Design and Characteristics of Acrylate Polymers with Alicyclic Lactone Group for ArF resists

Katsumi Maeda, Kaichiro Nakano, and Masamitsu Shirai*

*Jisso and Production Technologies Research Laboratories NEC Corporation
1120, Shimokuzawa, Sagami-hara, Kanagawa 229-1198, Japan*

**Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University
1-1 Gakuen-cho, Nakaku, Sakai, Osaka 599-8531, Japan*

We designed novel acrylate monomers with an alicyclic lactone group [3-oxa-4-oxotricyclo[5.3.1.0^{6,10}]undecanyl (OTCU) or 4,4-dimethyl-5-oxa-6-oxotetracyclo[7.2.1.0^{2,8}.0^{3,7}]dodecyl (OTCD) group] for an ArF chemically amplified resist. The polymers with these monomer units exhibited high transparency at 193 nm and good adhesion to a Si substrate. They were also extremely durable against dry etching. The etching durability of polymer with the OTCD group was superior to that of the polymer with the OTCU group. Furthermore, a chemically amplified positive resist comprised of terpolymer with an OTCD units and a photo-acid generator achieved a resolution of 130-nm L/S with an ArF exposure system.

Keywords: alicyclic lactone monomer, acrylate polymer, dry-etching durability, chemically amplified positive resist, ArF excimer laser lithography

1. Introduction

ArF excimer laser (193 nm) lithography is currently used to manufacture of ULSIs with 90-nm design rules. A chemically amplified positive resist composed of an acid-cleavable polymeric material and a photo-acid generator (PAG) is used as the ArF resist in practice. At present, acrylate polymers with an adamantyl group and a lactone group,^{1–5} are used as the base polymers. Immersion technology^{6–8}, which can improve both resolution and the depth of focus, has recently been recognized as an attractive technique of extending 193-nm lithography to the 65-nm, 45-nm, and 32-nm technology nodes. Therefore, improvements in lithographic characteristics such as resolution, dry-etching resistance, and sensitivity are required for ArF resist materials. Dry-etching resistance should especially be further improved because the resists are becoming thinner with rules for smaller designs.

We previously developed an acrylate polymer with a norbornane lactone unit and reported that a chemically amplified positive resist with this polymer achieved both superior resistance against

dry etching and excellent resolution characteristics.

It is well known that the durability of polymer materials against etching is derived from their high carbon content. We designed new acrylate monomers in current study having an alicyclic lactone structure (3-oxa-4-oxotricyclo [5.3.1.0^{6,10}]undecanyl (OTCU) and 4,4-dimethyl-5-oxa-6-oxotetracyclo[7.2.1.0^{2,8}.0^{3,7}]dodecyl (OTCD) group) with higher carbon content. This paper reports on the basic properties, i.e., the thermal stability, transparency, and dry-etching resistance of the new acrylate polymers. We also report on our evaluation of the lithographic capabilities of the resist polymers using the monomers we developed.

2. Experimental

2.1. Monomers

The chemical structures of the new alicyclic lactone monomers (AOTCU and OTCD) we developed and the norbornane lactone monomer (AHNL)³ we previously developed are outlined in Figure 1. These monomers were synthesized with the following procedure.

Figure 1. Chemical structures of lactone monomers.

2-Acryloyloxymethyl-3-oxa-4-oxotricyclo[5.3.1.0^{6,10}]undecane (AOTCU).

A solution of 50 g of *m*-chloroperbenzoic acid in 400 ml of dichloromethane was added to a mixture of 25.4 g of tricyclodecane-8-one and 42.6 g of NaHCO₃ in 150 ml of dichloromethane, dropwise, while stirring at 0-5°C. The mixture was stirred for 8 h at room temperature. The precipitated *m*-chlorobenzoic acid was filtered off and the filtrate was washed with 5% aqueous NaHSO₃, 5% aqueous Na₂CO₃, and brine. This dichloromethane solution was dried over MgSO₄ and evaporated under reduced pressure. The residue was distilled at 110-111°C at 0.35 mmHg to yield 24.8 g of 3-oxa-2-oxotricyclo[5.3.1.0^{6,10}]undecane (OTCU) (88%).

To 50 ml of 2M lithium diisopropylamide in THF was added dropwise 15 g of OTCU in 40 ml of anhydrous THF with stirring under an argon atmosphere at a temperature below -70°C. The resulting mixture was stirred at -78°C for 1 hr and it was then warmed to -30°C. Formaldehyde gas, which was generated by heating paraformaldehyde at 170°C, was bubbled through the reaction mixture for 30 min after which it was stirred at -20°C for 1 hr and acidified with 10% HCl. The solution was diluted with 300 ml of ethyl acetate and washed with 5% aqueous NaHCO₃ and brine. The ethyl acetate solution was dried over MgSO₄ and evaporated. The residue was purified by silica gel chromatography to yield 6.3 g of 3-oxa-4-oxotricyclo[5.3.1.0^{6,10}]undecane-2-methanol (OTCUM, 36%).

To a mixture of 5 g of OTCUM and 3.71 g of *N,N*-dimethylaniline in 30 ml of dried CH₂Cl₂ was added 2.54 g of acryloyl chloride with stirring under an argon atmosphere at 0-5°C. After stirring for 6 hr, the resulting mixture was diluted with 200 ml of diethyl ether and washed with 0.5N HCl, 3% aqueous NaHCO₃, and brine. The solution was dried over MgSO₄ and evaporated. The residue was purified with silica gel chromatography to

yield 6 g of the target acrylate (colorless liquid, 94%).

¹H-NMR (CDCl₃, ppm) δ 0.8-1.19 (2H, m), 1.28-1.43 (1H, m), 1.56-1.85 (2H, m), 1.93-2.11 (3H, m), 2.16-2.22 (1H, m), 2.34-2.45 (1H, m), 2.69-2.87 (2H, m), 4.44 (1H, d), 4.46 (1H, d), 4.51 (1H, s), 5.88 (1H, d), 6.14 (1H, dd), 6.44 (1H, d).

4,4-Dimethyl-5-oxa-6-oxotetracyclo[7.2.1.0^{2,8}.0^{3,7}]undecyl-10(11)-acrylate (OTCDA).

A mixture of 19.7 g of quadricyclane and 20 g of maleic anhydride in 50 ml of chloroform was refluxed for 6 hr. After cooling, the solution was evaporated and the residue was recrystallized from toluene to yield tricyclo[4.2.1.0^{2,5}]-7-nonene-3,4-dicarboxylic anhydride (TCND). We dropped 20 g of TCND in 200 ml of anhydrous THF into 110 ml of 1M methylmagnesium bromide in THF while stirring at 0-5°C under an argon atmosphere. The resulting solution was stirred for 2 hr at room temperature. After cooling, the solution was acidified with 10% HCl and stirred at 40°C for 40 min. The resulting mixture was diluted with 200 ml of diethyl ether and washed with 4% aqueous NaHCO₃ and brine. The diethyl ether solution was dried over MgSO₄ and evaporated. The residue was recrystallized from hexane/toluene to yield 6.92 g of 4,4-dimethyl-5-oxa-6-oxotetracyclo[7.2.1.0^{2,8}.0^{3,7}]undecene (OTCD, 32%).

To 7.8 g of OTCD in 20 ml of dried THF was added 21 ml of 1M borane-THF complex in THF with stirring under an argon atmosphere at 0-5°C. After 1 hr, the solution was stirred at room temperature for 1 hr after which 3 ml of H₂O, 7 ml of 3mol/L aqueous NaOH, and 4.6 ml of 30% H₂O₂ were added to the solution. After stirring for 2 h, it was diluted with 100 ml of diethyl ether and washed with brine. The ether solution was dried over MgSO₄ and evaporated to yield 4.88 g of 4,4-dimethyl-5-oxa-6-oxo-10(11)-hydroxy-tetracyclo[7.2.1.0^{2,8}.0^{3,7}]undecane (OHTCD).

To a mixture of 4.88 g of OHTCD and 3.99 g of

N,N-dimethylaniline in 40 ml of dried CH_2Cl_2 was added 2.38 g of acryloyl chloride with stirring under an argon atmosphere at 0-5°C. After stirring for 6 hr, the resulting mixture was diluted with 100 ml of diethyl ether and washed with 0.5N HCl, 3 % aqueous NaHCO_3 , and brine. The solution was dried over MgSO_4 and evaporated. The residue was purified with silica gel chromatography to yield 2.6 g of the target acrylate (colorless liquid, 43%).

$^1\text{H-NMR}$ (CDCl_3 , ppm) δ 1.287, 1.292, 1.47, 1.49 (6H, s), 1.51-1.81 (4H, m), 2.1-2.49 (5H, m), 2.78-2.84 (1H, m), 4.52-4.59 (1H, d), 5.82 (1H, dd), 6.09 (1H, dd), 6.38 (1H, d).

2.2. Radical polymerization

The homopolymers (poly(AOTCU) and poly(OTCDA)) and resist polymers were synthesized by using free radical polymerization as follows. The monomers were dissolved in dry THF. A polymerization initiator 2,2'-azobis-(isobutyronitrile) was added to the mixture. The solution was then heated to 60-65°C in an argon atmosphere for 2 hr. After cooling to room temperature, the mixture was poured into hexane to precipitate the polymer. The product was purified by carrying out two reprecipitations.

2.3. Monomer and polymer characterization

$^1\text{H-NMR}$ and ultraviolet absorption spectra were respectively measured on a Burcker AMX-400 and a Shimadzu UV-365 spectrometer. The average molecular weight and polydispersity were measured by gel permeation chromatography on a Shimadzu Gel Permeation Chromatography System. The thermal properties were analyzed with a Mack Science Thermal Analysis System 001. The dissolution rates were measured on an in-house dissolution monitor. The work of adhesion of the polymer to the Si substrate was calculated by Owens', Young's, and Dupré's formulas which use the measured contact angles of water and methylene iodide on polymer films and the Si substrate.

2.4. Lithographic evaluation

Triphenylsulfonium nonaflate (TPS-Nf) was used as a photo-acid generator. The resist films were spun to a thickness of 0.4 μm on an organic ARC-coated Si substrate and pre-baked at either 140°C or 150°C for 1 min. Exposure was carried out using a Nikon ArF Scanner (NA=0.6, annular illumination). The Exposed resists were post-exposure-baked at 140°C for 1 min on a

hot-plate and developed in a 2.38% tetramethylammonium hydroxide (TMAH) solution for 1 min.

3. Results and Discussion

3.1. Polymer properties

We first investigated the thermal stability of lactone homopolymers. The decomposition temperatures (T_d : 5% weight loss) are listed in Table 1. Although the new homopolymers (poly(AOTCU) and poly(OTCDA)) we developed have a lower T_d than that of the poly(AHNL) (T_d : 383 °C) we previously developed, they have sufficient thermal stability (T_d : 200°C and 293°C) for practical lithography processes. Additionally, poly(OTCDA) with a γ -lactone structure exhibited higher thermal stability than poly(AOTCU) with a δ -lactone structure. This may be derived from the rigid tetracyclododecene structure. We also evaluated the work of adhesion (Wps) of the polymers on a Si substrate (Table 1). The results indicate that the newly developed polymers have excellent adhesion to the Si substrate as well as the poly(vinylphenol) (78.9 mN/m), which is a base polymer used as a KrF resist.

Table 1. Decomposition temperatures and work of adhesion of homopolymers.

Homopolymers	T_d (°C) ¹⁾	Wps (mN/m) ²⁾
poly(AOTCU)	200	79.4
poly(OTCDA)	297	81.5
poly(AHNL)	383	88.6
poly(vinylphenol)	-	78.9

1) 5% weight loss. 2) work of adhesion of polymers on Si substrate treated with HMDS.

Hydrophilic monomers need to have high resistance against alkaline developers to apply them as positive resists. We therefore measured the dissolution rate of the homopolymers (Table 2). We found that the dissolution rate of the poly(AOTCU) was 2.5×10^{-6} $\mu\text{m/s}$ in a 2.38% TMAH solution, while the poly(OTCDA) was insoluble in the developer. This finding indicates that a hydrolysis reaction did not occur in the tertiary ester of γ -lactone moiety but in the δ -lactone moiety. A possible reaction of the δ -lactone polymer (poly(AOTCU)) with the alkaline developer is outlined in Figure 2. As the dissolution rate of poly(AOTCU) is very slow, this hydrolysis reaction is almost negligible during a practical development process (60-90 s).

Figure 2. Hydrolysis reaction of poly(AOTCU).

Table 2. Dissolution rate and dry-etching rate of homopolymers.

Homopolymers	Dissolution rate ($\mu\text{m/s}$) ¹⁾	Etching rate for CF_4 gas (rel.)
P(AOTCU)	2.5×10^{-6}	0.73
P(OTCDA)	- ²⁾	0.65
p(AHNL)	7.8×10^{-6}	1.0

1) in 2.38% TMAH. 2) insoluble.

The most important requirement is resistance against dry etching because resists are becoming thinner with rules for smaller designs. We investigated the durability of the polymers against dry etching. Table 2 summarizes the etching rate of the polymers for CF_4 gas. The lactone polymers we developed have higher dry-etching durability than poly(AHNL), i.e., the etch rate of the polymers was 0.65-0.73 times that of poly(AHNL). Furthermore, the durability of poly(OTCDA) against etching is superior to that of poly(AOTCU). This may be caused by the difference in the carbon content of the alicyclic lactone unit; poly(OTCDA) has 11 carbon atoms, while poly(AOTCU) has 10.

3.2 Lithographic capabilities

We applied the developed lactone monomers to a chemically amplified positive resist. The resist polymer structures are outlined in Figure 3.

We analyzed their thermal properties and

Figure 3. Chemical structures of resist polymers.

transparency. Table 3 lists their Td and transmittance. These polymers have a high thermal stability when used as resists (Td: 222 °C or 234 °C) and high transparency at 193 nm (74-79%/0.4 μm).

Table 3. Decomposition temperatures and transmittance of resist polymers.

Resist polymers	Td(°C) ¹⁾	T(%/0.4 μm) ²⁾
Polymer A	222	74
Polymer B	234	79

1) 5% weight loss. 2) at 193 nm.

2)

We also evaluated the resolution characteristics of a positive resist composed of the terpolymers and photo-acid generator using a Nikon ArF scanner. As we can see from Figures 4 and 5, the positive resists composed of polymers A or B and 2 wt% TPS-Nf resolved a 130-nm L/S pattern with annular illumination.

Figure 4. SEM micrographs of L/S patterns of resist with polymer A.

Figure 5. SEM micrographs of L/S patterns of resist with polymer B.

4. Conclusion

We designed novel acrylate monomers with an alicyclic lactone group [3-oxa-4-oxotricyclo[5.3.1.0^{6,10}]undecanyl (OTCU) or 4,4-dimethyl-5-oxa-6-oxo-tetracyclo[7.2.1.0^{2,8}.0^{3,7}]dodecyl (OTCD) group] for an ArF chemically amplified resist polymer. The polymers with these monomer units exhibited high transparency at 193 nm and good adhesion to a Si substrate. The polymers were also extremely durable against dry etching.

The durability against etching of the polymer with OTCD group was superior to that of the polymer with OTCU group. Furthermore, a chemically amplified positive resist comprised of terpolymers with these lactone monomer units and a photo-acid generator achieved a resolution of 130-nm L/S with an ArF exposure system.

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