193-nm Photoresists Based on Norbornene Copolymers with Derivatives of Bile Acid

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We synthesized new chemically amplified photoresists for 193-nm lithography. Norbornene substituted with a derivative of bile acid was copolymerized with maleic anhydride by free radical polymerization. The resulting copolymers have good transmittance at 193 nm and possess excellent thermal stability up to 260 °C. With the standard developer, the resists formulated with the copolymers form 0.15–0.18 μm patterns at doses of 6–7 mJ cm^{-2} using an ArF excimer laser stepper.

In 1992, Fujitsu's researchers first proposed an alicyclic incorporated polymer, "alicyclic polymer", realizing both high transparency at 193 nm and good dry-etching resistance of the resist.[1a] Since then, chemically amplified photoresists which have been designed for 193-nm lithography almost involve methacrylate-based polymers with pendant alicyclic moieties[1–5] and cycloolefin-maleic anhydride copolymers.[6–8] However, there have been difficulties in satisfying both high dry-etching resistance and good lithographic performance such as adhesion and resolution.

Previously we reported a norbornene copolymer with a derivative of cholic acid, poly(*t*-butyl 3α-(5-norbornene-2-carbonyloxy)-7α,12α-dihydroxy-5β-cholan-24-oate-co-maleic anhydride) (poly(TBNDHC-co-MA)), for 193-nm lithography.[9] Poly(TBNDHC-co-MA) had high transparency at 193 nm and showed better dry-etching resistance than the conventional KrF excimer laser resist for chlorine and oxygen mixed gas. The PMT etcher was used with flow rates of 20 sccm of chlorine and 4 sccm of oxygen at 800 W for 40 s. The resist formulated with poly(TBNDHC-co-MA) resolved 0.15 μm line and space patterns, but the patterns exhibited top-rounding profiles (Figure 1). The top-rounding is mainly caused by dark erosion due to dissolution of the unexposed resist in a developing solution. To improve the pattern profiles, the matrix polymer needs to be less hydrophilic than poly(TBNDHC-co-MA) while satisfying adhesion to silicon substrate.

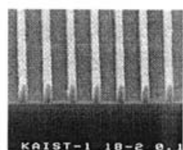

Figure 1. Scanning electron micrograph of 0.15 μm line and space patterns with poly(TBNDHC-co-MA).

We synthesized norbornene monomer with a derivative of lithocholic acid, *t*-butyl 3α-(5-norbornene-2-carbonyloxy)-5β-cholan-24-oate (TBNC). As TBNC does not have a hydroxyl group, it is less hydrophilic than TBNDHC which has two secondary hydroxyl groups. TBNC[10] was synthesized by one-step esterification of *t*-butyl lithocholate (TBLC) with 2-chlorocarbonyl-5-norbornene (CCN) in the presence of triethylamine. TBLC was synthesized by the method reported in the literature.[11] CCN was prepared by Diels-Alder reaction between cyclopentadiene and acryloyl chloride. As TBNC does not have any functional groups providing adhesion to silicon substrate, TBNC was copolymerized[12] with MA and 2-hydroxyethyl 5-norbornene-2-carboxylate (HENC) which has a primary hydroxyl group. HENC was synthesized by the method described in the literature.[13] The copolymer was synthesized by free radical polymerization using 2,2'-azobisisobutyronitrile (AIBN) as an initiator.[14] The chemical structure of the resulting copolymer is shown in Figure 2.

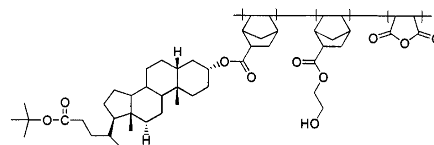

Figure 2. The chemical structure of poly(TBNC-co-HENC-co-MA).

A photoresist solution was prepared by dissolving 1.2 g of the copolymer and 0.024 g of triphenylsulfonium triflate as a photoacid generator in 6.0 g of propylene glycol monomethyl ether acetate (PGMEA). The photoresist solution was spin-coated on a hexamethyldisilazane treated silicon wafer and prebaked 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 illumination was off-axis and the mask was binary. The wafer was baked at 110 °C for 90 s and developed by dipping in a 0.262 M tetramethylammonium hydroxide aqueous solution. The resist formulated with the copolymer gave patterns of flat tops as expected. However, 0.18 μm patterns exhibited footing (Figure 3 (a)). Furthermore, 0.16 μm patterns were not separated completely due to severe footing in the exposure area (Figure 3 (b)).

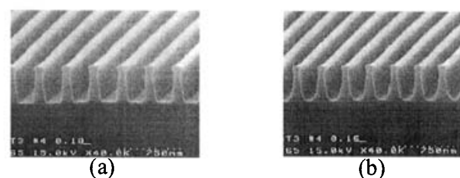

Figure 3. Scanning electron micrographs of 0.18 μm (a) and 0.16 μm (b) features with a thickness of 0.5 μm printed with poly(TBNC-co-HENC-co-MA) at a dose of 6 mJ cm^{-2}.

To investigate the cause of footing, the photoresist solution was spin-coated on NaCl cells and then the cells were prebaked at 110 °C for 90 s. The cells were exposed at a dose of 50 mJ cm^{-2} using a deep UV exposure tool. The exposed cells were

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baked for 90 s at 100 °C, 110 °C, and 130 °C, respectively. FT-IR spectra were measured before exposure, after postexposure bake (PEB) at 100 °C, 110 °C, and 130 °C, respectively (Figure 4). In Figure 4, the band intensity around 3700–2500 cm^{-1} due to carboxyl and hydroxyl groups decreases as the PEB temperature increases from 110 °C to 130 °C. It indicates that esterification reactions of primary hydroxyl groups with carboxyl groups generated from deprotection reactions of *t*-butoxycarbonyl groups occur as the PEB temperature increases from 110 °C to 130 °C. From the result of the change of FT-IR spectra on PEB temperature, it was thought that footing was caused by cross-linking reaction due to primary hydroxyl groups of HENC. Meanwhile, no sign of esterification reaction between secondary hydroxyl group in TBNHC and carboxyl groups was detected up to 130 °C under the same condition described above.

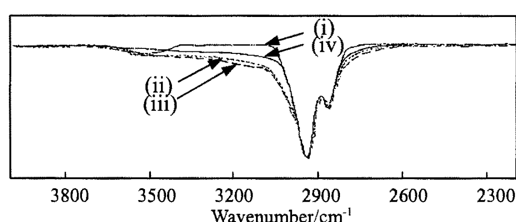

Figure 4. FT-IR spectra of poly(TBNC-co-HENC-co-MAN) before exposure (i), post-exposure-baked at 100 °C (ii), 110 °C (iii), and 130 °C (iv).

In order to improve pattern profiles, we synthesized *t*-butyl 3α-(5-norbornene-2-carbonyloxy)-12α-hydroxy-5β-cholan-24-oate (TBNHC) which has intermediate hydrophilicity between TBNDHC and TBNC, by one-step esterification of *t*-butyl deoxycholate (TBDC) with CCN in the presence of triethylamine.[15] TBDC was synthesized by the method described in the literature.[11] Poly(TBNHC-co-MA) was synthesized by free radical polymerization using AIBN as an initiator.[16] The chemical structure of the resulting copolymer is shown in Figure 5.

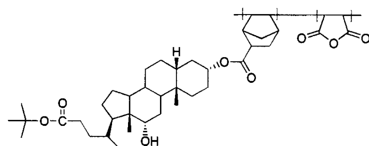

Figure 5. The chemical structure of poly(TBNHC-co-MA).

Photoresist solution was prepared in the same way as for the poly(TBNC-co-HENC-co-MA). Lithographic evaluation was also performed using the same procedure as for the poly(TBNC-co-HENC-co-MA). The resist formulated with poly(TBNHC-co-MA), 0.15 μm line and space patterns are well defined with flat tops and without footing (Figure 6).

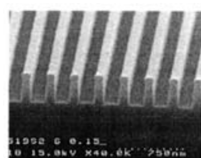

Figure 6. Scanning electron micrograph of 0.15 μm line and space patterns with a thickness of 0.38 μm printed with poly(TBNHC-co-MA) at a dose of 7 mJ cm^{-2}.

In conclusion, it was found that the degree of hydrophilicity of a matrix polymer affected the shape of patterns. Besides, type of hydroxyl group used to enhance adhesion to silicon substrate had decisive influence on resolution of the patterns.

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10 TBNC was obtained in a yield of 75% as a white powder. ^{1}H-NMR ($CDCl_3$, 300 MHz, TMS): 0.69 (3H, s, 18-methyl), 0.89 (3H, s, 19-methyl), 0.97 (3H, d, *J* = 6 Hz, 21-methyl), 1.01–2.02 (26H, m), 1.43 (9H, s, *t*-butyl), 2.19 (4H, m), 2.85 (2H, m), 3.16 (1H, m), 4.50 (1H, m, 3-H), 5.91 (1H, m, *endo*-olefinic proton), 6.11 (2H, m, *exo*-olefinc protons), 6.15 (1H, m, *endo*-olefinic proton). FT-IR (cm^{-1}): 3492 (OH), 2942 (alicyclic CH), 1729 (C=O of ester), 1151 (C-O of ester).
11 F. M. Houlihan, T. I. Wallow, O. Nalamasu, and E. Reichmanis, *Macromolecules*, **30** (21), 6517 (1997).
12 Feed ratio of the monomers is TBNC : HENC : MA = 42.5 : 7.5 : 50 (mol%). Poly(TBNC-co-HENC-co-MA) was obtained in a yield of 32% as a white powder. The M_w and MWD were 4970 g mol^{-1} and 1.5, respectively. The T_d was 261.1 °C and T_g was not detected. The absorbance of the polymer was 0.30 $μm^{-1}$ at 193 nm. Copolymers having feed ratio less than 7.5 mol% HENC cannot be used for lithographic evaluation due to loss of adhesion to silicon substrate.
13 J. C. Jung, M. H. Jung, and K. H. Baik, *J. Photopolym. Sci. Technol*., **11**, 481 (1997).
14 Polymerization was carried out in dry toluene using 1.0 mol% of AIBN at 65 °C under vacuum in a sealed ampoule for 20 h.
15 TBNHC was obtained in a yield of 72% as a white powder. ^{1}H-NMR ($CDCl_3$, 300 MHz, TMS): δ = 0.67 (3H, s, 18-methyl), 0.89 (3H, s, 19-methyl), 0.98 (3H, d, *J* = 6 Hz, 21-methyl), 1.02–2.03 (25H, m), 1.43 (9H, s, *t*-butyl), 2.19 (4H, m), 2.85 (2H, m), 3.16 (1H, m), 3.99 (1H, m, *J* = 3 Hz, 12-H), 4.51 (1H, m, 3-H), 5.92 (1H, m, *endo*-olefinic proton), 6.09 (2H, m, *exo*-olefinc protons), 6.14 (1H, m, *endo*-olefinic proton). FT-IR (cm^{-1}): 3488 (OH), 2943 (alicyclic CH), 1730 (C=O of ester), 1154 (C-O of ester).
16 Polymerization was carried out in dry THF using 1.0 mol% of AIBN at 65 °C under vacuum in a sealed ampoule for 20 h. Feed ratio of the monomers is TBNHC : MA = 50 : 50 (mol%). Poly(TBNHC-co-MA) was obtained in a yield of 31% as a white powder. The M_w and MWD were 5160 g mol^{-1} and 1.6, respectively. The T_d was 259.4 °C and T_g was not detected. The absorbance of the polymer was 0.31 $μm^{-1}$ at 193 nm.