Recent Progress in New Acetal-based Resist for Electron Beam Lithography

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In order to solve pattern collapse problems caused by high aspect ratio, new acetal-based chemically-amplified positive tone resists for electron beam lithography were investigated. Electron beam lithography is in the initial stages of utilization for device manufacturing and high-end mask making. The resist screening results using 70kV direct writing electron beam tool showed high resolution, good pattern profiles and reduced substrate influence. Dry etching resistance was also studied.

Keyword: acetal, chemically amplified resist, electron beam

1. Introduction

Chemically-amplified resists have already been applied in the area of KrF and ArF lithography. In next generation lithography such as electron beam lithography with high or low acceleration voltage [1-9], extreme UV lithography (EUV) and synchrotron radiation lithography [10-11], resist designs have taken advantage of these chemically-amplified systems. We generally classify the chemically-amplified resist systems into acetal or ketal chemistry type and thermal annealing of polymer films type. In the acetal based chemistry, positive tone resists are commonly designed with the base polymer of poly(hydroxystyrene) (PHS) attached with acetal protecting hydroxyl groups. This system is known to prevent substrate dependency and to be stable for environmental contaminations. However, the etch resistance of simple acetal based chemistry is relatively weak compared with that of thermal annealing type. The weak etch resistance would become a more significant problem when a thin film application is required to target more fine patterning.

This paper focuses on the characterization of new acetal-based chemically-amplified positive tone resists for electron beam lithography which target high resolution and low substrate dependency. An additional experiment on pattern collapse, which might limit the superior advantage of high aspect patterning utilizing electron beam lithography, is also examined.

2. Experimental

2.1 Resist sample preparations

All of the tested chemically-amplified positive tone resist samples consisted of a base polymer, photo acid generator (PAG), quencher, surfactant, and casting solvent. Four samples, A, B, C and D, were prepared with a variety of PHS polymers with bulky groups, while all other contents were identical. The sample composition is described in Table 1. The base polymer structure of Sample A and B was a PHS polymer protected by ethoxyethyl and adamantoxyethyl. Sample C was a styrene (PS) and PHS copolymer protected by adamantoxyethyl. Sample D was composed of PHS and poly(hydroxy adamantyl acrylate) (PHAdA) copolymer

with ethoxyethyl. The sample viscosity was adjusted with propylene glycol monomethyl ether 2-acetate (PEGMEA), targeting 400nm and 200nm film thickness.

Table 1. Main polymer of sample

Sample	Base Polymer	Protecting Group
A	PHS	ethoxyethyl
B	PHS	adamanthoxyethyl
C	PHS / PS	adamanthoxyethyl
D	PHS / PHAdA	ethoxyethyl
PAG: sulfuric acid type		
Quencher: long alkyl chain amine		
phenolic acid		

2.2 Electron beam exposure

The resist evaluations were done with a Hitachi HL-800D direct writing electron beam (DWEB) system with variable shaped beam. The system was operated under acceleration energy setting of 70kV.

2.3 Resist process and measurement

The resist was spin-coated on silicon substrates treated with hexamethyl disilazane (HMDS) or CrO_x on silicon. The coating thickness was adjusted for each thickness after a softbake, which was carried out at 90°C, 100°C or 110°C for 90 seconds on a hotplate. The exposed resist was then post-exposure-baked at 110°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 critical dimensions (CD) were measured with a Hitachi S-9220 top-down SEM.

2.4 Etch study

A blanket etch measurement was performed with CF_4 and O_2 mixture gases. The etch rate was calculated from the initial and remaining film thickness after etching. The relative etch selectivity was then normalized with the etch rates as referred Sample A without alicyclic structures.

3. Results and Discussions

3.1 Fundamental Resist Characteristics

The fundamental resist characteristics: beam size linearity, line width roughness (LWR), dose to size (D_{size}) and dose latitude (DL) were compared for the four resist samples, in order to observe any structural dependency of

the main polymer. The resist thickness in this examination was set at 400nm. First, the beam size linearity is described in Fig. 1 under the optimum dose of 150nm 1:1 lines and spaces. The beam size linearity, when normalized within $\pm 5\%$ CD variation, was down to 120nm except Sample C. However, it was confirmed that each resist indicated enough resolution at 150nm 1:1 lines and spaces. Second, data was collected on LWR, D_{size} and DL. These results are summarized in Table 2. LER was measured with the default algorithm set at 30% threshold of S-9220 and D_{size} of the dose for the target line width were calculated from the logarithmic approximation curve with CD change from varied exposure energies. The DL was defined with this equation,

$$\text{DL} [\%] = (D_{+10\%} - D_{-10\%}) / D_{\text{size}} * 100, (1)$$

where $D_{+10\%}$ and $D_{-10\%}$ are the doses that provide $\pm 10\%$ line width from the target 150nm lines.

Figure 1. Beam size linearity of Sample A, B, C and D 400nm film thickness with 70kV DWEB exposure

Table 2. LWR, D_{size} and DL of Sample A, B, C and D with 400nm film thickness

Sample	LWR	D_{size}	DL
A	8.6nm	$8.1 \mu\text{C}/\text{cm}^2$	23.1%
B	9.3nm	$8.0 \mu\text{C}/\text{cm}^2$	12.8%
C	8.0nm	$15.6 \mu\text{C}/\text{cm}^2$	16.3%
D	9.8nm	$7.6 \mu\text{C}/\text{cm}^2$	16.0%

From these fundamental data findings, no evident advantage was confirmed regardless of the formulation difference in each resist.

3.2 Resist Pattern Profile

The imaging results of 150nm lines and spaces are shown in Fig. 2. All cross-sections presented very steep resist sidewalls. However, Sample A, B and C have a round pattern profile and seem to show a slight film thickness loss at the unexposed area. Sample D has a rectangular pattern profile. It is interesting to note that Sample C and D have main polymers with more insolubility in comparison with PHS in alkali aqueous. The sample polymers consist of PHAdA and PS, respectively. The adamantyl and phenyl groups are hydrophobic groups, and therefore inhibitor in alkali aqueous. We believe that the insolubility site in alkali aqueous can provide a good image profile, however such excess insolubility generates a bad profile. In this case, the alcohol of PHAdA is more hydrophilic than an aromatic structure in PS, which is effective for imaging a good profile. Even if main polymers with adamantyl units, which provide high dry etch resistance, it is possible to introduce hydroxyl groups and similar structures that can control pattern profile.

Figure 2. 150nm lines and spaces pattern profile of Sample A, B, C and D 400nm film thickness

3.3 Dry etching study

We investigated the dry etch resistance of Sample A, B, C and D using a CF_4 / O_2 chemistry in Table 3. The Sample B, C and D with a main polymer prepared with an adamantyl unit showed higher etch resistance than Sample A, and agree with high Ring parameter value. In addition, Sample C had the lowest Ohnishi parameter value and correspondingly had the best etch resistance [12-13].

Table 3. Relative dry etch resistance data

Sample	Ohnishi parameter	Ring parameter	Relative etch resistance
A	2.73	0.50	1.0
B	2.54	0.61	1.3
C	2.47	0.62	1.4
D	2.85	0.53	1.2

Figure 3. 80nm and 100nm lines and spaces pattern profile of Sample A and D
(a): 400nm film thickness
(b) and (c): 200nm film thickness

3.4 Thin film thickness imaging

An additional thin film thickness 70kV DWEB experiment was performed on Sample A and D at 200nm film thickness. Results are in Figure 3. Sample D resolved 80nm lines and spaces without pattern collapse and maintained good profile at 200nm film thickness as in 400nm film thickness. Sample A displayed extensive film thickness loss in the unexposed area and could not resolve at 80nm lines and spaces.

3.5 Substrate dependency on CrO_x

The investigation of substrate dependency on CrO_x for mask making was done with Sample D. In general, chemically-amplified resists generate resist footing on CrO_x . The resist profile of Sample D indicates clean patterning. This result proves that acetal protecting systems are effective against CrO_x .

Figure 4. 300nm lines and spaces for Sample D imaged on silicon and CrO_x

4. Conclusions

The new acetal-based chemically-amplified positive tone resists were studied for reducing the pattern collapse problem. It was found that adequate insolubility sites in alkali aqueous provide good profiles and high resolution of 80nm lines and spaces at thin film thickness. The main polymer when introduced with an adamantyl unit of alicyclic showed higher dry etching resistance compared to aliphatic structures only, and agreed with Ring parameter. Furthermore, durability of CrO_x substrate is good. We have developed this resist for device manufacturing and high-end mask making with electron beam lithography.

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