Three-Component Photoresists Containing Thermally Crosslinkable Vinyl Ether Derivatives

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ABSTRACT: Poly(4-hydroxystyrene-*co*-4-methoxystyrene) (MEOST) was synthesized and MEOST-13 with the methoxystyrene content of 12.5 mol % was used as a binder polymer for a three-component photopolymer system. The MEOST-13 films containing a vinyl ether monomer and a photoacid generator are insolubilized in an aqueous base in a prebake step owing to the thermal crosslinking reaction between hydroxyl groups of MEOST-13 and vinyl ether groups. Upon exposure to light and subsequent postexposure bake, the crosslinks are decomposed by photogenerated acids, leading to effective solubilization of the exposed areas. The MEOST-13 films showed sufficient insolubilization at baking temperatures of 140°C or above. The conversion of vinyl ether groups increased rapidly with increasing baking temperature. The sensitivity of the MEOST-13 films increased abruptly with an increase in postexposure bake temperature because of the nature of chemical amplification. The MEOST-13 films showed a sensitivity of 33 mJ/cm^2 and afforded positive-tone images with the improved resolution of 0.30-μm line and space at 248-nm light. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 3399–3404, 2001

Key words: photoresist; thermal crosslinking; acidolytic cleavage; vinyl ether group; photoacid generator

INTRODUCTION

High sensitivity and resolution in photopolymers for microlithography can be achieved by the incorporation of chemical amplification concept into resist systems. Chemical amplification concept in resists means all the methods that induce effective quantum efficiency above one. Since a series of onium salts that photochemically generate strong acids were reported,[1–3] a number of chemically amplified resist systems have been reported. They involve the acid-catalyzed deprotection of acid-labile pendant groups,[4–9] acid-catalyzed depolymerization of polymer main chains,[10–13] and acid-catalyzed electrophilic aromatic substitution.[14–17]

The author previously reported a novel chemically amplified photopolymer based on thermal crosslinking and acidolytic cleavage of the crosslinks. Typical examples include a two-component photoresist composed of poly{4-hydroxystyrene-*co*-4-[2-(vinyloxy)ethoxy]styrene} and a photoacid generator (PAG), and a three-component photoresist composed of poly(4-hydroxystyrene) (PHS), a vinyl ether monomer and a PAG, and a two-component photoresist composed of

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PHS and a thermally crosslinkable PAG bearing vinyl ether groups in the structure.[18–22] On prebaking at high temperature before ultraviolet (UV) irradiation, vinyl ether groups react with hydroxyl groups of the Brönsted acid based-binder polymers by electrophilic addition reaction to form acetal crosslinks. After exposure to UV light and subsequent postexposure bake (PEB), the crosslinks are decomposed catalytically by photogenerated acids to give alcohol and aldehyde, and consequently, positive-working photoresists are obtained after alkaline development. In these resists, the loss of the film thickness of unexposed areas can be minimized simply by changing prebaking temperature without chemical modification. These resists also show dual-mode behavior, depending on the concentration of vinyl ether groups and process conditions such as prebaking temperature. When the content of vinyl ether groups is high and the films are prebaked at relatively low temperatures, the resist films that are not thermally crosslinked act as negative-working resists on the basis of cationic polymerization.[18]

In chemically amplified photoresists based on acid-catalyzed reactions, a decrease in the acidity of binder polymers improves the resist stabilities such as the reproducibility of the resist performance and the shelf life. The acidity of PHS can be decreased by introducing hydrophobic methyl groups to hydroxyl groups of the phenolic moiety. In the present report, the author synthesized poly(4-hydroxystyrene-*co*-4-methoxystyrene) (MEOST) having methyl groups in the structure and reviewed the possibility of application of the three-component photoresist composed of MEOST, a vinyl ether monomer and a PAG to lithography.

EXPERIMENTAL

Materials

All chemicals were purchased from Aldrich Chemical Company (Madison, WI) with the following exceptions. PHS (M_n = 9023, M_w = 10,106) was supplied by Nippon Soda Company (Tokyo, Japan) and used as received. Bis{4-[2-(vinyloxy)ethoxy]phenyl}-4-methoxyphenylsulfonium triflate (TPS-2VE-Tf) as a thermally crosslinkable PAG and 2,2-bis{4-[2-(vinyloxy)ethoxy]phenyl} propane (BPA-DEVE) as a crosslinking agent were synthesized according to the literature.[20–22]

Measurements

Fourier transform infrared (FTIR) spectra were measured with a Bomem MB 104 FT/IR spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL GSX-400 spectrometer. The molecular weights of the polymers were determined on a TOSO HLC 802 UR gel permeation chromatograph with a TSK-GEL H-type column in tetrahydrofuran (THF) using polystyrene as the standard. Glass transition temperature (T_g) was determined by differential scanning calorimetry (DSC) on a Rigaku Denki Co. CN805E1 thermal analyzer (heating rate: 10°C/min). Resist films were exposed to 248-nm light from KrF excimer laser stepper (numerical aperture: 0.45; Nikon). Film thickness was measured with a Tencor P-10 Surface Profiler.

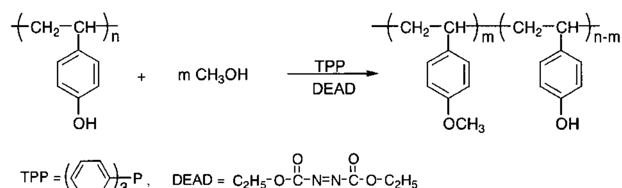
Synthesis of Copolymer (MEOST)[23,24]

PHS (0.1 mol, 12.0 g) was dissolved in distilled THF in a flask fitted with a paddle stirrer, reflux condenser, dropping funnel, and nitrogen inlet. Into the solution were placed in turn triphenylphosphine (TPP) (0.015 mol, 3.9 g) in THF, diethylazodicarboxylate (DEAD) (0.015 mol, 2.6 g) in THF, and methanol (0.015 mol, 0.5 g). The solution was stirred at room temperature for 2 h. The reaction mixture was reprecipitated five times in methylene chloride to afford white powder with the 4-methoxystyrene unit of 12.5 mol %. The methoxystyrene content was determined from ^{1}H-NMR spectra by comparing the integral ratio of each 4H for the benzene of the 4-hydroxystyrene and 4-methoxystyrene units at 6.2–7.0 ppm to 3H for the methyl group of the 4-methoxystyrene unit at 3.7 ppm.

FTIR (KBr, cm^{-1}): 1238, 1174 (CO stretching), 3349 (OH stretching), 1612, 1598, 1512, 1446 (C═C stretching of benzene ring). ^{1}H-NMR (300 MHz, CD_3OD, ppm): 0.8–2.1 (each 3H, CH_2CH of two repeating units), 3.7 (3H, methoxy), 6.2–7.0 (each 4H, benzene of two units). ^{13}C-NMR (300 MHz, CD_3OD, ppm): 155.8, 138.6, 129.9, 115.9, 114.6, 55.8, 45.0, 41.0.

Lithographic Evaluation

Resist films were prepared by spin-coating the photosensitive solutions dissolved in propylene glycol methyl ether acetate on bare Si wafers to give ca. 0.7 μm-thick films. The films were prebaked on a hot plate, exposed to 248-nm light from KrF excimer laser stepper, and postbaked.



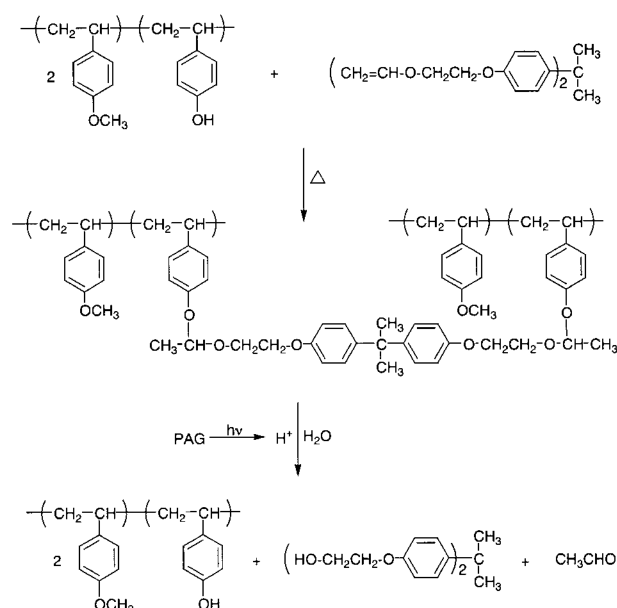
Scheme 1 Synthesis of MEOST copolymer.

Development was done in 2.38 wt % aqueous solution of tetramethylammonium hydroxide (TMAH). The thickness of the film remaining after development was measured as a function of the exposure energy. The film thickness was normalized to that obtained after PEB.

RESULTS AND DISCUSSION

MEOST resins were readily synthesized by allowing PHS to undergo the Mitsunobu reaction[23,24] with methanol in the presence of TPP and DEAD, as shown in Scheme 1. The products were obtained as white powder with relatively good yields above 70% and chemically identified by gel permeation chromatography, DSC, ^{1}H-NMR, ^{13}C-NMR, and FTIR.

Dissolution rates for the synthesized MEOST resins were measured in 2.38 wt % aqueous solution of TMAH. The dissolution rates of the MEOST films in the alkaline developer were decreased rapidly with an increase in the methyl moiety content, and were 29 and 22 nm/s for the resins containing 12.5 and 14.5 mol % methyl groups, respectively. The lithographic testing indicated that the dissolution rate of 22 nm/s was too low to attain the best resolution, and accordingly, the MEOST resin containing 12.5 mol % methyl groups (MEOST-13) was used in this study. Table I shows physical and chemical properties of MEOST-13 together with those of PHS.



Scheme 2 Thermal crosslinking and acidolytic cleavage mechanism of MEOST films containing BPA-DEVE and a PAG.

The T_gs and average molecular weights of both polymers were analogous.

The author clarified the mechanism of the thermal crosslinking and acid-catalyzed acidolysis for three-component photoresists composed of PHS, a vinyl ether monomer, and a PAG in the previous reports.[18,20] On the basis of the results, the mechanism for three-component photoresists consisting of MEOST, a vinyl ether monomer, and a PAG is recognized as shown in Scheme 2: the vinyl ether groups react with the hydroxyl group of MEOST in the prebake step to form acetal crosslinked networks. Upon irradiation with UV and subsequent PEB, the crosslinks are catalytically decomposed by photogenerated acids to give MEOST, alcohol, and acetaldehyde.

As exemplified in Figure 5, the lithographic testing revealed that the improved resolving ca-

Table I Physical and Chemical Properties of Binder Polymers

Polymers	Components (mol %) 4-Hydroxystyrene	Components (mol %) 4-Methoxystyrene	Average Molecular Weight[a] M_n	Average Molecular Weight[a] M_w	Average Molecular Weight[a] M_w/M_n	T_g[b] (°C)	Dissolution Rate (nm/s)
PHS	100	0	9.023	10,106	1.12	181	158.5
MEOST-13	87.5	12.5	9.172	10,320	1.13	170	29.0

[a] Measured by GPC (relative to polystyrene standards).
[b] Measured by DSC.

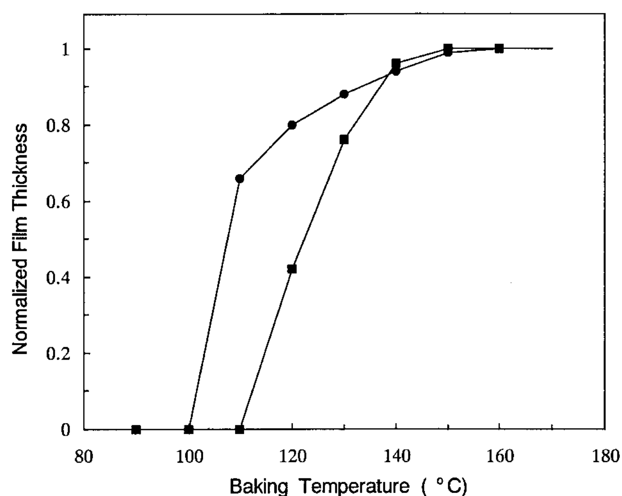


Figure 1 Insolubilization curves of MEOST-13 (●) and PHS (■) films containing 3 mol % BPA-DEVE and 0.4 mol % TPS-2VE-Tf. Baking: 90 s; developer: 2.38 wt % TMAH.

pacity could be achieved with MEOST-13 containing 3–4 mol % vinyl ether monomers, and accordingly resist formulations containing vinyl ether monomers within the limits were used for the performance evaluation. Figure 1 shows insolubilization curves for MEOST-13 and PHS films containing 3 mol % BPA-DEVE and 0.4 mol % TPS-2VE-Tf. Each film was baked for 90 s on a hot plate and developed for 1 min in 2.38 wt % aqueous solution of TMAH.

When baked at 100°C, the MEOST-13 film started to become insoluble, whereas the PHS film showed no insolubilization at the same baking temperature and began to come insolubilized at 110°C. Both MEOST-13 and PHS films also showed analogous insolubilization fractions at baking temperatures of 140°C or above. The insolubilization fractions of both films were ca. 0.95 at 140°C and 1.0 at 150°C or above. This result can be interpreted as follows.

The dissolution rate of MEOST-13 resin is only one-sixth that of PHS resin, as can be seen from Table I. Accordingly, the MEOST-13 films containing BPA-DEVE and TPS-2VE-Tf begin to become insoluble even with low crosslinking density at relatively low baking temperatures. Consequently, the MEOST-13 films exhibit higher insolubilization rates at baking temperatures of 100–130°C than the PHS films. However, the PHS resin with the higher acidity has the higher thermal crosslinking reactivity as compared with the MEOST-13 resin bearing methyl groups in the structure. Accordingly, despite their relatively high solubility in the TMAH, the PHS films containing BPA-DEVE and TPS-2VE-Tf show high insolubilization fractions when aided by sufficient thermal energy. As a result, the insolubilization fractions of both MEOST-13 and PHS films become analogous at baking temperatures of 140°C or above.

The conversion of vinyl ether groups for the MEOST-13 and PHS films is shown in Figure 2. The measurements were made with the films on Si wafers and the curves were obtained by tracing the absorption peak due to δ_{CH} (982 cm^{-1}) of vinyl ether groups on FTIR spectra.

The MEOST-13 films showed increasing conversion with increasing baking temperature and time. The MEOST-13 films also showed an abrupt increase of the conversion during the initial 90 s. Especially at the baking temperature of 140°C, the conversion was 54% after initial baking for 90 s, whereas it increased only by 9% after prolonged baking for 90 s. Both prebake and PEB for the lithographic process in this study were conducted for 90 s, except that PEB in Figure 5 was performed for 60 s. That is, unexposed areas undergo the thermal crosslinking reaction for 180 s. Accordingly, it is found that insolubilization of the MEOST-13 films due to the thermal crosslinking mainly depends on a prebake step. Actually, the insolubilization fraction was 94% after initial

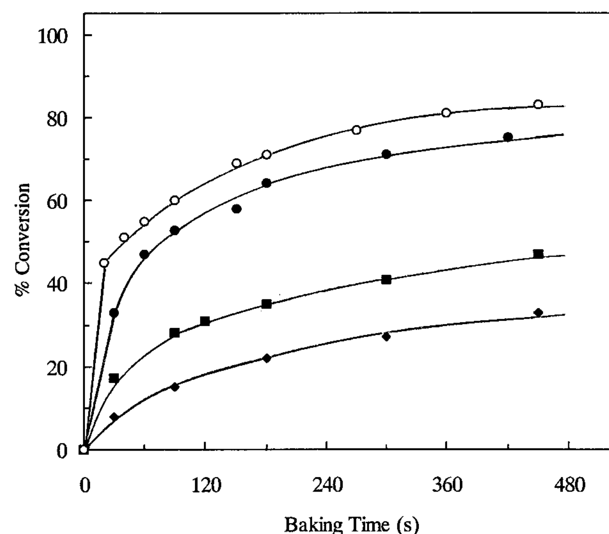


Figure 2 Conversion of vinyl ether groups for MEOST-13 and PHS films containing 3 mol % BPA-DEVE and 0.4 mol % TPS-2VE-Tf. (♦) MEOST-13 film at 90°C; (■) MEOST-13 film at 110°C; (●) MEOST-13 film at 140°C; (○) PHS film at 140°C.

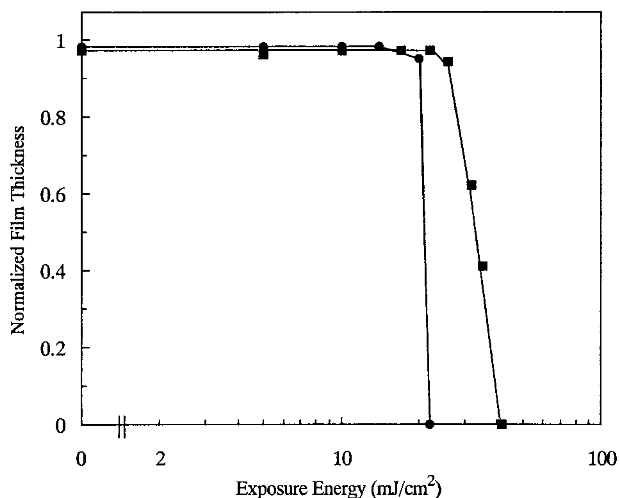


Figure 3 Characteristic curves for MEOST-13 (■) and PHS (●) films containing 3 mol % BPA-DEVE and 0.4 mol % TPS-2VE-Tf. Prebake and PEB at 140°C for 90 s; developer: 2.38 wt % TMAH.

baking for 90 s at 140°C, as shown in Figure 1, but it increased only by 3% after the prolonged 90 s, corresponding to PEB. However, when baking was performed at 140°C, the PHS films showed the higher conversion by ca. 7% than the MEOST-13 films. The conversion of the PHS film after initial baking for 90 s at 140°C was 60%.

Figure 3 shows characteristic curves for the MEOST-13 and PHS films. Each film was composed of a resin, 3 mol % BPA-DEVE, and 0.4 mol % TPS-2VE-Tf. Both prebake and PEB were done at 140°C for 90 s.

As can be seen in Scheme 2, the crosslinks are cleaved by photogenerated acids and return to the initial structure before crosslinking. That is, the binder polymer with higher solubility in an aqueous base before crosslinking offers the product with higher solubility after acidolytic cleavage in the presence of enough photogenerated acids and thermal energy. The dissolution rates of the resins in 2.38 wt % aqueous solution of TMAH are 29 nm/s for MEOST-13 and 158.5 nm/s for PHS, as shown in Table I, indicating that the dissolution rate of PHS is higher than MEOST-13. As a result, the MEOST-13 films containing the MEOST-13 resin with lower solubility as a binder polymer revealed the sensitivity of 44 mJ/cm^2, whereas the PHS films containing the PHS resin with higher solubility revealed the higher sensitivity of 23 mJ/cm^2.

Figure 4 shows characteristic curves for the MEOST-13 films containing 3 mol % BPA-DEVE and 0.4 mol % TPS-2VE-Tf when PEB temperatures are varied from 90 to 160°C. Prebake was done at 140°C for 90 s and PEB time was for 90 s.

The MEOST-13 film revealed the low sensitivity of 340 mJ/cm^2 at the PEB temperature of 90°C, and further, when no PEB was performed, the insolubilization fraction did not decrease to less than 0.33 even under enough exposure. However, the sensitivity increased quickly with an increase in PEB temperature, and the improved sensitivity of 33 mJ/cm^2 was exhibited at the PEB temperature of 160°C.

This rapid sensitivity enhancement may be attributed to the nature of chemical amplification. As shown in Scheme 2, the crosslinks are cleaved by photogenerated acids. In the cleavage process, the acid is regenerated and continues to be available for subsequent reaction. Such a dark reaction is activated by the rise of PEB temperature.

The optimum exposure energy to achieve the high resolving capacity is generally located in the range of 1.5 to 2 times the sensitivity on characteristic curves. A scanning electron micrograph of positive patterns printed in 0.7-μm-thick film is exhibited in Figure 5. The MEOST-13 film containing 3 mol % BPA-DEVE and 0.4 mol % TPS-2VE-Tf was prebaked at 140°C for 90 s and exposed at a dose of 84 mJ/cm^2 to 248-nm light from a KrF excimer laser stepper (numerical aperture: 0.45), followed by PEB for 60 s at 140°C. Development was done in 2.38 wt % aqueous solution of

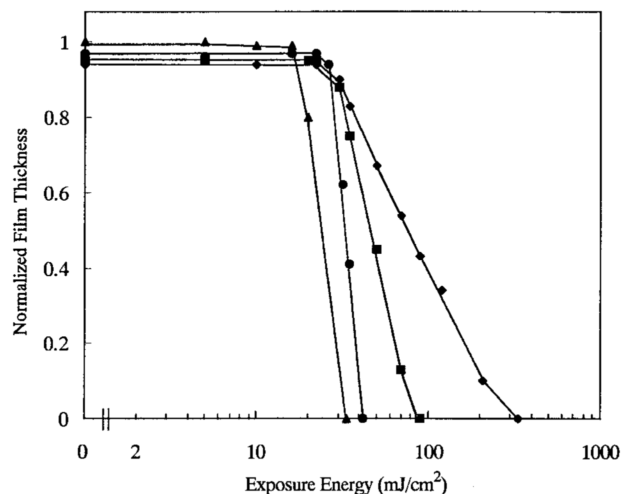


Figure 4 Characteristic curves for MEOST-13 films containing 3 mol % BPA-DEVE and 0.4 mol % TPS-2VE-Tf. Prebake at 140°C for 90 s; PEB time for 90 s; developer: 2.38 wt % TMAH. PEB: (♦) 90°C; (■) 120°C; (●) 140°C; (▲) 160°C.

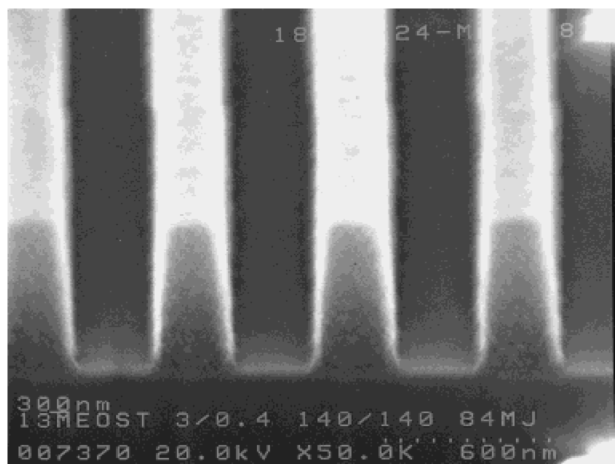


Figure 5 A scanning electron micrograph of 0.30-μm line and space positive patterns obtained on the MEOST-13 film containing 3 mol % BPA-DEVE and 0.4 mol % TPS-2VE-Tf. Prebake at 140°C for 90 s; PEB at 140°C for 60 s; dose: 84 mJ/cm^2 to 248-nm light; development: puddle in 2.38 wt % TMAH.

TMAH. The micrograph exhibits that 0.30-μm line and space patterns are resolved. However, the resolution of this resist can be improved by chemical modification of each component of the resist, and recently we have demonstrated 0.14-μm resolution at 248 nm from a KrF excimer laser stepper (numerical aperture: 0.60). The results will be described elsewhere.

CONCLUSION

MEOST-13 was readily synthesized through the Mitsunobu reaction. The MEOST-13 films containing 3 mol % BPA-DEVE and 0.4 mol % TPS-2VE-Tf showed sufficient insolubilization at baking temperatures of 140°C or above. The insolubilization fractions and conversions at 140°C were 0.94 and 54% after initial baking for 90 s, and 0.97 and 63% after the prolonged 90 s, implying that insolubilization of the films mainly depends on a prebake step. The PHS films showed the higher sensitivity than the MEOST-13 films in the presence of sufficient acids and thermal energy. Positive-tone images with the improved resolution of 0.30-μm line and space were obtained at 248-nm light.

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