Improvement of Defect Issues for Advanced 193nm Resist

KyungMee Kim, Yeouyoung Yoon, JaeHo Kim, YoungHo Kim, SangMun Chon

Manufacturing Technology Team, Technology & Engineering Center,

SAMSUNG Electronics Co., LTD., San #16 Banwol-Ri, Taejeon-Eup,

Hwasung-City, Gyeonggi-Do, Korea

kkm0209@samsung.com

The first generation 193nm resist for sub-90nm DRAM device has brought up defect issues in mass production. Improvement from several aspects has been applied along three different types of defect, 1) micro-bridge, 2) gel-like defect, 3) nozzle drying defect. Diversified attempts were considered from monomer design and polymerization to resist purification process via solvent selection as keys for defect-free solution. Polymerization and following purification process should be well considered to reduce high molecular size fraction. Co-solvent system for resist was also effective to avoid drying out of resist on coating nozzle tip. Also material design of monomers was essentially important to keep composition uniformity in polymer chain and not to generate defect precursor.

Keywords: ArF(193nm) device, defect, u-bridge, nozzle defect

1. Introduction

As design rules approach sub 100nm and below, the lithography used to produce these device should rely on 193nm(ArF) resist. Continuous effort on 193nm resist has been done to improve process window, line edge roughness, pattern collapse, etching durability and so on. Quality issues of photo resist became more important at the stage of mass production of sub-micron devices.

Defectivity has been one of the most important issues for device production. However solution of defect in the litho cell is an area where significant improvement can be realized, guaranteeing 100 percent defect-free resist is a difficult task. Developer and developing recipes have been considered to affect defect level as well as lithographic performance.^{1,2,3} Rinse liquid also affects pattern collapse and defect.⁴

Regarding resist component, a lot of study on line edge roughness (LER) after development and etching has been reported. Polymer homogeneity model by reducing the difference of polymerization rate of monomers was reported to effective to reduce LER.⁵ Polarity of functional unit has been studied for lithographic performance and pattern profile.^{6,7}

As lithography has become more complex with thinner resist and sub-wavelength optics, the effective defect-solution program has requested. It is due to decrease likelihood of causing yield loss and rework wafer. In this report, diversified attempts to improve three different types of defect, **I)** micro-bridge, **II)** gel-like defect, **III)** nozzle drying defect are described (Figure 1), considering from monomer design and polymerization to resist purification process via solvent selection as keys for defect-free solution.

Figure 1. Three different type of Defect

2. Experimental

2-1. Polymer Preparation

Structures of the monomers employed in this study are listed on **Table 1**.

Polymers were prepared as follows; Typical polymerization, employing such monomers, was carried out under nitrogen atmosphere.

Relative reactivity of the acid labile monomers are evaluated experimentally by co-polymerization with a typical polar monomer, norbornanelactone

Table 1. Structure of the monomers

Acid Labile Monomer	MAdMA	EAdMA	Monomer D
Structure			Methacrylate of bulky tertiary alkyl
Polar Monomer	NBLMA	GBLMA	Monomer O
Structure			Methacrylate of hydrophilic bulky lactone

methacrylate (NBLMA). Considering relative reaction rates at the radical terminals in co-polymerization of two different kinds of monomers, component ratio of the resulting polymer can be approximated by Mayo-Lewis equation.⁸ According to Fineman-Ross method, relative rate constant, "r-value" can be calculated from the component ratio of the copolymer.⁹

2-2. Resist Preparation

Resist materials were prepared as follows; Polymers, PAGs, basic compounds and surfactants were dissolved in PGMEA. Co-solvents were added in some cases. The mixtures were filtered with 0.03μm filter to obtain the desired resist materials.

2-3. Lithography and Defect Analysis

Resist materials were coated at 270nm thickness on 8 inch Si wafers which had been coated with BARC in advance. The wafers were exposed with ArF exposing tool (Nikon) and 90nm line / 90nm space patterns were obtained after post-exposure bake and development. The patterned wafers were analyzed with Win-Win 50 1200L defect detecting tool (Acretech Micro Technologies).

3. Results and Consideration

3-1. Monomer Design

A u-bridge defect as Figure 2 was considered as outbreak by un-uniformity property of dissolution rate in exposed area. And there is important factor improving dissolution rate uniformity of ArF resist, polymer disperse by polymer preparation. For improving the polymer uniformity, it is very important that selection of each one of monomers. Firstly, we calculated r-value of the acid labile monomers to compare their polymerizability (Table 2).

Figure 2 u-defect in sub 90nm L/S

If the reactivity difference among monomers in co-polymerization is too big, high polymer (very large Mw) and blocky polymer could be generated and they might become the potential defect precursors. In general, the polymerizability of acid labile unit, usually bulky tertiary alkyl ester, is lower than that of polar unit. In order to obtain polymer with good homogeneity, it is desirable to utilize the monomers that have similar reactivity.

Table 2. r-Value of the acid labile monomer

Monomer 1	MAdMA	EAdMA	Monomer D
Monomer 2	NBLMA	NBLMA	NBLMA
$r_{\text{Monomer 1}}$	1.11	0.66	1.06
$r_{\text{Monomer 2}}$	1.28	1.72	1.25

We need to use an acid labile unit with low E_a (activation energy in acid catalyzed elimination reaction) to realize better lithographic performance. However, EAdMA, which was the most widely used low E_a unit, could not be optimal because of its relatively poor polymerizability. It seemed to be difficult for us to obtain "uniform" copolymer using EAdMA as a main monomer. Thus, a defect-free

resist material might also be a hard target. Dozens of new monomers were synthesized and evaluated. Eventually, we found Monomer D, as a potential candidate, which has even lower E_a than EAdMA and good relative polymerizability.

Next, we started the screening of polar monomer. NBLMA is the most well-known and popular polar unit because of its good balance of lithographic performance and etching durability. However, its norbornane structure seems to be somewhat too hydrophobic and the affinity for developer is not sufficient. There is an apprehension that the Blocks of NBLMA might become defect precursors, and that is a fatal disadvantage of NBLMA in our application.

GBLMA can be another candidate as its cLogP value¹⁰ is much smaller than that of NBLMA (Table 3). However, it has a problem of etching durability though it seems to be sufficiently hydrophilic. We searched the alternative polar monomer with both good hydrophilicity and etching durability, and finally discovered Monomer O, methacrylate of hydrophilic bulky lactone, which has lower cLogP value than GBLMA and higher etching durability than NBLMA. In addition, lithographic performance of Monomer O is satisfactory, almost compatible to NBLMA.

Table 3. cLogP value of polar monomers

Monomer	NBLMA	GBLMA	Monomer O
cLogP	0.63	0.34	0.20

From the discussion above, Monomer D and Monomer O were determined as standard monomers for our experiment. In the following description, "copolymer" means the copolymerized product of Monomer D, Monomer O and 3-hydroxy-1-adamantyl methacrylate unless some special notes were written.

3-2. Polymerization and Purification

A Gel-like (Figure 3) defect was brought by high molecular weight polymer in the resist. Because of inducing high molecular weight polymer by different reactivity of each monomers it need to feed method optimization.

Figure 3 Typical Gel-Like defect in L/S

Monomer feed method is greatly influential in defect. We tried three methods, feed at once (Method A), continuous feed (Method B) and advanced continuous feed (Method C), and investigated the relationship between feeding method and defect count.

By Method A, high polymer and blocky polymer could be easily formed and the defect count was extremely high. Under the condition of Method A, Monomer O, the most reactive monomer in this case, was rapidly consumed in the early stage of co-polymerization, and Monomer D was introduced in the latter period. As a result, the product inevitably contained successive O or D sequences, -O-O-O- or -D-D-D-, which were extremely hydrophilic or hydrophobic, and such parts eventually gathered and formed gels.

In the case of Method B, monomers and catalysts were continuously supplied into the reaction mixture, so that the difference of monomer consumption was much smaller than Method A. In Method C, feed lines for monomers and catalysts were separated and feed speed was optimized considering the co-polymerizability of each monomer. Thus, homogeneity of copolymer became even better and the generation of defect precursors could be suppressed.

Even with the special care in the co-polymerization step such as Method C above, we could not prevent the defect completely. We should struggle to remove defect precursors as well as not to generate them. For further improvement, an additional filtration step was adopted in the work-up process of the polymer production. This step was introduced before the precipitation and it could remove hardly soluble component in the reaction mixture such as extraordinarily high molecular weight polymer.

3-3. Resist Formulation

Filtration of PGMEA solution of the polymer before PR formulation was also known as a means of improving defect. In the formulation step, many components such as PAGs, quenchers, surfactants and co-solvents are added and some of them act as "solubility enhancers", which can help the polymer to dissolve in PGMEA. Unexpectedly, Nozzle defect was viewed in ArF resist differ from KrF. It is owing to lack of solubility in the resist.

Figure 4 nozzle defect by resist solubility

In the formulation step, adding some co-solvents can reduce defects, because they strongly make the polymer soluble in the solvent and prevent the gel formation. Especially, they were effective to reduce nozzle-drying defects, which could be generated even in the case that the precursors of micro-bridge or gel-like defect were completely removed. The higher co-solvent content, the less nozzle drying defect could be accomplished. However, co-solvents are influential in lithographic performance, so that the solvent ratio should be optimized with great care.

The results of the investigation above are shown in Table 4 and 5.

Table 4. The results of the Defect count -1

Polymerization		Formulation		Defect Count Micro-bridge & Gel-Like
Feed	Post filtration	Pre filtration	Co solvent	
A	-	-	with	> 30000
B	-	-	with	> 1000
C	-	-	with	88
C	With	-	with	38
C	With	with	with	13

4. Conclusion

Improvement from several aspects has been applied to reduce three different types of defects.

Table 5. The results of the Defect count -2

Polymerization		Formulation		Defect Count Nozzle Drying
Feed	Post filtration	Pre filtration	Co solvent	
C	With	with	with	102
C	With	with	with (x3)	18

Structural design of monomers with appropriate polymerization rate and polarity was essentially important to enhance composition uniformity in polymer sequence and then to realize defect-free lithographic performance. Polymerization process by proper monomer feeding rate was also effective to avoid generation of defect precursors. Resist formulation process and solvent choice were also important. We accomplished the first generation 193nm resist for Samsung's sub-90nm DRAM device through this series of investigation.

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