Adhesion-promoted copolymers for 193-nm photoresists without cross-linking during lithographic process

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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, and shelf life stability of resist. 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. Sub-0.15 μm line and space patterns were obtained at a dose of 10.5 mJ cm⁻² using an ArF excimer laser stepper.

Keywords: ArF excimer laser lithography, Adhesion, Cross-linking, Shelf life stability

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 have some drawbacks such as severe hydrophobicity causes poor adhesion of resist film to a silicon substrate and unavailability of conventional developer, and severe rigidity causes cracks in resist film, respectively.

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] We also found that the polymer containing hydroxyl moiety shows insufficient shelf life stability.

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 and shelf life stability. 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 used without further purification. Triethylamine (TEA) was purchased from Junsei Chemical Company and purified by distillation. Triethylamine (TEA) was purchased from Junsei Chemical Company and purified by distillation. Triethylamine (TEA) was purchased from Junsei Chemical Company and purified by distillation. Triethylamine (TEA) was purchased from Junsei Chemical Company and purified by distillation. 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. 

2.2. Measurements

Infrared spectra were recorded on a Bio-Rad FTS-165 FT-IR spectrometer. Proton n.m.r. spectra were obtained with a Bruker AM-300 FT-NMR spectrometer in CDCl₃ at 25°C. The number-average molecular weight (Mₙ) and molecular weight distribution (MWD) were determined on a Waters GPC-150C in tetrahydrofuran using a calibration curve of polystyrene standards. The thickness of resist film was measured with a KLA & Tencor α-Step 500 surface profiler.

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 colorless liquid. 1H n.m.r. (CDCl₃, 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, -OCH₃), 3.54 (2H, m, - CH₂OCH₃), 3.64 (4H, m, -CH₂OCH₂), 4.18 (2H, m, -C(O)OCH₂), 5.94 (1H, m, olefinic proton), 6.18 (1H, m, olefinic proton). FTi.r. (cm⁻¹): 2940 (alicyclic CH), 1735 (C=O of ester).

2.4. Polymerization

All of 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. Poly(TBNLC-co-HNC-co-MA) was synthesized by method described in the literature.[10]

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 2,000 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°C and 150°C, respectively. FT-IR spectra were measured before exposure, after PEB at 110°C, and 150°C, respectively.

2.6. Solubility test

The polymer and 2 wt% TPSTf were dissolved in appropriate solvent: propylene glycol methyl ether acetate, 2-methoxy ethyl ether, and cyclohexanone. The solution was spin-coated on silicon wafers at 2,000 rpm and then the wafers were prebaked at 110°C for 90 s on a hot plate. The wafers were exposed at a dose of 100 mJ cm⁻². The exposed wafers were baked for 10 min at 150°C. The resist film was dissolved in tetrahydrofuran.

2.7. Storage for shelf life stability test

The polymer and 2 wt% TPSTf were dissolved in propylene glycol methyl ether acetate. The resist solution was stored at 25°C in a dark room. After certain period of time, the solution was spin-coated on silicon wafer at 2,000 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.

2.8. 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 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. [11-15]

![Fig. 1. Synthesis of MENC.](image1)

![Fig. 2. Synthesis of poly(BNC,co-MENC,co-NB,co-MA) and poly(BNC,co-HNC,co-NB,co-MA).](image2)

<table>
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<th>Table 1. Polymerization results</th>
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$a$ $M_n$ and MWD were determined by GPC with polystyrene standards.

$b$ Polymerization was carried out using HNC instead of MENC.

3.2. Cross-linking study

FT-IR spectra of the resists formulated with poly(BNC,co-MENC,co-NB,co-MA) and poly(BNC,co-HNC,co-NB,co-MA) are shown in Fig. 3(a) and Fig. 3(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°C 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°C 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 containing 2-(2-methoxyethoxy)ethyl ester groups instead of hydroxyl groups undergo deprotection without cross-linking as shown in Fig. 3(a).

### 3.3. Solubility test

Table 2 shows the solubility properties of the resist films formulated with the polymer containing various functional groups after PEB at 150°C for 10 min. The films containing a hydroxyl group were not dissolved in tetrahydrofuran. It is the result of cross-linking reaction of hydroxyl moiety with carboxyl or anhydride.

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<th>Polymer Structure</th>
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3.4. Shelf life

The better storage stability is accomplished by substituting HNC with MENC as shown in Fig. 4.

![Fig. 4. Shelf life stability of resist solution. The resist solution formulated with poly(BNC<sub>0.2</sub>-co-MENC<sub>0.1</sub>-co-NB<sub>0.2</sub>-co-MA<sub>0.5</sub>):C and poly(BNC<sub>0.2</sub>-co-HNC<sub>0.32</sub>-co-MA<sub>0.5</sub>):F](image)
hexamethylenedisilasane (HMDS). The work of adhesion of the resist increases linearly as the content of MENC increases as shown in Fig. 5.

![Work of Adhesion vs. MENC Content](image)

**Fig. 5.** Work of adhesion of resists as a function of MENC content.

3.6. Lithographic performance

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<th>Polymer Structure</th>
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Lithographic performance of the polymer was evaluated using an ArF exposure system (ISI, NA = 0.6). A 0.18 μm line space patterns of poly(TBNLC0.375-co-HNC0.125-co-MA45) was obtained by our group and there are severe foot profiles due to the insoluble layer resulted from the cross-linking of hydroxyl pendant, as shown in Fig. 6(a). On the other hand, 0.14 and 0.15 μm patterns of the resist formulated with poly(BNC0.2-co-MENC0.1-co-NB0.2-co-MA0.5) are well defined at a dose of 10.5 mJ cm\(^{-2}\) using a conventional 2.38 wt% 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. Sub-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. The resist solution of the polymer containing MENC also shows better shelf life stability.

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References
