Resist Characteristics with Electron Beam and SR Exposures

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The components of chemically amplified resist were investigated to meet the requirements for synchrotron radiation lithography, such as high sensitivity, low film thickness loss and good critical dimension uniformity. The three sigma of critical dimension (CD) uniformity achieved 11 nm for the 100 nm hole pattern with the resist optimization employed through adjustment of the protection ratio of the base polymer and the addition of an amine quencher.

Keywords: chemically amplified resist, synchrotron radiation, sensitivity, CD uniformity

1. Introduction

The chemically amplified resist system has been applied to the mass production of semiconductors with KrF lithography. This system is likely to be applied for resist designs of the next generation lithography (NGL), such as direct write electron beam exposure (DWEB), electron beam projection lithography (EPL), extreme UV lithography (EUV) and synchrotron radiation lithography (SR) [1-5]. The reason is that the small interaction between the exposed energy and photoresist components is still considered in their chemical reactions. From the standpoint of resist designing, the combination between NGL and the chemically amplification system seems to be most effective, however, the low absorbance of the sensitizers makes it obviously hard to achieve the required sensitivity of the exposure sources [6]. Recently, excellent sub-techniques for hole patterning have been investigated to extend the resolution limit determined by the exposure wavelength and illuminations [7]. However, there might be issues to avoid the unopened hole and to correct the proximity effect on the pattern pitch as the demand for smaller holes increases. The NGL mentioned above have advantages to simplify and to pattern smaller holes.

This paper focuses on designing positive tone resists with high sensitivity for the SR lithography

with some screening technique by electron beam exposure. To take account for the surface roughness involved by mask contrast [8], the resist components optimization is performed with variation of the protecting ratio of resist base polymer and photo acid generator (PAG). It also discusses on how to control the critical dimension (CD) uniformity from the standpoint of resist quencher mechanism.

2. Experimental

2.1. Resist sample preparations

Resist formulation was modified to present a well-balanced lithographic performance on resolution, sensitivity and CD uniformity. The co-polymers composed primarily of p-hydroxystyrene and t-butyl acrylate monomers were commercially obtained as a resist base polymer. A variation of t-butyl acrylate ratios was prepared by mixing two different copolymers. A variety of onium salts was investigated as a PAG. Amine quenchers were added to control the acid diffusion length. Acid derivatives were added as counter substances for amine quenchers. The resist samples were also diluted with propylene glycol monomethyl ether acetate (PGMEA) as a casting thinner along with a leveling surfactant.

2.2. Electron beam exposure (50kV DWEB)

The electron beam exposure was done with

HITACHI HL-750 direct writing system, where the acceleration energy was 50kV.

2.3. Synchrotron radiation exposure

The X-ray exposure was carried out by the Canon XFPA stepper using a 0.6 GeV superconducting storage ring at the Advanced Technology R&D Center of Mitsubishi Electric Corporation. The X-ray masks were made up of SiC membrane with a 0.3 μm thickness W-Ti absorber and the proximity gap was 10 or 20 μm .

2.4. Resist process and measurement

The resist was spin-coated on Si substrates treated with hexamethyl disilazane (HMDS). The coating thickness was measured at 500 nm after a softbake which was carried out at 150°C for 90 seconds on a proximity hotplate. The exposed resist was then post-exposure-baked at 150°C for 90 seconds and developed for 60 seconds in NMD-3 2.38% (Tokyo Ohka Kogyo Co.) of 0.26N aqueous tetramethylammonium hydroxide (TMAH) solution. The CD was measured for 81 points per exposure field with in-line SEM.

3. Results and Discussion

3.1. Sensitivity and film thickness loss

First, the correlation for sensitivity was investigated between the 50kV DWEB and the SR exposure. Figure 1 indicates that there is a clear correlation between the sensitivities. This correlation was convenient for the resist optimization with two different exposure systems.

Fig. 1. Resist sensitivity correlation between 50kV DWEB and SR exposure

The relationship between resist sensitivity and thickness loss was investigated in a matrix of base polymer with different copolymer ratios and three types of PAG with the 50kV DWEB exposure. Triethanol amine was used as a quencher for this experiment. The amount of quencher was 9.4E-04 mol in relation to the 1.0 mol of base polymer.

The tested samples are listed in Table I.

In Fig. 2 and 3, higher sensitivity was achieved with decreasing the t-butyl acrylate ratio, but the thickness loss got worse at the same time. When considering high sensitivity and low thickness loss, the possible composition of resist was found to be determined by both the copolymer ratio and the PAG types. For example, the optimum copolymer ratio for t-butyl acrylate was over 32% when normalizing 5% of thickness loss or less. The SR exposure was performed for two samples with the base resin of 32% and 40% t-butyl acrylate from S11-S14, as shown in Fig. 4. Because of the significant surface roughness for the sample with 40% t-butyl acrylate ratio, the upper limit was suggested to be under 40%.

Table I. Resist preparation for PAG dependency

Sample ID	PAG structure	Amount (mol)
S1-S5	Dimethylphenylsulfonium triflate (DMPS-Tf)	1.2E-02
S6-S10	Triphenylsulfonium perfluoro-1-butanesulfonate (TPS-PBS)	1.2E-02
S11-S14	Triphenylsulfonium triflate (TPS-Tf)	1.2E-02

Fig. 2. Unexposed film thickness loss with 50kV DWEB by changing the copolymer ratio (t-butyl acrylate)

Fig. 3. Resist sensitivity (Do: dose to clear) with 50kV DWEB by changing the copolymer ratio (t-butyl acrylate)

Fig. 4. Surface roughness for resists with different copolymer ratio by SR exposure

3.2. Critical Dimension Uniformity

The structural dependency of the amine quencher was investigated for the CD uniformity with the SR exposure system. Five resist samples were prepared with varied amine quenchers, as shown in Table II. In these samples, TPS-Tf was used as a PAG with $1.2\text{E-}02$ mol in relation to 1.0 mol of the base resin. Data was obtained for 180 nm line and space and calculated for 3-sigma as shown in Fig. 5. It was found that a minimum value was given by selecting a certain type of amine structure. For example that hydroxyl amines indicated smaller value than that of alkyl amines. However, no correlation was found for the chemical properties such as molecular weight (Mw), boiling point (b.p.) and acidity (pKa), as listed in Table III.

Table II. Resist sample preparation for amine quencher structure

Sample ID	Amine structure	Amount (mol)
S15	Triethylamine	$6.3\text{E-}04$
S16	Tripropyl amine	$6.3\text{E-}04$
S17	Tripenyl amine	$6.3\text{E-}04$
S18	Diethanol amine	$6.3\text{E-}04$
S19	Triethanol amine	$6.3\text{E-}04$

Fig. 5. CD uniformity vs. amine quencher: exposure dose S15 70mJ/cm^2 , S16 75mJ/cm^2 , S17 90mJ/cm^2 , S18 70mJ/cm^2 and S19 90mJ/cm^2

Table III. Properties for amine quenchers

Amine structure	Mw	b.p. ($^{\circ}\text{C}$)	pKa	Reference
Triethyl amine	101	89.4	10.72	[9, 10]
Tripropyl amine	143	156.5	10.3	[11, 12]
Tripenyl amine	227.43	240-245	9.3	[13, 14]
Diethanol amine	105.1	269.1	8.1	[15]
Triethanol amine	149.2	360	7.76	[13, 14]

For further investigation on amine quencher, four samples were prepared by changing the quencher quantities from $6.3\text{E-}04$ to $1.6\text{E-}03$ mol, as shown in Table IV. The proximity gap of the SR exposure system was $10\text{ }\mu\text{m}$ for this investigation. The sensitivity and the CD uniformity for each sample were measured for 100 nm hole pattern as shown in Fig. 6. The resist sensitivity degraded gradually with increasing quencher amount. But an optimum amount existed with consideration to CD uniformity. In Fig. 7 and 8, each measurement data was compared for samples S19 and S20. Although the quencher amount range from around $9.4\text{E-}04$ to $1.3\text{E-}03$ presented the minimum value for 3-sigma, the resist composition of S20 was actually effective to compensate high sensitivity and good CD uniformity. The 3-sigma was 11 nm for 100 nm hole.

The pattern profile of S20 presented high aspect ratio contact hole with 100 nm resolution, as shown in Fig. 9.

Table IV. Resist sample preparation for quencher amount

Sample ID	Amine structure	Amount (mol)
S19	Triethanol amine	$6.3\text{E-}04$
S20	Triethanol amine	$9.4\text{E-}04$
S21	Triethanol amine	$1.3\text{E-}03$
S22	Triethanol amine	$1.6\text{E-}03$

Fig. 6. CD uniformity and sensitivity by changing amine quencher amount

Fig. 7. CD uniformity and sensitivity of S19

Fig. 8. CD uniformity and sensitivity of S20

Fig. 9. 100 nm hole pattern profile of S20: exposure dose 100mJ/cm², resist thickness 500 nm, softbake 150°C-90s, PEB 150°C-90s, Development NMD-3 2.38% 60s

4. Conclusions

The relationship between the copolymer ratio and resist characteristics was studied with 50kV DWEB and SR exposure system. It was found that there was an optimum copolymer ratio with consideration to the resist sensitivity and the film thickness loss at unexposed area. The quencher loading also was investigated for the CD uniformity. The adequate selection and addition of amine quencher are important to improve the CD variation and to achieve high sensitivity for SR lithography from the standpoint of resist design.

The 3-sigma of the CD valuation for 100 nm holes was given as 11 nm in the exposure field.

5. References

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