Newly developed acrylic copolymers for ArF photoresist

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We have developed novel acrylic copolymers for ArF photoresist which have more etching durability than usual. The excellent one of those copolymers in handling contains 8- or 9-methacryloyloxy-4-oxatricyclo[5.2.1.0^{2,6}]decan-3-one (OTDMA) and γ,γ -dimethyl- α -methylene- γ -butyrolactone (DMMB). OTDMA is a new methacrylic ester monomer having a lactone unit with bridged structure. DMMB introduces a lactone structure to the main chain of acrylic copolymers. It was suggested that the solubility of monomers depends on the hindrance of their polar group, and the role of the hydrophilic monomers has been discussed from the standpoint of the position of their hydrophilic parts.

Keywords: ArF photoresist, acrylic copolymer, etching durability, OTDMA, DMMB, hydrophilic part, solubility

1. INTRODUCTION

ArF lithography is now being introduced into the device manufacture for the 130 nm technology node. Methacrylate based platforms are prime candidates for the positive photoresist for this lithography.¹⁻⁴ In recent reports, we described the properties of a copolymer consisting of β -hydroxy- γ -butyrolactone methacrylate (HGBMA) and 2-methyl-2-adamantyl methacrylate (MAdMA) as a photoresist (Figure 1), including the most fitted compound as quencher, and the effect of end group structures on photoresist performances.^{5,6} Outstanding properties of the copolymer are its sensitivity and resolution.

To provide sufficient etching durability, the methacrylate copolymers contain the monomer with highly annelated carbon ring structure like 2-methyl-2-adamantyl group at side chain. However, as the current trend in the ArF lithography is towards the shorter integration scale from 180 nm to 130, 100 nm, the copolymer should have the higher resolution and the more etching durability. Monomers which improved the properties have emerged. Some of the monomers have more reactivity in the acidic condition.^{7,8} And others have a hydrophilic part incorporated in an annelated structure.^{8,9}

There are two solutions for the enhancement of etching durability. One is to give higher carbon density to their hydrophilic parts. The other is to introduce structural rigidity to their main chains. According to this methodology, we explored to develop novel materials and successfully synthesized a copolymer containing OTDMA and DMMB. We tried to optimize the polymer structure simultaneously considering the distance between their hydrophilic parts in its side chain and main chains.

In this paper, we would like to report the concept of our molecular design and the predictions of the copolymer properties by computer simulation. We also show the lithographic performances of the copolymer, including the synthesis of OTDMA monomer, DMMB monomer and the copolymerization

Figure 1. Structure of poly (MAdMA-HGBMA).

2. EXPERIMENTAL

2.1 Calculation parameter

Relative etching rate of the homopolymer was calculated by Ohfujii model,¹⁰ normalized in such a way that Nobolac resist =1. Octanol / water partition coefficient (Log P) of monomer was calculated by Villar's method¹¹ and Ghose, Pritchett and Crippen's method¹² using SPARTAN V. 5.1.1 (Wavefunction Inc.). Solubility parameter (Sp) of the homopolymer at 25 °C was calculated by Feders-like method and van Krevelen-like method¹³ using Insight II (Accelrys).

2.2 Synthesis and characterization of monomers

OTDMA was prepared as follows:

A reduction of 5-norbornene-2,3-dicarboxylic anhydride with sodium borohydride furnished norbornenelactone. A hydration under acidic conditions yielded hydroxynorbornenelactone. Finally, OTDMA was synthesized by esterification.

DMMB was prepared as follows:

The alkylation of dimethyl malonate led to the methallyl derivative. Treatment with formaldehyde, followed by decarboxylation and cyclization, afforded DMMB.

The solubility of hydrophilic monomers was investigated as follows:

A 1g of a monomer was added in a 1g, 3g and 9g of solvent, respectively. The mixture was stirred at 25 °C for 8 hours to examine whether the solution was homogeneous.

2.3 Preparation of copolymers

The copolymers were prepared as follows:

Mixture of monomers and AIBN as the initiator were dissolved in 1,4-dioxane and were polymerized at 80°C for 8 hours. All the polymerizations were carried out under N₂ flow. The polymerized solution was precipitated by addition dropwisely to excess methanol. The obtained copolymer was dried overnight in vacuo.

2.4 Characterization of copolymers

Gel permeation chromatography (GPC) analyses of the copolymers were performed at a flow rate of 1.0mL/min in tetrahydrofuran (THF) using Toso HPC-8220GPC system equipped with RI detector. The column was calibrated using polystyrene standards.

The composition of copolymers was determined by proton nuclear magnetic resonance (¹H-NMR) spectra (JEOL GSX-400) in CDCl₃ at 40°C.

The solubility of the copolymers was investigated as follows:

A 1g of the copolymer was added in a 3g of solvent. The mixture was stirred at 25 °C for 8 hours to examine whether the solution was homogeneous.

2.5 Photoresist performances

The photoresist films were prepared as follows:

A 4.7g of copolymer powder, a 70mg of triphenylsulfonium triflate as photo acid generator (PAG) and a 3mg of 1-cyclohexyl-2-pyrrolidinone as quencher were dissolved in 30.1g of propylene glycol methyl ether acetate (PGMEA) / γ -butyrolactone (90/10 wt%). The solution was filtered through a membrane filter with pore size of 0.2 μ m (Advantec Toyo DISMIC-13), and was spin-coated on silicone wafer pre-treated with hexamethyldisilazane (HMDS). After baking at 120°C for 60sec, the resist film with about 400nm thickness was formed on the wafer.

The sensitivity of resist film was measured using ArF flood exposure instrument (Nikon model SP-193) and 2.38wt% tetramethylammonium hydroxide (TMAH) aqueous solution as a developer at room temperature for 60sec. The development rate was analyzed by a development rate monitor (DRM) (Litho Tech Japan RDA-790EB).

The relative dry-etching rates compared to a Novolak resist were measured using Showa Shinku SPE-220T system in CF₄ / O₂ plasmas. The etching conditions were 95 sccm of CF₄, 5 sccm of O₂ and 14 Pa at 200 W of microwave power. The film thickness loss was measured using Dainippon Screen Lambdaace VM-8000J system after etching for 2 min.

3. RESULTS AND DISCUSSION

3.1. Design and synthesis of the monomers

On the development of novel polymers, we prepared two monomers on the basis of different methods using computer simulation. Chemical structures of the monomers and those used as a standard reference are shown in Figure 2. The result of simulation is shown in Table 1.

Figure 2. Structural formulae of the monomers.

Table 1. Result of a simulation on the properties of the monomers.

Monomer	Homopolymer relative etch rate ^{*1} (Ks)	LogP		Homopolymer Sp [(MPa) ^{1/2}]	
		Villar	Ghose-Crippen	Fedors-like	van Krevelen-like
MAdMA	0.87 (0.29)	2.68	3.22	19.29	16.86
EAdMA	0.87 (0.29)	2.91	3.70	19.28	16.88
HGBMA	2.31 (0.42)	0.15	0.55	22.24	18.03
MAHNCL	1.09 (0.29)	0.71	1.16	21.74	17.72
OTDMA	1.06 (0.29)	0.74	1.25	21.58	17.71
MB	1.82 (0.42)	0.23	0.48	22.59	18.10
DMMB	1.60 (0.42)	0.87	1.02	20.23	16.60

*1 Normalized in such a way that Nobolac resist =1

To give higher carbon density to the hydrophilic parts, we adopted tricyclo[5.2.1.0^{2,6}]decane system comprising a lactone unit, which was expected to be superior to HGBMA and equal to 5-methacryloyloxy-6-hydroxynorbornene-2-carboxylic 6-lactone (MAHNCL)⁹ in etching durability by Ohfui Model. Although the calculated value of Log P was suggested to be contrary, it was also predicted that the lactone unit on this relatively planar system was less hindered than that incorporated in an annelated structure, such as MAHNCL, so OTDMA appeared more advantageous in adhesion to the substrate and solubility in organic solvents. Good solubility contributes to handling in the polymerization process.

To introduce structural rigidity to the main chains, we paid attention to simple exomethylene cyclic monomers with hydrophilic functional group. It is known that α -methylene- γ -butyrolactone (MB) is an acrylic-like monomer capable of free-radical polymerization.¹⁴⁻¹⁶ But Poly (MB) is soluble only in dimethyl sulfoxide and dimethyl formamide (DMF)^{15,16} and its calculated etch rate value was high. As a result of investigation, we selected DMMB whose homopolymer was soluble in many common organic solvents with improved etching durability by simulation.

HGBMA, OTDMA and DMMB were also expected to play a different role since they differed in the distance between their hydrophilic parts and vinyl group.

Figure 3 shows synthetic route of OTDMA and DMMB. On the first step of OTDMA synthesis, anhydride converted to lactone by selective reduction. Subsequent hydration to a reactive double bond of norbornene ring proceeded smoothly, followed by esterification. The monomer obtained was a mixture of isomers. In DMMB, reaction of dimethyl malonate with methallyl halide occurred easily. The resultant diester underwent facile decarboxylation and vinylation. In either case, starting material is readily available and the product is obtained in a high yield through short steps.

Figure 3. Synthetic route of OTDMA and DMMB.**Table 2.** The solubility of the monomers at 25 °C.

Polymer Code	PGMEA	Ethyl lactate	4-Butyrolactone	1,4-Dioxane	Acetonitrile	DMF	Cyclohexanone
A	good	good	good	good	poor	good	good
B	poor	good	good	good	poor	good	good
C	poor	good	good	good	poor	good	good
D	good	good	good	good	poor	good	good
E	good	good	good	good	poor	good	good
F	good	good	good	good	poor	good	good

excellent: $\leq 50\text{wt}\%$ soln., good: 25-50wt%soln., normal: 10-25wt%soln., poor: $> 10\text{wt}\%$ soln.

3.2. Properties of the monomers

To confirm the simulation results, we investigated the solubility of hydrophilic monomers (Table 2). HGBMA, MB and DMMB had good solubility in various organic solvents and OTDMA had similar solubility except in PGMEA and ethyl lactate. On the contrast, MAHNCL had poor solubility and required more amount of solvent. As we expected, OTDMA was superior to MAHNCL in solubility. The difference of solubility among monomers is due to that of the hindrance of their hydrophilic parts, and presumably has an effect on adhesion to the substrate of the resulting copolymer.

Figure 4. Structure of poly (MAdMA-OTDMA).

Figure 5. Structure of poly (EAdMA-OTDMA).

Figure 6. Structure of poly (EAdMA-OTDMA-DMMB).

We synthesized a series of copolymers containing the new hydrophilic monomers in a variety of monomer feeds. We adopted MAdMA and 2-ethyl-2-adamantyl methacrylate (EAdMA) as the pair to them. EAdMA had as high etch rate and 2.5 times as high reactivity to acid as MAdMA.⁷ Chemical structures of the copolymers we prepared are shown in Figure 4-6. The values of M_n , M_w , M_w/M_n and composition of the copolymers are listed in Table 3. Poly (MAdMA-HGBMA) was also synthesized as a standard reference (Polymer A). Each copolymerization gave a good yield.

3.3. Lithographic performances of the copolymers

We evaluated the sensitivity and the etch rate of the copolymers (Table 4). We also investigated the relation between the development rate and exposure dose of 193 nm light for them (Figure 7). Polymer B, where OTDMA was used as a substitute for HGBMA, had lower sensitivity and more etching durability than Polymer A. A decrease in sensitivity meant that OTDMA did not have acid cleavability. Drastic enhancement of sensitivity observed in Polymer C may depend on having changed MAdMA into EAdMA. The introduction of DMMB had little influence on sensitivity as shown in Polymer D-F. Since the etch rate was remarkably improved by Polymer B-F, OTDMA and DMMB proved to be more durable monomer for etching process. The result obtained about OTDMA was in agreement with the assumption based on our simulation. Since Polymer D-F were similar to Polymer C in the etch rate, it was suggested that Poly (DMMB) had more etching durability than we had supposed.

Then we investigated solubility of the copolymers (Table 5). The result demonstrated that what contained OTDMA was not so dissolved in PGMEA as what contained HGBMA and an addition of DMMB was effective.

The results obtained led the conclusion that the introduction of OTDMA to the copolymer makes improvement to etching durability remarkably and of DMMB makes improvement to both etching

Table 3. Characteristics of the copolymers.

Polymer Code	Monomer M1/M2/M3	M_n	M_w	M_w/M_n	Composition ratio M1/M2/M3
A	MAdMA/HGBMA	7300	11000	1.51	44/56
B	MAdMA/OTDMA	6800	13200	1.94	52/48
C	EAdMA/OTDMA	5800	10800	1.86	47/53
D	EAdMA/OTDMA/DMMB	4500	7000	1.68	49/38/13
E	EAdMA/OTDMA/DMMB	4300	6700	1.57	45/31/24
F	EAdMA/OTDMA/DMMB	4100	7400	1.81	48/40/12

durability and solubility. Each hydrophilic monomer, HGBMA, OTDMA and DMMB, plays a different role corresponding to the position of a lactone unit. We can obtain the copolymers with desired properties by selecting the best out of the monomers.

Table 4. Lithographic performances of the copolymers.

Polymer Code	Monomer M1/M2/M3	Composition ratio M1/M2/M3	Sensitivity (mJ/cm ²)	Relative etch rate ^{*1}
A	MAdMA/HGBMA	44/56	1.76	1.29
B	MAdMA/OTDMA	52/48	4.68	1.14
C	EAdMA/OTDMA	47/53	0.98	1.16
D	EAdMA/OTDMA/DMMB	49/38/13	1.22	1.16
E	EAdMA/OTDMA/DMMB	45/31/24	1.22	1.16
F	EAdMA/OTDMA/DMMB	48/40/12	1.46	1.12

*1 Normalized in such a way that Nobolac resist =1

Figure 7. The development rate vs. exposure dose for the copolymers.

Table 5. The solubility of the copolymers at 25 °C.

Polymer Code	PGMEA	Ethyl lactate	4-Butyrolactone	1,4-Dioxane	Acetonitrile	DMF	Cyclohexanone
A	good	good	good	good	poor	good	good
B	poor	good	good	good	poor	good	good
C	poor	good	good	good	poor	good	good
D	good	good	good	good	poor	good	good
E	good	good	good	good	poor	good	good
F	good	good	good	good	poor	good	good

good: $\leq 25\text{wt}\%\text{soln.}$, poor: $> 25\text{wt}\%\text{soln.}$

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