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Poly(*t*-butyl-3α-(5-norbornene-2-carbonyloxy)-7α,12α-dihydroxy-5β-cholan-24-oate-co-maleic anhydride) for a 193-nm photoresist

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Abstract

A copolymer of *t*-butyl-3α-(5-norbornene-2-carbonyloxy)-7α,12α-dihydroxy-5β-cholan-24-oate and maleic anhydride was synthesized as a matrix polymer for ArF excimer laser lithography. The polymer has an excellent transmittance at 193 nm and possesses good thermal stability up to 255°C. The resist formulated with the polymer showed better dry-etching resistance than the conventional KrF excimer laser resist for chlorine and oxygen mixed gas. A 0.15 μm line and space patterns were obtained at a dose of 18 mJ cm^{-2} using an ArF excimer laser stepper. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: 193-nm photoresist; Norbornene; Dry-etching resistance

1. Introduction

Photolithography using 193-nm (ArF excimer laser) exposure tools is one of the promising technologies for producing patterns below 0.18 μm. However, high performance resists suitable for these exposure tools must be designed before it can be put into practical application. Photoresists (193-nm) should possess high imaging properties and dry-etching resistance, as well as compatibility with 2.38 wt.% tetramethylammonium hydroxide (TMAH) aqueous developer. The main problem in developing such resists is to keep a balance between dry-etching resistance and transparency at 193 nm. Conventional resist materials, for example, novolac resins for g/i-line lithography and poly(hydroxystyrene) for KrF excimer laser lithography, have satisfactory resistance toward plasma etching process. However, they could not be used due to their strong absorption at 193 nm.

Recently, methacrylate copolymers with pendant alicyclic moieties [1–4] and cycloolefin–maleic anhydride copolymers [5–7] have been proposed for their high transparency and good dry-etching resistance. However, there have been difficulties in satisfying both high dry-etching resistance and good requisite material properties for lithographic performance simultaneously. The photoresists having adequate dry-etching resistance with the help of alicyclic units tend to be brittle, poor in adhesion, and seldom dissolve in 2.38 wt.% TMAH developer. On the other hand, the decreased alicyclic units results in improved lithographic performance at the cost of dry-etching resistance.

In this study, we introduced alicyclic groups into both main and side chains of the matrix polymer in order to enhance the dry-etching resistance. Synthesis, physical properties, and lithographic performance of the newly designed polymer are described.

2. Experimental

2.1. Materials

Cholic acid, trifluoroacetic anhydride, and *t*-butyl alcohol were purchased from Aldrich Chemical Company and used without further purification. Acryloyl chloride and maleic anhydride (MA) were purchased from Aldrich Chemical Company and purified by vacuum distillation and crystallized in chloroform, respectively. Triethylamine (TEA) was purchased from Junsei Chemical Company and purified by distillation. 2-Chlorocarbonyl-5-norbornene (CCN) was prepared by the Diels–Alder reaction [8–11] between cyclopentadiene and acryloyl chloride. The reaction product was purified by vacuum distillation. Triphenylsulfonium

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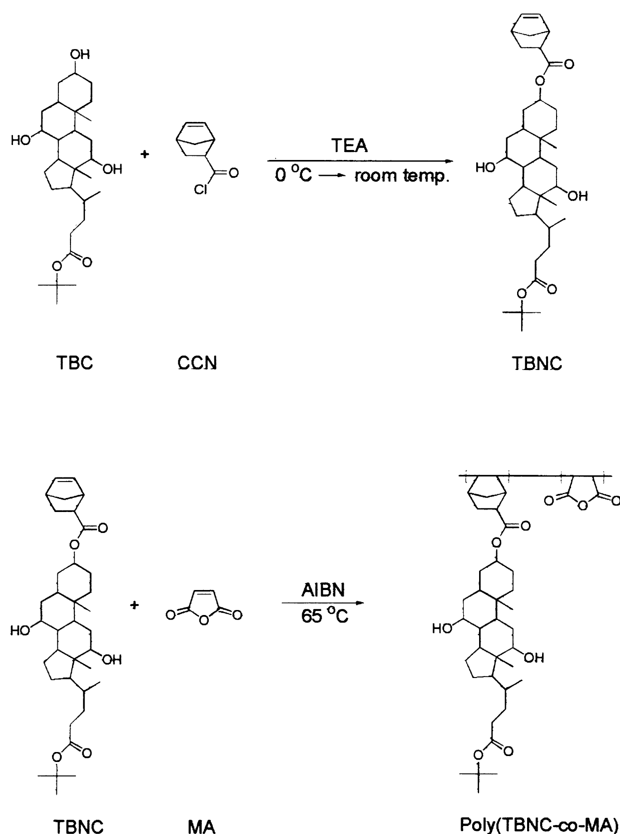

Fig. 1. Synthesis of TBNC and poly(TBNC-co-MA).

triflate (TPSTf) as a photoacid generator (PAG) was prepared by the literature method [12,13].

2.2. Synthesis of t-butyl cholate and t-butyl-3α-(5-norbornene-2-carbonyloxy)-7α,12α-dihydroxy-5β-cholan-24-oate (TBNC)

t-Butyl cholate was synthesized by the method previously reported [14]. TBNC was synthesized as follows. 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 ($CaCl_2$) was charged with 10.0 g (0.022 mol) of *t*-butyl cholate, 3.0 ml (0.021 mol) of TEA, and a stir bar. Then, 200 ml of dry diethyl ether was added under a nitrogen atmosphere. The solution was stirred and cooled to 0°C, and 3.3 g (0.021 mol) of 2-chlorocarbonyl-5-norbornene in 30 ml of dry diethyl ether was added drop-wise 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. TBNC was obtained with a yield of 5.6 g (45%) as a white powder. Elemental analysis, calculated for $C_{36}H_{56}O_6$: C, 73.93; H, 9.65; found: C, 73.87; H, 9.61. ^{1}H NMR ($CDCl_3$, ppm): 0.68 (3H, s, 18-Me), 0.88 (3H, s, 19-Me), 0.96 (3H, d, $J = 6$ Hz, 21-Me), 1.0–2.02 (24H, m), 1.43 (9H, s, *t*-butyl), 2.19 (4H, m), 2.85 (2H, m), 3.16 (1H, m), 3.83 (1H, m, $J = 3$ Hz, 7-H), 3.98 (1H, m, $J = 3$ Hz, 12-H), 4.50 (1H, m, 3-H), 5.89 (1H, m, *endo*-olefinic proton), 6.09 (2H, m, *exo*-olefinc protons), 6.13 (1H, m, *endo*-olefinic proton). FTIR (cm^{-1}): 3484 (OH), 2940 (alicyclic CH), 1728 (C=O of ester), 1152 (C–O of ester).

2.3. Synthesis of poly(TBNC-co-MA)

A copolymer of TBNC and MA was synthesized by free radical solution polymerization in a sealed ampoule. TBNC (5.0 g (8.6 mmol)) and MA (0.84 g (8.6 mmol)) were dissolved in 6.0 g of dry tetrahydrofuran, and 0.028 g (0.17 mmol) of *N,N*-azobisisobutyronitrile (AIBN) was added to this mixture solution as a radical initiator. Polymerization was performed at 65°C for 20 h under a nitrogen atmosphere. After the reaction, the polymer was precipitated twice into a mixed solvent (petroleum ether:diethyl ether, 5:1 volume ratio) and dried at reduced pressure. Poly(TBNC-co-MA) was obtained with a yield of 1.96 g (34%) as a white powder.

2.4. Lithographic evaluation

A photoresist solution was prepared by dissolving 4 g of poly(TBNC-co-MA) and 0.08 g of TPSTf in 24 g of propylene glycol methyl ether acetate. The solution was filtered twice through a 0.2 μm membrane filter prior to the application to the silicon substrate. A resist film was prepared by spin coating of photoresist solution on a hexamethyldisilazane treated silicon wafer and baking at 100°C for 90 s, and exposed at 193 nm with a ISI ArF excimer laser stepper with 0.6 NA. The exposed wafer was baked again at 130°C for 120 s and developed by dipping in 2.38 wt.% TMAH aqueous solution for 40 s. Resist film thickness was measured with an Alpha-Step 500 Profiler (Tencor Instrument). The line-widths were measured on a Hitachi S-800 CD-SEM and cross-section profiles were obtained by a Hitachi S-8820 SEM.

2.5. Evaluation of dry-etching resistance

The dry-etching rates of the polymers were obtained by measuring the thickness of the polymer films before and after the reactive ion etching for chlorine and oxygen mixed gas. The dry-etching rates were measured on a PMT etcher.

2.6. Measurements

Infrared spectra were obtained using a Bruker EQUINOX 55. Proton NMR spectra were obtained using 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 RICO

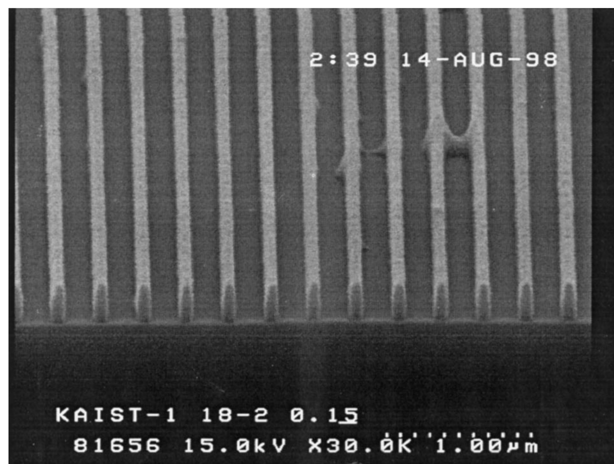

Fig. 2. Scanning electron micrograph of a 0.15 μm line and space patterns with a thickness of 0.35 μm printed with poly(TBNC-co-MA).

CHNS-932. 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 for polystyrene standards. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) data were obtained on a Perkin–Elmer TA 7 series system at a heating rate of 20°C min^{-1}.

3. Results and discussion

A monomer of TBNC and poly(TBNC-co-MA) were synthesized. Proton NMR spectra of *t*-butyl cholate and TBNC showed that TBNC was formed from the reaction between 3α-hydroxyl group of *t*-butyl cholate and 2-chlorocarbonyl-5-norbornene. The synthetic scheme of TBNC and poly(TBNC-co-MA) is shown in Fig. 1. It is well known that free radical copolymerizations of electron donating norbornene derivatives and electron accepting MA produce alternating copolymers [15–19]. TBNC serves three functions for a 193-nm photoresist. *t*-Butoxy carbonyl group of TBNC provide an acid-cleavable function which is responsible for creating a radiation-induced solubility change. The alicyclic ring system and two hydroxyl groups of TBNC provide a dry-etching resistance and adhesion to silicon substrate, respectively.

The M_n and MWD of the polymer were 3500 g mol^{-1} and 1.2, respectively. The glass transition temperature was not detected and the onset decomposition temperature (T_d) was 255°C due to loss of isobutene in the *t*-butoxy carbonyl group. On the other hand, T_d was 98°C in the presence of a photoacid generator. The polymer exhibits excellent transmittance at 193 nm. The absorbances of the polymer and the polymer containing 2 wt.% TPSTf were 0.32 and 0.68 μm^{-1} at 193 nm, respectively.

Table 1
Dry-etching rates of polymers

Polymer	Dry-etching rate[a]
Poly(TBNC-co-MA)	1.39
Poly(hydroxystyrene) (TOK, DP015)	1.43
Novolac resin (JSR, PFI-38)	1.00

[a] Etching conditions: Cl_2 gas = 20 sccm; O_2 gas = 4 sccm; 800 W; 40 s.

Lithographic performance of the polymer was evaluated using an ArF exposure system (ISI, NA = 0.6). The scanning electron micrograph of the line and space patterns for the resist, formulated with poly(TBNC-co-MA) was shown in Fig. 2. A 0.15 μm line and space patterns with a thickness of 0.35 μm are well defined at a dose of 18 mJ cm^{-2} using a conventional developer.

As listed in Table 1, the dry-etching rate of poly(TBNC-co-MA) relative to the novolac resist was 1.39 for chlorine and oxygen mixed gas. This rate was slower than that of the poly(hydroxystyrene) resist. This result shows that poly(TBNC-co-MA) has excellent dry-etching resistance.

4. Conclusion

We have synthesized a new type of matrix polymer which has alicyclic groups in both the main and side chains. A 0.15 μm line and space patterns were obtained at a dose of 18 mJ cm^{-2} using an ArF excimer laser stepper and 2.38 wt.% TMAH aqueous solution as a developer. The dry-etching resistance of this resist was better than that of the poly(hydroxystyrene) resist for chlorine and oxygen mixed gas.

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