Negative resists of silicone-containing graft polymer for bilayer resist system

Yoshio Tachibana, Yasutaro Yasuda and Tetsuji Jitsumatsu
Research Laboratory, Toagosei Chemical Industry Co. Ltd, 1-1, Funami-cho, Minato-ku, Nagoya-shi, Aichi 455, Japan

and Ken'ichi Koseki and Tsuguo Yamaoka*
Faculty of Engineering, Chiba University, 1-33, Yayoi-cho, Chiba-shi, Chiba 260, Japan
(Received 15 July 1989; revised 7 September 1989; accepted 18 September 1989)

Photocrosslinkable silicone-containing graft polymers were synthesized using silicone-macromonomer; 0.5 μm line and space patterns were accurately fabricated by O_2RIE using the graft polymers as the top layer on phenol novolak resin. TEM observation of the graft polymer indicated the phase separation of the silicone chain from the hydrocarbon chain. The phase separation enhanced the photocrosslinking efficiency of the graft polymer.

(Keywords: silicone macromonomer; graft polymer; negative resist; azido group; photocrosslinking; phase separation)

INTRODUCTION

The minimum pattern size in the very large scale integrated circuit (VLSI) reaches sub-halfmicron dimensions. The multilayer resist system is one of the promising candidates which enables the transfer of sub-halfmicron patterns with high resolution and high aspect ratio. While a trilayer resist system provides successfully high resolution, it requires a rather complicated manufacturing process.

A bilayer resist system was proposed as an alternative to simplify the trilayer system. The bilayer resist system is composed of a top layer for pattern formation on a thick polymer layer for planarization. The top layer must be provided with high resistance to oxygen reactive ion etching (O_2RIE) for transferring the pattern to the bottom layer.

A number of Si-containing resists which are sensitive to deep u.v., electron beam or X-ray have been demonstrated as the top layer for imaging[1–8].

Hatzakis[1] first demonstrated the bilayer system by using poly(methylvinyl siloxane) on a hard-baked AZ-1350J layer in which the top resist was exposed with deep u.v. or electron beam. Morita[2] reported chloromethylated poly(diphenylsiloxane) which has a high T_g and the high sensitivity to deep u.v., electron beam, and X-ray. Saigo[3] developed a near u.v. resist consisting of poly(allyl dimethylsilyl-α-methylstyrene) and bisazide. Granger[4] reported poly[γ-methacryloyloxypropyl tris(trimethylsiloxy)silane] as a negative electron beam resist.

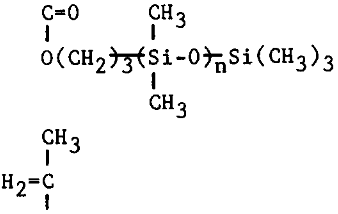
In the present paper, photosensitive Si-containing graft polymers were prepared and their characteristics for the bilayer resist are described below. As has been suggested by a number of reports[9–11] phase separation, induced by the different property of the grafted side chains from the main chain, was observed in our graft polymer and the effects on sensitivity are also discussed.

EXPERIMENTAL

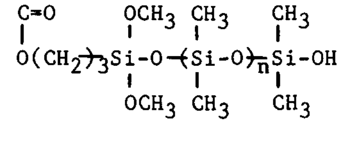
Synthesis of silicone macromonomers

Silicone macromonomers, MM(1) and MM(2) were prepared as follows: 0.5 g of metallic potassium and 5 g of *n*-hexane were placed in a flask, and then 10 ml methanol was added dropwise for 30 min at 0–5°C under an N_2 atmosphere. After excess methanol and *n*-hexane were removed under reduced pressure, 40 ml dry tetrahydrofuran (THF) and 40 ml octamethyl cyclotetrasiloxane were added to the solution, and refluxed for 4 h. After the solution was cooled to room temperature, 10 wt% γ-methacryloxypropyl dimethylchlorosilane in THF was added dropwise to the solution. Then the reacted potassium chloride was removed by filtration, and the silicone macromonomer MM(1) was isolated by reprecipitation with methanol.

α,ω-Dihydroxypolydimethylsiloxane, γ-methacryloxypropyltrimethoxysilane and potassium acetate was reacted for 20 h at 150°C under an N_2 atmosphere. After cooling, toluene was added to the solution, and then potassium acetate was removed by filtration. The MM(2) thus prepared was isolated by reprecipitation with methanol. The molecular structures of MM(1) and MM(2) are shown below


$\mathrm{CH_2{=}C(CH_3)\text{-}C({=}O)\text{-}O(CH_2)_3(Si(CH_3)_2\text{-}O)_nSi(CH_3)_3}$

MM(1)


$\mathrm{CH_2{=}C(CH_3)\text{-}C({=}O)\text{-}O(CH_2)_3Si(OCH_3)_2\text{-}O(Si(CH_3)_2\text{-}O)_nSi(CH_3)_2\text{-}OH}$

MM(2)

---

* To whom correspondence should be addressed

0032-3861/90/081553–06

Synthesis of graft polymers by polymerization of MM samples

MM(1) ($M_n = 1000$) (30 g), methyl methacrylate (30 g) and glycidyl methacrylate (40 g) were dissolved in 150 ml toluene with 1 g 2,2'-azobis-iso-butyronitrile (AIBN) as an initiator. The solution was reacted for 5 h at 85°C under an N_2 atmosphere to prepare the graft terpolymer, then acrylic acid (AA), cinnamic acid (CA) or *p*-azidobenzoic acid (N_3) were added to the solution. The solution was stirred at 80°C with bubbling air using tetra-*n*-butylammonium bromide (TBAB) as an esterification catalyst. In the case of esterification of acrylic acid, hydroquinone dimethyl ether was added as an inhibitor of thermal polymerization of the acryloyl group. The end point of esterification was determined by acid value of the polymer with a 0.1 M ethanol solution of potassium hydroxide, using bromothymol blue as an indicator. Finally, the photosensitive silicone-containing graft polymers were isolated and purified by repeating reprecipitation with *n*-hexane or methanol.

GP was prepared by copolymerizing MM(2) and methylmethacrylate in toluene with AIBN. After polymerizing for 5 h at 85°C under an N_2 atmosphere, the reacting solution was poured into *n*-hexane to precipitate GP. The polymerization and the esterification steps and the abbreviations of the photosensitive graft polymers are summarized in *Scheme 1*. The terpolymerization ratio of the graft polymers was obtained by controlling the amount of the respective monomer in feed. The structures and the molecular weights of the photosensitive graft polymers and GP were characterized by ^{1}H n.m.r. and g.p.c. (a Toso Model HLC-802UR), respectively. The molecular parameters and the compositions of these polymers are summarized in *Table 1*.

Lithographic evaluation

A solution (10 wt%) of the graft polymer added with triplet sensitizer, photoinitiator or 4,4'-diazidochalcone if necessary, was spun on a silicon wafer and prebaked at 80°C for 30 min to form a 0.2 μm thick layer. The polymer layer was exposed to 365 nm light to determine sensitivity to *i*-line, and to 254 nm light (a low pressure mercury lamp) to determine sensitivity to deep u.v. light. After exposure the polymer layer on the silicon wafer was developed with iso-amylacetate for GP(AA), GP(CA) and GP(N_3) and with the 1:1 mixed solution of toluene and *n*-hexane for GP, followed by rinsing with *n*-hexane.

The ratio of the film thickness before and after development was defined as the gel fraction. The characteristic curve of the polymer was obtained by plotting the gel fraction against the exposure energy.

Scheme 1

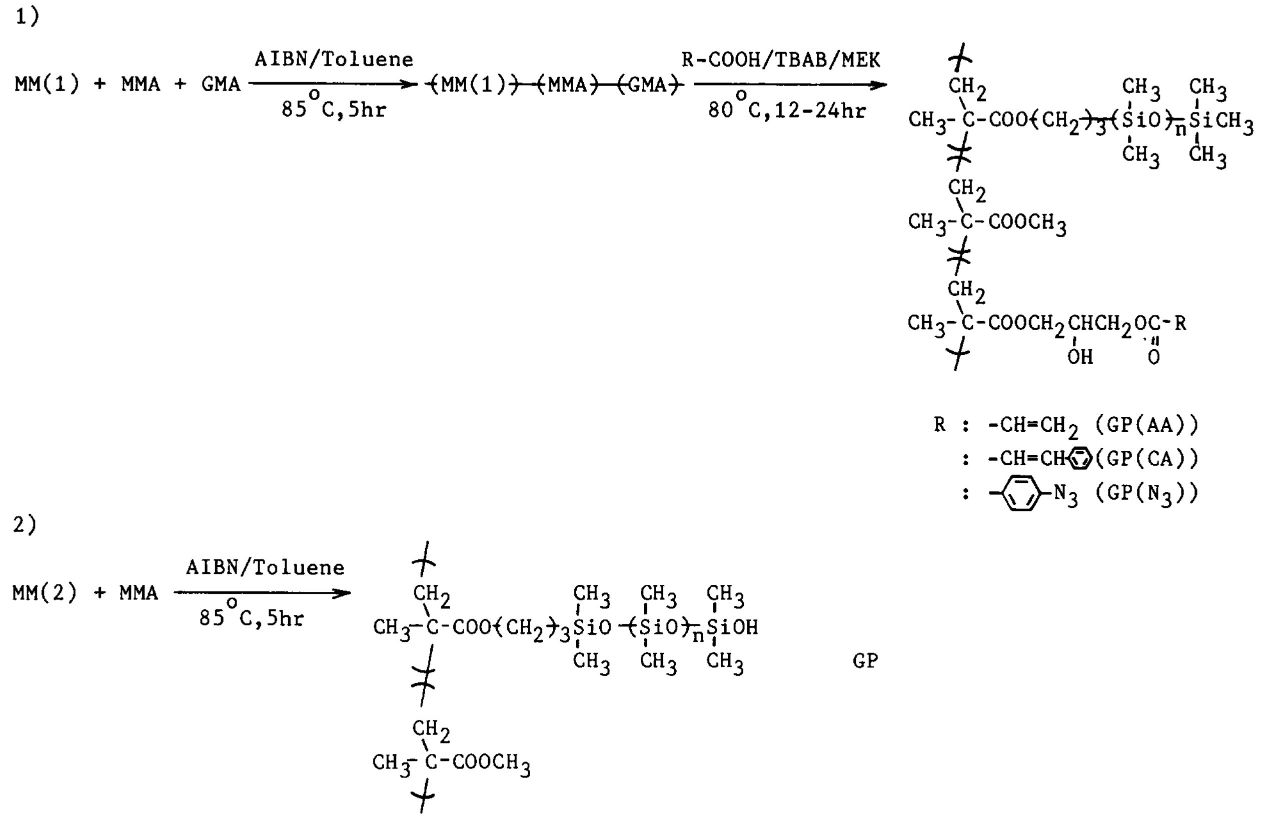


Table 1 Molecular parameters of silicone-containing graft polymers

	Molecular parameters			Composition of polymers (mol%)			
Abbreviation	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	MM(1)	MM(2)	MMA	GMA
GP	4400	67600	15	–	0.7	99.3	–
GP(AA)	14000	76200	5.4	3.4	–	49.8	46.8
GP(CA)	14800	53700	3.6	3.5	–	47.5	49.0
GP(N_3)	18200	40800	2.2	3.8	–	45.0	51.2

Sensitivity was defined by $D_g^{0.5}$ (the exposed energy, mJ/cm^2 required to gelate half the initial film thickness). D_g^i is the exposed energy where gelation starts. The contrast of the polymer (γ) was defined as the slope of the characteristic curve at $D_g^{0.5}$.

Patterning by dry etching

On 1 μm thick layer of novolak resin, a pattern was formed with the graft polymer, and dry-etched by oxygen reactive ion etching (O$_2$RIE). The patterns produced are evaluated by s.e.m. observation.

Observation of phase separation

The polymer spin coated on a PET film to form 0.3 μm thick layer was dyed by keeping it in a closed chamber saturated with the vapour from 1% aqueous solution of ruthenium(VIII) oxide. The polymer film removed from PET film was observed with TEM.

RESULTS AND DISCUSSION

Photosensitivity of graft polymers

GP(CA) and GP(N$_3$) are photosensitive by themselves because they contain the photocrosslinkable cinnamoyl group and phenyl azide group, respectively. GP(AA) is not photosensitive by itself but can be photosensitized by adding a small amount of photoinitiator. GP is not photosensitive by itself because no photosensitive group is present in the structure, but can be photosensitized by adding photocrosslinking agents such as bisazide compound.

Figure 1 shows the electronic spectra of GP(CA) and GP(N$_3$). GP(CA) has an absorption peak at 280 nm due to the cinnamoyl group and GP(N$_3$) has a peak at 274 nm due to the *p*-azidobenzoyl group. The presence of absorptions in these wavelength regions indicates that GP(CA) and GP(N$_3$) are sensitive to light at wavelengths shorter than 320 nm. *Figure 2* shows the sensitivity curves of GP(CA) and GP(N$_3$) on irradiation of 254 nm light. The sensitivity values ($D_g^{0.5}$) of GP(CA) and GP(N$_3$) are 13.5 mJ/cm^2 and 5.7 mJ/cm^2, respectively. Photocrosslinking of GP(CA) is based on photodimerization of the cinnamoyl group, and may follow the second order kinetics. On the other hand, GP(N$_3$) is crosslinked by the reaction of nitrenes transiently produced by the photolysis of azide groups. Hydrogen abstraction, coupling to form azo compounds, and addition to ethylene double bonds are also known as the main reactions of nitrenes. With these reactions, nitrenes react not only with other nitrenes but also the surrounding polymer chains to form a crosslinking structure.

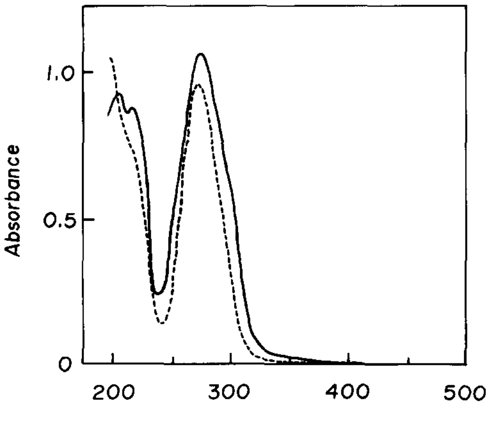


Figure 1 Electronic spectra of ——, GP(CA) and ----, GP(N$_3$) film. Film thickness: 0.2 μm

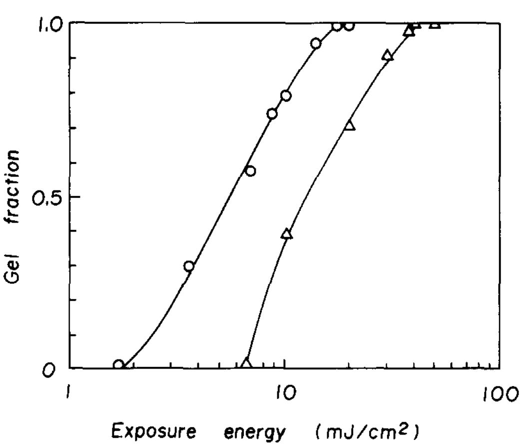


Figure 2 Characteristic curves of —△—, GP(CA) and —○—, GP(N$_3$) on irradiation of 254 nm light

Because photochemical reactions of both cinnamoyl group and azide group are known to occur via the lowest excited triplet state, the spectral sensitivity of GP(CA) and GP(N$_3$) may be extended to the near ultraviolet region by the use of an appropriate triplet sensitizer. When 8 wt% Michler's ketone (MK) was added as the triplet sensitizer, GP(CA) and GP(N$_3$) exhibited the sensitivity of 18.5 mJ/cm^2 and 6.2 mJ/cm^2, respectively, to 365 nm (*i*-line) light.

Because the crosslinking of GP(AA) is accomplished by photopolymerization of the acryloyl group, GP(AA) can be photosensitized by the addition of a radical generating photoinitiator. GP(AA) to which 5 wt% photoinitiator (α,α-dimethoxy-α-phenylacetophenone) was added, exhibited the sensitivity of 22 mJ/cm^2 to 365 nm of light. GP sensitized with 7.7 wt% 4,4′-diazidochalcone showed the sensitivity of 87 mJ/cm^2 to 365 nm of light. The resist characteristics of GP, GP(CA), GP(N$_3$), and GP(AA) are summarized in *Table 2*.

The dependence of sensitivity on the concentration of the photocrosslinking group was investigated by varying the terpolymerization ratio of GP(N$_3$). As is shown in *Table 3*, terpolymers containing differing amounts of glycidylacrylate (from 11.5 mol% to 36.6 mol%) were prepared.

As azidobenzoyl group is added to glycidyl group, GP(N$_3$) with different azide group content can be prepared. The sensitivity to 365 nm light of these three polymers from GP(N$_3$)$-$10 to GP(N$_3$)$-$30 were measured by adding MK as a triplet sensitizer. As can be seen in *Figure 3*, the sensitivity of these polymers to 365 nm light is between 2.2–4.1 mJ/cm^2 for $D_g^{0.5}$ and 1.0–3.0 mJ/cm^2 for D_g^i. The sensitivity when exposed to 254 nm is in the range of 0.58–4.4 mJ/cm^2. Because the sensitivity of photocrosslinking type polymers depends on the molecular weight, we also investigated the dependence of sensitivity on the content of phenylazide group by comparing $1/D_g^i \times \bar{M}_w$ for GP(N$_3$) samples. According to the theory of gelation, the number of crosslinking units required to gelate are inversely proportional to the initial weight-average molecular weight[12,13]. Consequently, the term of $D_g^i \times \bar{M}_w$ indicates

Table 2 Composition of photosensitive graft polymers and the lithographic parameters

Graft polymer	Sensitizer or photocrosslinker (wt% to polymer)	Wavelength of exposure light (nm)	Sensitivity $D_g^{0.5}$ (mJ/cm^2)	γ
GP(AA)	α,α-Dimethoxy-α-phenylacetophenone, 5	365	22	0.8
GP(CA)	–	254	13.5	1.2
GP(CA)	Michler's ketone, 8	365	18.5	1.5
GP(N_3)	–	254	5.7	1.1
GP(N_3)	Michler's ketone, 8	365	6.2	1.4
GP	4,4′-Diazidochalcone, 15	365	87	2.2

Table 3 Molecular parameters of silicone-containing graft polymers

Abbreviation	Molecular parameter			Composition of polymer (mol%)			Sensitivity $D_g^{0.5}$ (mJ/cm^2)	
	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	MM(1)	MMA	GMA	254 nm	365 nm[a]
GP(N_3)–10	27400	118500	4.3	3.3	85.2	11.5	4.4	4.1
GP(N_3)–20	43800	122100	2.8	3.1	75.0	21.9	0.79	3.1
GP(N_3)–30	31900	133200	4.2	2.8	60.6	36.6	0.58	2.2

[a] Sensitized with Michler's ketone

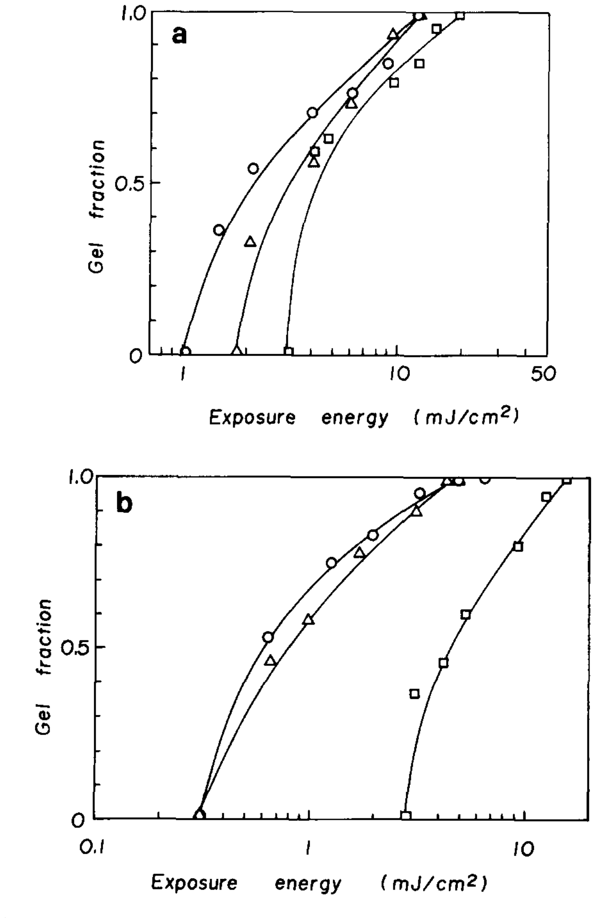


Figure 3 (a) I-line sensitivity characteristics curves of GP(N_3) samples sensitized with Michler's ketone. □, GP(N_3)–10; △, GP(N_3)–20; ○, GP(N_3)–30. (b) Deep u.v. (254 nm) sensitivity characteristic curves of GP(N_3) samples. □, GP(N_3)–10; △, GP(N_3)–20; ○, GP(N_3)–30

the photosensitivity of the polymer gelation where the variation of molecular weight is normalized. *Figure 4* shows the relationship between the concentration of phenylazide group and $1/D_g^i \times \bar{M}_w$ for GP(N_3) samples. With increases in the content of the phenylazide group in the polymer, $1/D_g^i \times \bar{M}_w$ increases.

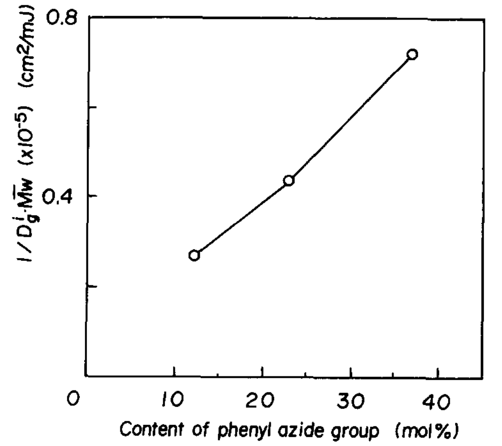
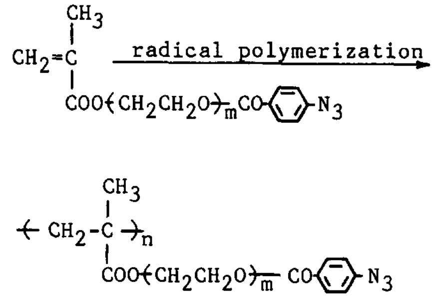


Figure 4 The relationship between the concentration of phenylazide group and $1/D_g^i \times \bar{M}_w$ for GP(N_3) samples

A number of polymers involving the phenylazide group as a photocrosslinking group have been reported[14,15]. We have also studied the relationship between the length of the side chain and the sensitivity of crosslinking using azide polymers which have the following structures. The methods of preparation and characterization have been reported in a previous paper[16].



$$CH_2{=}C(CH_3)COO(CH_2CH_2O)_mCO\text{-}C_6H_4\text{-}N_3 \xrightarrow{\text{radical polymerization}} {+}CH_2\text{-}C(CH_3)(COO(CH_2CH_2O)_mCO\text{-}C_6H_4\text{-}N_3){+}_n$$

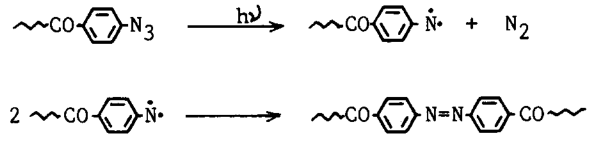
The degree of substitution of photosensitive azide group is 100% because the polymers were radical-polymerized from the parent monomers. As is indicated by the sensitivity values in *Table 4*, sensitivity increases with an increase in the length of the side chain. This means that the mobility of the side chains is important

Table 4 The sensitivity values of azide polymers having different side chain length

m	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	D_g^i	$D_g^{0.5}$	$1/D_g^i \times \bar{M}_w$
1	172000	3.9	15	69	3.0×10^{-7}
2	145000	2.7	7	25	9.0×10^{-7}
3	77000	2.1	2	13	6.4×10^{-6}

for crosslinking efficiency, and suggests that the encounter of photochemically produced nitrenes results in the crosslinking structure.

In other words, among the various reactions of nitrenes, the coupling reaction of nitrenes to form azo bonds may be the most important mechanism for crosslinking.



Values of $1/D_g^i \times \bar{M}_w$ for these polymers are from 3×10^{-7} to 6.4×10^{-6}. Compared with these values, the $1/D_g^i \times \bar{M}_w$ for GP(N_3) samples gives much higher values from 0.3×10^{-5} to 0.8×10^{-5}. The higher values of the crosslinking efficiency of GP(N_3) samples may be brought about by the structure of the graft polymers.

Phase separation in Si-containing graft polymer

The silicone-containing graft polymers prepared in the present study are consisting of hydrocarbon chains and siloxane chain segments which are different from each other in solubility parameters.

Figure 5 shows a TEM photograph of the film surface of the silicone-containing graft polymer, GP. The TEM photograph shows that the polymer surface is not homogeneous, and exhibits minute specks. This appearance of the polymer surface suggests that phase separation is occurring in the polymer.

The surface of the polymer film was slightly etched by oxygen reactive etching (O_2RIE). While most organic compounds are ashed by O_2RIE, Si-containing compounds are not completely ashed by O_2RIE. When Si-containing organic compounds are etched by O_2RIE, the organic portions of the compounds are ashed. Si elements, however, are not ashed but converted to SiO_2 which remains.

The s.e.m. photograph of the polymer surface after etching with O_2RIE, shows that the minute specks are not ashed whilst other portions of the surface are ashed out (*Figure 6*). This suggests that the specks are rich in the Si element. In other words, the hydrocarbon portion and the siloxane portion in the polymer are incompatible and are phase separated. As a result of the phase separation, phenylazide groups are locally concentrated. The local concentration of phenylazide group in the polymer may make the crosslinking reaction more efficient.

Application to bilayer resist system

Phenol–novolak resin was spin-coated on a silicon wafer in 1.5 μm thickness and hard-baked at 200°C for 60 min. On the hard-baked phenol–novolak resin layer, the photosensitive graft polymer was spin-coated to form 0.2–0.3 μm layer. After image-wise exposure with 254 nm of light, it was developed for 60 s in isoamylacetate (GP(AA), GP(CA) and GP(N_3)), and rinsed for 20 s in *n*-hexane. The patterns thus formed were transferred to the underlying phenol–novolak resin layer by O_2RIE (O_2 flow: 30 sccm, pressure: 2.3 mTorr, power: 1000 W, etching time: 2.5 min). *Figure 7* demonstrates 0.5 μm and 1.0 μm line patterns after O_2RIE formed with GP sensitized by adding 7.7 wt% diazidochalcone. Other graft polymers also offered similar patterns. The results show that the silicone-containing graft polymers show high resistance against O_2RIE and act as the bilayer resist.

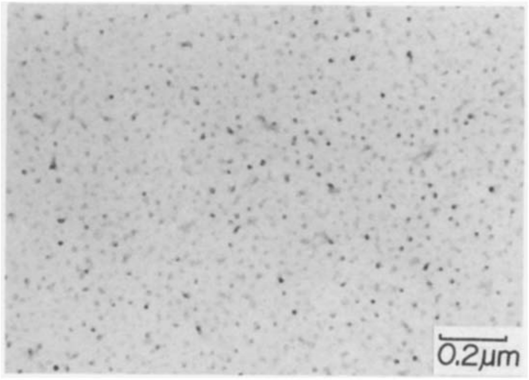


Figure 5 TEM photograph of the film surface of silicone-containing graft polymer, GP on a PET film

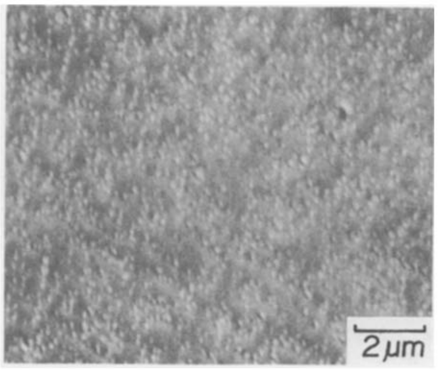


Figure 6 SEM photograph of the polymer surface after etching with O_2RIE

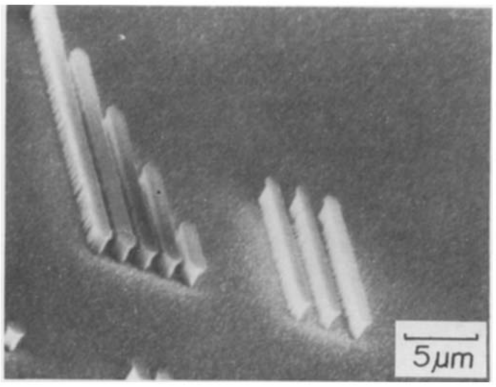


Figure 7 SEM photograph of 0.5 μm and 1.0 μm line patterns after O_2RIE formed with GP/diazidochalcone

REFERENCES

1 Hatzakis, M., Paraszczak, J. and Show, J. In *Proc. Microcircuit Engineering Conf.*, Lausanne, 1981, p. 386

2 Morita, H., Imamura, S., Tanaka, A. and Tamamura, T. *J. Electrochem. Soc.* 1984, **131**, 2402

3 Saigo, K., Watanabe, F. and Ohnishi, Y. *J. Vac. Sci. Technol.* 1986, **B4**, 692

4 Granger, D. D., Miller, L. J. and Lewis, M. M. *J. Vac. Sci. Technol.* 1988, **B6**, 370

5 Ohnishi, Y., Suzuki, M., Saigo, K., Saotome, Y. and Gokan, H. *Proc. SPIE* 1985, **539**, 62

6 Allen, R. D., McDonald, S. A. and Willson, C. G. In 'Polymers for High Technology', ACS Symp. Ser. No. 346, American Chemical Society, Washington, DC, 1987, p. 101

7 Kudo, T., Ishikawa, A., Okamoto, H., Miyauchi, K., Murai, F., Mochiji, K. and Umezaki, H. *J. Electrochem. Soc.* 1987, **134**, 2607

8 Todokoro, Y., Kajiya, A. and Watanabe, H. *J. Vac. Sci. Technol.* 1988, **B6**, 357

9 Ichimura, K. and Hayashi, K. *Bull. Res. Inst. Polym. Text.* 1986, **155**, 119

10 Serre, B. and Worsfold, D. J. *Polymer* 1987, **28**, 881

11 Bakhshaee, M., Hayward, D., Affrossman, S., Sherrington, D. C. and Pethrick, R. A. *Polymer* 1988, **29**, 1407

12 Stockmayer, W. H. *J. Chem. Phys.* 1944, **12**, 125

13 Ku, H. Y. and Scala, L. C. *J. Electrochem. Soc.* 1969, **116**, 980

14 Kodak Co. US Patent 3 096 311, 1963

15 Koseki, K., Koshiba, M., Nakamura, A., Yamaoka, T. and Tsunoda, T. *Kobunshi Ronbunshu* 1980, **37**, 235

16 Koseki, K., Shibata, T. and Yamaoka, T. *Kobunshi Ronbunshu* 1987, **44**, 173