diffused. We obtained the acid diffusion length based on the quantity of film removed by the development[8]-[9]. We calculated the acid diffusion coefficient after varying the exposure value and repeating the measurement. For this report, we also performed measurements to determine how differences in PAG anion size, amount of quencher additive, and PEB temperature affected the value of the acid diffusion coefficient. We entered the measurements obtained into the PROLITH simulator[10] to explore the effects of acid diffusion on pattern profiles.

2. Measurement Methods

Figure 1 shows the beamline configuration, which uses light emitted from the bending magnet of the NewSUBARU[2] storage ring as its light source. The electron beam of the NewSUBARU facility has an energy of 1.0 GeV. Figures 2 and 3, respectively, show a schematic diagram and a photo of the resist exposure equipment, consisting of an optical mirror chamber, an exposure chamber, and a load lock chamber used to change samples[11]. Each chamber incorporates a magnet-levitation turbomolecular pump and an oil-free scroll. One concave mirror and two plane mirrors are installed inside the...
optical mirror chamber; the concave mirror reflects light once, while the two plane mirrors reflect light 6-times. The incident angle and reflection angles are 5 deg. from the perpendicular. The 7-times reflection by the Mo/Si multilayer reflecting mirrors achieves an actual exposure reflection spectrum of six-mirror exposure optics (Figure 4). Graphs (a) and (b) in Figure 5 give the measured reflectance spectra of the Mo/Si multilayer concave mirror and Mo/Si multilayer plane mirror, respectively. These reflectance spectrum measurements were obtained using the reflectometer of the NewSUBARU BL3 beamline. Graph (c) in Figure 5 shows the calculated result for the reflectance spectrum on the sample surface based on the measured reflectance spectra. The center wavelength is 13.57 nm, while the reflectance at the center wavelength is 2.3%. The beam size on the sample surface is approximately 4 x 4 mm². Each 4-inch sample was subjected to a 9-shot exposure, making it easy to obtain the resist sensitivity curve. The base pressure in the chamber was maintained at about 2 x 10⁻⁵ Pa.

To adjust resist exposure values, we used a high-speed electromagnetic shutter inside the four-quadrant slit chamber located upstream of the resist exposure equipment. This high-speed electromagnetic shutter was controlled externally with a shutter control software program written in C++ and running on a Windows PC. The flux on sample surfaces was approximately 0.33 mW/cm² with a ring storage current of 200 mA.

Since irradiation times are approximately 30 s for a high-sensitivity resist of 10 mJ/cm², we set the irradiation time to around 100 ms to obtain the sensitivity curve. The time resolution of the high-speed shutter was 11 ms, a value that meets the specification requirement [1].

Figure 1  NewSUBARU synchrotron radiation facility

Figure 2  Resist exposure evaluation line (BL3)

Figure 3  External view of the EUV exposure evaluation system

Figure 4  6-mirror optics

Figure 5  Reflectance spectra of Mo/Si multilayer mirror: (a) top left, (b) top right, (c) bottom
3. Experimental

For the experiment, we used resin bound with blocking groups as a first layer. Specifically, we chose GMH resin, \[10\]-\[12\] a lactone-based polymer. This resin contained GBLMA/MAdMA/HAdMA (40/40/20 (mol%) (“GMH” hereinafter) without PAG (Figure 6). For the second layer, we used 4-methyl-2-pentanol to dissolve a JSR-manufactured alkali-soluble TC material (28.8 wt%) and added PAG. The amount of PAG added was 4 mol% of the TC resin used. Figure 7 shows the structure of the PAG used.

![GMH (With blocking group)](image1)

![PAG-A (TPS-TF)](image2)

![PAG-B (TPS-PFBS)](image3)

![PAG-C (TPBDPS-PFBS)](image4)

Figure 6 Polymer structures

Figure 7 PAG structures

We used the following three types of triphenylsulfonium-base PAG with different molecular weights: TPS-TF (Triphenylsulfonium triflate, MW = 412.45) TPS-PFBS (Triphenylsulfonium perfluorobutanesulfonate, MW = 562.47) TBPDPS-PFBS (Triphenylbutyl-diphenylsulfonate-perfluorobutanesulfonate, MW = 618.57) (all manufactured by Toyo Gosei Kogyo Co., Ltd.). The amount of PAG added was 4 mol (molar concentration in the TC resin). In the experiment involving quencher additive, we used triethanolamine (MW = 149.19) as the quencher, varying the amount used among 0, 0.1, 0.5, 0.75, and 1.0 mol, based on the ratio in the resin.

Figure 8 is schematic diagram of the measurement method. We applied a coat of GMH polymer \[13\] (first layer) to a Si substrate, then applied a PAG-containing TC (second layer) on top of that coat (a). We exposed this sample to irradiation ranging from 0 to 20 mJ/cm\(^2\) using EUV open-frame exposure equipment (b), then performed the PEB process (c). The acid generated in the second layer during the exposure diffused into the first layer during the PEB process, after which we performed development (d). The parts of the first layer into which the acid had diffused dissolved during development. We measured the amount (depth) of film thickness loss in the first layer, regarding this as the acid diffusion length. Due to the relatively minute loss of film thickness, we used an ellipsometer to measure the thickness of the residual film and assessed the amount of film thickness lost. On this basis, we determined the relationship between exposure value and film thickness loss.

The photo in Figure 9 shows the sample after the PEB and development processes. The areas of reduced film thickness are readily visible. Figure 10 shows film thickness after development and the relationship between film thickness loss and exposure value. Also given here are the results of fitting with the modified equation (1) of Fick’s second law. We applied equation (1) to obtain the acid diffusion coefficient.

\[
\Delta d = \sqrt{2 \times D (E - E_0)}
\]

where

- $\Delta d$: Amount of film thickness loss (nm)
- $D$: Acid diffusion coefficient
- $E$: Exposure value (mJ/m\(^2\))
- $E_0$: Exposure value at which film thickness loss begins (mJ/cm\(^2\))
4. Results and Discussion

4.1 Effect of PAG type

We calculated the acid diffusion coefficient using three types of PAG with different anion structures. We formed the first layer film by baking at 130°C for 60 seconds. We set the film thickness to 50 nm, then formed the second layer film by baking at 90°C for 60 seconds. We set the film thickness to 100 nm. The amount of PAG added to the second layer TC in all samples was 4% mol (concentration in TC resin). Figure 11 shows the results.

Figure 11 Relationship between diffusion length and exposure value; results of fitting (PAG with different anion sizes)

Figure 12 shows the relationship between PAG molecular weight and diffusion length (at 20 mJ/cm²). As shown in this figure, the acid diffusion length increases with smaller anion structures.

4.2 Effect of quencher

We added triethanolamine in amounts of 0, 0.1, 0.5, 0.75, and 1.0 mol (based on the ratio in resin) to the first layer and studied the relationship between the amount of quencher added and acid diffusion length. We used PAG-B for the second layer. The amount of PAG-B added was 4 mol%. Figure 13 shows the results.

Figure 14 indicates the relationship between diffusion length (at 20 mJ/cm²) and quencher concentrations. The higher the quencher...
Figure 13 Relationship between diffusion length and exposure value; fitting results (different amounts of quencher)

Figure 14 Relationship between acid diffusion coefficient and quencher concentration

Figure 15 Relationship between diffusion length and exposure value; fitting results (different PEB temperatures)

concentration, the shorter the acid diffusion length. The quencher captures the moving acid, reducing the apparent diffusion length. This result suggests that this effect is more noticeable at higher quencher concentrations.

4.3 Effects of PEB temperature

We also examined the effects of PEB temperature. We added no quencher to the first layer, but added PAG-B to the second layer. The amount of PAG-B added was 4 mol%. Figure 15 shows the results.

Figure 16 shows the Arrhenius plot showing the relationship between acid diffusion length and PEB temperature. The graph indicates that the acid diffusion coefficient increases with rising PEB temperatures, suggesting that the acid diffuses faster and travels farther at higher temperatures. We see a linear relationship between the acid diffusion coefficient and the inverse (1/T) of the absolute temperature. The relationship between acid diffusion and temperature can be explained by chemical kinetics.

Figure 16 Relationship between acid diffusion coefficient and PEB temperature (Arrhenius plot)

5. Simulation

We performed simulations by using Prolith of pattern profiles by varying the amount of quencher added under the following conditions: exposure wavelength, 13.5nm; NA of 0.3; use of Annular illumination (Outer σ =0.7/Inner σ =0.3); and pattern size of 24-nm line and space. We set the resist film thickness to 50 nm and set the exposure value to make pattern sizes equal to design dimensions. Figure 17 shows the simulation results. Increasing the amount of quencher reduces LER and improves pattern profile. The results confirm that suppressing acid diffusion improves LER. A
quencher concentration of 0.5 mol produces excellent resist profiles; when quencher concentrations exceed 0.75 mol, the resulting pattern profiles are tapered, while resolution is degraded.

Figure 17 Profile simulations using different quencher amounts (results of LER calculations)

6. Conclusions

Using a method for measuring the diffusion coefficient of the acid generated from PAG in the TC, we examined the effects of PAG attributable to differing anion sizes, the amount of quencher added, and PEB temperatures. Table 1 gives the diffusion lengths and diffusion coefficients obtained for each measurement condition.

Table 1 Measurements result of diffusion length and diffusion coefficient

Based on our research results, we draw the following conclusions: (1) Larger PAG anions correlate with smaller acid diffusion coefficients; (2) adding more quencher reduces the acid diffusion coefficient; and (3) higher PEB temperatures correlate with greater acid diffusion coefficients. These findings are consistent with research results reported by Kawakami et al. We also performed simulations to explore the relationship between amount of quencher added and pattern profiles. The simulation results indicate that increasing the amounts of quencher suppresses acid diffusion and improves LER.

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