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Synthesis and characterization of norbornene-based polymers with 7,7-dimethyloxepan-2-one acid labile groups for chemically amplified photoresists

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Abstract

The present paper describes a novel class of norbornene-based copolymers containing 7,7-dimethyloxepan-2-one acid labile groups. Poly(3-(bicyclo[2.2.1]hept-5-en-2-ylhydroxymethyl)-7, 7-dimethyloxepan-2-one-co-5-((2-decahydronaphthyl)oxycarbonyl)-norbornene-co-5-norbornene-2-carboxylic acid-*co*-maleic anhydride) was synthesized and evaluated as a potential chemically amplified resist for ArF lithography. The 7,7-dimethyloxepan-2-one group of the matrix polymer was readily cleaved and the carboxylic acid functionality was formed by acid-catalyzed ring-opening reaction in the exposed region after post-exposure bake. The resist patterns of 0.12 μm feature size were obtained at a dose of 10 mJ cm^{-2} with a conventional developer, 2.38 wt% tetramethylammonium hydroxide aqueous solution, using an ArF excimer laser stepper. © 2002 Published by Elsevier Science Ltd.

Keywords: Chemically amplified resist; 7,7-Dimethyloxepan-2-one; ArF lithography

1. Introduction

Since the proposal of the concept of 'chemically amplified photoresists (CARs)' [1–3], the field of 193 nm photoresists using ArF excimer laser has advanced remarkably in the past few years due to the efforts of resist designers around the world [4]. The majority of recently published work on 193 nm resists involves the design of new etch resistant polymers, focusing on new backbone polymer chemistry [5–7], alicyclic pendant groups [8,9], and acid labile protecting groups [10–12]. For chemical amplification process, *tert*-butyl, ethoxyethyl, and tetrahydropyranyl groups have been used extensively as protecting groups for carboxylic acid in the matrix polymers for 193 nm CARs. However, the polymers with those protecting groups release the volatile byproducts such as isobutene, ethyl vinyl ether, and 3,4-dihydro-2H-pyran by acid-catalyzed deprotection reaction, inducing the necessary solubility changes for the practical imaging applications.

Our goal in this investigation is to apply a novel method of polarity change, ring-opening instead of conventional deprotection for a deep UV chemically amplified resist system. We propose a new acid labile group, 7,7-dimethyloxepan-2-one, which is introduced into the norbornene-based polymers for positive CARs. Upon exposure and post-exposure bake (PEB), the 7,7-dimethyloxepan-2-one group is readily cleaved by ring-opening reaction and the carboxylic acid functionality is formed by acid-catalyzed reaction in the exposed region. Therefore, the resist can be developed by a conventional 2.38 wt% tetramethylammonium hydroxide (TMAH) developer. In this article, we discuss the synthetic method, physical properties, and lithographic performance of the newly designed polymer.

2. Experimental

2.1. Materials

5-Norbornene-2-carboxaldehyde, 5-norbornene-2-carboxylic acid (NC), 2-decahydronaphthol, and acryloyl chloride were purchased from Aldrich Chemical Company and used without further purification. Maleic anhydride (MA) was purchased from Aldrich Chemical Company and purified by recrystallization in benzene. Triethylamine (TEA) was purchased from Junsei Chemical Company and purified by distillation. 2,2-Dimethyl cyclohexanone was prepared as

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described by Ireland [13]. 2-Chlorocarbonyl-5-norbornene (CCN) was prepared via Diels–Alder reaction [14] between cyclopentadiene and acryloyl chloride. The reaction product was distilled under reduced pressure. *N*,*N*′-Azobisisobutyronitrile (AIBN) was purified by recrystallization in methanol. Triphenylsulfonium triflate (TPSOTf) as a photoacid generator (PAG) was given by Midori Kagaku Co., Ltd.

2.2. Measurements

^{1}H and ^{13}C NMR spectra were obtained using a Bruker AM-300 FT-NMR spectrometer in $CDCl_3$ at 25 °C. Infrared spectra were obtained using a Bruker EQUINOX 55. Ultraviolet spectra were recorded as spin-coated films on quartz plates with a Hewlett–Packard Model 8453 spectrophotometer. Elemental analysis data were obtained on a RICO CHNS-932. The weight-average molecular weight (M_w) and molecular weight distribution (MWD) were determined in tetrahydrofuran (THF) by a Waters GPC-150C calibrated with polystyrene standards. Thermogravimetric analysis (TGA) data were obtained on a Perkin–Elmer TA 7 series thermal system. TGA measurement was made at a heating rate of 20 °C min^{-1}. The work of adhesion value of a polymer on a silicon substrate was calculated using formulas with contact angles of water (H_2O) and methylene iodide (CH_2I_2) on the polymer film and substrate as set forth by Owens and Wendt's [15], Young's [16], and Dupre's equations.

2.3. Synthesis of 3-(bicyclo[2.2.1]hept-5-en-2-ylhydroxymethyl)-7,7-dimethyloxepan-2-one (BHMDMO)

The monomer 3-(bicyclo[2.2.1]hept-5-en-2-ylhydroxymethyl)-7,7-dimethyloxepan-2-one (BHMDMO) was synthesized as follows. All the following reaction procedures were conducted under dry nitrogen.

2.3.1. 7,7-Dimethyloxepan-2-one

To a solution of 41.46 g (185 mmol) of *m*-chloroperoxybenzoic acid (*m*-CPBA, 77% purity) and 5.19 g (62 mmol) of sodium bicarbonate in 450 ml of methylene chloride was added a solution of 15.6 g (124 mmol) of 2,2-dimethylcyclohexanone in 50 ml of methylene chloride. The resulting mixture was stirred at 40 °C for 5 h. The excess peracid was reduced by addition of aqueous sodium sulfite. The mixture was diluted with methylene chloride, washed with aqueous K_2CO_3 and brine, and dried over Na_2SO_4. The solvent was removed, and the crude product was purified by distillation under reduced pressure. The product was obtained in a yield of 13.6 g (77%). Bp 54 °C (0.1 mmHg). ^{1}H NMR ($CDCl_3$, ppm): δ 1.43 (6H, s, CH_3), 1.65–1.84 (6H, m, $(CH_2)_3$), 2.63–2.67 (2H, t, CH_2CO_2). ^{13}C NMR ($CDCl_3$, ppm): δ 23.4, 24.27, 28.5, 37.2, 40.2, 81.29, 174.8. FTIR (cm^{-1}): 2940 (alicyclic CH), 1716 (C=O of lactone), 1110 (C–O–C of lactone).

2.3.2. 3-(Bicyclo [2.2.1]hept-5-en-2-ylhydroxymethyl)-7,7-dimethyloxepan-2-one

The lithium enolate of the caprolactone was formed at −78 °C by adding a solution of 5 g (35 mmol) of 7,7-dimethyloxepan-2-one in 80 ml of dry THF to a solution of 20 ml (38.6 mmol) of 2 M lithium diisopropylamide. After stirring for 20 min, 4.55 g (37 mmol) of 5-norbornene-2-carboxaldehyde in 20 ml of dry THF was added and the resulting mixture was subjected to −20 °C for 3 h. The reaction mixture was neutralized by addition of aqueous NH_4Cl, and diluted with diethyl ether. The organic layer was washed with water and dried over Na_2SO_4. The solvent was removed, and the crude product was purified by recrystallization in a mixture of diethyl ether and *n*-hexane (3:2 volume ratio). BHMDMO was obtained in a yield of 5.02 g (54%). ^{1}H NMR ($CDCl_3$, ppm): δ 1.04–2.1 (8H, m), 1.4 (3H, s, CH_3–C–O_2C), 1.5 (3H, s, CH_3–C–O_2C), 2.6 (1H, m, CH–C–O), 2.9 (2H, m), 3.1 (1H, m, CH–CO_2), 3.2 (1H, m, CH–O), 3.6 (1H, d, OH), 5.83–6.2 (2H, m, olefinic proton). ^{13}C NMR ($CDCl_3$, ppm): δ 176.4 (lactone). FTIR (cm^{-1}): 3520 (OH), 2965 (alicyclic CH), 1698 (C=O of lactone), 1127 (C–O–C of lactone). Anal. calcd for $C_{16}H_{24}O_3$; C, 72.69; H, 9.15. Found: C, 72.61; H, 9.09.

2.4. Synthesis of 5-((2-decahydronaphthyl)oxycarbonyl)-norbornene (DNN)

To a solution of 15.4 g (0.10 mol) of 2-decahydronaphthol in 300 ml of dry diethyl ether was added 17.2 g (0.11 mol) of 2-chlorocarbonyl-5-norbornene at 0 °C and then, slowly added 16.7 ml (0.12 mol) of TEA. The reaction mixture was allowed to warm to room temperature and stirred for 6 h. The mixture was washed with water and dried over anhydrous $MgSO_4$. The solvent was removed, and the crude product was purified by distillation under reduced pressure. The product was obtained in a yield of 21.95 g (80%). Bp 106 °C (0.1 mmHg). ^{1}H NMR ($CDCl_3$, ppm): δ 1.02–2.02 (20H, m), 2.9 (2H, m), 3.17 (1H, m), 4.62–4.80 (1H, m), 5.86–6.16 (2H, m, olefinic proton). FTIR (cm^{-1}): 2924 (alicyclic CH), 1731 (C=O of ester), 1130 (C–O–C of ester).

2.5. Polymerization

All of the polymers were prepared by free radical polymerization in sealed ampoules. A typical polymerization is as follows.

A copolymer of BHMDMO, 5-((2-decahydronaphthyl)-oxycarbonyl)-norbornene (DNN), NC, and maleic anhydride was synthesized. 0.82 g (3.1 mmol) of BHMDMO, 1.70 g (6.2 mmol) of DNN, 0.14 g (1.0 mmol) of NC, and 1.01 g (10.3 mmol) of maleic anhydride were dissolved in 3.8 g of dry dioxane, and 0.067 g (0.41 mmol) of *N*,*N*′-azobisisobutyronitrile was added to this mixture solution as a radical initiator. Polymerization was performed at 65 °C for 24 h under a nitrogen atmosphere. After the reaction, the solution was diluted with tetrahydrofuran and precipitated twice into a mixed solvent (petroleum ether/diethyl ether, 2:1 volume ratio) and dried at reduced pressure. The polymer was obtained with a yield of 1.65 g (45%) as a white powder.

2.6. Acid-catalyzed cleavage of 7,7-dimethyloxepan-2-one

In order to demonstrate the acid-catalyzed cleavage reaction of the protecting group, 7,7-dimethyloxepan-2-one as the model compound was studied using ^{13}C NMR spectroscopy. Deuterium chloride (DCl, 20 wt% solution in D_2O) was used as an acid catalyst. A solution was prepared by dissolving 7,7-dimethyloxepan-2-one in 0.7 ml of DMSO-d_6 with 100 μl of the DCl solution. The sample was heated at 120 °C for 60 s. Then, the spectra were obtained using a Bruker AM-300 FT-NMR spectrometer in DMSO-d_6 at 25 °C. The ^{13}C NMR spectra were compared before and after heating of the sample.

2.7. Lithographic evaluation

A photoresist solution was prepared by dissolving 1 g of the polymer and 0.02 g of TPSOTf in 5 g of cyclohexanone. The solution was filtered twice through a 0.2 μm membrane filter prior to application on the silicon substrate. A resist film was prepared by spin coating of the photoresist solution on a hexamethyldisilazane-treated silicon wafer and baking at 110 °C for 90 s. Exposure was carried out at 193 nm with a ISI ArF excimer laser stepper with 0.6 NA. The exposed wafer was baked again at 120 °C for 90 s and developed by dipping in a 2.38 wt% tetramethylammonium hydroxide (TMAH) aqueous solution for 40 s. The linewidths were measured on a Hitachi S-800 CD-SEM and cross-section profiles were obtained by a Hitachi S-8820 SEM.

3. Results and discussion

The synthetic scheme of BHMDMO and poly(BHMDMO-*co*-DNN-*co*-NC-*co*-MA) is shown in Fig. 1. 2,2-Dimethylcyclohexanone was transformed into the seven-membered lactone by a Bayer–Villiger oxidation using *m*-CPBA. The monomer, BHMDMO, was prepared by reaction of lactone with 5-norbornene-2-carboxaldehyde. DNN was synthesized from the reaction between 2-chlorocarbonyl-5-norbornene and 2-decahydronaphthol in the presence of TEA. The lactone group of BHMDMO provides an acid-cleavable function which is responsible for creating a radiation-induced solubility change based on the chemical amplification, and adhesion to silicon substrate. The hydrophobic property was provided by the DNN structure and was introduced as a dissolution inhibitor. NC was also introduced to increase the sensitivity. Poly(BHMDMO-*co*-DNN-*co*-NC-*co*-MA) was prepared by free radical polymerization and the polymerization results are summarized in Table 1. The weight-average molecular weights of poly(BHMDMO-*co*-DNN-*co*-NC-*co*-MA) were in the range of 4300–6070 g mol^{-1} and the polydispersities were 1.27–1.55. Yields were 41–47%.

Table 1

Radical polymerization of BHMDMO, DNN, NC, and MA (polymerizations were carried out at 65 °C for 24 h in dioxane; mol% of AIBN based on the total amount of monomers is 2 mol% in all cases; *M*/*S* (the ratio of the weight of monomer relative to the weight of solvent) is 1 in all cases)

Polymer	Molar feed ratio (BHMDMO/DNN/NC/MA)	Yield (%)	M_w	MWD
A	50/0/0/50	47	6077	1.27
B	40/10/0/50	46	5351	1.31
C	30/20/0/50	43	4925	1.50
D	25/25/0/50	43	4728	1.46
E	20/30/0/50	41	4300	1.55
F	15/30/5/50	45	4758	1.53

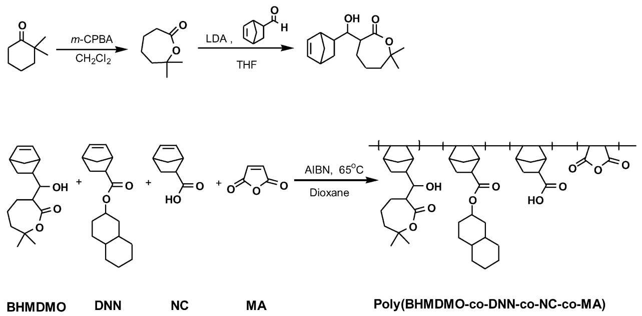

Fig. 1. Synthesis of BHMDMO and poly(BHMDMO-*co*-DNN-*co*-NC-*co*-MA).

TGA thermograms show that the onset decomposition temperature (T_d) is 248 °C in the absence of the photogenerated acid (Fig. 2a). From this temperature, a rapid weight loss takes place due to the loss of the pendant groups such as hydroxy, lactone, and alkyl ester. The onset decomposition temperature is 92 °C in the presence of the acid (Fig. 2b). The first weight loss between 92 and 180 °C is 7.2 wt% and this value corresponds to the elimination of water, followed by the evolution of carbon dioxide from the structures of β-hydroxy carboxylic acid or α,β-unsaturated carboxylic acid produced by the photogenerated acid.

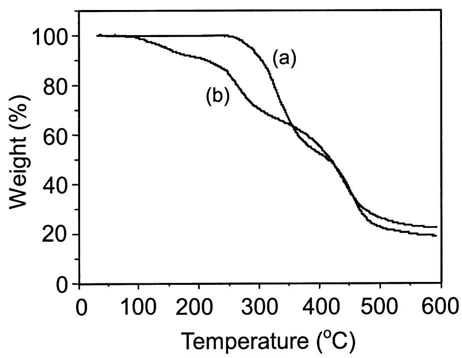

Fig. 2. TGA thermograms of polymer F containing 2.0 wt% TPSOTf (a) before and (b) after UV exposure of 40 mJ cm^{-2}.

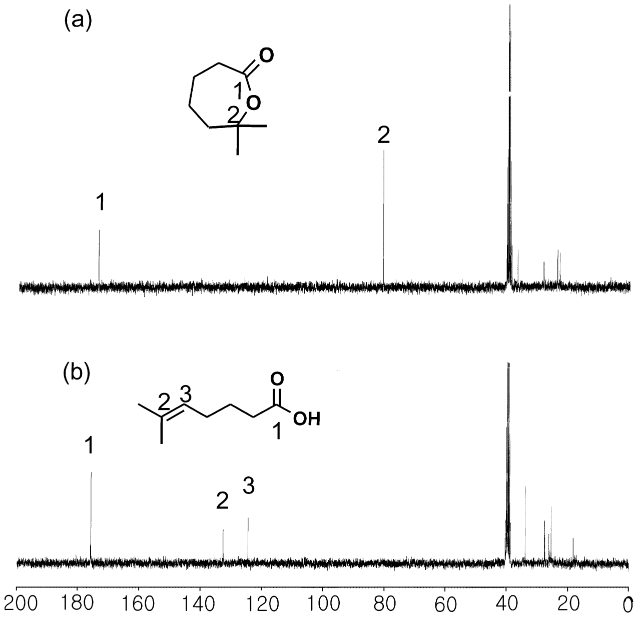

Fig. 3. ^{13}C NMR spectral change of 7,7-dimethyloxepan-2-one (a) before and (b) after heating at 120 °C for 60 s.

These phenomena result from the structure of β-hydroxy lactone in the matrix polymer [17].

The acid-catalyzed cleavage of 7,7-dimethyloxepan-2-one was studied using ^{13}C NMR spectroscopy (Fig. 3). After thermal treatment in the presence of DCl, the peak of the carbon adjacent to the ester group (CO_2–*C*) at 80.7 ppm and that of the ester group at 173.7 ppm, which are shown in the spectrum of 7,7-dimethyloxepan-2-one, completely disappeared. On the other hand, the vinylic carbon peaks at 124.4 and 132.5 ppm and the carboxylic carbon at 175.6 ppm were observed. This indicates that the vinylic carboxylic acid was formed by the ring-opening reaction of 7,7-dimethyloxepan-2-one in the presence of an acidic catalyst.

The acid-catalyzed cleavage of poly(BHMDMO-*co*-MA) was also confirmed by FTIR. Fig. 4 shows that the cleavage reaction results in the disappearance of the lactone group and the formation of the carboxylic group in the polymer. After exposure (dose = 40 mJ cm^{-2}) and PEB, the absorption at 3100–3600 cm^{-1}, which is due to the carboxylic acid and hydroxy group, increased remarkably. In contrast, the absorption at 1700 cm^{-1}, which is due to the ester structure of the lactone, decreased. Also, the C–O–C band of the lactone unit at 1125 cm^{-1} decreased. Therefore, the acid-catalyzed reaction in the resist film is attributed to the ring-opening reaction of the lactone to the acid, as shown in Fig. 5. As a result, the solubility of the polymer in the exposed areas changes significantly after exposure and bake. Due to the formation of polar carboxylic moieties, the exposed areas are easily developed in an alkaline aqueous medium. It can be used in resists for ArF excimer laser lithography.

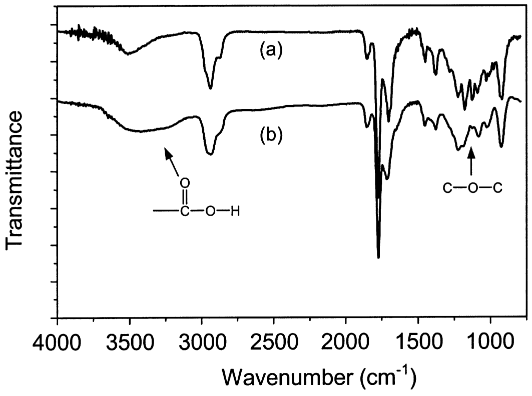

Fig. 4. FTIR spectral change of poly(BHMDMO-*co*-MA) (a) before and (b) after acidolysis with PEB at 140 °C for 90 s.

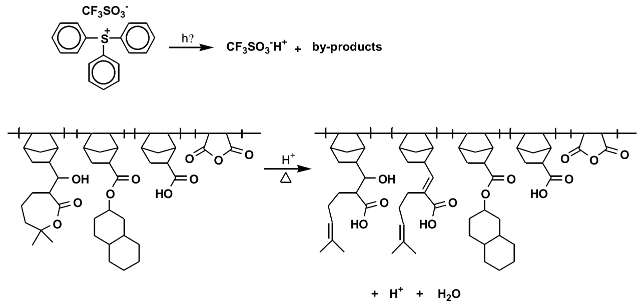

Fig. 5. Acid-catalyzed deprotection of poly(BHMDMO-*co*-DNN-*co*-NC-*co*-MA).

The polymer exhibits relatively good transmittance. The absorbencies of polymer F and the polymer containing 2 wt% TPSOTf were 0.52 and 0.76 μm^{-1} at 193 nm, respectively.

Works of adhesion of polymers on silicon substrates (W_{ps}) were calculated from the measured contact angles of water and CH_2I_2, and summarized in Table 2. The copolymers revealed the much improved adhesion properties to silicon substrates in comparison with the commercially available PVP-based resist (APEX-E). Poly(BHMDMO-*co*-MA) was too hydrophilic to be coated on a HMDS-primed silicon wafer, but it could be coated on a HMDS-free silicon wafer.

Table 2
Contact angles of H_2O and CH_2I_2, and work of adhesion of polymers

Sample	Contact angle (°)		W_{ps} [b] (dyn cm^{-1})
	H_2O	CH_2I_2	
Polymer A	58.7	25.4	109.47[a]
Polymer C	59.2	26.7	86.43
Polymer E	59.9	27.1	82.81
Polymer F	61.1	28.4	81.97
PVP-based resist (APEX-E)	54.8	73.5	70.36
HMDS-free Si	27.1	40.2	–
HMDS-primed Si	61.9	58.3	–

[b] Work of adhesion of polymers on a HMDS-primed silicon wafer.

[a] Work of adhesion of polymer A on a HMDS-free silicon wafer.

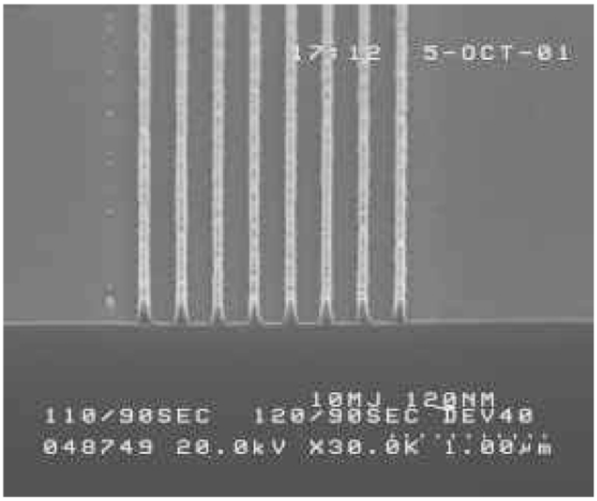

Fig. 6. SEM image of 0.12 μm line and space patterns at 10 mJ cm^{-2} printed with polymer F using an ArF excimer laser system (ISI, NA = 0.6).

Lithographic evaluation was performed on a poly(BH-MDMO-*co*-DNN-*co*-NC-*co*-MA)-based resist using an ArF exposure system (ISI, NA = 0.6). The scanning electron micrograph for the resist, formulated with polymer F, was shown in Fig. 6. The resist patterns of 0.12 μm feature size were resolved at a dose of 10 mJ cm^{-2} using a conventional developer.

4. Conclusion

We designed and synthesized a new type of matrix polymer containing the 7,7-dimethyloxepan-2-one groups as acid labile groups. Infrared spectroscopy investigation confirmed the acid-catalyzed ring-opening reaction of the 7,7-dimethyloxepan-2-one group with the carboxylic acid occurred in the exposed region. The matrix polymer does not release the gaseous byproducts due to the ring-opening reaction during and after exposure, different from other polymers containing *tert*-butyl ester or tetrahydropyranyl ether protecting groups. The resist patterns of 0.12 μm feature size were obtained at a dose of 10 mJ cm^{-2} using an ArF excimer laser stepper and 2.38 wt% TMAH aqueous solution as a developer.

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