Photocurable Positive Photoresist-Comprising Copolymers Having Pendant Alkoxy Ethyl Moieties

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ABSTRACT: A series of copolymers based on methacrylic acid (MAA), methyl methacrylate (MMA), *n*-butyl methacrylate (BM), and bornyl methacrylate (BMA) with various feed molar ratios were synthesized. To introduce the protecting alkoxy ethyl moieties onto copolymers, the pendant carboxyl groups were further reacted with alkyl vinyl ether. The pendant alkoxy ethyl groups on copolymers could be deprotected by acid catalyst. Characterization of positive-tone photoresist-comprising copolymers having pendant alkoxy ethyl groups was carried out. Effects of alicyclic bornyl groups on the sensitivity and thermal properties of copolymers were investigated. It was found that the existence of bornyl groups in polymer might interfere with the hydrogen bonding produced by pendant carboxyl groups, leading to the decrease of thermal resistance. Acid-catalyzed dehydration crosslinking of pendant carboxyl groups of copolymers was also investigated. The exposure characteristic curves and the lithographic evaluation of the positive-tone photoresist were all investigated. Effects of alicyclic bornyl groups on the plasma etching resist of copolymers were also evaluated.
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Key words: photoresist; photoacid generator (PAG); bornyl methacrylate; lithography; acid-catalyzed dehydration

INTRODUCTION

Positive photoresists are materials that become soluble in solvent or water-based developing solutions when exposed to optical radiation. Many articles describing various mechanisms for positive-tone photoresists have been published.[1–7] Particularly, the *t*-butoxy carbonyl (*t*-BOC) deprotection mechanism offering a high sensitivity and contrast by acid-catalyzed deprotection has attracted interest in the development of high-performance photoresist.[8–9]

Recently, syntheses and applications of photoresists were developed within a widespread research area. The technological applications of photoresists are applied in the fields of microlithography,[10–11] printing materials,[12] liquid crystalline,[13–14] and nonlinear optical materials.[15] To increase the density of semiconductor devices, the lithography process of producing high-resolution images on substrates was one of the most significant processes in semiconductor manufacturing. It is widely believed that optical lithography will continue to be the dominant technique for mass fabrication of advanced semiconductor devices in the future. The use of a chemical amplification photoresist, in addition to greatly increased sensitivity of the photoresist, also improves the contrast and resolution of the photoresist pattern.[16–17]

In our previous article, we reported a novel acid-catalyzed dehydration crosslinking for nega-

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tive-tone photoresist-comprising copolymers having pendant carboxyl groups.[18] To connect the applications of the acid-catalyzed dehydration crosslinking on the positive-tone photoresist, in this article, a series of copolymers having pendant carboxyl and alkoxy ethyl groups were synthesized. Thermogravimetric properties of copolymers, exposure characteristic curves, and lithographic evaluation of the positive-tone photoresist were all investigated. Effects of alicyclic bornyl groups on the plasma-etching resistance of copolymers were also investigated.

EXPERIMENTAL

Materials

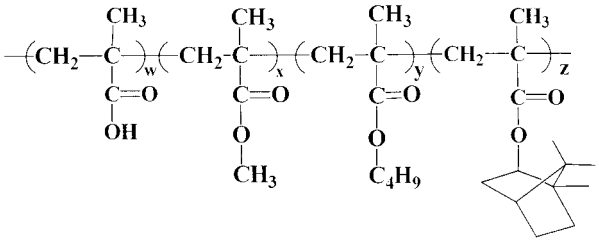
Methacrylic acid (MAA), methyl methacrylate (MMA), butyl methacrylate (BA), butyl vinyl ether (BVE), and ethyl vinyl ether (EVE) were purchased from Acros and purified by general methods. Triarylsulfonium hexafluoroantimonate as ionic photoacid generator (PAG) was purchased from Aldrich. The initiator azobisisobutyronitrile (AIBN) was purified by recrystallization in ethanol. Organic solvents used in this investigation were all distilled and dried with molecular sieves prior to use.

Measurements

The UV–visible spectra of films of the photoresist on quartz substrates were measured with a Jasco UV/Vis 7850 double-beam spectrometer. The photoresist was exposed with a Karl Suss MJB-3 aligner. The film thickness was measured with a Tencor Instrument alpha-step 200-film-thickness monitor. Dissolution rate is defined as the changes of photoresist film thickness per development time. The resist pattern profiles were evaluated by using a Jeol JSM-35 and JAX-840 scanning electron microscope. Thermal properties and functional groups of polymers were evaluated and analyzed by using a DuPont 910 differential scanning calorimeter, a Perkin–Elmer TGA-7 thermogravimetric analyzer, and a Jasco FTIR spectrometer, respectively. Elemental analyses were calculated with a Heraeus CHN-O rapid elemental analyzer. TOA pH meter was used to measure the pH values of developing aqueous solutions.

Preparation and Functionalization of Copolymers

Copolymers were obtained by the copolymerization of monomers in tetrahydrofuran (THF) in the presence of 1 wt % AIBN at 60°C for 12 h. Comonomers were poured into a glass polymerization tube equipped with a sealing cap, which was degassed in vacuum by using a freeze–thaw technique, and then sealed off. After completion of the polymerization, copolymers were precipitated from a large amount of water/methanol (1 : 1 in volume) solution and then washed with distilled water completely. To introduce the pendant alkoxy ethyl groups, copolymers (5 g) dissolved in THF (5 g) with excess alkyl vinyl ether (5 g) were poured into a glass tube equipped with a sealing cap and then sealed off. The mixture was heated at 70°C for 24 h, then precipitated by pouring the reaction mixture into a large amount of distilled water, and washed with water completely.



Scheme 1

Lithographic Evaluation

A resist solution was made by dissolving 1.5 g copolymer and 0.15 g PAG in 10 ml THF. The photosensitive solution was filtered through a 0.45-μm filter and then spin-coated onto a clean silicon wafer surface at 1000 rpm for 10 s, 2500 rpm for 20 s, and then prebaked at 90°C for 2 min. A 1- to 3-μm-thick film will be obtained. The photoresist was exposed with a Karl Suss MJB-3 aligner. After exposure, the resist was postexposure baked (PEB) at 110°C for 2 min and then developed with a 20-s immersion in 0.5 wt % sodium carbonate developer. A clear pattern was obtained when rinsed completely with distilled water. The relief polymeric materials were then exposed with UV light and further heat treated at 150°C for 60 min. At this stage, the dehydration of pendant carboxyl groups led to the crosslinking of copolymers. Resolution of the photoresist was estimated by SEM technique.

RESULTS AND DISCUSSION

Scheme 1 shows the copolymer structure. The MMA unit in the copolymer was introduced to

Table I Results of Copolymerization of Comonomers[a]

Polymer	MAA[b]	MMA[c]	*n*-BMA[d]	(±)-BMA[e]	T_{dc}[f] (°C)	Yield (%)	$M_w \times 10^{-4}$[g]
1	10[h]	10	10	0	247	70	4.6
2	20	10	10	10	198	85	3.4
3	10	10	10	10	195	84	1.5

[a] Copolymerized in THF at 60°C for 12 h in the presence of 1 wt % of AIBN.
[b] Methacrylic acid.
[c] Methyl methacrylate.
[d] *n*-Butyl methacrylate.
[e] (±)-Bornyl methacrylate.
[f] Decomposition temperature measured by TGA.
[g] Estimated by GPC with polystyrene standards.
[h] Mmol of feed monomers.

improve adhesion and mechanical properties and minimize shrinkage after exposure-bake processing steps. The MAA unit in the copolymer was introduced to be functionalized as photosensitive groups and also to induce crosslinking of the relief polymeric patterns through the acid-catalyzed dehydration by the PAG. In addition, MAA plays an important role in the resist becoming base-developable. BA was introduced to give good adhesion on silicon substrate and to improve the developing properties. BMA was utilized to improve the dry etching resistant.

The results of polymerization of comonomers are summarized in Table I. All polymers shown in Table I could be dissolved in alkali aqueous solution. Figure 1 shows the results of thermogravimetric analyses of polymers 1, 2, and 3. As can be seen, polymer 1 without a bornyl methacrylate (BMA) unit has higher thermal resistance than polymers 2 and 3. Feed monomer content of BMA in polymers 2 and 3 are 20 and 25 mol %, respectively. As can be seen in Scheme 1, the bornyl group is a large alicyclic group and has a large steric hinderance. In our previous article,[7] it was found that thermal resistant of copolymers increased with an increase in the content of pendant BMA unit. In this case, however, the existence of the large amount of BMA in the copolymer may interfere with the formation of the hydrogen bonds produced by carboxyl groups, leading to the decrease of thermal resistance.

As shown in Scheme 2, alkoxy ethyl groups were introduced onto the copolymers. The introduced pendant alkoxy ethyl groups are acid labile, which will be decomposed by acid catalyst. To investigate the functionalization of copolymers, the FTIR spectra of copolymer 1 before and after functionalization were measured. As Figure 2 shows, the OH absorption of copolymer 1 decreased obviously after functionalization by ethyl vinyl ether. Figure 3 shows the FTIR spectra of copolymer 4 functionalized by ethyl vinyl ether with 10 wt % PAG before and after UV irradiation. An obvious OH absorption was observed after UV irradiation and a sufficient PEB. The results suggest that the pendant ethoxy ethyl groups were decomposed by acid catalyzation. The deprotection mechanism is shown in Scheme 2.

To investigate the effects of alkoxy groups on the thermo properties of copolymers, ethoxy ethyl and butoxy ethyl groups were introduced onto the copolymers. The results of the thermo properties are summarized in Table II. As Table II shows,

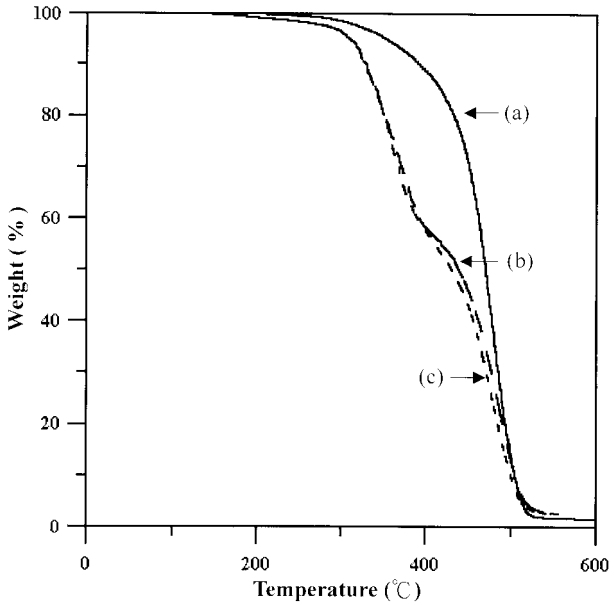
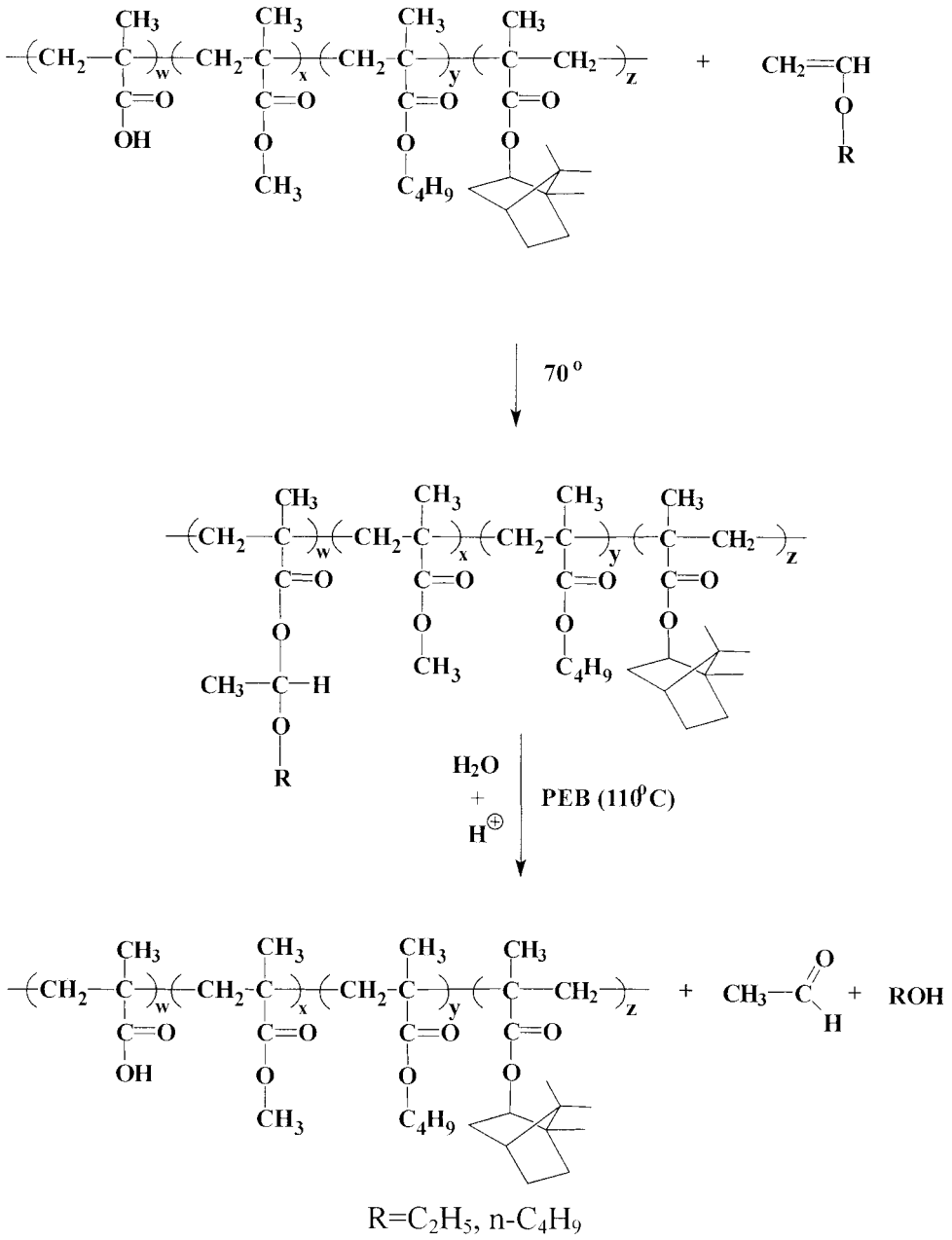


Figure 1 Thermogravimetric curves measured by TGA (20°C/min) in nitrogen. (a) Copolymer 1; (b) copolymer 2; (c) copolymer 3.



R=C_2H_5, n-C_4H_9

Scheme 2

the deprotection temperature and the decomposition temperature of copolymers having butoxy ethyl groups are all lower than those of copolymers having ethoxy ethyl groups. Before functionalization, the decomposition temperature of copolymer 2 is about 198°C. After functionalization by EVE and BVE, the decomposition temperatures were decreased to 185 and 180°C, respectively. As can be seen in Table II, the acid-catalyzed deprotection of the ethoxy ethyl group and butoxy ethyl group of copolymers 6 and 7 will occur at 105 and 95°C, respectively. The deprotection of pendant groups will increase the hydrophilicity and alkaline solubility of copolymers.

As shown in Scheme 3, acid-catalyzed dehydration of pendant carboxyl groups may occur at 150°C heat treatment, leading to the crosslinking of copolymers. As described in our previous article, the crosslinked polymer could be confirmed by FTIR spectra.[7] To investigate the acid-catalyzed dehydration, copolymer 6 with 10 wt % PAG photoresist was irradiated with UV light for 60 s and

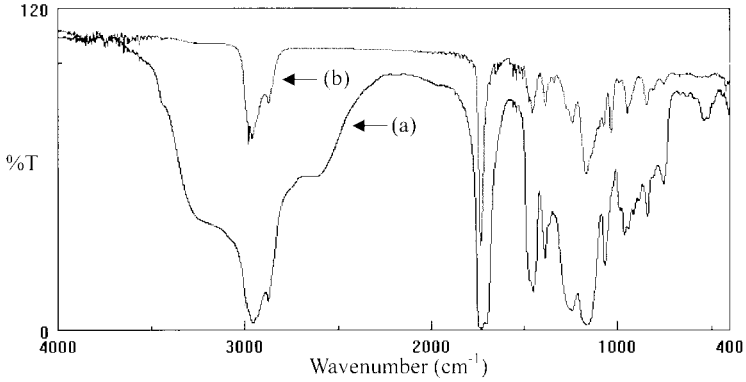


Figure 2 FTIR spectra of copolymer 3 (a) before and (b) after functionalized with ethyl vinyl ether.

then PEB at 150°C for 1 h. Curves (a), (b), and (c) in Figure 4 show the results of thermogravimetric analyses of copolymer 6 with 10 wt % PAG before UV irradiation, after UV irradiation, and after UV irradiation then PEB at 150°C for 60 min, respectively. As can be seen in curve (b), the pendant ethoxy ethyl groups will be decomposed in the initial stage. After UV irradiation and a sufficient PEB heat treatment at 150°C for 60 min, as shown in curve (c), deprotection of ethoxy ethyl groups and dehydration crosslinking of pendant carboxyl groups both completely led to the increase of the thermal resistance of polymer.

To find a suitable developer, the solubility of polymer 4 with various concentrations of sodium carbonate aqueous solution was investigated. The results are summarized in Figure 5. As Figure 5 shows, 0.5 wt % of sodium carbonate aqueous solution can be used as a developer for this photoresist system. The photoresist appears as good resistance for the developer without any UV irradiation and PEB treatment.

Figure 6 shows the exposure characteristic curves of the photoresist comprising the copolymers 4 and 5. As mentioned in Table II, the deprotection temperature of polymers having butoxy ethyl groups (copolymer 5) is lower than that of polymers having ethoxy ethyl groups (copolymer 4). The contrast of copolymer 4, however, is better than that of copolymer 5. This may be due to the fact that the acidity of butanol (bp = 117.7°C), a by-product of acid-catalyzed decomposition of copolymer 5, is greater than that of ethanol (bp = 78°C) from copolymer 4. Furthermore, the ethanol from polymer 4 should be readily evaporated during the PEB procedure. The existence and greater basicity of butoxy may induce a large barrier for photoacid transfer in polymer matrix, leading to the decrease in acid-catalyzed deprotection of polymers. Figure 7 shows the pH dependence of 0.01 g PAG in 10 ml ethanol and butanol on UV irradiation time. The pH value of PAG in ethanol is about 3.6, which is much lower than in butanol (about 5.5) after a sufficient UV irradia-

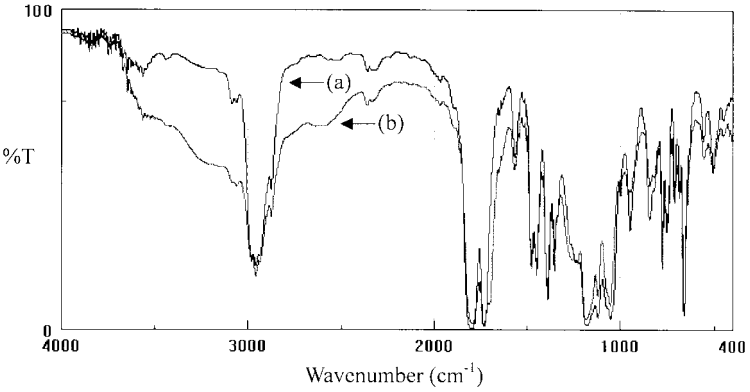


Figure 3 FTIR spectra of (a) copolymer 4 with PAG and (b) after UV irradiation for 60 s and PEB at 110°C for 2 min.

Table II Thermal Properties of Polymers[a]

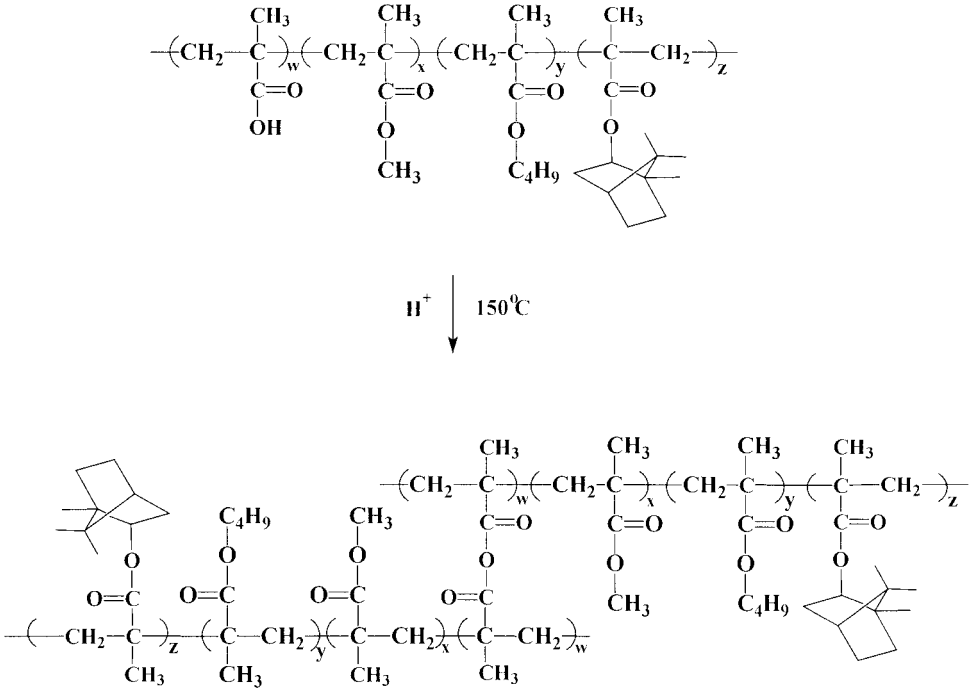
Polymer	Polymer Matrix	Protective Compound[b]	T_{dp}[c] (°C)	T_{dc}[d] (°C)	Yield (%)
4	Polymer 1	EVE	125	240	81
5	Polymer 1	BVE	117	237	78
6	Polymer 2	EVE	105	185	83
7	Polymer 2	BVE	95	180	88
8	Polymer 3	EVE	127	190	85
9	Polymer 3	BVE	120	187	75

[a] Functionalized in THF at 70°C for 24 h.
[b] EVE, ethyl vinyl ether; BVE, butyl vinyl ether.
[c] Deprotection temperature measured by DSC.
[d] Decomposition temperature measured by TGA.

tion for 180 s. The results suggest that the acidic environment is unfavorable for the decomposition of the PAG. The results are consistent with those obtained in Figure 6.

As shown in Figures 8 and 9, the existence of a great amount of alicyclic bornyl groups in copolymers 8 and 9 will interfere with the acid deprotection of alkoxy ethyl groups, leading to the decrease of sensitivity and contrast of the photoresist. In theory, an increase in the feed molar ratio of MAA (copolymer 2) will increase the content of pendant carboxyl groups, which could be functionalized by alkyl vinyl ether, leading to an increase in sensitivity.

Copolymer 4 with no alicyclic bornyl groups has better sensitivity and contrast than those of copolymer 8. For dry-etching lithography, however, it is necessary to introduce the alicyclic structures to enhance dry-etching resistance. To investigate the effects of alicyclic bornyl groups on the etching resistance, the etching rate of copolymers 4–9, poly(methyl methacrylate), and novolac resins were investigated with CH_4/Ar plasma etching. Table III shows the results of the etching rates of the polymers normalized to the novolac resin. The etching rates of polymers with no bornyl groups are 1.90 and 1.98 times the novolac resin. Polymers 6–9 with bornyl groups



Scheme 3

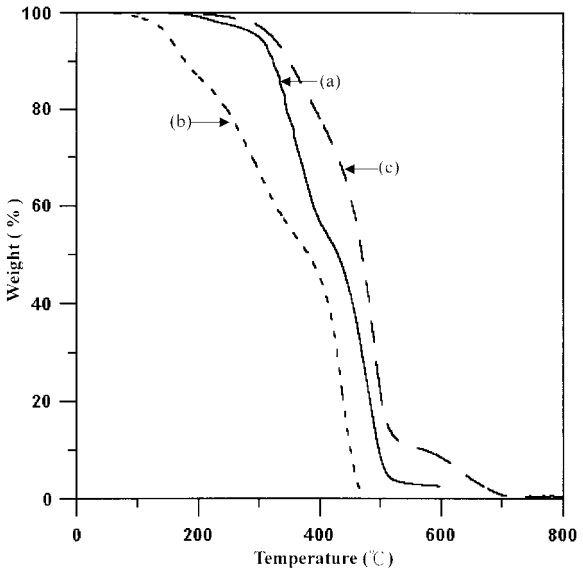


Figure 4 Thermogravimetric curves of copolymer 6 with 10 wt % PAG measured by TGA (20°C/min) in nitrogen: (a) before UV irradiation; (b) after UV irradiation; (c) after UV irradiation and PEB at 150°C for 60 min.

give better etching resistance than that of PMMA. Polymer 8 has an especially similar etching resistance to that of the novolac resin.

The SEM of lithographic performance was evaluated by polymer 6 with 10 wt % PAG, spin coated on a silicon wafer, and irradiated with a Karl Suss MJB-3 aligner through a line space

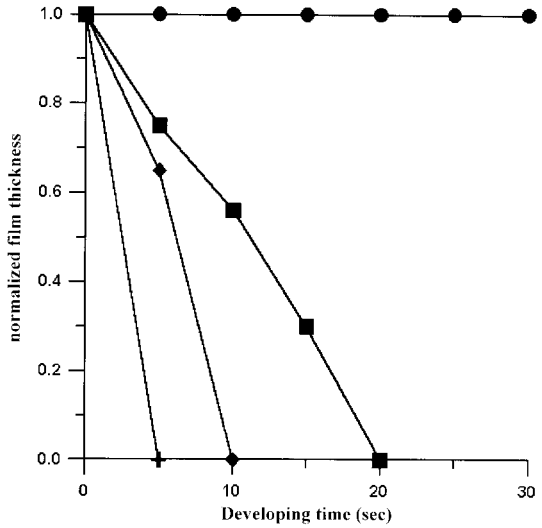


Figure 5 Dependence of normalized copolymer 4 film thickness on developing time in various concentrations of sodium carbonate: (+) 5 wt %; (◆) 3 wt %; (■) 1 wt %; (●) 0.5 wt %.

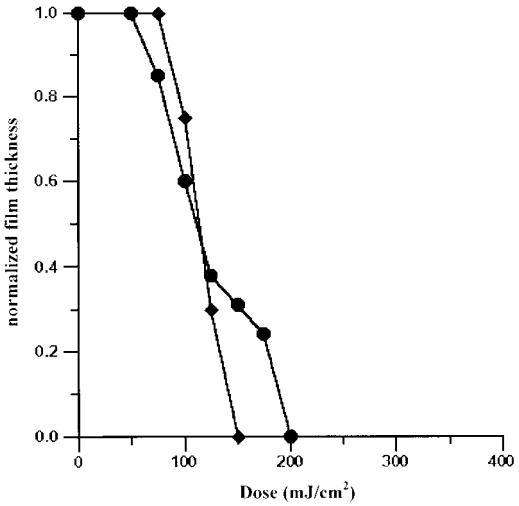


Figure 6 Exposure characteristic curves of positive photoresist comprising various copolymers: (◆) copolymer 4; (●) copolymer 5.

photomask. After exposure, the resist film was PEB at 120°C for 2 min, developed in 0.5 wt % sodium carbonate developer, and then washed with distilled water. Figure 10 shows the results of lithography; a 0.25-μm line and space pattern is achieved.

CONCLUSION

Copolymers having acid-labile pendant alkoxy ethyl groups were synthesized and could be used

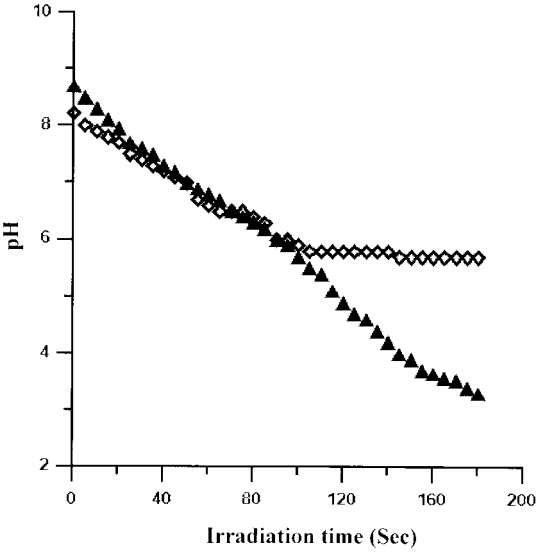


Figure 7 Dependence of pH values on UV irradiation time, 0.01 g PAG in 10 ml (▲) ethanol; (△) *n*-butanol.

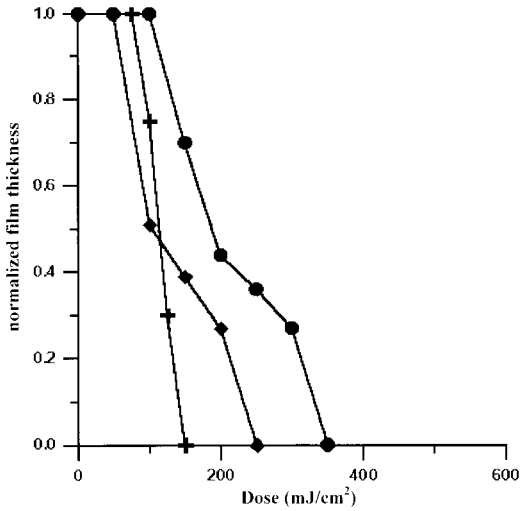


Figure 8 Exposure characteristic curves of positive photoresist comprising various copolymers: (+) copolymer 4; (◆) copolymer 6; (●) copolymer 8.

as a polymer matrix for positive-tone photoresist. The deprotection of pendant alkoxy ethyl groups was carried out by UV irradiation and then PEB at 110°C for 2 min. The presence of alicyclic bornyl groups in copolymers will decrease the sensitivity and contrast but increase the plasma-etching resistance of photoresist. Dehydration crosslinking of pendant carboxyl groups will occur in the presence of photoacid by heat treatment at 150°C for 1 min. The great acidity of butanol formed in the photoreaction may induce a large

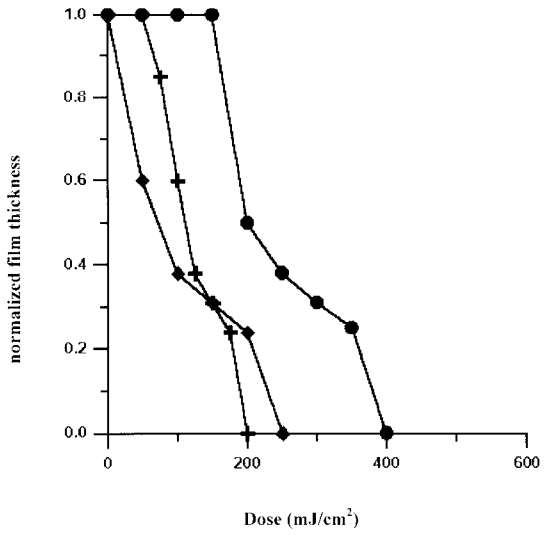


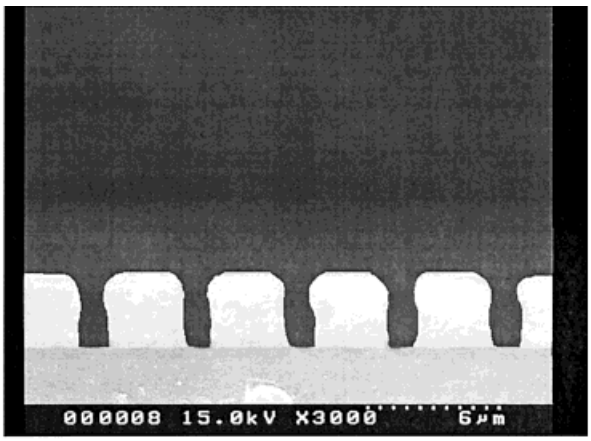
Figure 9 Exposure characteristic curves of positive photoresist comprising various copolymers: (+) copolymer 5; (◆) copolymer 7; (●) copolymer 9.

Table III Etching Rate of Polymers[a]

Polymer	Etching Rate
4	1.90
5	1.98
6	1.43
7	1.52
8	1.11
9	1.19
PMMA	1.80
Novolac resin	1.00

[a] CF_4 : Ar = 8 : 1 standard cubic centimeters per minute gas flow, 6×10^{-2} Torr, 650 W, 600 s.

barrier for photoacid formation, and a transfer in polymer matrix led to a decrease of sensitivity and contrast of photoresist-comprising polymers having pendant butoxy ethyl groups.



(a)

(b)

Figure 10 SEM photographs of resolution patterns.

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