Investigation of Resist Characteristics of Fluoropolymer for 157nm Lithography

Toshiyuki Ogata, Koutaro Endo, Hiromitsu Tsuji, and Hiroshi Komano

*Advanced Material Development Division 1, TOKYO OHKA KOGYO CO., LTD.
1590 Tabata, Samukawa-machi, Koza-gun, Kanagawa, 253-0114 Japan*

Recently, fluoropolymers have become promising base resins for single-layer resist uses in 157nm lithography. The 157nm positive-tone resists we studied displayed good optical transparency at 157nm (absorption coefficient of 1.9 to 2.7 μm^{-1}). In addition, these polymers showed good exposure sensitivities ranging from 3.5 to 5 mJ/cm², and high contrast for their dissolution rate curves using an improved dissolution rate monitor for thin film thickness. One of the modified 150nm film thickness resists has achieved 100nm lines and space pattern resolution on SiON substrate using a 157nm stepper (NA 0.60, σ 0.3) with a phase shift mask.

Keywords: fluoropolymer, 157nm resist, dissolution rate

1. Introduction

A new lithographic approach with F₂ laser is drawing attention as the successor of post ArF lithography for the 65nm node. One of the major challenges for 157nm technology is the fact that most conventional resists applied in manufacturing of semiconductors indicate an extremely high absorption at the wavelength of 157nm, therefore new base polymers with high transparency are necessary for 157nm photoresists.

Recently, several promising results have been reported for fluoropolymers to obtain high transparency at this wavelength and are therefore being studied intensively [1-5]. Specifically, there are reports of dissolution rates for fluoropolymer measured by using the quartz-crystal-microbalance (QCM) method [6, 7]. In addition to high transparency, the base polymer for single-layer resists must meet many requirements. These requirements include but are not limited by: aqueous-base solubility, strong adhesion to varying substrates, limited dark film thickness loss and excellent etch properties. Of most interest to us is the dissolution behavior of resist consisting of fluoropolymer during development. The control of the dissolution rate is critical in order to obtain high-resolution resist, good resist pattern profile and wide process

window at thin film thickness for 157nm lithography.

This paper describes the results of our first attempt to manipulate the dissolution behavior of fluoropolymer positive-tone resists measured by using an improved dissolution rate monitor for thin film thickness during development.

2. Experimental

2.1. Materials

The resist samples were formulated with fluoropolymer, photo acid generator (PAG), quencher and casting solvent. All samples were worked as positive-tone and applied a chemically amplified resist system. Fluoropolymers utilizing hexafluoroisopropanol groups, which indicated the polymer glass transition temperature (T_g) around 140°C, were used for aqueous-base solubility. The resist samples consisted of triphenylsulfonium perfluoro-1-butanefluoroborate as PAG and tri-isopropanol amine as quencher. We prepared three resist samples for the fundamental study of contrast and dissolution property measurement. In each resist, the amount of PAG was the same but the molar ratios of protecting group as well as the protecting group were different. 157nm absorption coefficient of samples and the relationship of protecting molar ratio and groups

are described in Table 1.

Table 1. Sample description in regards to absorption coefficient, protecting molar ratio and group

Sample	Absorption Coefficient (μm^{-1})	Molar Ratio	Group
Resist A	1.9	Low	a
Resist B	2.7	High	a
Resist C	2.1	Low	b

The fluorine containing ratio was calculated to be in the range of 35-40 weight percent of the total solid components. The sample viscosity was adjusted with propylene glycol monomethyl ether 2-acetate (PGMEA), targeting 150nm film thickness.

2.2. Optical Properties Measurements

Absorbance data was obtained from resist films coated on MgF_2 substrates and baked at 110°C for 90 seconds, where a VUV-200 spectrophotometer (JASCO) was utilized. The collected absorbance data was also calculated to the absorption coefficient.

2.3. Dissolution Rate Measurements

Resist formulations were prepared as described above and coated onto silicon. The coated wafers were soft baked (SB) at 110°C or 130°C for 90 seconds, and post exposure bakes (PEB) occurred at 110°C or 130°C for 90 seconds. Exposures at 157nm were performed on a 157nm open frame exposure system of VUVES-4500 manufactured by Litho Tech Japan Co. The resists were developed using a dissolution rate monitor MODEL RDA-808 RB manufactured by Litho Tech Japan Co. The developer used was NMD-3 2.38% (Tokyo Ohka Kogyo Co.) at 23°C. The clearing exposure energy (E_0) was defined as the exposure dose necessary to develop the resist film. Minimum dissolution rates ($R_{\min}$) were determined by measuring film thickness in an unexposed area of the resist film thickness before and after development. Maximum dissolution rates ($R_{\max}$) were also determined from the highest dissolution rate during development from the dissolution rate curve. Contrast was estimated from the dissolution rate curve by varied the exposure energy.

2.4. Lithographic Characterization

Resist formulations were prepared as described above and coated on SiON substrate. The coated wafers were soft and post exposure baked at varied temperature for 90 seconds, and developed for 60

seconds in NMD-3 2.38% (Tokyo Ohka Kogyo Co.) of 0.26N TMAH. Exposures at 157nm were performed on an Exitech stepper (NA 0.60, σ 0.3) at International SEMATECH using a phase shift mask. The critical dimensions (CD) were measured with a Hitachi S-9220. E_{size} was determined to be an optimum exposure energy when the mask size was given. Cross-sectional resist profiles were observed by using scanning electron microscope with Hitachi S-4700.

3. Results and Discussions

3.1. Dissolution Rate Studies

The traditional technique was applied to measure the film thickness loss after development, as is shown in Figure 1. Resist A, B and C indicated good clearing doses, from 3.5 to 5 mJ/cm^2 , and almost no film thickness loss in the unexposed area during development. In addition, the similar resist slope was displayed from the curves. But these curves were simply calculated from the resist thickness changes before and after development. Therefore we had to monitor the dissolution behavior during development to obtain more information.

Figure 1. Resist film thickness change curves after development for Resist A, B and C: SB/PEB 110°C/110°C

Dissolution rate studies were initially aimed to confirm the effect of molar ratios of protecting group and difference of protecting group. The dissolution rate curves by varied exposure dose for Resist A, B and C were collected and plotted in Figure 2. To compare with the curves in the classical resist film thickness measurement, it was found that this dissolution rate measurement has

succeeded to monitor the difference between the samples with 157nm exposure, even for the thin film thickness evaluation.

Figure 2. Dissolution rate curves for Resist A, B and C: 150nm resist film thickness, SB/PEB 110°C/110°C

Dissolution rate studies were initially aimed to confirm the effect of molar ratios of protecting group and difference of protecting group. The dissolution rate curves by varied exposure dose for Resist A, B and C were collected and plotted in Figure 2. To compare with the curves in the classical resist film thickness measurement, it was found that this dissolution rate measurement has

succeeded to monitor the difference between the samples with 157nm exposure, even for the thin film thickness evaluation. The new detection method of RDA-808 RB effectively contributed the dissolution rate in thin film measurement. The dissolution properties are abstracted in Table 2.

Resist A indicated a high $R_{\min}$ and a medium $R_{\max}$ in this evaluation. In the same manner, Resist B and C indicated a very low $R_{\min}$, thus mean that a very small value of film thickness loss at the unexposed area is expected during development. However, it was cleared that there was a significant difference on $R_{\max}$ between Resist B and C. For example, the $R_{\max}$ of Resist C indicated the value of 54, and then calculated to around 3000nm resist film dissolution during the 60 seconds development. From the view points of resist formulation, the results of dissolution rate measurement enable to discuss the following comparisons. In the difference of protecting agents between Resist A and C, it is suggested that the bulky protecting group decrease the both $R_{\min}$ and $R_{\max}$. In the comparison of Resist A and B, where the same protecting agents were introduced, it is mentioned that the dissolution rate curves are controllable by changing the protecting molar ratio.

The dissolution measurement is very efficient to discuss on resist properties, as well as to design resist formulations.

Table 2. Dissolution Rate Properties for Resist A, B and C

Resist	E_0 (mJ/cm ²)	$R_{\min}$ (nm/s)	$R_{\max}$ (nm/s)	Contrast
A	3.5	0.043	1056	9.1
B	4.0	0.0032	4669	18.3
C	5.0	0.0032	54	9.7

3.2 Bake Dependency

Dissolution properties for the bake temperature dependency of Resist A are shown in the dissolution rate curves in Figure 3. Three bake conditions were examined in the combination of SB and PEB, and plotted as of 110/110, 110/130 and 130/110. The E_0 were found to be 3.5mJ/cm², 3.5mJ/cm² and 1.5mJ/cm², respectively. To discuss the PEB temperature, the curves of 110/110 and 110/130 were compared. With regardless of

the PEB temperature, no significant difference was observed in E_0 , $R_{\min}$, and $R_{\max}$. This implies that the decomposition of protecting agent was simultaneously done under those PEB conditions. Otherwise, the exited PAG effectively diffused in the resist film and resulted in the decomposition under the glass transition temperature of the formulated fluoropolymers. Interestingly, as the SB temperature increases, the shape of the dissolution rate curves changes dramatically. The

major difference in the curves was a result of changing E_0 value and the contrast.

To follow up on the SB temperature dependency, the relationship for pattern profile and E_{size} were collected in Figure 4. The observed pattern was 70nm isolate lines with utilized an Exitech 157nm micro stepper at International SEMTECH. The imaging was performed on SiON substrate. As shown in the dissolution rate measurement, the value of E_{size} tended to decrease with increasing the SB temperature.

Figure 3. Dissolution rate curves on bake dependency of Resist A: 110/110 indicated the condition under 110°C SB and 130°C PEB, 110/130 and 130/110 meant in the same manner

Figure 4. SB temperature dependency for E_{size} and pattern profile of Resist A: Substrate SiON, PEB 105°C, Exposure tool Exitech 157nm stepper (NA 0.60, σ 0.3) with a PSM, Pattern 70nm isolated lines

In the pattern profile, a T-top formation was observed at low SB temperature below the polymer Tg of 140°C. The problem was dramatically reduced when the SB temperature was above the polymer Tg. To combine the results of dissolution rate and imaging, it is pointed out that there was a huge SB temperature dependency. It is also suggested that there are some possibility of large free volume that comes from either residual solvent or resin matrix in the resist film. However, at the same time, this phenomenon would be consistent with the annealing concept [8]. Thus implies that fluoropolymer resists may be susceptible to airborne contaminants.

3.3 Film Thickness Dependency

The additional samples with 200nm and 250nm film thickness were prepared for Resist A. Then the film thickness dependency was investigated under the condition of the SB of 130°C and the PEB of 110°C temperatures. Curiously, Figure 5 displays no significant difference in R_{min} , R_{max} and contrast for the varied resist film thickness from 150nm to 250nm. The transparency at the 157nm exposure wavelength for the 150nm and 250nm film thickness of Resist A was calculated to be 52% and 34%, respectively. The dissolution rate curves should not be characterized with the optical density in enough imaging transparency.

Figure 5. Dissolution rate curves on film thickness dependency of Resist A: SB/PEB 130°C/110°C, Resist film thickness 150nm, 200nm and 250nm

3.4 Lithographic Evaluation

When considering controlling the dissolution rate, we further modified a resist for SiON substrate. The resist showed an absorption

coefficient of $2.0 \mu\text{m}^{-1}$ at 157nm. The cross section profiles are shown in Figure 6. The mask size linearity is shown in Figure 7. The resolution has achieved 100nm 1:1 lines and spaces and 70nm isolated lines with 420nm pitch with a phase shift mask. The evaluation was done with a 150nm film thickness. The exposure energy was read to be $34.5\text{mJ}/\text{cm}^2$ under the condition where a 0.3 sigma aperture was set in the beam line. The pattern profile has a slight T-top formation in the dense line pattern and the isolate pattern is slightly round, however, this modified resist shows good mask linearity performance on SiON substrate, as shown in Figure 8. There were no scumming and adhesion issues.

Figure 6. SEM pictures of the optimized resist with 150nm film thickness on SiON: (a) 83nm lines with 200nm pitch, (b) 71nm lines with 420nm pitch

Figure 7. Mask size linearity for dense lines and spaces and isolated lines

4. Conclusions

The dissolution rate for the 157nm resists, which consisted of fluoropolymer, has successfully been characterized under the thin film thickness conditions with utilizing the new monitoring tool. The dissolution rate curves are controllable by changing the protecting molar ratio and group of

fluorinated base polymer. However, it was found that the fluorinated resist formulation indicated the relatively strong bake dependency on SB temperature, not on PEB. One of the good signals is that no significant film thickness dependency was confirmed up to 250nm film thickness application. It might be contributed by the high transparency of resist film. Furthermore, we have obtained 100nm lines and space pattern and 70nm lines with 420nm pitch using a phase shift mask on SiON substrate when exposing with an Exitech 157nm stepper (NA 0.60, σ 0.3).

Acknowledgment

The authors acknowledge the 157nm Lithography Group at International SEMATECH for 157nm lithography and processing as well as Dr. Sekiguchi and Mr. Miyake of Litho Tech Japan Corporation for their expert support in this work.

References

1. M. K. Crawford, A. E. Feiring, J. Feldman, R. H. French, V. A. Petrov, F. L. Schadt III, R. J. Smalley, and F. C. Zumsteg, *Proc. SPIE*, **4345**, (2001) 429
2. T. Itani, M. Toriumi, T. Naito, S. Ishikawa, S. Miyoshi, T. Yamazaki, M. Watanabe, *J. Vac. Sci. Technol.* **B19** (2001) 2705
3. H. Ito, G. M. Wallraff, N. Fender, P. J. Brock, W. D. Hinsberg, A. Mahorowala, C. E. Larson, H. D. Truong, and R. D. Allen, *J. Vac. Sci. Technol.* **B19** (2001) 2678
4. R. R. Dammel, R. Sakamuri, T. Kubo, A. Romano, L. Rhodes, R. Vicari, C. Hacker, W. Conley, and D. Miller, *J. Photopolymer Sci. Technol.* **14** (2001) 603
5. M. Shirai, T. Shinozuka, H. Okamura, M. Tsunooka, S. Kishimura, M. Endo, M. Sasago, *J. Photopolymer Sci. Technol.* **14** (2001) 621
6. H. Ito, G. M. Wallraff, N. Fender, P. J. Brock, C. E. Larson, H. D. Truong, G. Breyta, D. C. Miller, M. H. Sherwood, and R. D. Allen, *J. Photopolymer Sci. Technol.* **14** (2001) 583
7. S. Ishikawa, M. Toriumi, S. Miyoshi, T. Naito, T. Yamazaki, M. Watanabe, and T. Itani, *J. Photopolymer Sci. Technol.* **14** (2001) 595
8. H. Ito, G. Breyta, and D. Hofer, *Proc. SPIE*, **2438**, (1995) 53