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Adhesion-promoted copolymers based on norbornene derivatives and maleic anhydride for 193-nm photoresists

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Abstract

A copolymer of *t*-butyl 5-norbornene-2-carboxylate, 2-(2-methoxyethoxy)ethyl 5-norbornene-2-carboxylate, norbornene, and maleic anhydride was synthesized as a matrix polymer for ArF excimer laser lithography. Hydrophilic 2-(2-methoxyethoxy)ethyl ester groups are introduced into side chains of the matrix polymer in order to improve adhesion to a silicon substrate without causing cross-linking during a lithographic process. The resist formulated with the polymer shows better adhesion to a silicon substrate as the mole fraction of 2-(2-methoxyethoxy)ethyl 5-norbornene-2-carboxylate increases. 0.15 μm line and space patterns were obtained at a dose of 10.5 mJ cm^{-2} using an ArF excimer laser stepper. © 2000 Published by Elsevier Science Ltd. All rights reserved.

Keywords: ArF excimer laser lithography; Adhesion; Cross-linking

1. Introduction

The technology for 193-nm lithography is developing rapidly to satisfy the requirements that envision printing features of 0.16 μm and below. However, high performance resists suitable for these exposure tools must be designed before they can be put into practical application. 193-nm photoresists should possess optimum range of transparency at 193 nm, high imaging property, and good adhesion property as well as compatibility with a 2.38 wt% tetramethylammonium hydroxide (TMAH) aqueous developer. Unfortunately, the existing phenolic resist absorbs far too much radiation at 193 nm to be useful. New chemistries for 193-nm resists differ completely from those of their predecessors: Alicyclic-based polymers replace phenolic-based polymers and deprotonation of carboxylic acid moieties, rather than phenolic hydroxyl groups, most often serves as the principal mechanism for aqueous base solubility.

The alicyclic polymers have the necessary transparency and etch resistance, but their incorporation gives rise to poor adhesion, cracks in resist film, and lowers resist sensitivity. Therefore, hydrophilic moiety such as a hydroxyl group should be incorporated in the polymer. However, we found that the resist formulated with the polymer containing hydroxyl group showed "foot" profiles, and it is suggested that the hydroxyl group causes cross-linking during a lithographic process [1].

In this study, we introduced 2-(2-methoxyethoxy)ethyl ester groups into side chains of the matrix polymer in order to improve adhesion to a silicon substrate without causing the cross-linking. Synthesis, physical properties, and lithographic performance of the newly designed polymer will be described.

2. Experimental

2.1. Materials

t-Butyl acrylate (TBA) and 2-hydroxyethyl acrylate (HEA) were purchased from Aldrich Chemical Company and purified by vacuum distillation. Dicyclopentadiene, di(ethylene glycol) methyl ether (DEGME), and norbornene (NB) were purchased from Aldrich Chemical Company and used without further purification. Cyclopentadiene (CPD) was prepared by cracking of dicyclopentadiene. Acryloyl chloride and maleic anhydride (MA) were purchased from Aldrich Chemical Company and purified by distillation and crystallization in chloroform, respectively. Triethylamine (TEA) was purchased from Junsei Chemical Company and purified by distillation. 2-Chlorocarbonyl-5-norbornene (CCN) was prepared by Diels–Alder reaction [2–5] of CPD with acryloyl chloride. The reaction product was purified by vacuum distillation. *t*-Butyl 5-norbornene-2-carboxylate

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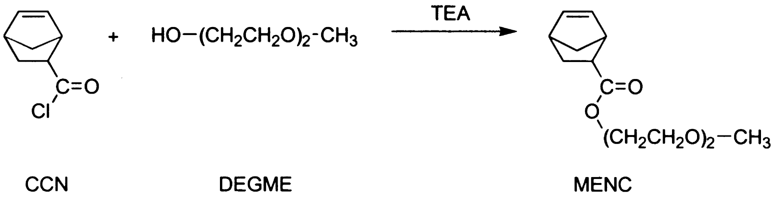

Fig. 1. Synthesis of MENC.

(BNC), 2-hydroxyethyl 5-norbornene-2-carboxylate (HNC) [6], and triphenylsulfonium triflate (TPSTf) [7,8] were prepared by the method described in the literature.

2.2. Measurements

Infrared spectra were recorded on a Bio-Rad FTS-165 FT-IR spectrometer. Proton NMR spectra were obtained with a Bruker AM-300 FT-NMR spectrometer in $CDCl_3$ at 25°C. 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 Carlo Erba. The number-average molecular weight (M_n) and molecular weight distribution (MWD) were determined on a Waters GPC-150C in tetrahydrofuran using a calibration curve of polystyrene standards. 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 Owens and Wendt's [9], Young's [10], and Dupré's equations [11]. The contact angles were calculated from the volumes and the diameters of water and methylene iodide drops [12].

2.3. Synthesis of 2-(2-methoxyethoxy)ethyl 5-norbornene-2-carboxylate (MENC)

A well dried 250 ml three-necked 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 (0.083 mol) of DEGME, 8.4 g (0.083 mol) of TEA, and 200 ml of dry diethyl ether. The solution was stirred and cooled to 0°C, and 13.0 g (0.083 mol) of CCN in 30 ml of dry 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 TEA salt was removed by filtration and the reaction mixture was purified by column chromatography on silica gel with ethyl acetate/*n*-hexane (1/3) as eluent. The desired fractions were combined and dried at reduced pressure. MENC was obtained in a yield of 17.0 g (85.2%) as colourless liquid. ^{1}H NMR ($CDCl_3$, ppm): 1.27 (1H, d), 1.41 (2H, m), 1.82 (1H, m), 2.89 (1H, br. s), 2.98 (1H, m), 3.21 (1H, br. s), 3.37 (3H, s, $-OCH_3$), 3.54 (2H, m, $-CH_2OCH_3$), 3.64 (4H, m, $-CH_2OCH_2-$), 4.18 (2H, m, $-C(O)OCH_2-$), 5.94 (1H, m, olefinic proton), 6.18 (1H, m, olefinic proton). FT-IR (cm^{-1}): 2940 (alicyclic CH), 1735 (C=O of ester).

2.4. Polymerization

All the polymers were synthesized by free radical polymerization in sealed ampoules. Monomers and 1 mol% *N*,*N*′-azobis(isobutyronitrile) (AIBN) were dissolved in tetrahydrofuran, and the resulting mixture was heated at 65°C under vacuum for 30 h. After the polymerization, the solution was diluted with tetrahydrofuran and precipitated into a mixed solvent (petroleum ether:diethyl ether = 5:1 volume ratio). The precipitated polymer was collected by filtration and washed with the precipitating solvent. After drying under vacuum for 6 h, white powdery material was obtained.

2.5. IR spectral study

The polymer and 2 wt% TPSTf were dissolved in propylene glycol methyl ether acetate. The solution was spin-coated on NaCl cells at 2000 rpm and then the cells were prebaked at 110°C for 90 s on a hot plate. The cells were exposed at a dose of 100 mJ cm^{-2}. The exposed cells were baked for 3 min at 110 and 150°C, respectively. FT-IR spectra were measured before exposure, after PEB at 110, and 150°C, respectively.

2.6. Lithographic evaluation

A photoresist solution was prepared by dissolving 4 g of poly(BNC-*co*-MENC-*co*-NB-*co*-MA) and 0.08 g of TPSTf in 32 g of propylene glycol methyl ether acetate. The solution was filtered two times through a 0.2 μm membrane filter. A resist film was prepared by spin coating of the photoresist solution on a 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 110°C for 90 s and developed by dipping in a 2.38 wt% TMAH aqueous solution for 40 s. The cross section profiles were obtained by a Hitachi S-8820 SEM.

3. Results and discussion

3.1. Synthesis of monomers and polymers

New hydrophilic monomer, MENC, was synthesized by esterification as shown in Fig. 1. Poly(BNC-*co*-MENC-*co*-NB-*co*-MA) and poly(BNC-*co*-HNC-*co*-NB-*co*-MA) with

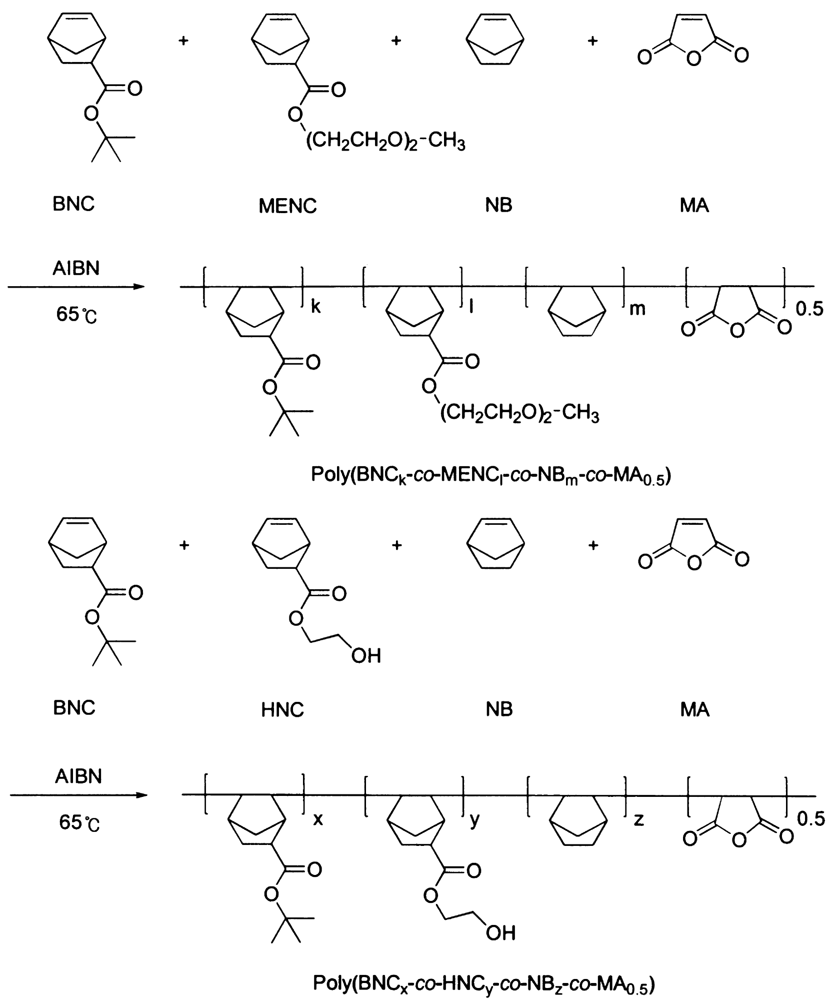

Fig. 2. Synthesis of poly(BNC_k-*co*-$MENC_l$-*co*-NB_m-*co*-$MA_{0.5}$) and poly(BNC_x-*co*-HNC_y-*co*-NB_z-*co*-$MA_{0.5}$).

various molar feed ratios were obtained using 1 mol% AIBN as a radical initiator. The synthetic schemes are shown in Fig. 2. The polymerization results are summarized in Table 1. It is well known that free radical copolymerizations of electron donating norbornene derivatives and electron accepting maleic anhydride produce alternating copolymers [13–17].

Table 1
Polymerization results

Polymer	Molar feed ratio (BNC/MENC/NB/MA)	Copolymer composition[a] (BNC/MENC/NB/MA)	Yield (%)	M_n[b]	MWD[b]
A	50/0/0/50	50/0/0/50	37	4470	1.472
B	20/5/25/50	19.6/4.7/25.7/50	36	4030	1.732
C	20/10/20/50	19.7/9.8/20.5/50	35	4050	1.746
D	20/15/15/50	19.6/14.7/15.7/50	36	4000	1.742
E	20/20/10/50	19.8/19.6/10.6/50	34	4060	1.717
F	20/10[c]/20/50	19.8/9.7[c]/20.5/50	34	4010	1.744
G	17/33[c]/0/50	17.9/32.1[c]/0/50	35	4100	1.620

[a] Copolymer composition calculated from elemental analysis on the basis of the content of MA is 50 mol%.

[b] M_n and MWD were determined by GPC with polystyrene standards.

[c] Polymerization was carried out using HNC instead of MENC.

3.2. Cross-linking study

FT-IR spectra of the resists formulated with poly($BNC_{0.2}$-*co*-$MENC_{0.1}$-*co*-$NB_{0.2}$-*co*-$MA_{0.5}$) and poly($BNC_{0.17}$-*co*-$HNC_{0.33}$-*co*-$MA_{0.5}$) are shown in Fig. 3(a) and (b), respectively. In Fig. 3(a), the band intensity around 3600–2300 cm^{-1} due to carboxyl groups augments as the postexposure bake (PEB) temperature increases from 110 to 150°C. Therefore, more BNC units undergo deprotection reactions at the higher PEB temperature. On the contrary, as shown in Fig. 3(b), the band intensity around 3600–2300 cm^{-1} due to carboxyl and hydroxyl groups decreases as the PEB temperature increases from 110 to 150°C. It indicates that esterification reactions of hydroxyl groups coincide with deprotection reactions of the *t*-butyl groups. The polymer containing hydroxyl groups in the side chains causes cross-linking reactions that make the resist film insoluble in a developer. However, our newly designed polymer

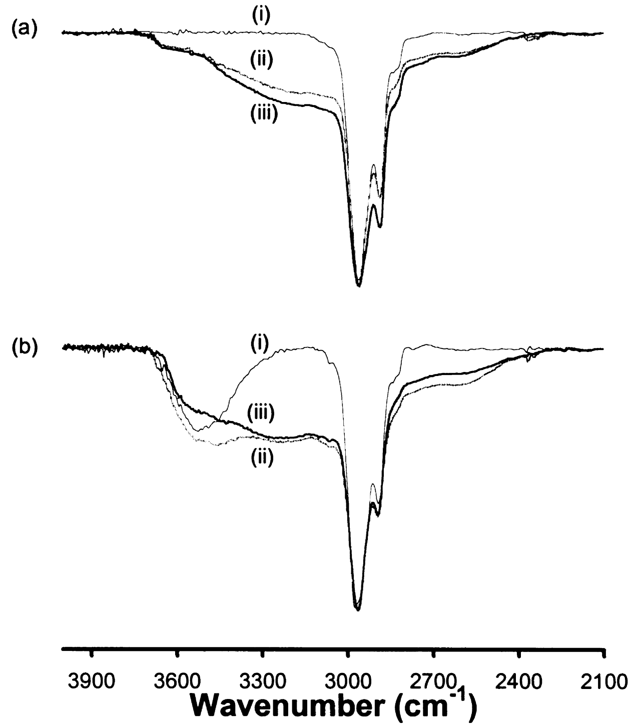

Fig. 3. FT-IR spectra of (a) poly($BNC_{0.2}$-*co*-$MENC_{0.1}$-*co*-$NB_{0.2}$-*co*-$MA_{0.5}$) and (b) poly($BNC_{0.17}$-*co*-$HNC_{0.33}$-*co*-$MA_{0.5}$) before exposure (i), after exposure and PEB at 110°C (ii), and 150°C (iii) for 3 min.

containing 2-(2-methoxyethoxy)ethyl ester groups instead of hydroxyl groups undergo deprotection without cross-linking as shown in Fig. 3(a).

3.3. Adhesion property

The adhesion properties of the polymers were evaluated from the work of adhesion between a polymer film and a silicon substrate primed with hexamethylenedisilasane (HMDS). The contact angles of water and methylene iodide, and the work of adhesion of polymers on silicon substrates (W_{ps}) are summarized in Table 2. The work of adhesion of the resist increases linearly as the content of MENC increases as shown in Fig. 4. Poly($BNC_{0.2}$-*co*-$MENC_{0.2}$-*co*-$NB_{0.1}$-*co*-$MA_{0.5}$) shows similar W_{ps} to that of poly($BNC_{0.2}$-*co*-$HNC_{0.1}$-*co*-$NB_{0.2}$-*co*-$MA_{0.5}$).

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

Polymer	Contact angle (°)		W_{ps}[a] (dyne cm^{-1})
	H_2O	CH_2I_2	
A	80.2	57.2	64.6
B	77.9	53.0	66.7
C	76.4	52.4	68.0
D	74.7	49.0	69.7
E	73.6	47.1	70.7
F	73.5	47.6	71.8
Novolac resist	70.0	44.8	73.5

[a] Work of adhesion of a polymer on a HMDS primed silicon substrate.

3.4. Absorbance at 193 nm

The polymers exhibit good transparency at 193 nm. The absorbance data of the polymer films with and without 2 wt% TPSTf are summarized in Table 3. Based on the absorbance data of the copolymers, it is confirmed that copolymerization with MENC did not increase optical density at 193 nm.

3.5. Lithographic performance

Preliminary lithographic evaluations of the resists formulated with poly(BNC-*co*-MA) using a DUV exposure system showed that features with dimensions below 0.5 μm were lifted off during development. This is due to

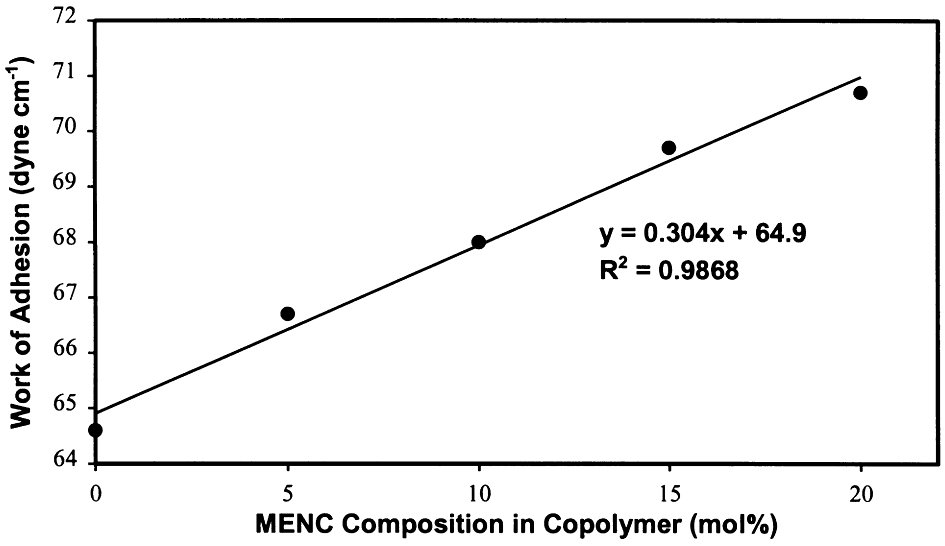

Fig. 4. Work of adhesion of resists as a function of MENC content.

Table 3
UV absorbances of polymers at 193 nm

Polymer	UV absorbance at 193 nm (μm^{-1})	
	Without PAG	With 2 wt% PAG
A	0.44	0.68
B	0.46	0.71
C	0.47	0.73
D	0.49	0.76
E	0.48	0.74
F	0.46	0.72

poor adhesion of the polymer to a silicon substrate. However, the polymers possessing more than 5 mol% of MENC were not peeled off.

As the hydrophilic MENC content increased, dark-erosion was observed since the penetration of hydrophilic TMAH into resists film is promoted. However, the polymers containing less than 15 mol% MENC were not dark-eroded and showed high dissolution contrast.

Lithographic performance of the polymer was evaluated using an ArF exposure system (ISI, NA = 0.6). The scanning electron micrograph of patterns by the resist formulated with poly($BNC_{0.2}$-*co*-$MENC_{0.1}$-*co*-$NB_{0.2}$-*co*-$MA_{0.5}$) are shown in Fig. 5. 0.15 μm line and space patterns with thickness of 0.35 μm are well defined at a dose of 10.5 mJ cm^{-2} using a conventional 2.38 wt% TMAH developer.

4. Conclusion

MENC is introduced into the matrix polymer in order to improve adhesion of a resist on a silicon substrate without causing cross-linking during PEB. The work of adhesion of the resist increases as the content of MENC increases. 0.15 μm line and space patterns were obtained using a resist based on the copolymer containing MENC at a dose of 10.5 mJ cm^{-2} with an ArF excimer laser stepper and the standard developer.

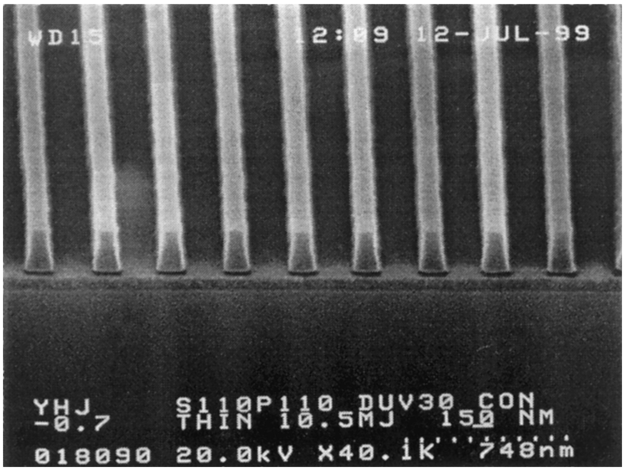

Fig. 5. Scanning electron micrograph of 0.15 μm line and space positive images with poly($BNC_{0.2}$-*co*-$MENC_{0.1}$-*co*-$NB_{0.2}$-*co*-$MA_{0.5}$) at a dose of 10.5 mJ cm^{-2}.

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