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Three-component photoresists based on thermal crosslinking and acidolytic cleavage

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Abstract

Three vinyl ether monomers, 2,2-bis(4-[2′-(vinyloxy)ethoxy]phenyl(propane, 1,3,5-tris[2′-(vinyloxy)ethoxy]benzene, and 1,1,1-tris(4-[2′-(vinyloxy)ethoxy]phenyl)-ethane were synthesized and studied as thermal crosslinking agents in a three-component chemically amplified photoresist system. During prebake the resists were completely insolubilized in aqueous base through thermal crosslinking between poly(*p*-hydroxystyrene) binder polymer and the vinyl ether monomers. Upon exposure to UV and subsequent postexposure bake, the crosslinks were cleaved by photogenerated acid, leading to effective solubilization of the exposed areas. The thermal crosslinking and acid-catalyzed cleavage of the crosslinks were investigated by infrared (IR) spectroscopy. Degree of conversion of vinyl ether groups, dissolution rate and photosensitivity of the resists are strongly dependent on prebaking temperature. The resists showed relatively high sensitivity at 365 nm, and afforded positive-tone images by alkaline development. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Photoresist; Thermal crosslinking; Vinyl ether group

1. Introduction

Since Ito et al. incorporated “chemical amplification” concept into photoresist [1,2], a number of chemically amplified resist systems have been reported. They involve the acid-catalyzed deprotection of acid-labile pendant groups [3–10], acid-catalyzed depolymerization of the polymer main chain [11–16], and acid-catalyzed electrophilic aromatic substitution [17–22]. In addition, electron beam-induced polymerization of pendant oxirane ring [23] and free radical polymerization of acrylated diols [24] are important examples.

The authors previously reported a novel chemically amplified photoresist system based on thermal crosslinking and acidolytic cleavage of the crosslinks. Typical examples include two-component photoresists composed of poly(4-hydroxystyrene-*co*-4-[2-(vinyloxy)ethoxy]styrene) and a photoacid generator (PAG), and three-component photoresists composed of terpolymers bearing carboxyl groups, a vinyl ether monomer and a PAG [25,26]. The vinyl ether groups react with hydroxyl groups of the binder polymers at high temperature through electrophilic addition reaction to form crosslinked networks. The crosslinks are cleaved acid-catalytically by photogenerated acid. The resists exhibit either positive- or negative-working behavior depending on process conditions such as prebaking temperature.

In the present study, we report a new three-component photoresist system composed of poly(*p*-hydroxystyrene) (PHS), a monomer having vinyl ether groups and a PAG. The vinyl ether groups of the monomer undergo a thermal crosslinking reaction with the PHS binder polymer in the prebake step, thereby forming acetal crosslinked networks. Upon irradiation with UV and subsequent postexposure bake (PEB), a strong acid generated from a PAG catalyzes cleavage reaction of the crosslinks, and consequently, a positive-working photoresist is obtained after alkaline development.

2. Experimental

2.1. Materials and instruments

PHS ($M_n = 2400$, $M_w = 4300$) from Maruzen Petrochemical Co. Ltd., and bisphenol A, phloroglucinol, and 2-chloroethyl vinyl ether from Tokyo Kasei Kogyo Co. Ltd., and 1,1,1-tris(4-hydroxyphenyl)ethane from Aldrich

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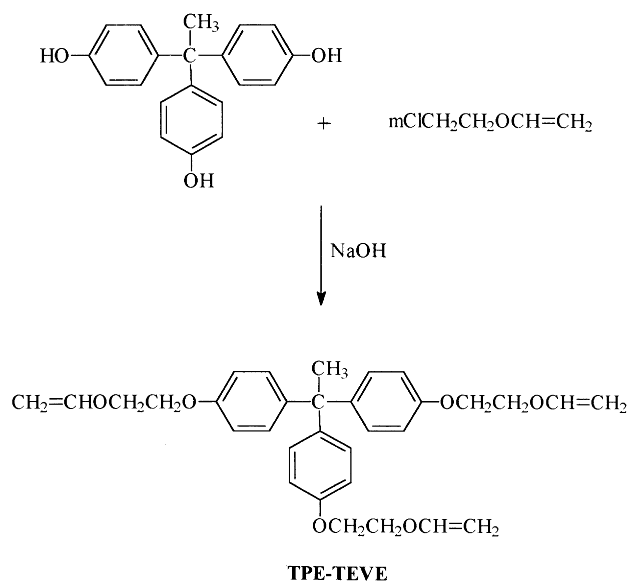


Scheme 1.

Chemical Co. were used as received. Diphenyliodonium 8-anilinonaphthalene-9,10-dimethoxyanthracene-2-sulfonate (DIAS) was synthesized according to the literature [27–30].

Fourier transform infrared (FTIR) spectra were measured with a Horiba FT-200 FTIR spectrometer. NMR spectra were recorded on a JEOL GSX-400 spectrometer. Melting points were measured at a heating rate of 10°C min^{-1} on a Rigaku Denki Co. model CN805E1 differential scanning calorimeter (DSC). Resist films were exposed to 365-nm light with a filtered super-high-pressure mercury lamp (Ushio Inc., 250 W). Film thickness was measured with a Tencor Alphastep 200.

2.2. Synthesis of vinyl ether monomers

Three vinyl ether monomers were synthesized in a similar manner. A typical example is given as follows. Into a 300-ml flask fitted with an overhead stirrer, reflux condenser, thermometer, dropping funnel and nitrogen inlet were placed 0.10 mol of 1,1,1-tris(4-hydroxyphenyl)ethane, 50 ml of DMSO, and 0.45 mol of NaOH pellets. The flask contents were stirred at 60°C for 1 h, and then 0.45 mol of 2-chloroethyl vinyl ether (CEVE) was added. After stirring at 70°C for 5 h, the reaction mixture was diluted with distilled water, and transferred into a separatory funnel with diethyl ether. After recrystallization in water, white crystalline 1,1,1-tris(4-[2-(vinyloxy)ethoxy]phenyl)ethane (TPE-TEVE) was obtained.

1,1,1-tris(4-[2-(vinyloxy)ethoxy]phenyl)ethane (TPE-TEVE): m. p. 98°C, ^{1}H NMR (400 MHz, in $CDCl_3$), δ (ppm): 2.12 (s, 3H, methyl), 4.02–4.28 (m, 18H, vinyloxyethoxy), 6.52–6.59 (q, 3H, vinyl), 6.85–7.13 (m, 12H, benzene). ^{13}C NMR (400 MHz, in $CDCl_3$), δ (ppm): 156.5, 151.6, 142.1, 129.6, 113.7, 86.9, 66.3, 50.6, 30.7. IR (KBr), ν (cm^{-1}): 1611 (C=C stretching of vinyl ether), 1200 (C–O–C stretching of vinyl ether), 982 (CH bending of vinyl ether). Elemental analysis: calculated for $C_{32}H_{36}O_6$, C 74.39, H 7.02; found, C 74.42, H 7.03.

2,2-bis(4-[2-(vinyloxy)ethoxy]phenyl)propane (BPA-DEVE): m.p. 59°C, ^{1}H NMR (400 MHz, in $CDCl_3$), δ (ppm): 1.61 (s, 6H, methyl), 3.98–4.26 (m, 12H, vinyloxyethoxy), 6.53–6.59 (q, 2H, vinyl), 6.85–7.13 (m, 8H, benzene). ^{13}C NMR (400 MHz, in $CDCl_3$), δ (ppm): 156.4, 151.7, 143.5, 127.7, 114.0, 87.0, 66.4, 66.3, 41.7, 31.0. IR (KBr), ν (cm^{-1}): 1612 (C=C stretching of vinyl ether), 1201 (C–O–C stretching of vinyl ether), 982 (CH bending of vinyl ether). Elemental analysis: calculated for $C_{23}H_{28}O_4$, C 74.97, H 7.66; found, C 75.02, H 7.84.

1,3,5-tris[2-(vinyloxy)ethoxy]benzene (THB-TEVE): m.p. 29°C, ^{1}H NMR (400 MHz, in $CDCl_3$), δ (ppm): 3.98–4.25 (m, 18H, vinyloxyethoxy), 6.49–6.97 (m, 6H, vinyl and benzene). ^{13}C NMR (400 MHz, in $CDCl_3$), δ (ppm): 158.6, 151.6, 107.9, 87.0, 67.1, 66.4. IR (KBr), ν (cm^{-1}): 1611 (C=C stretching of vinyl ether), 1200 (C–O–C stretching of vinyl ether), 981 (CH bending of vinyl ether). Elemental analysis: calculated for $C_{18}H_{24}O_6$, C 64.27, H 7.19; found, C 64.35, H 7.24.

2.3. Lithographic evaluation

Resist films were prepared by spin-coating the photosensitive solutions on bare Si wafers, followed by prebake, and the film thickness was measured to be 0.6–1.0 μm. The films were exposed to 365 nm light and postbaked. Development was performed using a 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.

3. Results and discussion

The three vinyl ether monomers, bifunctional BPA-DEVE and trifunctional TPE-TEVE and THB-TEVE, were readily synthesized by reacting 2-chloroethyl vinyl ether with corresponding phenolic compounds, as exemplified by the preparation of TPE-TEVE (Scheme 1). The monomers were obtained as white crystals in relatively good yields above 70%. The structures of three monomers were confirmed by ^{1}H and ^{13}C NMR spectra, IR spectra, and elemental analysis.

In the previous report [25], the authors had clarified the mechanism of thermal crosslinking and acid-catalyzed cleavage of a two-component photoresist system composed of a phenolic resin bearing vinyl ether groups in the side chains and a PAG by using spectroscopic methods such as FTIR, ^{1}H NMR, ^{13}C NMR and FAB-MS. The lithographic testing indicated that the best resolving capacity could be achieved with the polymers containing 9–13 mol% pendant vinyl ether groups. Accordingly, resist formulations containing

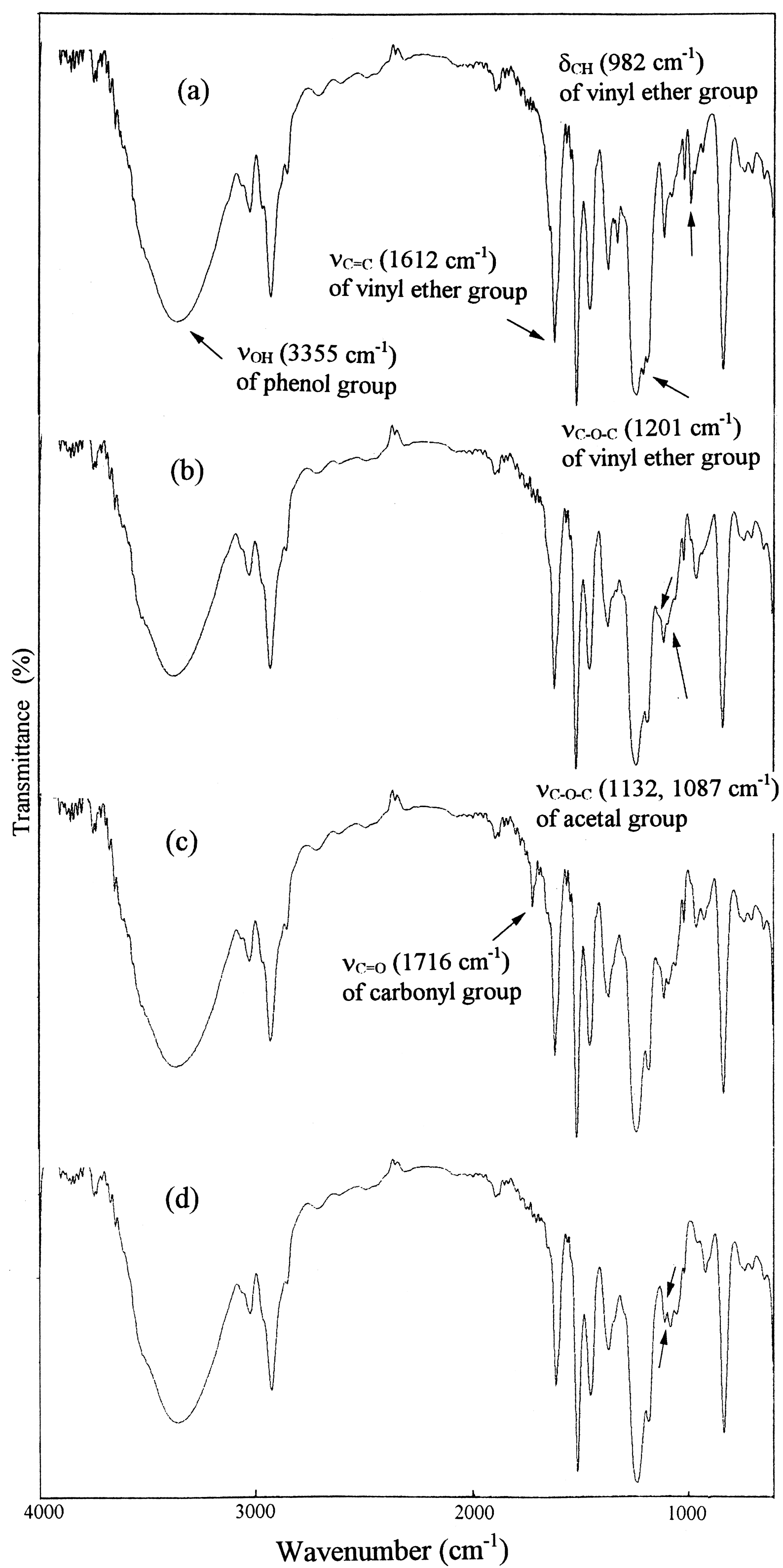
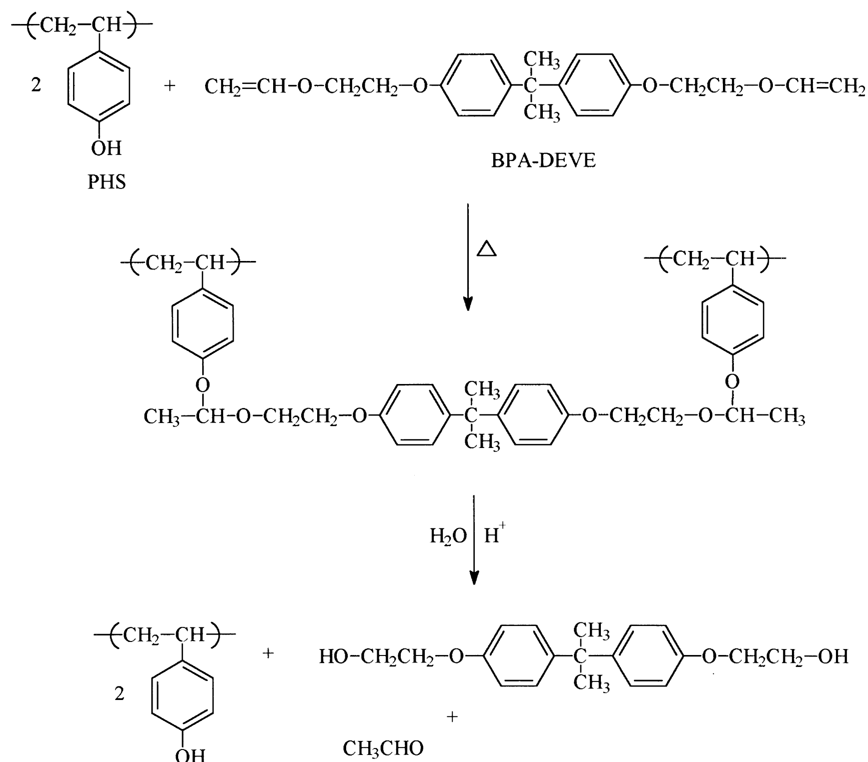


Fig. 1. Infrared spectra of PHS film containing 13 mol% BPA-DEVE and 7 wt% DIAS: (a) before prebaking; (b) after prebaking at 130°C for 15 min; (c) after exposure to 56 mJ cm^2 of UV light at 365 nm; (d) after postexposure baking at 130°C for 10 min.



Scheme 2.

13 mol% vinyl ether monomers were employed in this study.

Fig. 1 shows the changes in FTIR spectra for a resist film formulated from the PHS resin, 13 mol% BPA-DEVE, and 7 wt% DIAS. The film was prebaked at 130°C for 15 min, exposed to 365 nm light with 56 mJ cm^{-2}, and then post-baked at 130°C for 10 min. After prebake, the absorption peaks due to ν_{C-O-C} (1201 cm^{-1}) and δ_{CH} (982 cm^{-1}) of the vinyl ether group, and ν_{OH} (3355 cm^{-1}) of the phenol group decreased. The peak due to $\nu_{C=C}$ (1612 cm^{-1}) of the vinyl ether group overlapping $\nu_{C=C}$ (1612, 1600, 1511, 1455 cm^{-1}) of benzene ring also decreased after prebake. In addition, the weak absorption peaks due to ν_{C-O-C} (1104, 1070 cm^{-1}) of the ether group changed to the peaks due to ν_{C-O-C} (1132, 1087 cm^{-1}) of the acetal group. These results suggest that the vinyl ether groups reacted with the hydroxyl groups to form crosslinked networks with acetal structure during the prebake.

On the other hand, the absorption peak due to $\nu_{C=O}$ (1716 cm^{-1}) of acetaldehyde, which would appear when the acetal groups decompose by acids, appeared after exposure and disappeared after PEB. This indicates that

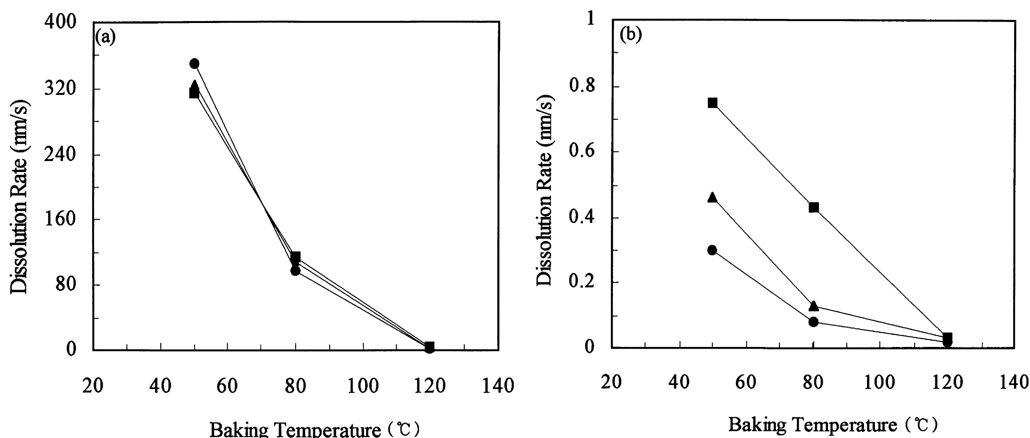


Fig. 2. Change in dissolution rates for PHS films containing BPA-DEVE (■), TPE-TEVE (▲) and THB-TEVE (●); developer (a) PGMEA and (b) TMAH 2.38 wt%.

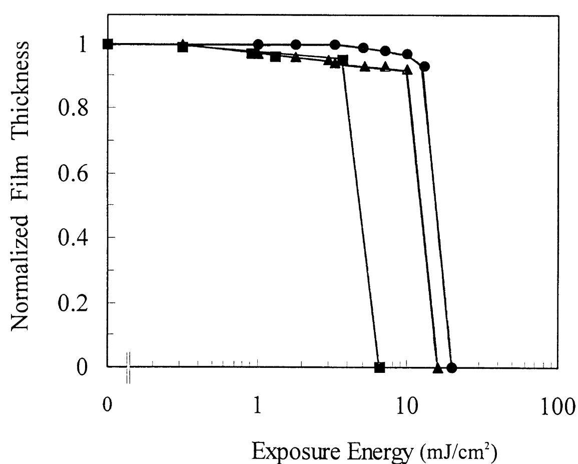


Fig. 3. Sensitivity curves for PHS films containing 13 mol% BPA-DEVE (▲), TPE-TEVE (●) and THB-TEVE (■): DIAS 7 wt%; prebake and PEB at 80°C for 10 min; developer TMAH 2.38 wt%.

the cleavage reaction proceeds slightly in the presence of photogenerated acid even at room temperature. After PEB, the peak due to ν_{OH} (3355 cm^{-1}) of the phenol group increased while the peaks due to ν_{C-O-C} (1132, 1087 cm^{-1}) of the acetal group disappeared completely.

This spectral behavior agrees well with the authors' previous results [25,26]. Therefore, the resist chemistry of the present three-component system is recognized as shown in Scheme 2: the thermal crosslinking of PHS occurs through electrophilic addition reaction with vinyl ether groups in the prebake step, and upon exposure and subsequent PEB, the crosslinks with acetal structure are cleaved by photogenerated acid to give PHS, alcohol and acetaldehyde. In the cleavage process, the acid (H^+) is regenerated and continues to be available for subsequent reaction, hence the amplification nature of the system.

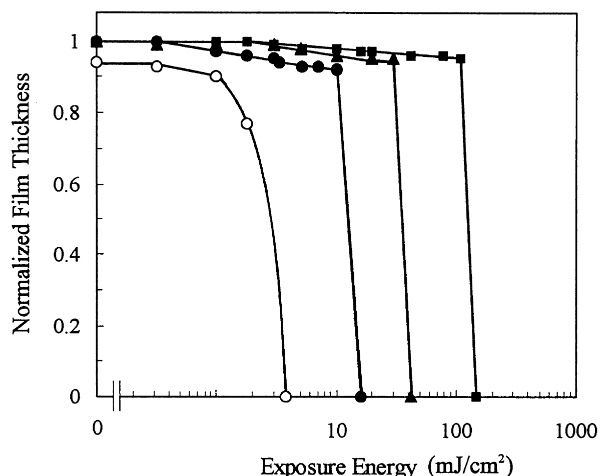


Fig. 4. Sensitivity curves for PHS films containing 13 mol% BPA-DEVE and 7 wt% DIAS: PEB at 80°C for 10 min; developer TMAH 2.38 wt%. (○) prebake at 50°C for 10 min; (●) prebake at 80°C for 10 min; (▲) prebake at 100°C for 10 min; (■) prebake at 120°C for 10 min.

With PHS films containing BPA-DEVE, THB-TEVE and TPE-TEVE, dissolution rates were measured after prebaking at different temperatures (Fig. 2). Each film with 13 mol% vinyl ether monomer was baked in a convection oven for 10 min and developed either in propylene glycol methyl ether acetate (PGMEA), which was used as the solvent for all the resist formulations in this study, or in a 2.38 wt% aqueous solution of TMAH.

When prebaked at 50°C for 10 min and developed in PGMEA, the films showed the dissolution rates of 310–350 nm s^{-1} as shown in Fig. 2(a), which were almost unchanged even after prolonged baking for 60 min. A PHS film containing no vinyl ether monomer dissolved in PGMEA at a rate of 321 nm s^{-1}. These results imply that the thermal crosslinking reaction does not occur at 50°C. However, after prebaking at 80°C for 10 min, the dissolution rates decreased greatly to ca 110 nm s^{-1}, and the rates further decreased on prolonged baking at the same temperature. When prebaking was conducted at 120°C, the films showed very low dissolution rates below 3 nm s^{-1}. The results indicate that the PHS films undergo the thermal crosslinking reaction based on Scheme 2 at the baking temperatures of 80 and 120°C.

When the aqueous TMAH was employed as a developer, a PHS film containing no vinyl ether monomer showed a dissolution rate of 155 nm s^{-1}, while the films with BPA-DEVE, THB-TEVE and TPE-TEVE showed much lower dissolution rates of 0.75, 0.46 and 0.30 nm s^{-1}, respectively, even when they were prebaked at 50°C for 10 min (Fig. 2(b)). Since the thermal crosslinking reaction does not occur on baking under the conditions, this result implies that the vinyl ether monomers act as dissolution inhibitors for the PHS resin in aqueous base. When prebake was conducted at 80°C, the dissolution rates further decreased due to the thermal crosslinking. The films prebaked at 120°C were almost completely insolubilized in the alkaline solution on the basis of the thermal crosslinking reaction as well as the dissolution inhibition effect.

UV irradiation and PEB of the crosslinked films resulted in their effective solubilization in aqueous base. Sensitivity curves for the PHS films containing 13 mol% vinyl ether monomers and 7 wt% DIAS, are shown in Fig. 3. Both the prebake and PEB were done at 80°C for 10 min, and development was performed using the aqueous TMAH for 1 min. The resist film with trifunctional THB-TEVE exhibited the highest sensitivity of 7 mJ cm^2, and those containing BPA-DEVE and TPE-TEVE showed the sensitivities of 17 and 20 mJ cm^2, respectively.

The photosensitivity of the three-component photoresists was found to be greatly affected by the prebaking temperature. For PHS films formulated with 13 mol% BPA-DEVE and 7 wt% DIAS, sensitivity was measured after prebaking at various temperatures. PEB for all the films was done at 80°C for 10 min. The resist sensitivity decreased with increasing prebaking temperature as shown in Fig. 4. The resist showed a relatively high sensitivity of 17 mJ cm^2

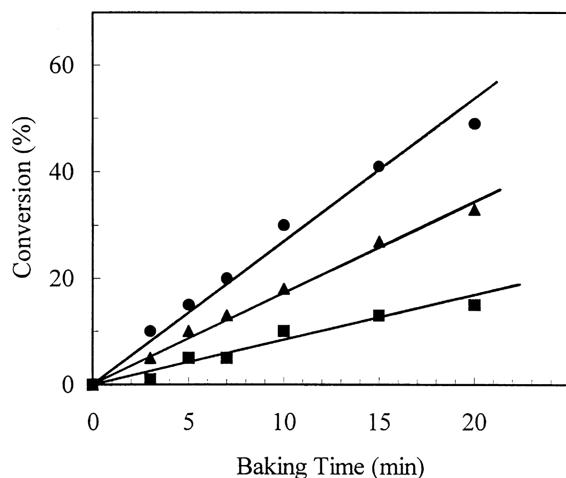


Fig. 5. Conversion of vinyl ether groups for the PHS films containing 13 mol% TPE-TEVE. Prebake: (■) 80°C; (▲) 100°C; (●) 120°C.

when prebake was performed at 80°C, while it had the lowest sensitivity of 150 mJ cm^2 when prebaking temperature was 120°C. This result could be interpreted as follows: the crosslinks due to the thermal crosslinking reaction have higher crosslinking density when prebake was done at higher temperature. The higher the crosslinking density is, the more difficult the diffusion of photogenerated acid becomes.

A resist film prebaked at 50°C showed the highest sensitivity of 3.5 mJ cm^2, but thickness loss of unirradiated areas during development was ca 6% (Fig. 4). The solubilization of the film by irradiation and PEB might be due to hydrolysis of vinyl ether moiety by photogenerated acid, which was demonstrated in our previous work [25].

The effect of varying prebaking temperature on the degree of conversion of vinyl ether groups was investigated for the PHS films containing 13 mol% TPE-TEVE (Fig. 5). The curves were obtained by tracing absorption change of

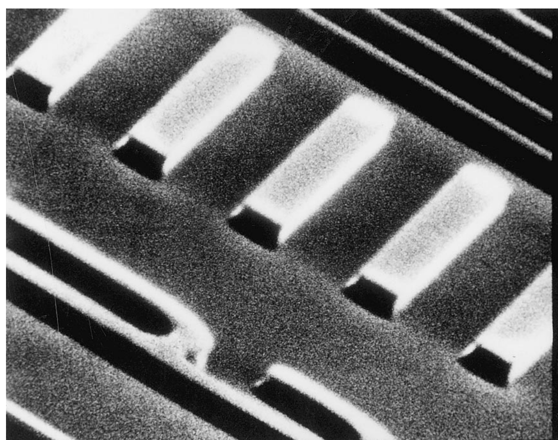


Fig. 6. A scanning electron micrograph of 1.0 μm line and space positive patterns in the PHS film containing 5 mol% TPE-TEVE and 2 mol% DIAS: exposure to 365 nm light (46 mJ cm^2) by a contact mode; prebake and PEB at 110°C for 10 min; developer TMAH 2.38 wt%.

vinyl ether groups (δ_{CH}, 982 cm^{-1}) on FTIR spectra. The conversion increases with increasing prebaking temperature, implying that the films have higher crosslinking density when prebaked at higher temperature.

Both prebake and PEB in the lithographic process in this study were carried out for 10 min. That is, unirradiated areas undergo the thermal crosslinking reaction for 20 min. As can be seen in Fig. 5, the conversion of vinyl ether groups was 13% when the film was baked at 80°C for 20 min, and nearly 50% when baked at 120°C for 20 min.

Fig. 6 shows a scanning electron micrograph of a positive-tone image printed in a 0.65 μm thick PHS film containing 5 mol% TPE-TEVE and 2 mol% DIAS. The resist film was prebaked at 110°C for 10 min, exposed to 365 nm light at a dose of 46 mJ cm^2 by a contact mode, and postbaked at 110°C for 10 min. Development was done in 2.38 wt% aqueous solution of TMAH. The micrograph shows that 1 μm lines and spaces are resolved.

4. Conclusions

Bi- or trifunctional vinyl ether monomers, BPA-DEVE, THB-TEVE and TPE-TEVE were readily synthesized and used as effective thermal crosslinking agents in a three-component chemically amplified photoresist system. The matrix polymer, PHS, is quite soluble in 2.38 wt% aqueous TMAH, but its solubility greatly decreases when a vinyl ether monomer is added to the resin, due to the dissolution inhibition effect of the monomers. Upon prebaking, the resist films were almost completely insolubilized in the aqueous base by the thermal crosslinking reaction. When exposed to UV light and postbaked, the crosslinks decompose by photogenerated acid, leading to solubilization of the exposed areas. The resist sensitivity decreased with an increase in prebaking temperature and is in the range of 7–20 mJ cm^2. Positive-tone images were obtained by irradiation of the crosslinked resist films with 365 nm light and subsequent PEB, followed by development using the TMAH developer.

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