JSR EUV Resist Development toward 22nmhp Design and Beyond

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In order to achieve targeted resist performance for EUV in practical applications, we have developed new materials such as molecular glass (MG), PAG, and acid amplifiers (AA). Protected NORIA, a molecular glass, was examined for extending resolution limits. The resist with protected NORIA showed 22 nm hp resolutions under EUV exposure. PAG acid diffusion effect on LWR was also investigated. It was found that acid diffusion control was one of the most important factors for LWR improvement. To improve sensitivity, application of AA (acid amplifier) was investigated. The resist with AA gained 25% sensitivity improvement over the original formulation. Elemental technologies for major progress of EUV resist were made.

Keyword: lithography, EUV, molecular glass, acid amplifier, PAG

1. Introduction

ArF immersion lithography is capable of extending the optical lithography limit down to 4xnm hp process. Double patterning process can then lower optical lithography limits down to 2xnm hp. Several double patterning processes were reported but they become increasingly expensive. From the technical point of view, further lithography progress would be necessary for 22 nm hp and beyond. Extreme ultraviolet (EUV) lithography is one of the most promising candidates for next generation lithography (NGL), which can print 22 nm hp and beyond. Once EUV technology is in place, lithography costs would be suppressed since the high contrast of EUV permits relatively simple processes when compared to double patterning. There still exist multiple issues for EUV technology for practical application, although considerable progress in exposure tool, mask and resist were done in the last few years. Still resist remains as one of the

critical items that require significant improvement. The most difficult technical issue for EUV resist is the need for simultaneous improvement in resolution, line width roughness (LWR), and sensitivity. Many research groups are developing new materials such as molecular glass (MG)¹, polymer bound photo-acid generator^{2,3}, high quantum yield PAG⁴, sensitizer⁵ and high absorption resin^{6,7} to achieve these simultaneous improvements. In this study, we focused on MG, PAG, and acid amplifier to break the trade-off relationship among resolution, line width roughness (LWR), and sensitivity (further discussions reference the term RLS).

2. Experimental

2.1. Materials

The structure of raw materials and PAGs' anion classification in this paper are shown in Figure 1. Polyhydroxystyrene, poly[(meth acrylicacid)-co-(lactone)], protected NORIA,

hybrid type resin and acid amplifier (AA) were synthesized in our lab. Sulfonium salts were synthesized and used as PAGs. Resist samples were obtained by mixing resin or protected NORIA, PAG, quencher, and solvent. The mixed solution was then filtered using a 0.5µm PTFE filter prior to evaluation. The resist formulations are described in Table 1.

Figure 1. Structure of Raw Materials.

Table 1. Formulation of resists used in this study.

Resist	Resin/MG	PAG	Additive
Resist A	Protected NORIA	TPSX	
Resist B	Hybrid type	TPSOTf	
Resist C	Hybrid type	TPSONf	
Resist D	Hybrid type	TPSY	
Resist E	Hybrid type	TPSZ	
Resist F	Hybrid type	TPSZ	
Resist G	Hybrid type	TPSZ	Acid amplifier
Resist H	Hybrid type	TPSZ	
Resist I	Hybrid type	PDA-PAG	

2.2. Measurement of acid diffusion length

Acid diffusion length with various PAGs was investigated with the following procedure^{8,9}. Resist was spin-coated on a bare Si wafer to a 3000 angstrom film thickness after soft-bake, then exposed with a Nikon NSR S203B. Exposed resist powder was obtained by removing the resist film from the Si wafer with a razor. This powder acts as an acid source layer (Layer A in Figure 2) for the measurement of diffusion length. Resist was again coated on a new bare Si

wafer to a 3000 angstrom film thickness (Layer B in Figure 2). Layer A was put on layer B as a pellet. This stack was then baked to simulate the PEB process and acid was allowed to diffuse from layer A to layer B. The stack was then developed with 0.26N TMAH solution for 60 sec. In the end, thickness loss (ΔL), which is the difference between exposed and unexposed area thicknesses, was measured with DNS Lambda Ace ($\lambda=633\text{nm}$). Acid diffusion coefficient (D) was calculated using eq. (1),

$$\Delta L = 2(Dt_{\text{PEB}})^{1/2} \text{erfc}^{-1}(E_{\text{crit}}/E) \quad \text{eq. (1)}$$

ΔL is the film thickness loss, D is the acid diffusion coefficient, t_{PEB} is the PEB time, erfc is the error function complement, E_{crit} is the exposure dose at which film thickness loss was observed for the first time, and E is the exposure dose in equation (1).

Infrared spectra were recorded on a Horiba FT-720 spectrometer. ^1H and ^{13}C -NMR spectra were obtained on a Bruker DPX-300 spectrometer. Molecular weights were determined by a gel permeation chromatography (GPC) with polystyrene calibration using a HITACHI D-7100-G equipped with column in THF at 40 °C. Thermal analyses were performed on a Seiko EXSTAR 6000-TG / DTA6300 thermal analyzer at a heating rate of 10 °C · min⁻¹ for thermogravimetric (TG) under nitrogen.

Figure 2. Experimental method for acid diffusion

Results and Discussion

3.1. Technology to improve resolution

Molecular glass (NORIA)

Several molecular glasses based on star-shaped molecules^{10,11}, calix[n]arene derivatives¹², and dendrimers¹³ were screened as candidates for resist materials. Cholic acid derivatives and adamantane derivatives were examined for 193nm resists¹⁴.

Cholic acid derivatives were also evaluated as EB resist¹⁵. In addition, partially t-BOC protected calix[4]resorcinarene were applied for positive-tone resist systems¹⁶. Some polyphenol derivatives showed high resolution under EUV exposure¹⁷, however these molecules have insufficient T_g (glass transition temperature) to withstand the thermal requirements of the lithographic processes.

Nishikubo *et al.* prepared a new polyphenol compound named NORIA, which has a three-dimensional structure, like a waterwheel, and showed unique characteristics¹⁸. As NORIA has been confirmed to have high thermal stability due to its unique structure, the resist properties using NORIA as a molecular glass were investigated.

At first, dissolution rate of NORIA was compared to typical resins for photo resists. Dissolution rate of 100% de-protected NORIA was measured to know the possible maximum dissolution rate. Table 2 shows the dissolution rate of de-protected NORIA, polyhydroxystyrene, and poly[(methacrylic acid)-co-(lactone)] in 0.026N TMAH aqueous solution.

As is evident from the relative dissolution rate values, de-protected NORIA is expected to show higher dissolution rate than polyhydroxystyrene and poly[(methacrylic acid)-co-(lactone)]. Taking this into account, we believe that protected Noria would possess strong potential to show high resolution.

Resist A using protected NORIA was exposed by an EUV exposure tool (NA: 0.30, Quadrupole). Figure 3 shows the top-down profile of Resist A where it can be clearly seen that 22 nm hp patterns are well-resolved. This result clearly establishes NORIA as a cutting-edge high resolution resist capable of resolving <22nm hp. Resolution is limited by line collapse and therefore, several studies, such as swelling suppression, profile control and additional process are currently on going.

All peaks were well assigned to the expected polymer structure. The molecular weight of polymer **3** was estimated (relative to a polystyrene standard) by gel permeation chromatography (GPC) in THF. The chromatogram of polymer **3** was a unimodal distribution with a polydispersity of 3.9.

The weight-average molecular weight (M_w) was determined as 21,000.

Table 2. Dissolution rate of de-protected NORIA, polyhydroxystyrene, and Poly[(methacrylic acid)-co-(lactone)]

	De-protected NORIA	Polyhydroxystyrene	Poly[(methacrylic acid)-co-(lactone)]
Structure
DR*	100	<1	10

* Dissolution rate (Relative value)

Figure 3. Top-view SEM images of line and space pattern of Resist A under EUV exposure (NA: 0.30, Quadrupole).

3.2 Technology to Improve LWR

3.2.1 Acid Diffusion Control

Various PAGs were synthesized in this study and their classification is described in Figure 1. Diffusion length of these PAGs' was determined and is summarized in Table 3.

Table 3. Acid diffusion coefficient D

PAG	Anion classification	Acid diffusion coefficient D (nm ² /s)
TPSOTf	Small	110
TPSONf	Middle	80
TPSY	Bulky	50
TPSZ	Middle with polar unit	20

The acid diffusion coefficient D of TPSOTf, TPSONf, TPSY, and TPSZ were 110, 80, 50, and 20 nm²/s, respectively. Many studies have already shown that an increase of PAG anion size makes acid diffusion length shorter. However, TPSZ does not have this proportional relationship

between the anion size and acid diffusion length. It is possible that the polar unit in TPSZ has affinitive properties to the polymer backbone, and thus leading to its unique acid diffusion length behavior. Resist B, C, D, and E containing TPSOTf, TPSONf, TPSY, and TPSZ, respectively, were exposed using an EUV exposure tool (NA: 0.3, Annular). Table 4 shows the top-down profile of Resist B, C, D, and E. To see the effect of acid diffusion coefficient D on LWR, the LWR of 45 nm hp patterns for Resist B, C, D, and E was measured and found to be 6.4 nm, 5.8 nm, 6.0 nm and 4.8 nm, respectively. This result suggests that acid diffusion control provides a good way to improve LWR.

Table 4. Top-view SEM images of line and space pattern of resist B, C, D, and E under EUV exposure (NA: 0.3, Annular).

Resist	PAG	LWR
Resist B	TPSOTf	6.4nm
Resist C	TPSONf	5.8nm
Resist D	TPSY	6.0nm
Resist E	TPSZ	4.8nm

3.2.2 Special rinse process

Recently, Chandhok et al. reported¹⁹ LWR reduction techniques such as vapor smoothing, hardbake, ozonaton, rinse etc. More recently, Matsunaga et al. reported²⁰ development processes to improve LWR. In this study, a special rinse process was tested on Resist E. Z-factor helps in quantifying resist performance and is calculated with equation (2)²¹.

$$\text{Z-factor} = (\text{Resolution})^3 \times (\text{LER})^2 \times (\text{Sensitivity}) \quad \text{eq. (2)}$$

Table 5 shows the top-down profile, resolution, LWR, sensitivity, and Z-factor of Resist E with normal rinse process and with special rinse process. The LWR of the normal rinse process and the special rinse process were 3.9 nm and 3.1 nm, respectively. It was found that with the special rinse process 20% LWR improvement was gained while maintaining resolution and sensitivity. Z-factor improvement from 4.6E-08 to 3.0E-08 represents overcoming of RLS trade off relationship with the use of ancillary rinse agents.

Table 5. Resist performance of Resist E under EUV exposure (NA: 0.30, Quadrupole).

Resist	Resist E (Normal rinse)	Resist E (Special rinse)
Profile (30 nm hp)
Resolution	26 nm hp	26 nm hp
LWR @30nm hp	3.9 nm	3.1 nm
Sensitivity @30nm hp	22.3 mJ/cm ²	23.5 mJ/cm ²
Z-factor	4.6E-08	3.0E-08

3.3 Technology to Improve Sensitivity

3.3.1 Acid amplifier

Recently, Brainard and co-workers reported^{22,23} one unique way of beating RLS trade-off with the application of acid amplifier (AA). In this study, we developed EUV resist using sulfonate AA. The AA structure is shown in Figure 1.

Resist F (without AA) and Resist G (with AA) were exposed using an EUV exposure tool (NA: 0.30, Quadrupole).

Table 6. Resist performance of Resist F and G under EUV exposure (NA: 0.30, Quadrupole)

Resist	Resist F (without AA)	Resist G (with AA)
Profile (30 nm hp)
Resolution	26 nm hp	24 nm hp
LWR @30 nm hp	4.7 nm	5.5 nm
Sensitivity @30 nm hp	30.6 mJ/cm ²	14.9 mJ/cm ²
Z-factor	9.1E-08	6.1E-08

Table 6 shows the top-down profile, resolution, LWR, sensitivity, and Z-factor of resists F and G. Sensitivity of 30nm hp patterns for Resist F and G were found to be 30.6 mJ/cm² and 14.9 mJ/cm², respectively. It was found that resist G significantly improved sensitivity compared to Resist F. Furthermore, Resist G improved Z-factor from Resist F as well. This result suggests that AA has possibility to beat the RLS trade off. Certain structural modifications of AA

have been identified that will likely result in improved performance and further optimization along these lines is on-going.

3.3.2 Photo Destructive Anion PAG (PDA-PAG)

Photo destructive anion PAG (PDA-PAG) was developed to control acid diffusion length. PDA-PAG contains both a photo acid generation unit and a photo destructive unit in the same molecule. Here photo acid generation happens first, followed by the decomposition of the remaining anion part. Therefore, this PAG works as a bulky anion at low dose areas consequently having short acid diffusion length. On the other hand at higher dose areas the anion is decomposed in such a way that a smaller acid is obtained that has longer diffusion length. This property matches the resist design concept of having high sensitivity and resolution at the same time. The PAG has short acid diffusion length in the border of exposed/unexposed areas which is desirable for high resolution. Long acid diffusion length in the exposed area is desirable for high sensitivity.

Resist H with TSPY and Resist I with PDA-PAG were exposed using an EUV exposure tool (NA: 0.30, Quadrupole). Table 7 shows the top-down profile, resolution, LWR, sensitivity, and Z-factor of Resist H and I. Sensitivity of 30nm hp patterns for Resist H and I were found to be 22.4 mJ/cm² and 16.7 mJ/cm², respectively. It was found that Resist I improved sensitivity compared with resist H while maintaining resolution and LWR. Resist I improved Z-factor compared to resist H. This result suggests that PDA-PAG has capability to beat the RLS trade off. Further formulation optimization with PAD-PAG is on-going.

Table 7. Resist performance of Resist H and I by EUV exposure (NA: 0.30, Quadrupole).

Resist	Resist H	Resist I
PAG	TSPZ	PDA-PAG
Profile 30 nm hp
Resolution	24 nm hp	24 nm hp
LWR @30 nm hp	4.4 nm	4.2 nm
Sensitivity @30 nm hp	22.4 mJ/cm ²	16.7 mJ/cm ²
Z-factor	5.9E-08	4.0E-08

3. Conclusion

In this study, multiple technical progresses were done which are contributing to EUV resist improvement. Protected NORIA for resolution extension and new PAG designs to overcome the RLS trade off showed major progress. In addition to material development, post development rinse processes showed capability to improve LWR. Now multiple items to improve resist properties are ready. Results of this study will push EUV technology for practical application from the resist requirement point of view.

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