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A One-Component Negative Photoresist Based on an Epoxy Terpolymer Containing Oxime-Urethane Groups as a Photobase Generator

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Abstract: For their application as one-component photoresists, we prepared epoxy terpolymers containing oxime-urethane and benzophenone groups by the radical polymerization of glycidyl methacrylate (GMA), methacryloxyethyl benzophenoneoxime urethane (MBU), and *N*-(4-benzoyl)phenylmaleimide (BPMI). The terpolymer composition was optimized to provide the most photosensitive photoresist. The photo-decomposition reaction of the oxime-urethane groups in the terpolymer was monitored by UV absorption spectroscopy, and the photo-crosslinking reaction of the epoxy terpolymer was observed by measuring the normalized thickness. The photosensitivity of the epoxy terpolymer increased as the amount of BPMI and MBU units increased up to 16 and 24 mol%, respectively. Among the terpolymers we prepared, terpolymer T-II(contents of GMA, MBU, BPMI are 75, 19, 6.1 mole%, respectively) exhibited the highest photosensitivity ($D_c^{0.5}$ = 430 mJ/cm^2) and had a moderate contrast (γ_p = 1.23). Negative-tone micropatterns having a line width of ca. 10 μm were obtained by developing the system with chloroform.

Keywords: photoresist, photocrosslinking, photobase generator, terpolymer, micropattern formation.

Introduction

Epoxy polymers have been widely used in coatings, adhesives, moulding compounds and polymer composites due to their superior thermomechanical properties and excellent processability. They also have been used in electric and electronic industry as insulating materials because of their excellent dielectric properties, high mechanical strength, high thermal stability, and good adhesion property. In resent years, the use of epoxy polymers becomes increasingly important and diversified according to the development of the microelectronic industry. For example, epoxy polymers have been used as epoxy molding compounds for electronic devices, integrated circuit packaging materials, printed circuit boards (PCBs), laminates, insulating materials, and electrically insulating adhesives,[1] etc.

Photoresists based on the epoxy polymers are another kind of an application of the epoxy polymers in microelectronic industry. They have been used to the manufacture of various types of the PCBs as reported in the patents,[2-5] since they have useful properties such as their high thermal resistance, high resolution and sensitivity, good adhesion, and low thermal expansion coefficient. Moreover, they can be useful in a wide variety of applications in the field of offset printing plates, thermoset vesicular images, microimages for information storage, decoration of paper, glass, and packages, and light-curable coatings.[6]

The general composition of the epoxy polymer as photoresist was made of an epoxy polymer, a photopolymerization initiator, curing agent, and other additives. Amines are generally used for the thermal curing agent for the epoxy polymers in coatings, adhesives, sealants, and paint applications. However, the mixture of epoxy polymers and amines is very unstable due to the high reactivity of the amines. Therefore, photoinduced amine formation from thermally stable photobase generators and their application to epoxy polymers are a very important concept in the industrial technology, since they can solve the problem of storage instability of epoxy polymer formulations.

Previously, we reported that the photolysis of oxime-urethane derivatives led to the photochemical formation of amines, inducing a cross-linking reaction in the epoxy polymer upon heating.[7,8] The epoxy polymers containing oxime-urethane groups were effectively cross-linked with the photochemically produced pendant amino groups.[9,10] The photocrosslinking reaction of a polymeric photobase generator containing oxime-urethane groups increased in the presence

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of benzophenone.[11]

Even though photocross-linking reaction of the epoxy polymers induced by the photobase generators has been reported,[9,10,12-16] there is only a few reports on its application to the preparation of photoresist based on the epoxy polymer.[17,18] The present paper reports stable, one-componant epoxy photoresist containing oxime-urethane and benzophenone groups, since 1) the photoresists containing epoxy groups are useful for the formation of micro-images for the various applications, 2) the one-componant photoresist system[22-24] should be free of compatibility problems of the added benzophenone and photobase generator, and 3) the processing steps could be simplified through the preparation of one-component photoresist system. The photochemical reaction of the epoxy terpolymer containing various amounts of benzophenone and oxime-urethane groups was compared in order to obtain the most photosensitive epoxy polymer composition, and the most photosensitive epoxy terpolymer was applied to negative photoresist.

Experimental

Materials and Instruments. 4-Aminobenzophenone and isocyanatoethyl methacrylate were obtained from the Aldrich and Tokyo Casei Chemical Company, respectively. Glycidyl methacrylate (GMA) was purchased from the Fluka Chemical Company and used after vacuum distillation. Methacryloxyethyl benzophenoneoxime urethane (MBU)[19] and *N*-4-benzoylphenyl maleimide (BPMI)[20] were prepared using the reported procedure.

Gel permeation chromatography (GPC) was carried out with a Young-in model 910 solvent delivery module equipped with a Young-Lin M720 absorbance detector. Shodex AT-806MS and AT-80M/S columns were used in the measurement of molecular weight determination. Molecular weight was calibrated using polystyrene standards. Micropatterns were observed using a Zeiss model Axiolab A optical microscope equipped with a digital camera. Irradiations were carried out on a Rayonet photochemical reactor (The Southern New England UV Company, model 208), equipped with 310 nm fluorescent lamps. One module of the photochemical reactor was placed in a horizontal position and irradiated. The light intensity measured using a Vilber Lourmat radiometer (model VLX-3W) was 0.99 mW/cm^2 at 310 nm. The film thickness was measured using a α-step 500 surface profiler (Tencor Instrument, Model AS-500).

Polymerization. The conditions for the preparation of polymers are shown in Table I. A typical procedure was as follows: MBU (0.70 g, 2.0 mmol), BPMI (0.28 g, 1.0 mmol), GMA (0.96 mL, 7.0 mmol), and AIBN (0.01 g, 0.5 wt%) were dissolved in THF (5.0 mL). The solution containing monomers and an initiator was purged with nitrogen for 15 min, after which polymerization was then carried out at 60 °C for 20 hrs. The polymer was isolated by double precipitation from THF solution into methanol (yield 71%).

IR (KBr pellet, cm^{-1}): 3408 (N-H), 2997, 2945 (C-H), 1728 (C=O), 1660, 1602, 1500, 1446 (aromatic), 1255 (C-N), 962 (N-O). ^{1}H-NMR (CDCl$_3$): δ 7.75-7.9 (aromatic protons of BPMI units), 7.25-7.6 (aromatic protons of BPMI and MBU units), 6.7-6.9 (NH protons of MBU units), 4.5-3.38 (-CH$_2$- protons of GMA and MBU units), 3.2-3.0 (CH protons of epoxy groups), 2.6-2.9 (-CH$_2$- protons of epoxy groups), 0.8-2.2 (aliphatic protons of the polymer main chain).

Relative Photodecomposition. The absorbance of the spin-coated terpolymer film on a quartz plate was 1.5 at 256 nm. The relative photo-decomposition of the oxime-urethane groups in the polymer, upon irradiation with a 310 nm UV light, was measured from the changes in absorbance (A_t/A_o) at 256 nm, where A_o was the absorbance at 254 nm at t=0 and A_t was that at $t = t$, respectively.

Normalized Thickness. The terpolymer films were prepared using a spin coating method. A 10 wt% solution of a polymer (0.1 g) in THF (1 mL) was filtered through a membrane filter. The solution was then spin coated on a quartz plate or a silicon wafer using a spin coater, at 1,000 rpm for 10 seconds on the 1st run, and 2,000 rpm for 10 seconds on the 2nd run, respectively. The resulting polymer film was dried at 40 °C for 4 hrs. The thickness of the film was 0.95 μm.

The terpolymer film on a silicon wafer was irradiated with 310 nm UV light. The irradiated film was dipped in THF for 1 min, and then dried at 40 °C for 4 hrs. The normalized thickness of the film was determined from the difference between absorbance at 2949 cm^{-1} before and after dipping in THF.

$$\text{Normalized thickness} = \frac{\text{Absorbance at 2949 cm}^{-1}\text{ after dipping in THF}}{\text{Absorbance at 2949 cm}^{-1}\text{ before dipping in THF}}$$

Micropattern Formation. The terpolymer T-II (0.1 g) was dissolved in 1.0 mL *N*-methylpyrrolidone (NMP) and the resultant polymer solution was filtered using a Milipore filter. The solution was then spin coated on a silicon wafer, which was pretreated with H$_2$O$_2$,[20] by a spin coater at 1,000 rpm for 70 sec on the 1st run and 2,000 rpm for 70 sec on the 2nd run, respectively. The thickness of the film was 0.83 μm after drying it at 40 °C for 12 hrs. The film on the silicon wafer was covered with a photomask and irradiated with 1.0 J/cm^2 of 310 nm UV light. The irradiated film was then dipped in chloroform for 30 sec, and then dried at 40 °C for 4 hrs. The resultant micropattern formed on the silicon wafer, was observed using an optical microscope.

Results and Discussion

Polymerization. It was reported that the photodecompo-

sition reaction of oxime-urethane groups was more efficient in the presence of benzophenone as a photosensitizer.[11] Therefore, in order to improve the efficiency of photo-crosslinking reactions of the epoxy polymer, both the photo-reactive groups and the photosensitizing groups were incorporated into the polymer chain. The monomers used in the preparation of the epoxy terpolymer, containing oxime-urethane groups and benzophenone groups, were prepared as shown in Scheme I. MBU, a monomer containing the oxime-urethane group, was prepared by the reaction of benzophenone oxime and isocyanatoethyl methacrylate. BPMI, a monomer containing the benzophenone group, was prepared by the reaction of maleic anhydride and 4-aminobenzophenone through two reaction steps.

The epoxy terpolymer was prepared through the polymerization of GMA, MMA, and BPMI in accordance with the molar ratios shown in Table I. The amount of MBU and BPMI units in the terpolymer, which was determined using a 300 MHz NMR spectrum, was lower than that of the feed, but the amount of GMA units was higher than that of the feed. This seems to be due to the higher reactivity of GMA than MBU or BPMI. The molecular weight of the epoxy terpolymers was measured using a GPC in THF, ranging between 13,000 and 29,000, relative to polystyrene standards. The molecular weight increased with the amount of the GMA units in the terpolymer. The polydispersity was in the range of 2.5-4.5, which showed a relatively broad molecular weight distribution. The glass transition temperature (T_g) increased with the amount of BPMI units in the terpolymer, since BPMI contains a rigid maleimide structure. The terpolymers were stable at room temperature for several months without any changes in DSC analyses.

Optimization of Polymer Composition. The polymer composition of the epoxy terpolymer containing oxime-urethane and benzophenone groups was optimized through the study of the photo-crosslinking reaction of the epoxy polymer. In order to find out the most photosensitive epoxy terpolymer composition, the photochemical reaction of the epoxy terpolymer was studied through the UV absorption spectroscopy and the measurement of normalized thickness.

Figure 1 shows the UV absorption spectral changes of a T-II terpolymer film on a quartz plate upon irradiation with 310 nm UV light. The absorption band around 254 nm decreased upon irradiation, while that around 310 nm increased. An isosbestic point was observed at 281 nm. The photo-decomposition of oxime-urethane groups in the terpolymer took place efficiently upon irradiation with 310 nm UV light. This seems to be due to the fact that the photodecomposition reaction of the oxime-urethane groups took place at its excited triplet state.[8]

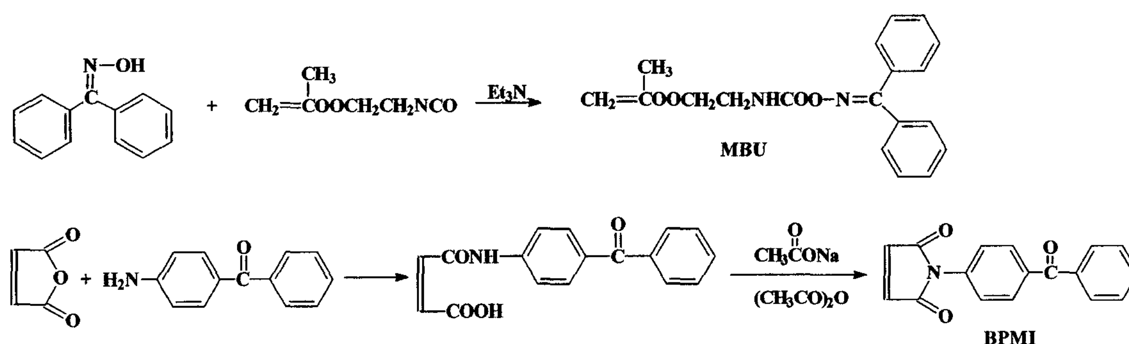
The relative photodecomposition of oxime-urethane groups in the terpolymer chain can be observed from the changes of

Table I. Composition and Physical Properties of the Epoxy Terpolymer

Polymer	Monomer Feed (mol %)			Content of Unit (mol %)[a]			Yield (%)	$\overline{M}_n$ [b]	$\overline{M}_w/\overline{M}_n$	T_g [c] (°C)
	GMA	MBU	BPMI	GMA	MBU	BPMI				
T-I	80	10	10	83	9.3	7.7	84	24,000	2.62	85
T-II	70	20	10	75	19	6.1	71	27,000	3.08	86
T-III	60	30	10	68	24	8.0	65	22,000	2.52	95
T-IV	77	20	3.0	79	18	2.9	80	29,000	3.07	75
T-V	60	20	20	64	20	16	69	13,000	2.51	103
C-I	78	22	0	81	19	0	70	42,000	4.53	74

[a]Determined from 300-MHz ^{1}H NMR spectra in $CDCl_3$. [b]By GPC measurements with THF as an eluent.
[c]Glass transition temperature measured by DSC at a heating rate of 10 °C /min under N_2.

Scheme I



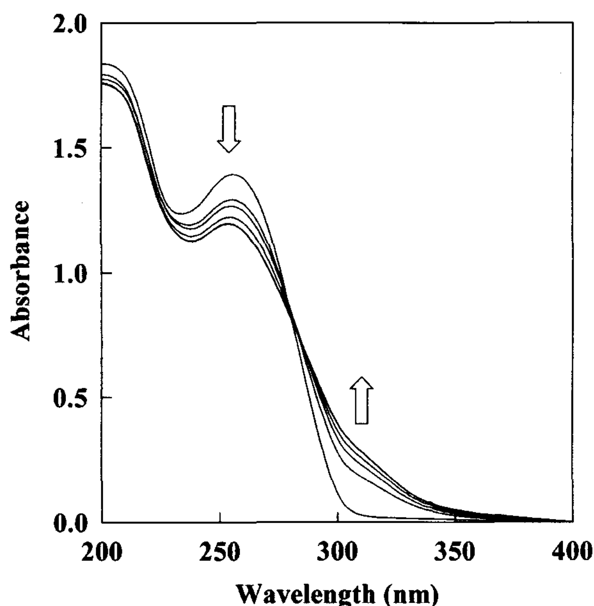


Figure 1. UV absorption spectral changes of a terpolymer T-II film on a quartz plate upon irradiation with a 310 nm UV light at 0, 0.2, 0.4, 0.6 and 1.0 J/cm^2.

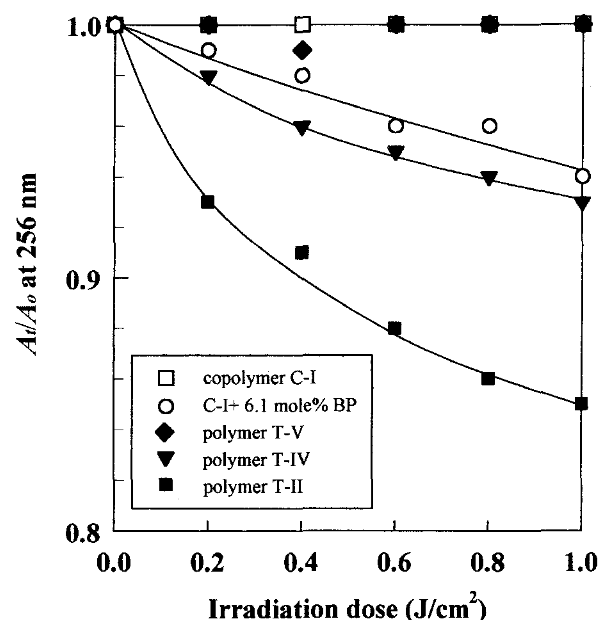


Figure 2. A_t/A_o changes of the polymer films on the quartz plates at 256 nm as a function of irradiation doses at different BPMI amounts. Irradiations were carried out with a 310 nm UV light.

the UV absorbance at 254 nm upon irradiation with 310 nm UV light. The absorbance of the terpolymer films for the UV experiments was adjusted 1.5 at 256 nm in order to maintain the thickness of the film constant.

Figure 2 illustrates the A_t/A_o changes of the terpolymer films on the quartz plates at 256 nm as a function of irradiation doses with a constant amount of MBU units (18~20 mole%) but containing different amounts of BPMI units (from 0 to 16 mole%). The relative photo-decomposition rates of the oxime-urethane groups in the terpolymer, increased in the order of copolymer C-1 (which contains 0 mole% BPMI units) < terpolymer T-V (16 mole%) < copolymer C-I after addition of 6.1 mole% benzophenone < terpolymer T-IV (2.9 mole%) < T-II (6.1 mole%). This results indicate that the relative photo-decomposition rates of oxime-urethane groups in the terpolymer increased with the amount of BPMI units in the range of 0~6.1 mole%, while it was completely quenched for the terpolymer T-V, which contains 16 mole% of BPMI units. This may be attributed to the fact that benzophenone triplets are self-quenching[21] at the higher amount of benzophenone groups in the terpolymer.

The effect of the physical state of benzophenone groups in the terpolymer, on the photodecomposition of oxime-urethane groups was compared. The efficiency of the photodecomposition rate of the oxime-urethane groups in a terpolymer T-II film, containing 6.1 mole% BPMI units, is far more efficient than that of the copolymer C-I film after the addition of 6.1 mole% benzophenone. This result indicates that the incorporation of the benzophenone groups into a polymer chain is a very efficient way to increase the photodecomposition reaction of the oxime-urethane groups in a polymer. This seems to be due to the homogeneous mixing of the photosensitizer groups and an efficient intramolecular energy transfer in the polymer chain.

Figure 3 shows the A_t/A_o changes of the terpolymer films at 256 nm as a function of irradiation doses at a constant concentration of BPMI units (6~8 mole%) in the terpolymer, while the MBU units varied from 9.3 to 24 mole%. The A_t/A_o value decreased in the order of the terpolymer T-I (containing 9.3 mole% of MBU units) > T-II (19 mole%) > T-III (24 mol%). This result indicates that the relative photo-decomposition rates of the oxime-urethane groups in the terpolymer decreased with the amount of oxime-urethane groups in the terpolymer, at a constant concentration of the benzophenone groups.

The photo-crosslinking reaction of the epoxy terpolymer films was observed by measuring the changes of normalized thickness as a function of the irradiation doses. Figure 4 shows the changes in the normalized thickness of the terpolymer films, containing similar amounts of MBU units (18~20 mole%) but having different amounts of BPMI units (0~16 mole%) as a function of the irradiation doses, when development was carried out in THF. The normalized thickness of the terpolymer films increased consistently with the irradiation doses. It increased in the order of copolymer C-I, or terpolymer T-V < T-IV < T-II. This result indicates that the normalized thickness increased with the amount of BPMI units in the terpolymer except with the terpolymer, T-V.

The change in the normalized thickness of the terpolymer T-V, which contains 16 mole% BPMI units, was similar to

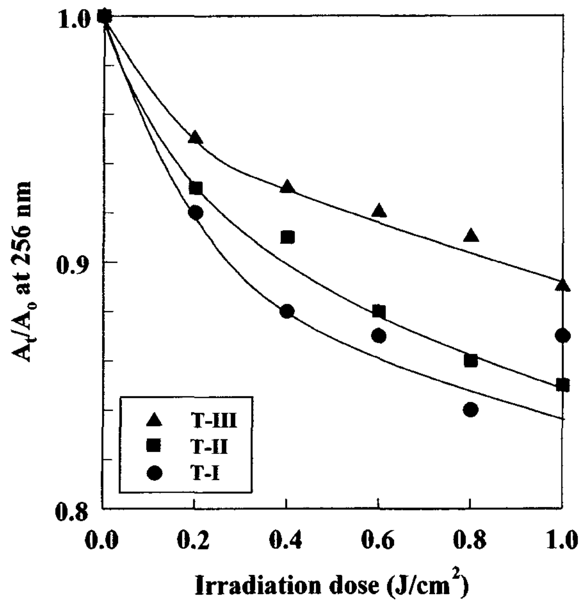


Figure 3. A_t/A_0 changes of the terpolymer films on the quartz plates at 256 nm as a function of irradiation doses at different MBU amounts. Irradiations were carried out with a 310 nm UV light.

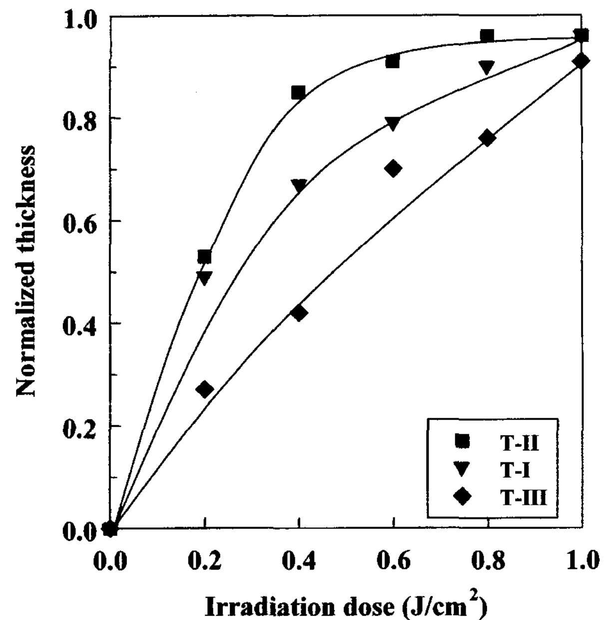


Figure 5. Changes in the normalized thickness of the terpolymer films on a silicon wafer as a function of irradiation doses at different MBU amounts. Development was carried out in THF.

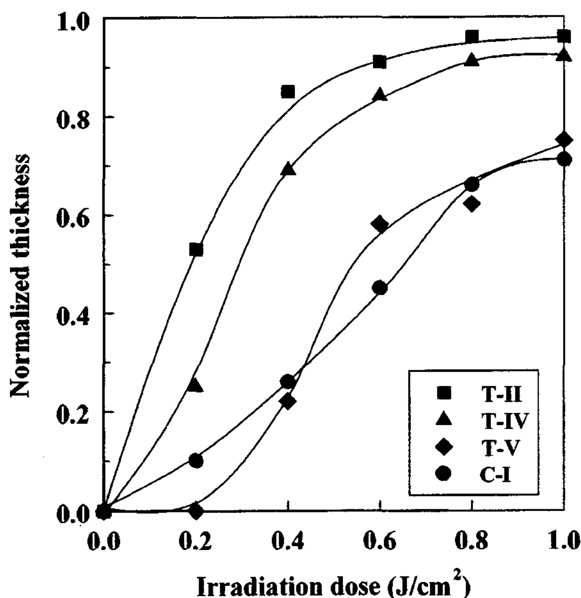


Figure 4. Changes in the normalized thickness of the polymer films on a silicon wafer as a function of irradiation doses at different BPMI amounts. Development was carried out in THF. Film thickness = 0.95 μm.

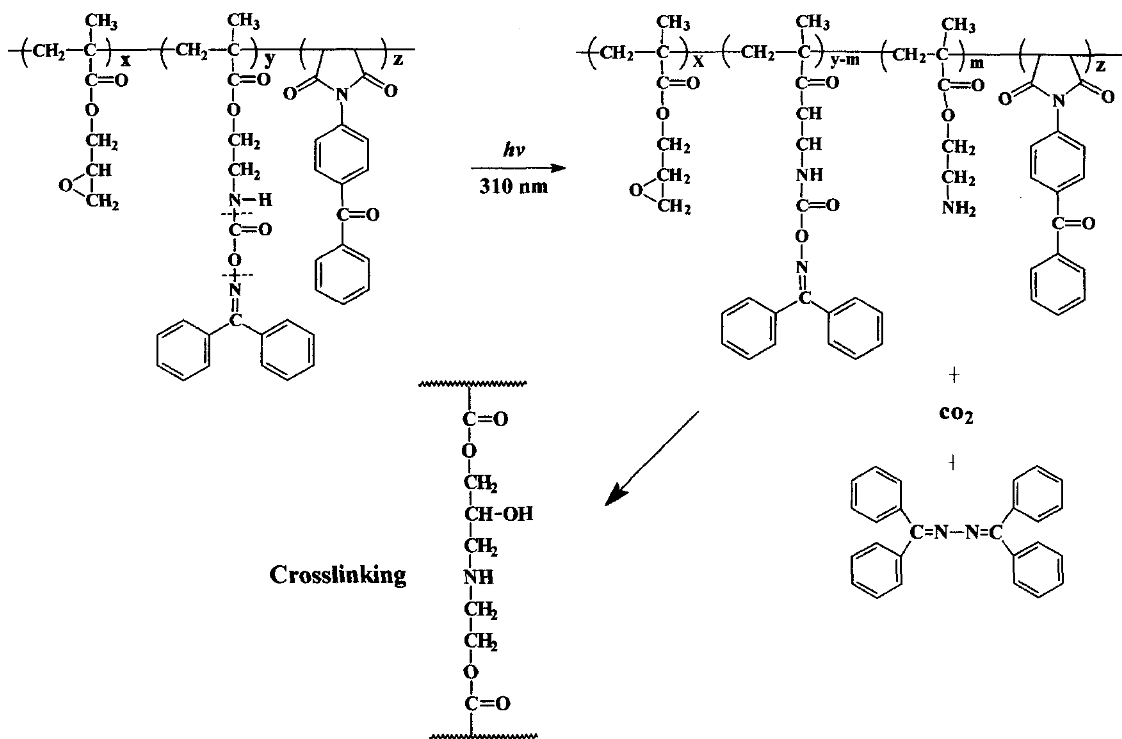
that of copolymer C-I, which had no sensitizer groups. This can be explained by two reasons. Firstly, the amount of the epoxy groups in the GMA units in the terpolymer T-V was 64 mole%, whilst that of the terpolymer T-II and T-IV was 75 and 79 mole%, respectively. Therefore, the polymerizable epoxy groups in the terpolymer T-V was smaller than that of the terpolymer T-II or T-IV. The other reason for the low reactivity of the terpolymer T-V is due to the fact that the photodecomposition of oxime-urethane groups in the polymer was inefficient with a high concentration of benzophenone groups, due to the self-quenching reaction of the benzophenone triplet, as discussed in Figure 2.

Figure 5 depicts the changes in the normalized thickness of the terpolymer films, containing a similar amount of BPMI units (6~8 mole%) but with a different amount of MBU units (9.3~24 mole%) as a function of irradiation doses. The normalized thickness increased in the order: T-III < T-I < T-II. This indicates that the normalized thickness increased with the amount of MBU units in the polymer except for the terpolymer T-III. The relatively low efficiency of the photocross-linking reaction of the terpolymer T-III seems to be due to the low amount of GMA units when compared with the terpolymer T-I or T-II.

Scheme II illustrates photo-crosslinking reaction of the epoxy terpolymer. Upon irradiation with 310 nm UV light, the oxime-urethane groups in the epoxy terpolymer underwent photosensitized decomposition reaction to form amino groups. The reaction of the amino groups with the epoxy group in the GMA units resulted in the formation of cross-linking.

Photopatterning. The terpolymer T-II was tested for its use as photoresist since it was the most photosensitive

Scheme II



epoxy terpolymer prepared. $CHCl_3$ was used for a developing solvent instead of THF, since a clearer micropattern could be obtained by developing with $CHCl_3$. Figure 6 shows the changes in the normalized thickness of a T-II film on a silicon wafer as a function of log (exposure dose) by developing with $CHCl_3$. The curve is known as a photosensitive curve featuring a typical negative type of photoresist. The sensitivity ($D_g^{0.5}$), which displays the energy for 50% cross-linking, was 430 mJ/cm^2 and the contrast (γ_n) was 1.23, respectively.

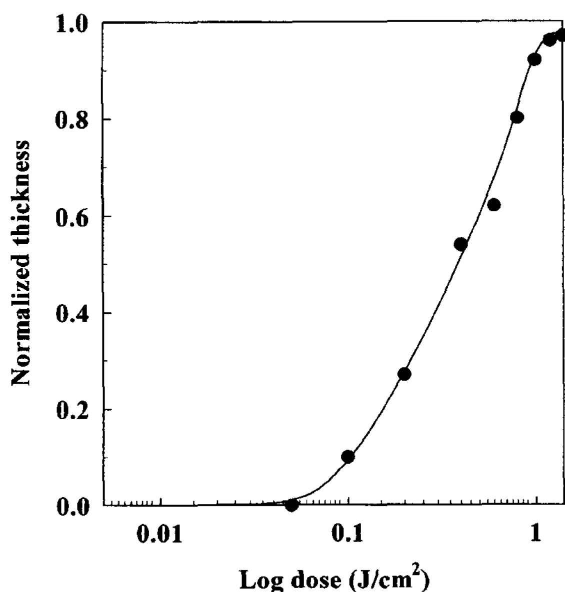
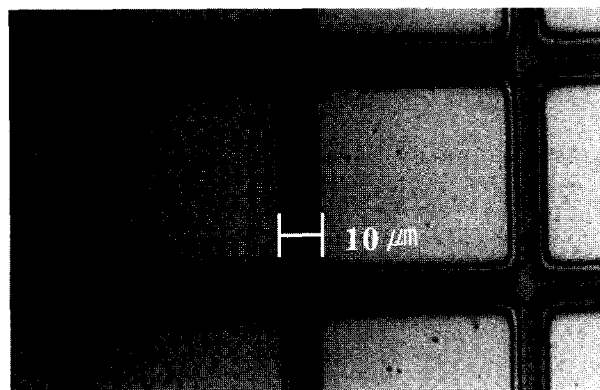


Figure 6. The normalized thickness of the terpolymer T-II film on a silicon wafer, as a function of exposure dose at a film thickness of 0.83 μm. Development was carried out with $CHCl_3$ at room temperature.

Figure 7 shows SEM image of a negative micropattern that was obtained through developing with $CHCl_3$. The developing process was not optimized, but a clear micropattern, with a line width of ~ 10 μm, was obtained.



X 200

Figure 7. An optical microscope image of a negative micropattern of a terpolymer T- II film, on a silicon wafer after irradiation at 1.0 J/cm^2. Development was carried out with $CHCl_3$ for 30 sec at room temperature.

Conclusions

The photo-decomposition of the oxime-urethane groups in the epoxy terpolymer increased with the amount of benzophenone groups at the constant amount of oxime-urethane groups. The photo-crosslinking reaction of the epoxy terpolymer film increased with the amount of benzophenone and oxime-urethane groups in the terpolymer, while it decreased when the amount of benzophenone and oxime-urethane groups was more than 16 and 24 mole%, respectively. The photosensitivity of the terpolymer could be increased through the incorporation of benzophenone groups into the polymer chain. A clear negative micropattern with a line width of ~10 μm was obtained with a terpolymer T-II film, which was the most photosensitive terpolymer prepared. Thus, the epoxy terpolymer containing oxime-urethane and benzophenone groups is useful for the application to a negative type, one-component epoxy photoresist, which has high photosensitivity and good storage stability.

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