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Poly(5-((2-trimethylsilyl-2-propyl)oxycarbonyl)-norbornene-*co*-maleic anhydride) for 193-nm lithography

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Abstract

A copolymer of 5-((2-trimethylsilyl-2-propyl)oxycarbonyl)-norbornene and maleic anhydride) was synthesized and evaluated as a chemically amplified resist for ArF lithography. The polymer has excellent transmittance at 193 nm and possesses good thermal stability up to 195°C, whereas in the presence of an acid the cleavage of the 2-trimethylsilyl-2-propyl ester group begins at 76°C in a catalytic manner. The 0.18 μm line and space patterns were obtained at a dose of 10 mJ cm^{-2} using an ArF excimer laser stepper. © 2000 Published by Elsevier Science Ltd. All rights reserved.

Keywords: 193-nm photoresist; Norbornene; Silicon-containing polymer

1. Introduction

Explosive growth in microelectronic device industry has been supported by microlithography and photoresist technologies. Optical lithography will continue to be the dominant technique for the mass fabrication of the advanced semiconductor devices. It is widely believed that ArF excimer laser lithography is the most promising candidate for the future microelectronics fabrication [1,2]. Polyhydroxystyrene derivatives, which are typically used for 248-nm photoresists, are incapable for 193-nm resists because of their strong absorbance at 193 nm.

Recently, methacrylate copolymers with pendant alicyclic groups [3–6] and cycloolefin–maleic anhydride copolymers [7–9] have been proposed for their high transparency and good dry-etching resistance. The acid labile protecting groups of the matrix polymer for chemically amplified resists (CARs) are various [10]. *t*-Butyl ester, tetrahydropyranyl ether, and tetrahydrofuranyl ether are well-known protecting groups of the matrix polymers for 193-nm CARs. Previously, we reported new silicon-containing methacrylate polymers bearing an acid labile side group, 2-trimethylsilyl-2-propyl (TMSP) ester, for a dry-developable CAR [11–13]. Upon exposure and post-exposure bake (PEB), the silicon-containing protecting groups were easily removed. Therefore, the resist could be developed by a conventional 2.38 wt.% tetramethylammonium hydroxide (TMAH) developer and be also dry-developed utilizing the silicon content difference between the exposed and unexposed regions. However, poly(2-trimethylsilyl-2-propyl methacrylate) is expected to be poor in dry-etching resistance since it does not contain alicyclic groups.

In this paper, a new cycloolefin–maleic anhydride copolymer, poly(5-((2-trimethylsilyl-2-propyl)oxycarbonyl)-norbornene-*co*-maleic anhydride) (poly(TMSPN-*co*-MA)), was synthesized in order to improve dry-etching resistance and thermal stability and the physical properties and lithographic performance were evaluated.

2. Experimental

2.1. Materials

Acryloyl chloride was purchased from Aldrich Chemical Company and used without further purification. Maleic anhydride (MA) was purchased from Aldrich Chemical Company and purified by crystallization in benzene. 2-Chlorocarbonyl-5-norbornene (CCN) was prepared via Diels–Alder reaction [14–17] 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 (TPSTf) as a photoacid generator (PAG) was prepared by the literature methods [18,19].

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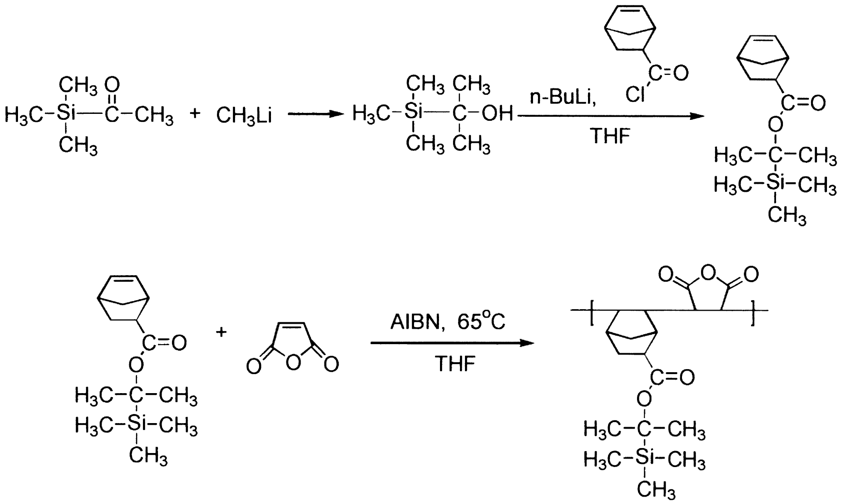

Fig. 1. Synthesis of TMSPN and poly(TMSPN-*co*-MA).

2.2. Measurements

Proton n.m.r. spectra were obtained using a Bruker AM-300 FT-NMR spectrometer in $CDCl_3$. 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. The number-average molecular weight (M_n) and molecular weight distribution (MWD) were determined in tetrahydrofuran (THF) by a Waters GPC-150C calibrated with polystyrene standards. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) data were obtained on a Perkin–Elmer TA 7 series thermal system. TGA and DSC measurements were made at heating rates of 10 and 20°C/min, respectively.

2.3. Synthesis of 5-((2-trimethylsilyl-2-propyl)oxycarbonyl)-norbornene (TMSPN)

2-Trimethylsilyl-2-propyl alcohol was synthesized by the method of the previously reported paper [11]. To a solution of 25 g (0.2 mol) of 2-trimethylsilyl-2-propyl alcohol in 200 ml tetrahydrofuran was added 110 ml (0.22 mol) of *n*-butyllithium (1.5 M) at 0°C, and the reaction mixture was allowed to warm to room temperature. After being stirred for 30 min, it was cooled again to 0°C. 2-Chlorocarbonyl-5-norbornene (36 g, 0.22 mol) was added slowly 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 reaction solvent was removed in a rotary evaporator. After diethyl ether and aqueous saturated sodium bicarbonate solution were added, the ethereal layer was separated. The organic layer 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. TMSPN was obtained in a yield of 38.4 g (76%). b.p. 58°C (0.02 mmHg). ^1H NMR ($CDCl_3$, ppm): 0.06 (9H, s, $Si(CH_3)_3$), 0.14 (6H, s, $O–C(CH_3)_2$–Si), 1.2–2.0 (4H, m), 2.7–3.3 (3H, m), 5.89–6.13 (2H, m, endo-olefinic proton, exo-olefinc proton). FTIR (cm^{-1}): 2940 (alicyclic CH), 1721 (C = O of ester), 842 ($Si(CH_3)_3$).

2.4. Preparation of poly(TMSPN-co-MA)

A copolymer of TMSPN and maleic anhydride was synthesized by free radical polymerization in a sealed ampoule. TMSPN (2.57 g, 10 mmol) and 1.0 g (10 mmol) of maleic anhydride were dissolved in 3.5 g of dry tetrahydrofuran and 0.033 g (0.20 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 polymerization, the solution was diluted with tetrahydrofuran and precipitated into a mixed solvent of petroleum ether and diethyl ether. The precipitated polymer was collected by filtration and washed with the precipitating solvent. After drying under

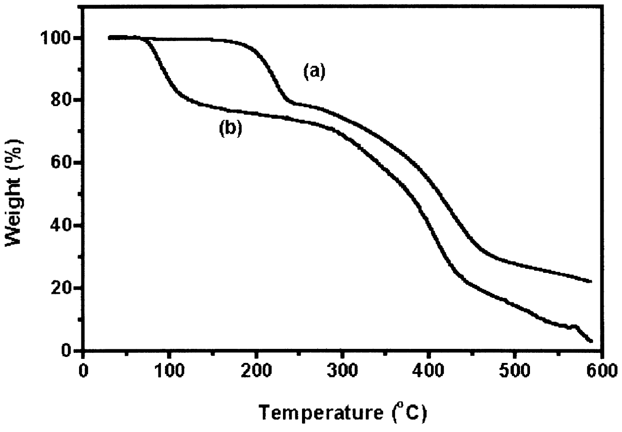

Fig. 2. Comparison of t.g.a. thermograms of poly(TMSPN-*co*-MA) containing 2.0 wt.% TPSTf before (a) and after (b) UV exposure of 10 mJ cm^{-2}.

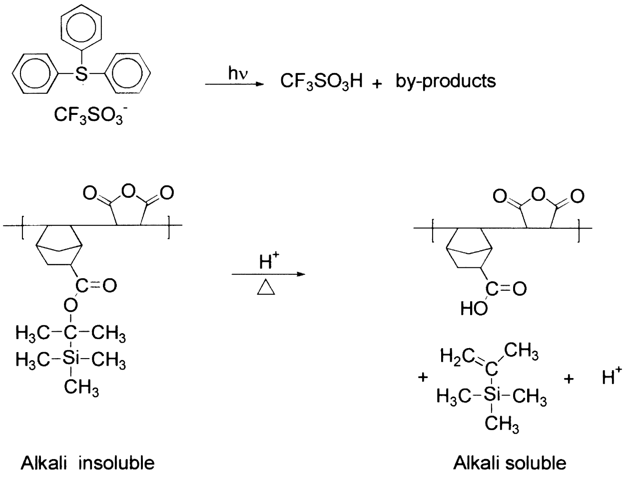

Fig. 3. Acid-catalyzed deprotection of poly(TMSPN-*co*-MA).

vacuum for 24 h, poly(TMSPN-*co*-MA) was obtained in a yield of 1.07 g (30%) as a white powder.

2.5. Lithographic evaluation

A photoresist solution was prepared by dissolving 2 g of poly(TMSPN-*co*-MA) and 0.04 g of TPSTf in 14 g of propylene glycol methyl ether acetate (PGMEA). The solution was filtered twice through 0.2 μm membrane filter prior to application to silicon substrate. A resist film was prepared by spin coating of the photoresist solution on a hexamethyldisilazane treated silicon wafer and baking at 140°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 an aqueous 2.38 wt.% tetramethylammonium hydroxide solution for 60 s. Resist film thickness was measured with an Alpha-Step 500 Profiler (Tencor Instrument). The linewidths were measured on a Hitachi S-800 CD-SEM and cross-section profiles were obtained by a Hitachi S-8820 SEM.

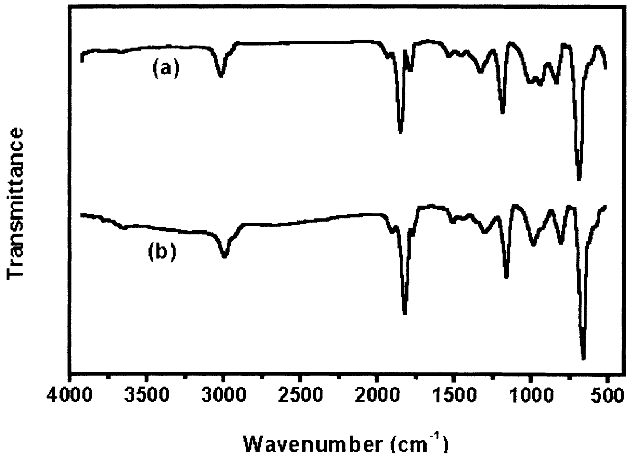

Fig. 4. IR spectral change of poly(TMSPN-*co*-MA) before (a) and after (b) acidolysis with post-exposure bake at 120°C for 90 s.

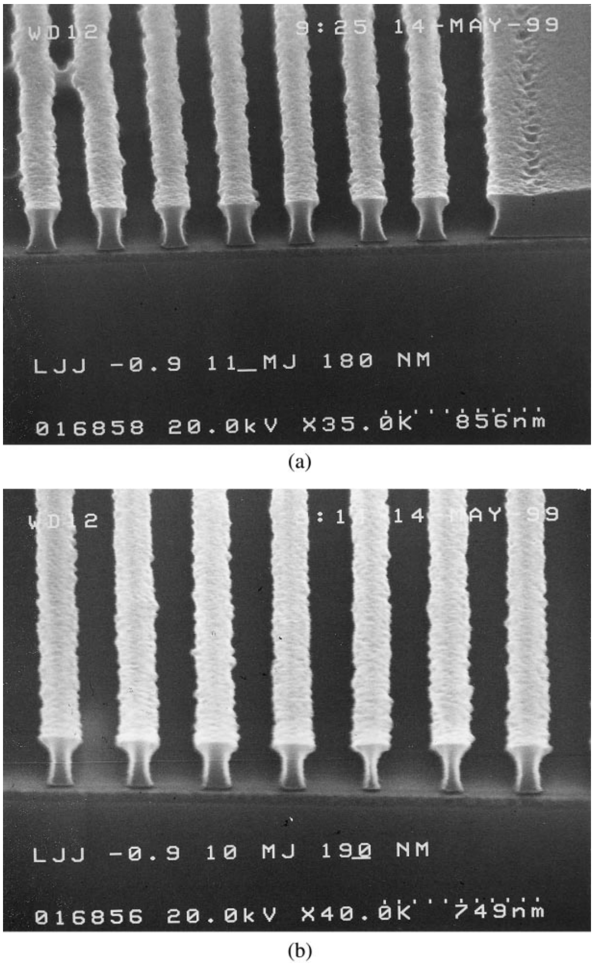

Fig. 5. SEM image of (a) 0.18 μm and (b) 0.19 μm line and space patterns printed with poly(TMSPN-*co*-MA) using an ArF excimer laser system (ISI, NA = 0.6) at 10 mJ cm^{-2}.

3. Results and discussion

The synthetic route of TMSPN and poly(TMSPN-*co*-MA) is shown in Fig. 1. 2-Trimethylsilyl-2-propanol was prepared by reacting acethyltrimethylsilane with methyl lithium. The monomer, TMSPN, was formed from the reaction between 2-trimethylsilyl-2-propanol and 2-chlorocarbonyl-5-norbornene. The number average molecular weight and polydispersity of the poly(TMSPN-*co*-MA) were 6700 g mol^{-1} and 1.58, respectively. The glass transition temperature was not detected up to the decomposition temperature of the polymer in the DSC thermogram. TGA thermograms show that the onset decomposition temperatures are 195°C in the absence of the photogenerated acid (Fig. 2a) and 76°C in the presence of the acid (Fig. 2b). The weight loss in the first decomposition temperature takes place due to evolution of 2,2,3-trimethyl-2-silabut-3-ene resulting from thermolysis of 2-trimethylsilyl-2-propyl groups of the polymer shown in Fig. 3. The cleavage reaction was confirmed by FTIR. Fig. 4 shows that the cleavage reaction results in the disapperance of the 2-trimethylsilyl-2-propyl group and the formation of the carboxylic group in the polymer. The Si–C stretching band at 840 cm^{-1} and the C–O–C band of TMSPN unit at 1110 cm^{-1} disappear, the carboxylic O–H stretching band appears at 3000–3400 cm^{-1}, and the C=O stretching band shifts from 1720 to 1703 cm^{-1} after exposure (dose = 10 mJ cm^{-2}) and post-exposure bake. The polymer exhibits relatively good transmittance and the absorbance of the polymer was 0.368 μm^{-1} at 193 nm. Therefore it can be used in resists for ArF excimer laser lithography.

Evaluation was performed on the poly(TMSPN-*co*-MA)-based resist. The sensitivity of the resist was 10 mJ cm^{-2} with PEB at 120°C for 90 s. Patterns of 0.18 μm line and space were resolved by the ArF excimer laser stepper using a conventional developer (Fig. 5). As the polymer contains silicon, we expect that the resist is applicable to the imaging layer of the conventional bilayer resist system.

Lithographic evaluation of this polymer as a dry-developable resist system is in progress, and the results will be published.

Acknowledgements

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