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Adhesion Enhancement of Norbornene Polymers with Lithocholate Substituents for 193-nm Resists

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ABSTRACT: Norbornene copolymers having derivatives of lithocholic acid were synthesized as matrix polymers for 193-nm lithography. Norbornene with a succinic acid ester group was introduced into the matrix polymers in order to improve adhesion to a silicon substrate without causing cross-linking during the post-exposure bake process. Dry-etching resistances of the polymers to CF_4-reactive ion etching are comparable to that of poly(4-hydroxystyrene), a typical matrix resin for 248-nm lithography. The resists formulated with the polymers gave 0.15 μm line and space patterns at a dose of 14 mJ/cm^2 using an ArF excimer laser stepper and a standard 2.38 wt% tetramethylammonium hydroxide aqueous solution.

KEY WORDS Lithocholic Acid / 193-nm Resist / Norbornene /

Chemically amplified resists for 193-nm lithography are the most promising materials for sub-100-nm patterns because of their sensitivities.[1,2] Matrix polymers for 193-nm lithography should have good transmittance at 193 nm, good adhesion property, high etch resistance, and also compatibility with a conventional developer. Alicyclic polymers have the necessary transparency and etch resistance, but their incorporation gives rise to poor adhesion to a silicon substrate. Therefore, hydrophilic moiety such as a hydroxyl group should be incorporated in the matrix polymer. However, the matrix polymer containing hydroxyl groups showed foot profiles due to cross-linking during a lithographic process.[3–6] In a negative resist system, acid-catalyzed insolubilization reactions by etherification between hydroxyl groups and esterification reaction between hydroxyl groups and carboxylic acid groups were utilized.[6]

In this paper, we propose a new matrix polymer containing succinic acid 2-(5-norbornene-2-carbonyloxy)-ethyl ester ethyl ester (SNEE) to enhance adhesion to silicon substrate without causing cross-linking during the post-exposure bake process. We expect SNEE can act as an adhesion promoter due to a large number of polar ester groups and have a good shelf life due to the absence of a reactive hydroxyl group. The synthesis, physical properties, and lithographic performance of the newly designed matrix polymer will be discussed.

EXPERIMENTAL

Materials

Dicyclopentadiene, ethyl 4-chloro-4-oxobutyrate, and lithocholic acid were purchased from Aldrich Chemical Company and used without further purification. Maleic anhydride (MA) and 2,2′-azobisisobutyronitrile (AIBN) were purchased from Aldrich Chemical Company and purified by recrystallization from diethyl ether and ethanol, respectively. Triphenylsulfonium trifluoromethanesulfonate (TPSTf),[7] *tert*-butyl lithocholate (TBLC),[8] norbornene-2-carboxylic acid *tert*-butyl lithocholate ester (NCBLC),[9] and 2-hydroxyethyl 5-norbornene-2-carboxylate (HENC)[4,9] were prepared as described in publications.

Synthesis of SNEE

A well-dried 250 mL 3-neck flask fitted with a dropping funnel, a nitrogen gas inlet, and a drying tube filled with anhydrous calcium chloride was charged with 10.0 g (0.055 mol) of HENC, 8.7 g (0.051 mol) of triethylamine, and 200 mL of diethyl ether. The solution was stirred and cooled to 0°C, and 10.0 g (0.061 mol) of ethyl 4-chloro-4-oxobutyrate in 30 mL of diethyl ether was added dropwise through the dropping funnel for 30 min and stirred vigorously. Then the reaction mixture was allowed to warm to room temperature and stirred for 6 h. The salt was removed by filtration and the reaction mixture was purified by column chromatography on

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silica gel with ethyl acetate/n-hexane (1/5) as eluant. The desired fractions were combined and dried at reduced pressure. SNEE was obtained in a yield of 9.7 g (57 %) as colorless liquid. ^{1}H NMR ($CDCl_3$, ppm): 1.19 (3H, t), 1.36 (2H, m), 1.86 (1H, m), 2.59 (4H, s), 2.89 (1H, s), 2.85 (1H, s), 2.93 (2H, m), 3.16 (1H, s), 4.11 (2H, m), 4.22 (4H, m), 5,87 (1H, m, endo-olefinic proton), 6.08 (2H, m, exo-olefinc protons), 6.14 (1H, m, endo-olefinic proton). FT-IR (cm^{-1}): 2975 (alicyclic CH), 1727 (C=O of ester), 1184 (C–O of ester).

Polymerization

The copolymers were synthesized with various monomer feed ratios using 1 mol% AIBN as a radical initiator in dried tetrahydrofuran at 65°C under vacuum in a sealed ampoule for 24 h. After the polymerization, the solution was diluted with tetrahydrofuran and precipitated into a mixed solvent (petroleum ether:diethyl ether = 2:1 by volume ratio). The precipitate was filtered, washed with the precipitating solvent, and dried under reduced pressure.

Adhesion Property

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 the substrate as set forth by Owen's, Young's, and Dupré's equations.

Storage Stability Test

The polymer and 2 wt% TPSTf were dissolved in propylene glycol methyl ether acetate. The resist solution was stored at 26°C in a dark room. After certain period of time, the solution was spin-coated on silicon wafer at 1,500 rpm and then the wafer was prebaked at 110°C for 90 s on a hot plate. The thickness of the resist film was measured.

Lithographic Evaluation

Resist solutions were formulated by dissolving poly(NCBLC-co-HENC-co-MA) or poly(NCBLC-co-SNEE-co-MA), and TPSTf (2 wt%) in propylene glycol methyl ether acetate (PGMEA) and then the solutions were filtered with a 0.2 µm teflon membrane filter. Resists were coated to yield 0.4 µm-thick film on silicon substrates and baked at 100°C for 90 s. Exposure was carried out with an ArF excimer laser stepper (ISI, NA = 0.6) using a conventional illumination method. Exposed resists were baked at 120°C for 90 s on a hot-plate and developed in a 2.38 wt% TMAH aqueous solution for 60 s.

RESULTS AND DISCUSSION

Synthesis of Monomers and Polymers

New hydrophilic monomer, SNEE, was synthesized by esterification reaction as shown in Figure 1. Poly(NCBLC-co-SNEE-co-MA) and poly(NCBLC-co-HENC-co-MA) with various molar feed ratios were obtained using AIBN as a radical initiator and the polymerization results are summarized in Table I. HENC was incorporated as a reference monomer which contains a hydroxyl group. The weight average molecular weights of polymers were 4730–8320 g/mol and the polydispersities were 1.50–1.85. Yields were 32–53 %.

Adhesion Property

The adhesion properties of the polymers were evaluated from the work of adhesion between a resist film and a silicon substrate. The work of adhesion of the polymers[10,11] on silicon substrates (W_{ps}) are summarized in Table I. The value of the polymer increased linearly as the content of SNEE increased (Figure 2). Thus, the succinic acid ester groups played a role in increasing the adhesion property of the resist material.

Etch Resistance

The dry-etching rates of the resist materials were obtained by measuring the time needed for etching the resist film completely during a reactive ion etching process. The dry-etching resistance was determined using an etcher under CF_4 plasma gas. Table II shows the etching rates of the polymers normalized to that of poly(4-hydroxystyrene). The dry-etching resistances of these resists are much better than that of poly(*tert*-butyl methacrylate) (PTBMA) and comparable to that of poly(4-hydroxystyrene).

Storage Stability

Poly(NCBLC-co-HENC-co-MA) showed relatively low storage stability because of the ring opening reaction between electrophilic acid anhydrides and potentially nucleophilic primary alcohols upon storage as a resist solution. The better storage stability is obtained by substituting nucleophilic HENC with SNEE as shown in Figure 3.

Lithographic Evaluation

The scanning electron micrographs of poly(NCBLC-co-HENC-co-MA) and poly(NCBLC-co-SNEE-co-MA) are shown in Figure 3. The resist formulated with poly(NCBLC-co-SNEE-co-MA) gave 0.15 µm line and space patterns (Figure 4b) and foot profile was not observed compared to that of poly(NCBLC-co-HENC-co-MA) (Figure 4a), which

Figure 1. The synthetic scheme of monomers and polymers.

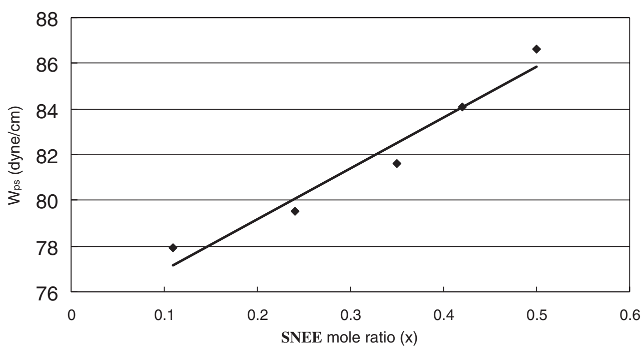


Figure 2. Work of adhesion of poly(NCBLC$_{0.5-x}$-co-SNEE$_x$-co-MA$_{0.5}$) as a function of SNEE content.

showed the foot profile as predicted in our previously published paper.[3] This indicates that the succinic acid ester is a good adhesion promoter without causing cross-linking.

CONCLUSION

The succinic acid ester group was introduced into the matrix polymer in order to improve adhesion on a silicon wafer without causing cross-linking during post-exposure bake. The work of adhesion of the resist increased as the content of SNEE increased. The dry-etch resistances of poly(NCBLC-co-SNEE-co-MA)

Table I. Polymerization results

Polymer	Molar Feed Ratio (NCBLC/HENC/SNEE/MA)	Copolymer Composition (NCBLC/HENC[a]/SNEE[b]/MA)	Mw[c]	MWD[c]	Wps[d]	Yield (%)
A	0.425/0.075/0/0.5	0.38/0.12/0/0.5	4,970	1.50	81.0	33
B	0.4/0.1/0/0.5	0.35/0.15/0/0.5	4,730	1.51	81.5	32
C	0.35/0.15/0/0.5	0.31/0.19/0/0.5	5,160	1.58	82.7	32
D	0.4/0/0.1/0.5	0.39/0/0.11/0.5	7,650	1.81	77.9	48
E	0.3/0/0.2/0.5	0.26/0/0.24/0.5	8,320	1.84	79.5	45
F	0.2/0/0.3/0.5	0.15/0/0.35/0.5.	7,870	1.78	81.6	53
G	0.1/0/0.4/0.5	0.08/0/0.42/0.5	7,540	1.85	84.1	51
H	0/0/0.5/0.5	0/0/0.5/0.5	8,120	1.79	86.6	52

[a] Copolymer composition ratio was determined by integration of the corresponding peaks in the ^{1}H NMR spectra. [b] Copolymer composition ratio was calculated from elemental analysis on the basis of the content of 50 mol% of MA. [c] The weight average molecular weight (Mw) and the molecular weight distribution (MWD) were determined by GPC with polystyrene standards. [d] The work of adhesion values of the polymers were calculated using Owen's, Young's, and Dupré's equations.

Table II. Etching rates of resist materials relative to poly(4-hydroxystyrene)

Material	Etching Rate[a] (Å/s)	Relative Etching Rate
PTBMA	18.5	1.71
Polymer C	12.1	1.12
Polymer E	12.9	1.19
Poly(4-hydroxystyrene)	10.8	1.0

[a] Etching conditions: flow rate of CF_4 gas = 30 sccm; RF power = 100 W; pressure = 200 mTorr.

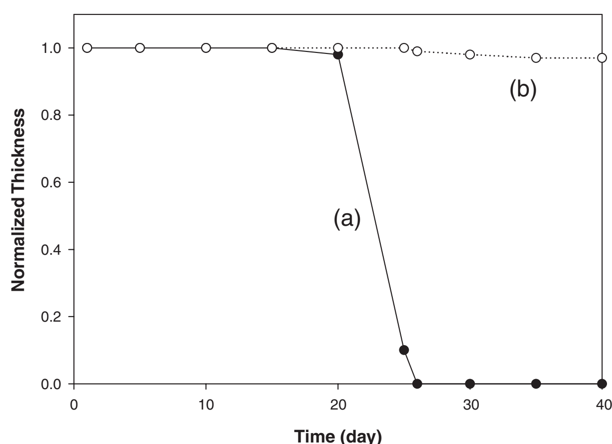
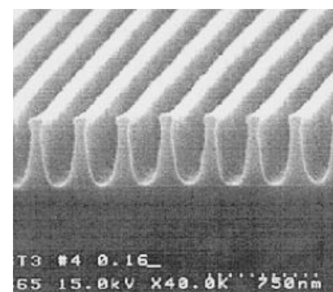
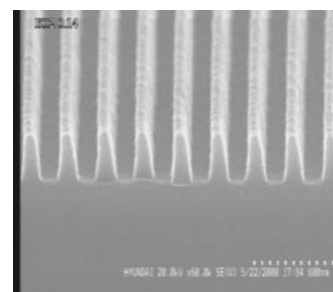


Figure 3. Storage stability of resist solution with poly-($NCBLC_{0.35}$-co-$HENC_{0.15}$-co-$MA_{0.5}$) (a) and poly($NCBLC_{0.3}$-co-$SNEE_{0.2}$-co-$MA_{0.5}$) (b).



(a)



(b)

Figure 4. Scanning electron micrographs of 0.16 µm line and space patterns with poly($NCBLC_{0.35}$-co-$HENC_{0.15}$-co-$MA_{0.5}$) (a) and 0.15 µm line and space patterns with poly($NCBLC_{0.3}$-co-$SNEE_{0.2}$-co-$MA_{0.5}$) (b).

are much better than that of poly(*tert*-butyl methacrylate) (PTBMA) and comparable to that of poly(4-hydroxystyrene). The resist formulated with poly-(NCBLC-co-SNEE-co-MA) gave 0.15 µm line and space patterns without foot profiles.

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