An Aqueous-Base Developable Photoresist Based on Light-Induced Cationic Polymerization: Resist Performance of Poly(Glycidyl Methacrylate-*co*-Methacrylic Acid)

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SYNOPSIS

An aqueous-base developable photoresist based on photoinduced cationic polymerization has been prepared by copolymerization of glycidyl methacrylate (GMA) and methacrylic acid (MAA). The copolymer containing 83 mol % of GMA unit is soluble in an aqueous base and crosslinked in the presence of photogenerated acid caused by acid-initiated ring-opening polymerization of pendant epoxide groups. Exposure results in the generation of acid and the subsequent baking process promotes the diffusion of photogenerated acid, which initiates the cationic crosslinking of the epoxide rings. It was also found that the sensitivity of the copolymer was remarkably enhanced when a divinyl ether monomer is added as a bifunctional crosslinker. The sensitivity enhancement may be caused by the high reactivity of the divinyl ether monomer in the presence of acid. The resist comprised of the copolymer, the vinyl ether monomer, and diphenyliodonium 9,10-dimethoxy-anthracene-2-sulfonate as photoacid generator exhibited the sensitivity of 20 mJ/cm^2. A good pattern profile with high resolution was attained by exposure to a 365 nm light followed by a postexposure bake at 60°C for 3 min. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Photopolymer systems are extensively used in modern technologies. Recently there has been a growing interest in cationic-induced polymerization because it is not inhibited by atmospheric oxygen in contrast to radical-induced polymerization. Crivello[1] found that diaryliodonium and triarylsulfonium salts having a complex metal halide counteranion are efficient photoinitiators for the cationic-induced polymerization.

Poly(glycidyl methacrylate) (PGMA) has a reactive epoxide ring in the side chain, and various functional groups can be introduced into PGMA by utilizing the reactivity of the epoxide ring.[2] For example, Nishikubo et al.[3-6] have reported the photopolymers prepared from the addition reaction of pendant epoxide groups of PGMA with the photosensitive groups. Schlesinger[7] and Crivello and Colon[8] have suggested the crosslinking reactions of polyfunctional epoxy compounds or vinyl ethers, respectively, using cationic photoinitiators such as aryldiazonium, diaryliodonium, and triarylsulfonium salts. Photocured epoxy resins give coating layers with good mechanical properties and a high chemical resistance, and have been employed for coatings, printing inks, recording materials, photoresists, and printing plates. Although the photoresist based on photocationic polymerization of epoxides or vinyl ethers have been reported, most of them are not alkaline developable. The use of organic solvents as developer results in environmental pollution. Moreover, developing by organic solvents causes an undesirable image distortion caused by swelling.[9] Recent studies have shown that negative resists based upon the crosslinking reaction exhibit no deformation of the image when developed in an aqueous base.[10-12] Only one example of an aqueous developable cationic photopolymerization system has been reported by Timpe et al.[13] This system is a

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function-separated type consisting of the aqueous-base soluble polymeric binder and the reactive epoxide monomer.

In the present study we have synthesized poly(glycidyl methacrylate-*co*-methacrylic acid) with varying copolymerization ratios and the application to negative-tone resist systems.

EXPERIMENTAL

Materials

All of the solvents used in this study are commercially available and were used after being dehydrated with molecular sieves. Glycidyl methacrylate (GMA), methacrylic acid (MAA), and azobis(isobutyronitrile) (AIBN) were purchased from Wako Pure Chemicals and used without further purification. Anthracene (Wako) was purified according to the literature.[14] Diphenyliodonium hexafluoroarsenate (DPI-AsF_6) was prepared according to the reported method.[15] The other photoacid generators, *p*-nitrobenzyl 9,10-dimethoxyanthracene-2-sulfonate (NAS),[16] *p*-nitrobenzyl 5-dimethylamino-1-naphthalenesulfonate (NDS),[17] and diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate (DIAS)[18] were prepared as described in the literature, respectively. Di(2-vinyloxy)ethyl ether of bisphenol-A (BPA-DEVE) was synthesized by reaction of bisphenol-A (Tokyo Kasei) with 2-chloroethyl vinyl ether (Tokyo Kasei) according to the previous reported method.[8] Other materials were from commercial sources and were not further purified.

Instrumentation

Infrared spectra were recorded on a Hitachi infrared spectrometer (Model 260-10) using film cast on NaCl disks and silicon wafers. ^{1}H-NMR spectra were obtained with a JEOL GSX-500 spectrometer in deuteriochloroform. Molecular weights and molecular weight distribution of the polymers synthesized in this study were determined by a TOSO HLC-802UR gel permeation chromatography (GPC) with a TSKGEL H type column (styrene gel column) at 40°C in THF. Molecular weights were calculated with reference to polystyrene standards. Thermal behavior was monitored by a Rigaku Denki Co. CN8085E1 thermal analyzer at 10°C/min for TGA and DSC under normal atmospheric conditions. Contact angle of H_2O on polymer film was measured with a Erma contact anglemeter, goniometer, model G-1.

Preparation of PGMA and Poly(Glycidyl Methacrylate-*co*-Methacrylic Acid)

PGMA was prepared in 70% yield by radical polymerization of GMA (10 g: 0.07 mol) using AIBN (0.2 g) in methyl ethyl ketone (MEK, 150 mL) at 62-3°C for 5 h under flowing nitrogen. The polymer solution was poured into *n*-hexane, and then the obtained polymer was purified by twice precipitating from MEK into *n*-hexane and drying at 25°C under reduced pressure. The epoxide equivalent of the obtained polymer measured by the reported method[19] was 150.1.

Copolymerization was carried out in 300-mL round-bottom, three-neck flasks equipped with a condensor, a nitrogen gas inlet, and a mechanical stirrer. After the required amounts of the two monomers (10 wt % in MEK) and AIBN had been added, the mixture was left stirring for 1 h prior to being heated to 62–3°C for 5 h. The polymerization mixture was allowed to cool, and then poured dropwise into an excess of *n*-hexane to precipitate the copolymer. Purification of the resulting copolymer was accomplished by two reprecipitations from MEK using *n*-hexane as the nonsolvent. All of the copolymers (**1–4**) were characterized by ^{1}H-NMR and IR spectroscopies.

Photosensitivity Measurement

A polymer and photoacid generator were dissolved in diethylene glycol dimethyl ether or 2-methoxyethanol. The solutions were filtered through a 1-μm Teflon filter prior to use. The solution was spun on a silicon wafer to form a 1-μm photosensitive film layer. The concentration of photoacid generator was adjusted to provide an absorbance of ca. 0.1 at 365 nm in a 1-μm film thickness. The absorbance of anthracene, which is a photosensitizer for DPI-AsF_6, was also optically matched with the other photoacid generators. The films on the wafer were exposed at 365-nm wavelength to the filtered super high pressure mercury lamp, developed for 30 s in tetramethylammonium hydroxide (TMAH) with a concentration of 1.5 wt %. Imagewise exposure was carried out in the contact mode with a quartz mask. The characteristic curve was obtained by a ratio of remained film thickness (gel fraction) against exposure energy. The intensity of incident light was measured with an Epply Model E-6 thermopile. The film thickness was measured by the multiplet interference method using a Nikon surface finish microscope.

Table I Preparation and Properties of PGMA and Copolymers 1–4

Polymer	Mole Fraction of GMA in Feed	Mole Fraction of GMA Component in Copolymer[a]	10^{-3} M_w[b]	10^{-3} M_n[b]	M_w/M_n[b]	T_g/°C[c]
PGMA	1		22	8.9	2.47	75.5
1	0.95	0.98	19	8.4	2.26	79.5
2	0.90	0.92	23	9.8	2.35	88.0
3	0.85	0.87	30	13	2.30	97.0
4	0.80	0.83	64	24	2.67	105

[a] Determined by ^{1}H-NMR spectroscopy.
[b] Measured by GPC.
[c] Measured by DSC.

RESULTS AND DISCUSSION

Copolymers consisting of GMA units, as cationic crosslinking moieties, and MAA units, as groups giving aqueous developability, were synthesized by varying the copolymerization ratios. Table I gives the physical properties of copolymers involving molecular weights and glass-transition temperatures. The composition of the copolymers was determined from their ^{1}H-NMR spectra by comparing the ratio of five protons around the epoxide ring to other aliphatic protons. Gel compounds were produced during the copolymerization reaction when the molar ratio of GMA was more than 30 mol % in feed. The gel products may be crosslinked copolymer formed by the reaction of the epoxide groups of GMA with carboxylic acids of MAA under the progress of copolymerization. Similarly, Nishikubo et al.[3] have reported that the gel compounds were obtained at the final stage of the addition reaction of poly(glycidyl methacrylate-*co*-methyl methacrylate) with carboxylic acids due to a side reaction of pendant epoxide groups with the resulting hydroxyl groups.

As can be seen in Table I, molecular weight of copolymers shows a tendency to increase with the decrease in the molar fraction of GMA, while the polydispersity weight-average/number average molecular weights (M_w/M_n) remains almost constant. A series of copolymers **4** with various molecular weights and a constant ratio of copolymerization was also prepared to study the effect of the molecular weight on the resist performance. As can be seen from Table II, the M_w is increased from 64000 to 131000 by decreasing the amount of AIBN used from 1.8 to 0.6 mol % relative to GMA monomer.

While the glass-transition temperature (T_g) of GMA homopolymer is 75.5°C, that of MAA homopolymer is about 230°C. The DSC curves of the copolymers in Figure 1 shows that the T_g values of copolymers are variable depending on the molar ratio of MAA. Copolymers 1–4 showed the glass transition temperatures between those of the respective homopolymers reflecting their molar composition (Fig. 2). Within the range of molecular weights prepared in this study, no significant change in T_g was observed for each copolymer with the same copolymerization ratio. For example, copolymers **4a–c**

Table II Preparation of Copolymer 4s of Different Molecular Weight

Copolymer	Mole Ratio of GMA/AIBN	10^{-3} M_w[a]	10^{-3} M_n[a]	M_w/M_n[a]	T_g[b]/°C
4	58	64	24	2.67	105
4a	39	41	17	2.41	102
4b	78	79	32	2.47	106
4c	117	131	52	2.52	105

[a] Measured by GPC.
[b] Measured by DSC.

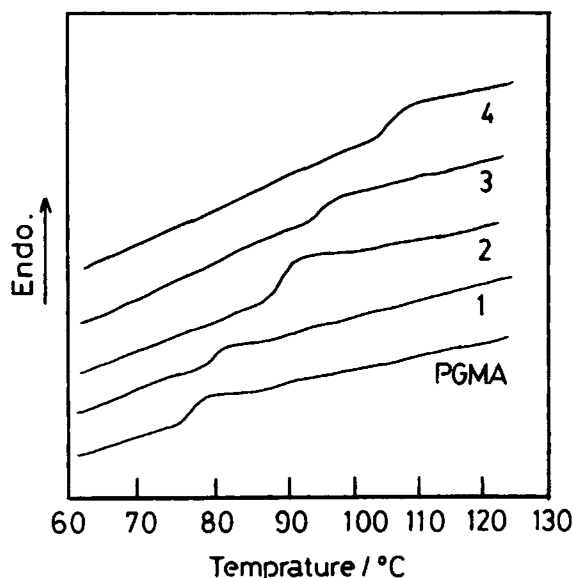


Figure 1 DSC curves of PGMA and copolymers **1–4** measured under normal atmospheric conditions.

that contain 83 mol % of GMA unit have T_g values of 102, 106, and 105°C, respectively.

Figure 3 shows contact angles of water on PGMA and copolymer films as a function of the copolymerization ratio. The contact angle of water on PGMA homopolymer is 55° and it decreases with an increase in the molar ratio of MAA, indicating that hydrophilicity of the copolymer increases with the increase in the molar ratio of MAA in the copolymer.

Among the copolymers **1–4**, only copolymer **4** is soluble in 1.5 wt % aqueous solution of TMAH.

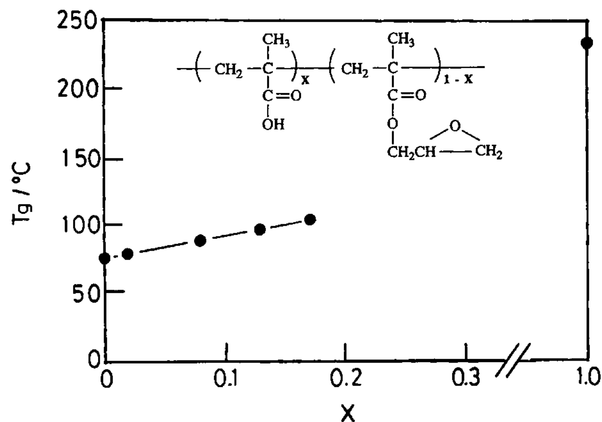


Figure 2 Glass-transition temperature of PGMA, copolymers **1–4** and PMAA.

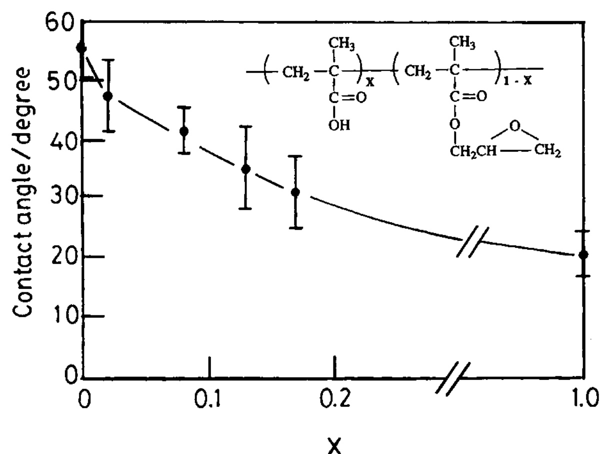


Figure 3 Contact angle/H_2O versus mole fraction of MAA in PGMA, copolymers **1–4** and PMAA.

Copolymer **1–4** are relatively stable against dark reaction and can be stored in the dark at room temperature for about 2 months without appreciable gel compounds. In the following imaging experiments copolymer **4** was used as the aqueous-base soluble polymeric binder for the photoinduced cationic polymerization system.

Lithographic Properties

The lithographic performance of copolymer **4** was investigated using DPI-AsF_6 sensitized by anthracene (AN/DPI-AsF_6), DIAS, NAS, and NDS as a

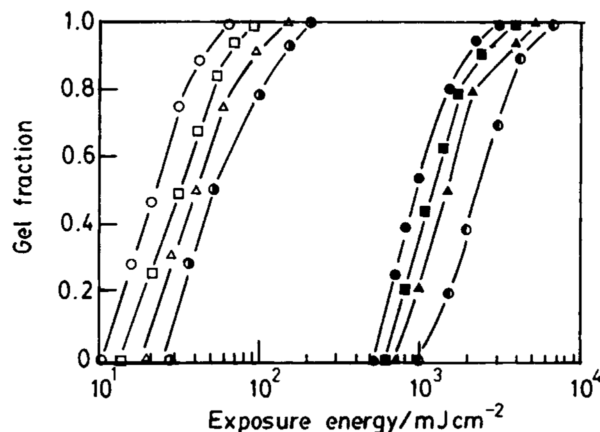
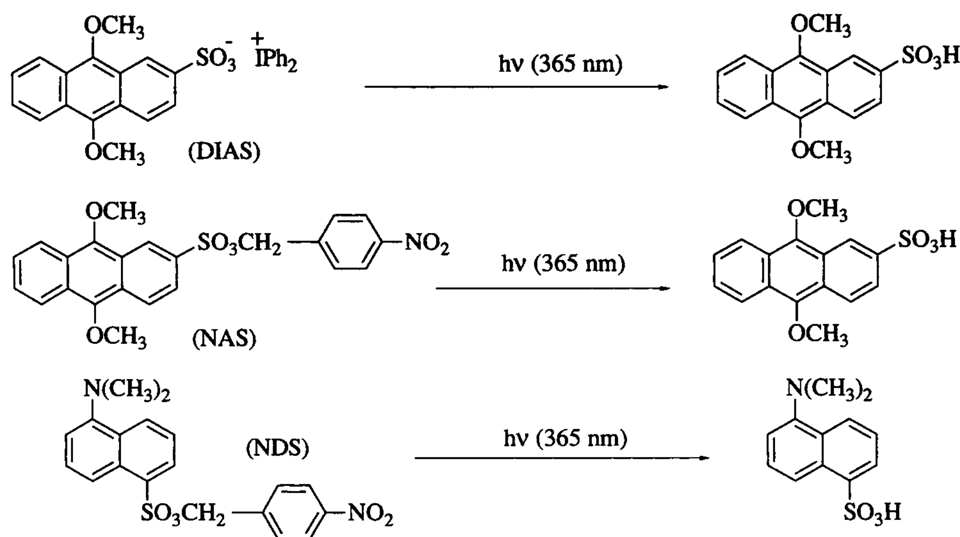


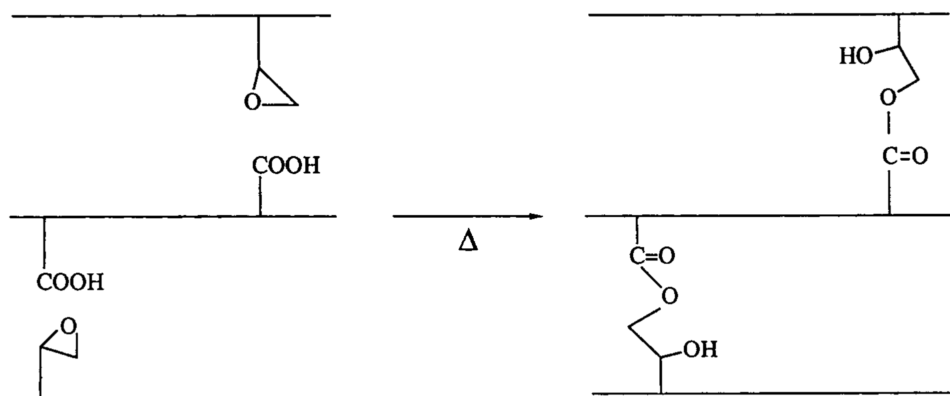
Figure 4 Characteristic curves of 2CS and 3CS. (●) **4**/DIAS; (■) **4**/AN/DPI-AsF_6; (▲) **4**/NDS; (◐) **4**/NAS; (○) **4**/DIAS/BPA-DEVE; (□) **4**/AN/DPI-AsF_6/BPA-DEVE; (△) **4**/NDS/BPA-DEVE; and (◑ **4**/NAS/BPA-DEVE.



Scheme 1

photoacid generator. Pappas et al.[20] have reported the photoinitiated polymerization of diepoxide by photosensitization of DPI-AsF_6 with anthracene. DIAS[18] and NAS[16] are photochemically decomposed to give 9,10-dimethoxyanthracene-2-sulfonic acid, and NDS[17] also photodissociates to produce the parent sulfonic acid (Scheme 1).

Polymer **4** films (1-μm thick) containing photoacid generator became insoluble in an aqueous-base developer by exposure to 365-nm light followed by postexposure bake (PEB) at 80°C for 5 min. The sensitivity of the resist formulated from copolymer **4** was evaluated by the characteristic curves shown in Figure 4. The exposure energy of 365 nm light to attain 0.5 gel fraction was defined as the sensitivity ($D_g^{0.5}$). The conditions of PEB process were controlled to prevent the process of thermal crosslinking reaction of copolymer **4** as shown in Scheme 2. DIAS, AN/DPI-AsF_6, NDS, and NAS offered the sensitivities of 0.9, 1.2, 1.3, and 2.5 J/cm^2 at 365 nm, respectively (Table III). The difference of the sensitivities for these systems may be mainly governed by the efficiency of acid formation from the photoacid generator, and the quantum yield of acid generation may be one of the most important factors in the photocationic polymerization to determine the resist sensitivity. It has been reported that the quantum yields of acid generation from DIAS, NDS, and NAS in degassed acetonitrile are 0.29,[18] 0.16,[17] and 0.11,[16] respectively. Both photoacid generators, DIAS and AN/DPI-AsF_6, generate Brϕnsted acid through the excitation of 9,10-dimethoxyanthracene



Scheme 2

Table III Sensitivities of 2CS and 3CS Using Various Photoacid Generators

Photoacid Generator	Copolymer 4[a]	4/BPA-DEVE[a]
DIAS	900	20
AN/DPI-PF_6	1200	32
NDS	1300	38
NBS	2500	50

[a] Units in mJ cm^{-2}.

moiety and anthracene, respectively. It was reported[18,20] that the photoacid generation of these compounds proceed via an electron transfer from excited singlet state of 9,10-dimethoxyanthracene moiety or anthracene to diphenyliodonium moiety. The free-energy change values accompanying the electron transfer for both DIAS and AN/DPI-AsF_6 systems are exothermic by more than 150 kJ/mol.[18,20] Although the rate constant of electron transfer in DIAS may be comparable to that in AN/DPI-AsF_6 according to the reported results mentioned above,[18,20] the quantum yield of acid generation is not reported for AN/DPI-AsF_6. The sensitivity of the resist by photo–cationic crosslinking is considered to be governed by the quantum efficiency of photoacid formation and the type of acid produced from the generator. The difference in sensitivity of both the resists is not clear presently because the type of acid formed from photodissociation of AN/DPI-AsF_6 is different from sulfonic acid formed by DIAS photolysis and the quantum yield is not determined for AN/DPI-AsF_6.

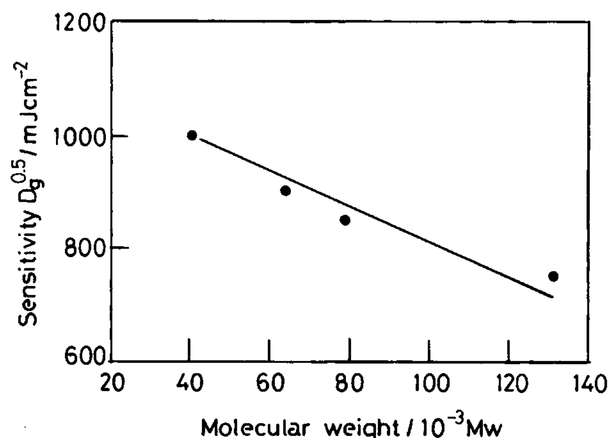


Figure 6 Sensitivity v molecular weight (M_w) for copolymers **4** and **4a–c**.

It was found that the sensitivities of two component resists (2CS) comprising copolymer **4**/photoacid generator are remarkably increased by the addition of the bifunctional vinyl ether monomer, BPA-DEVE, as the third component. The $D_g^{0.5}$ of the resists consisting of copolymer **4**, photoacid generator, and BPA-DEVE (3 component system, 3CS) was 20 mJ/cm^2 for DIAS, 32 mJ/cm^2 for AN/DPI-AsF_6, 38 mJ/cm^2 for NDS, and 50 mJ/cm^2 for NAS, respectively (Table III), with exposure to 365 nm light followed by PEB at 60°C for 3 min. Crivello and Colon[8] have shown from DSC analysis that the rate of photoinitiated cationic polymerization with diphenylidonium salts of aromatic divinyl ethers was much higher than that of cycloaliphatic diepoxides. Moreover, similar results on photocrosslinking re-

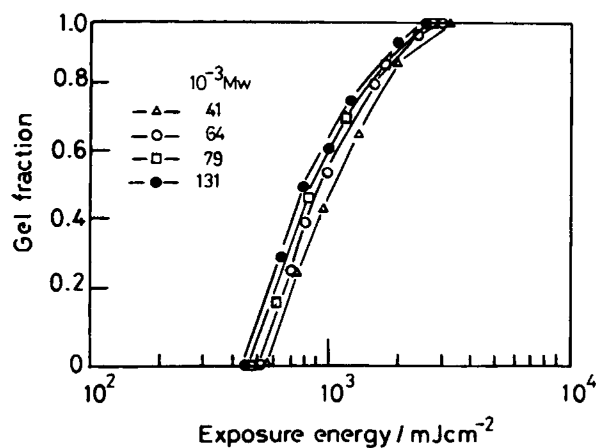


Figure 5 Dependence of characteristic curves of copolymer 4s with 10 wt % DIAS on number-average molecular weight (M_n).

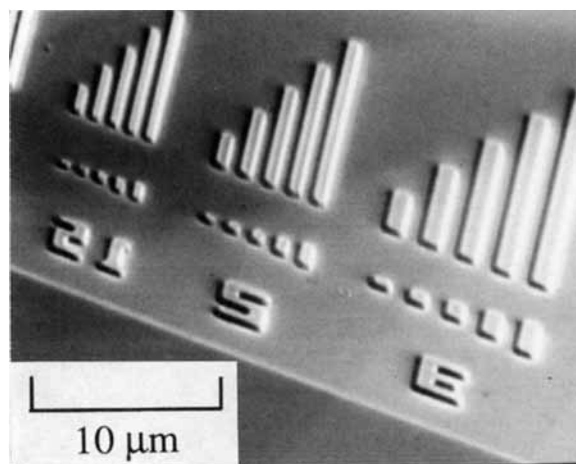


Figure 7 Scanning electron micrograph of a negative image obtained from 3CS using DIAS as a photoacid generator by exposure to 365 nm light.

actions of these monomers was also found by Nishikubo et al.[21] from the rates of gel production of divinyl ether and diglycidyl ether in dichloroethane. According to these data, we infer that the sensitivity enhancement in our 3CS is mainly attributable to the higher reactivity of the vinyl ether group than the epoxide group.

Figure 5 shows the dependence of sensitivity on the M_w for a series of copolymers 4's. The relationship between $D_g^{0.5}$ and M_w is shown in Figure 6. The sensitivity increases with increasing molecular weight. This result is reasonable from the viewpoint of the gelation theory[22] of polymer crosslinking and has been observed in other systems.[12,23,24]

Figure 7 shows the scanning electron micrograph of negative pattern printed with copolymer **4** containing 10 wt % DIAS and 100 wt % BPA-DEVE in a 1-μm film thickness. This picture shows that copolymer **4** reproduces a good pattern profile with high resolution by development with an aqueous base.

Figure 8 and 9 show IR spectra of the films of 2CS and 3CS using DIAS as the photoacid generator, before and after exposure to 365 nm light and PEB. In the case of 2CS, the IR spectra shows no remarkable change in spite of the exposure [Fig. 8(b)]. However, when the film was exposed and baked at 80°C for 5 min, the IR spectrum showed obvious changes. The absorption peak at 910 cm^{-1} was caused by the epoxide ring disappearing and a broad peak at 3500 cm^{-1} was caused by the hydroxy group increase as shown in Figure 8(c). These spectra indicate that crosslinkings of copolymer **4** (2CS) have taken place via ring-opening reactions of epoxide groups. The formation of hydroxyl groups in-

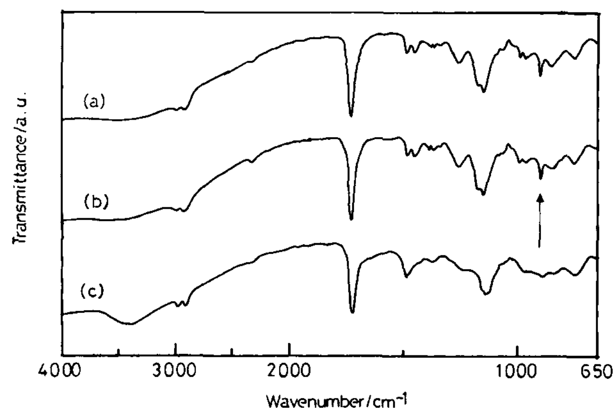


Figure 8 IR spectra of 2CS on silicon wafer (a) before exposure, (b) after exposure to 365 nm light, and (c) PEB at 80°C for 5 min.

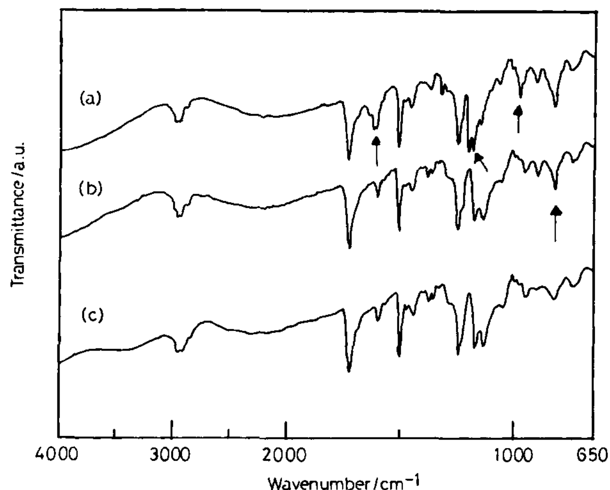


Figure 9 IR spectra of 3CS on silicon wafer (a) before exposure, (b) after irradiation at 365 nm, and (c) the subsequent heating at 60°C for 3 min.

dicates the addition reaction of epoxide ring with the acid.[2] On the other hand, IR spectra in Figure 9 shows that absorption peaks at 1620, 1205, and 990 cm^{-1}, which are assigned to carbon–carbon double bond in vinyl ether moiety, vinyl ether carbon–oxygen bond, and carbon–carbon double bond, respectively, disappeared after exposure to 365 nm light. After PEB at 60°C for 3 min, the absorption peaks at 910 cm^{-1} because the epoxide ring disappeared and the absorption peaks at 3500 cm^{-1} because the hydroxyl groups increased as is in the case of 2CS. These results indicate that the vinyl ether group is more reactive than the epoxide group and polymerizes without PEB if acid is present. Considering the reactivity difference between epoxide and vinyl ether groups, a comparison of Figures 8 and 9 indicates that the formation of interpenetrating polymer networks composed of epoxide and vinyl ether groups does not take place after the postexposure baking process. Consequently, the sensitivity is remarkably enhanced by the existence of BPA-DEVE (3CS) because the vinyl ether group of BPA-DEVE is polymerized by photogenerated acid and then epoxide groups crosslink in the successive PEB process.

CONCLUSIONS

A series of poly(GMA-*co*-MAA)s was prepared by the radical copolymerization of GMA and MAA in various ratios. Among the copolymers, the copoly-

mer consisting of 83 mol % GMA and 17 mol % MAA units gave the aqueous-base developable photoresist by the aid of a photoacid generator. The photoresist is insolubilized in aqueous-base developer after exposure and postexposure bake because of the acid catalyzed crosslinking reaction of the pendant epoxide rings. The photosensitivity of the resist is remarkably enhanced when the bifunctional vinyl ethermonomer (BPA-DEVE) is used in addition to the photoacid generator. From an IR spectroscopic study it was found that the sensitivity enhancement is accomplished by the much higher reactivity of the vinyl ether group of BPA-DEVE that polymerizes in the presence of acid without PEB. The copolymer prepared in this study offers high sensitive resist based on the cationic polymerization mechanism that is insensitive to oxygen in air.

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