A Novel Photoresist Based on Polymeric Acid Amplifiers

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Positive-working photopolymers substituted with acid amplifying units exhibiting enhanced photosensitivity are described.

Highly sensitive photopatternable polymer systems based on the concept of “chemical amplification” have been of great importance in electronics and coating industries.[1] The high sensitivity of chemical amplified photoresists (CAPs) stems from chemical transformation of the polymer systems catalyzed by acidic or basic species generated photochemically. On the other hand, we reported the concept of acid proliferation reactions consisting of autocatalytic acidolysis of “acid amplifiers”, which display autocatalytic decompositions catalyzed by a photogenerated strong acid to give newly generated sulfonic acids. Acid proliferation-type photoresists have been formulated by addition of the acid amplifiers to CAPs to enhance resist performances including photosensitivity.[2–7] Acid amplifiers developed so far are acetoacetate drivatives,[2] β-sulfonyloxyacetals,[3] 1,2-diol monosulfonates,[4] a trioxane derivative[5] and benzyl sulfonates.[6] Among them, 1,2-diol monosulfonates have been formulated to give acid proliferation photoresists applicable to the next generation photolithography.[4b,7] While the addition of these acid amplifiers enhances the photosensitivity, improvement of resolution powers of the photoresists has been required.[4a,4d] Taking notice of the facts that the resolution power of this type of photoresists is critically determined by diffusion of catalytic acidic molecules in resist films, we focused our attention on whether photosensitivity enhancement can be induced even when acid amplifier molecules are attached covalently to polymer backbones. We report here that this is the case.

We reported previously that pinanediol monosulfonates exhibit excellent thermostability in the absence of acidic species and suffer from acid-catalyzed rearrangement similar to pinacol rearrangement to release the corresponding sulfonic acid efficiently.[4c,7] It followed that 2-hydroxy-3-pinanyl *p*-styrenesulfonate (PSS)[8] **1** as a monomeric acid amplifier was synthesized by the esterification of (1*S*, 2*S*, 3*R*, 5*S*)-(+)-pinanediol with *p*-styrenesulfonyl chloride in the presence of triethylamine and 4-(dimethylamino)pyridine. Autocatalytic acidolysis behavior of **1** was followed by ^{1}H NMR spectra measurements of its chloroform-d_1 solution heated at 100 °C. It was observed that the quartet peak due to methine proton of the pinanyl units at δ = 4.89 ppm decreased, while new peaks at 2.1–2.3 ppm probably due to ketone derivative(s) appeared. Figure 1 shows time courses of the consumption of **1** in chloroform-d_1 at 100 °C. The appearance of this kind of a sigmoidal time course supports that the acidolysis proceeds autocatalytically to result in the proliferation of the acid. FT-IR spectroscopy was also conducted to monitor the ketone band of rearranged product(s) at around 1700 cm^{-1} to confirm the above solution.

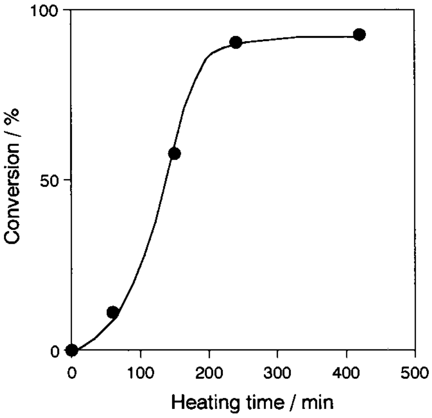

Figure 1. Time course of the consumption of **1** in chloroform-d_1 at 100 °C.

A homopolymer with the acid amplifying side chains **2** was synthesized by free radical copolymerization of in dry tetrahydrofuran using 2,2'-azobisisobutyronitrile (AIBN) as an initiator.[9] The acidolysis reaction of **2** was examined for a film doped with 5 wt% of diphenyl-(4-phenylthiophenyl)sulfonium hexafluoroantimonate (DTS) as a photoacid generator cast on a silicon wafer by means of FT-IR spectroscopy. The film was exposed to a 200-W Hg–Xe lamp of a 10 mJ·cm^{-2} dose and subsequently subjected to post-exposure bake (PEB) at 100 °C. The $\nu_{S=O}$ asymmetric band at 1360 cm^{-1} of the sulfonate was reduced while two sharp peaks at 1034 and 1006 cm^{-1} due to the $\nu_{S=O}$ symmetric band of the sulfonic acid appeared. As shown in Figure 2, changes of the intensity of these bands as a function of PEB time form sigmoidal curves, supporting the occurrence of non-linear acidolysis in a polymer film.

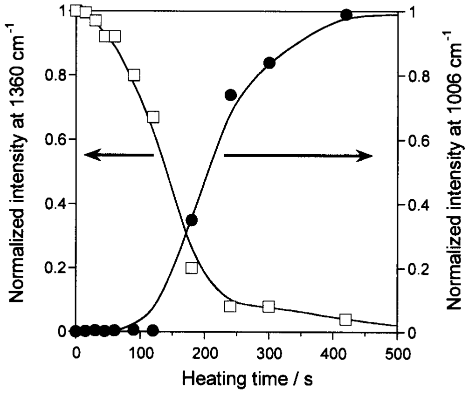

Figure 2. Time course of the consumption of the sulfonate of **2** (□) and the formation of the corresponding sulfonic acid (●) in resist films containing 5 wt% of DTS as a photoacid generator after exposure to 313 nm of a 10 mJ·cm^{-2} dose and subsequent post-exposure baking at 100 ℃.

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Sensitivity determination of the homopolymer **2** was conducted as follows. A solution of 0.1 g of **2** and 0.01 g of DTS as a photoacid generator in 1.0 g of cyclohexanone was spin-coated on a silicon wafer and prebaked at 100 °C for 60 s. Spin-cast films were exposed to 313 nm light from the Hg–Xe lamp through a bandpass filter, followed by PEB at 100 °C for 90 s. Subsequently, the wafer was dipped in a 2.5 wt% tetramethylammonium hydroxide (TMAH) aqueous solution and rinsed with water for 20 s. It was unexpectedly found that no thorough removal of a photoirradiated resist film is performed under the development conditions even though the cleavage of the acid amplifying residues occurred to give sulfonic side chains as revealed by the FT-IR spectra. This was probably because of the effect of the rearranged ketone product(s), which may act as a dissolution inhibitor.

Consequently, copolymers of **1** with *tert*-butyl methacrylate (tBMA) were prepared under the anticipation that the inhibitory effect of the rearranged product(s) on the solubility in alkaline solution is reduced to give positive-working photoresists according to the reaction scheme shown in Figure 3.[10] It was confirmed that the reduction of fractions of **1** in the copolymers results in thorough dissolution of their films after the photoirradiation and PEB. Figure 4 shows the sensitivity curve of a 10 : 90 copolymer of **1** and tBMA (poly(PSS_{10}-*co*-$tBMA_{90}$)) sensitized with DTS as an example. For comparison, the photosensitivity curve for tBMA homopolymer (ptBMA)[4c] in the presence of DTS is also shown in the Figure. The sensitivity of positive-working photoresists is defined as a minimum exposure dose required for thorough removal of resist films after development. As estimated by the sensitivity curve, poly(PSS_{10}-*co*-$tBMA_{90}$) exhibited higher photosensitivity of about 2 mJ·cm^{-2} when compared with ptBMA.

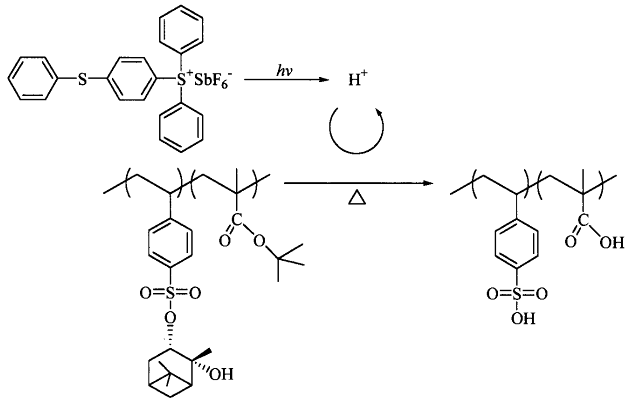

Figure 3. Acid proliferation reaction of a polymeric acid amplifier.

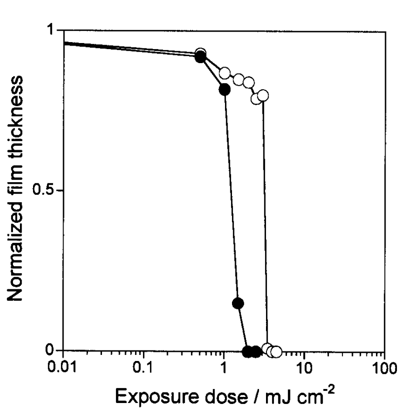

Figure 4. Photosensitivity curves of films of ptBMA (○) and poly(PSS_{10}-*co*-$tBMA_{90}$) (●), respectively, in the presence of 5 wt% of DTS as a photoacid generator.

In summary, we developed novel positive-working polymers with acid amplifying side chains exhibiting enhanced photosensitivity. Since the acid groups are fixed by covalent bonding to backbone polymers to suppress the mobility of acidic groups, the improvement of resolution power may be achieved. Evaluation of resist performances of this type of the copolymers is in progress.

References and Notes

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8 PSS was obtained in a yield of 48% as a yellowish syrup. ^1H NMR ($CDCl_3$, 200 MHz, TMS): δ 0.93 (s, 3H, CO–CH_3), 1.20–2.50 (m, 13H, $(CH)_2$, $(CH_2)_2$, C–$(CH_3)_2$ and OH), 4.89 (dd, J = 6.1, 9.6 Hz, 1H, O–CH), 5.50 (d, J = 10.9, 1H, H-C=C), 5.90 (d, J = 17.6, 1H, H–C=C), 6.77 (dd, J = 10.9, 17.6 Hz, 1H, CH=), 7.57–7.91 (m, 4H, aryl H). FT-IR (NaCl, cm^{-1}): 3537 (OH), 2925 (C–H), 1632 (C=C), 1455 (CH_2), 1359, 1181 (S=O). Anal. Found: C, 64.06; H, 7.20; S, 9.65%. Calcd for $C_{18}H_{24}SO_4$: C, 64.29; H, 7.14; S, 9.52%.

9 The poly(pinanyl *p*-styrenesulfonate) was obtained in a yield of 66% as a white powder. The M_w and M_w/M_n were 1.8 × 10^4 g·mol^{-1} and 5.9, respectively. The Tg was 112 °C.

10 Polymerization was carried out in dry THF using 1.0 wt% of AIBN at 70 °C for 7 h. Feed ratio of the monomers is PSS : tBMA = 16 : 84 (wt%). Poly(PSS_{10}-*co*-$tBMA_{90}$) was obtained in a yield of 50% as a white powder. The M_w and M_w/M_n were 4.7 × 10^4 g·mol^{-1} and 5.4, respectively. The Tg was 108 °C.