Articles

Negative Resists Using Acid-Catalyzed Dehydration of Phenylcarbinols: Correlation between Chemical Structure and Resist Sensitivity

K. Kojima,*,[†] S. Uchino, N. Asai,[‡] and T. Ueno[§]

Central Research Laboratory, Hitachi, Ltd., Kokubunji, Tokyo 185, Japan

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A series of phenylcarbinols have been evaluated as components of chemically amplified resists used for KrF excimer laser lithography. The character of the carbon atom to which the hydroxyl group is bonded to determines the insolubilization reactions, leading to differences in sensitivity. Resists using tertiary phenylcarbinol, which converts into polymeric compounds, exhibits the highest sensitivity while the resists using primary phenylcarbinol, which cross-links the phenolic resin, has the lowest sensitivity. Properties, such as sensitivity and chemistry, of the resist containing the secondary phenylcarbinol groups lie between those of the primary and tertiary phenylcarbinol containing resists.

1. Introduction

Phenylcarbinols can be classified as being primary, secondary, or tertiary based on the character of the carbon atom to which the hydroxyl group is directly bonded. Photoresists using primary phenylcarbinols and their derivatives as latent electrophiles have been investigated in detail by Fréchet et al.[1–7] According to their studies, primary phenylcarbinols are converted into benzyl cations, which cross-link the matrix polymer through acid-catalyzed reactions. On the other hand, Ueno et al. have examined tertiary phenylcarbinols as a component of highly sensitive and high contrast resist for I-line phase shift photolithography.[8] They have demonstrated that intramolecular dehydration reactions of tertiary phenylcarbinols are responsible for resist insolubilization, and the dehydration products act as dissolution inhibitors in phenolic resin. However, the correlation between resist sensitivity and the chemical structure of phenylcarbinols such as the character of the

carbon atom which the hydroxyl group was bonded to and the number of hydroxyl groups was not investigated. In this paper we report on the correlation between the chemical structure of the phenylcarbinols and the sensitivity of phenylcarbinol resists, as well as on the mechanism of the resist insolubilization.

2. Experimental Section

2.1. Materials. Diphenyliodonium triflate (DIT) used as a photoacid generator was synthesized by the conventional method.[9] Novolak resin (M_w 10 000) was obtained from Hitachi Chemical Co. Poly(4-hydroxystyrene) (M_w 5100, $M_w/M_n = 1.89$) was obtained from Maruzen Petrochemical Co. An aqueous base developer, 2.38 wt % tetramethylammonium hydroxide (TMAH) aqueous solution, was purchased from Tokyo Ohka Kogyo Co.

Benzyl alcohol (BZ-1) was purchased from Kanto Chemical Co., and α-methylbenzyl alcohol (BZ-2), α,α-dimethylbenzyl alcohol (BZ-3), α,α′-dihydroxy-1,3-diisopropylbenzene (MDIOL-3), *p*-xylylene glycol (PDIOL-1), and α,α′-dihydroxy-1,4-diisopropylbenzene (PDIOL-3) were purchased from Tokyo Kasei Kogyo Co. The other phenylcarbinols were synthesized as described below.

(1) m-Xylylene glycol (MDIOL-1): Sodium borohydride (2.00 g, 52.9 mmol) was added to a solution of *m*-phthalaldehyde (3.00 g, 22.4 mmol) in ethanol (25 mL) at 0 °C with stirring. The solution was stirred at room temperature for 3 h. The reaction mixture was concentrated under reduced pressure. Then, the residue was dissolved in water, extracted with ethyl acetate, and washed with saturated NaCl(aq). The organic layer was dried over anhydrous sodium sulfate and the solvent was removed. The crude product was chromatographed on silica gel using hexane and ethyl acetate (1:1) producing the desired product as a white powder (3.10 g, quantitative yield).

(2) α,α′-Dihydroxy-1,3-diethylbenzene (MDIOL-2): Sodium borohydride (1.60 g, 42.3 mmol) was added to a solution of 1,3-diacetylbenzene (1.62 g, 10.0 mmol) in ethanol (25 mL) at 0 °C with stirring. The solution was stirred at room temperature for 5 h. The reaction mixture was concentrated under reduced pressure. Then the residue was dissolved in water, extracted with ethyl acetate, and washed with saturated NaCl(aq). The

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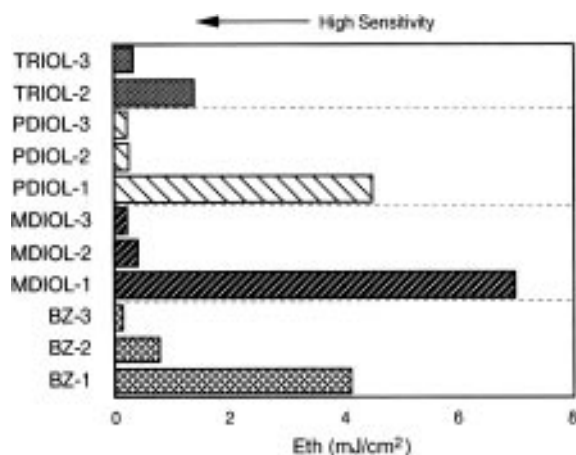(9) Crivello, J. V.; Lam, J. H. *J. Org. Chem.* **1978,** *43,* 305.

Figure 1. Sensitivity of the resists consisting of a phenylcarbinol, DIT, novolak.

Table 1. Phenylcarbinol Compounds Used in Experiments

Structure	Abbr.	Name	M.W.	m.p.
	BZ-1	benzyl alcohol	108.14	-15
	BZ-2	α-methylbenzyl alcohol	122.17	20
	BZ-3	α,α–dimethylbenzyl alcohol	136.19	32-34
	MDIOL-1	m-xylylene glycol	138.17	55
	MDIOL-2	α,α'-dihydroxy-1,3-diethylbenzene	166.22	69
	MDIOL-3	α,α'-dihydroxy-1,3-diisopropyl-benzene	194.28	124
	PDIOL-1	p-xylylene glycol	138.17	118
	PDIOL-2	α,α'-dihydroxy-1,4-diethylbenzene	166.22	89
	PDIOL-3	α,α'-dihydroxy-1,4-diisopropyl-benzene	194.28	144-146
	TRIOL-1	1,3,5-trihydroxymethyl-benzene	168.19	77
	TRIOL-2	α,α',α"–trihydroxy-1,3,5-triethylbenzene	210.26	125
	TRIOL-3	α,α',α"–trihydroxy-1,3,5-triisopropyl-benzene	252.35	150-152

organic layer was dried over anhydrous sodium sulfate, and the solvent was removed. The crude product was chromatographed on silica gel using hexane and ethyl acetate (1:1) producing the desired product as a white solid (1.62 g, quantitative yield).

α,α'-Dihydroxy-1,4-diethylbenzene (PDIOL-2) and α,α',α"-trihydroxy-1,3,5-triethylbenzene (TRIOL-2), respectively, were synthesized by reducing 1,4-diacetylbenzene and 1,3,5-triacetylbenzene, using the same method of the MDIOL-2 synthesis.

(3) 1,3,5-Trihydroxymethylbenzene (TRIOL-1): Lithium aluminum hydride (2.00 g, 52.7 mmol) was added to a solution of 1,3,5-benzenetricarboxylic acid (3.16 g, 14.8 mmol) and THF (100 mL) with vigorous stirring. The mixture was refluxed for 2 h. Then, water was slowly dripped into the reaction mixture at 0 °C. The mixture was filtered, and methanol was

added to the residue to extract the reaction product at 50 °C. The filtrate was concentrated, and the crude product was chromatographed on silica gel using ethyl acetate, producing the desired product as a white solid (1.49 g, 59% yield).

(4) α,α',α"-Trihydroxy-1,3,5-triisopropylbenzene (TRIOL-3): A THF solution of methylmagnesium iodide (0.91 mol/L, 38 mL) was slowly dripped to THF solution of 1,3,5-triacetylbenzene (2.04 g, 10.0 mmol) at 20 °C. The solution was refluxed for 1 h. After cooling to room temperature, saturated NH$_4$-Cl(aq) (50 mL) was added to the reaction mixture. The THF was removed from the solution, and the residue was extracted with ethyl acetate. The organic layer was washed with water and saturated NaCl(aq) and then dried over anhydrous sodium sulfate. After removal of the solvent in vacuo, the crude product was chromatographed on silica gel using hexane and ethyl acetate (1:1) producing a yellow-white solid (624 mg, 25% yield).

2.2. Resist Composition and Processing. Resist solutions were prepared by dissolving the phenolic resin, a photoacid generator, and a phenylcarbinol in cyclohexanone. The resists were spin-coated onto silicon substrates and the resist films were prebaked at 80 °C for 2 min then exposed to 2.48-nm light from a Xe—Hg lamp through an interference filter. After postexposure baking (PEB) on a hot plate, the films were developed in an aqueous base developer. Development time was defined as 4 times as long as the time required to dissolve the resist film in the developer. The film thickness was measured with a profilometer, Alpha-Step 200 (Tencor Instrument Co.). The dissolution rate was determined by measuring the time needed to clear the resist film in the developer. Lithographic performance of the resists were evaluated with a Canon KrF excimer laser stepper (0.45 NA).

2.3. Resist Characterization. UV absorption spectra were measured with a Hitachi U-3410 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer FT-IR 1720X spectrometer using spin-coated resist films on NaCl disks. Gel permeation chromatography (GPC) was performed using a Hitachi L-6000 liquid chromatography system equipped with Gelpak A-150, A-140, and A-120 GPC columns (Hitachi Chemical Co.). Molecular weights of the resists were described in terms of polystyrene equivalent molecular weight. A novolak resin without oligomeric components ($M_w = 1.38 \times 10^4$, $M_n = 5.26 \times 10^3$) was used for the GPC experiments.[10] The resist films were exposed at 365 nm to allow the light to reach the bottom of the resist films. The exposed resist samples were dissolved in tetrahydrofuran for the GPC measurements.

3. Results and Discussion

3.1. Sensitivity of Phenylcarbinol Resists. To determine the correlation between phenylcarbinol structure and resist sensitivity, a series of resists containing a phenylcarbinol (Table 1), a photoacid generator, and a matrix resin was formulated. Novolak resin was used as the matrix resin for sensitivity evaluation. To keep the number of phenylcarbinol molecules constant in the resist film, the resist composition was novolak/phenylcarbinol/DIT = 100 g/100 mmol/2.00 g, in order. TRIOL-1 was not sufficiently soluble in the solvent for the resist evaluation, so the sensitivity of the TRIOL-1 resist was not measured.

Sensitivity of the resists (E_{th}, mJ/cm^2), which was defined as the minimum dose for insolubilizing the resist film, is shown in Figure 1. The resist sensitivity mainly depends on the character of the carbon that the hydroxyl group is bonded to, as can be seen in Figures 1 and 2. The tertiary phenylcarbinols provide the highest sensitivity from among the phenylcarbinols

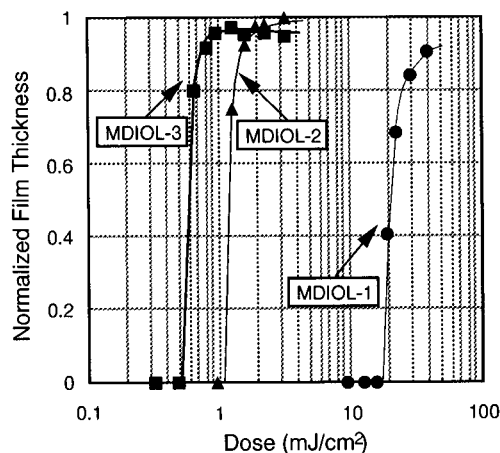(10) Shiraishi, H.; Fukuma, E.; Hayashi, N.; Tadano, K.; Ueno, T. *Chem. Mater.* **1991**, *3*, 621.

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Figure 2. Exposure characteristic curves for resists using MDIOLs.

Figure 3. Pseudo-Arrhenius plot of phenylcarbinol resist sensitivity.

having the same number of hydroxyl groups in a molecule. On the other hand, the resists using primary phenylcarbinols exhibit the lowest sensitivity from among the three types as shown in Figure 1. The sensitivity of the resist containing secondary phenylcarbinols is between the sensitivity of the primary and tertiary phenylcarbinol resists (Figure 1).

The resist sensitivity decreased to some extent when the number of hydroxyl groups in a molecule increased. This is because the hydroxyl group enhances the dissolution of novolak in an aqueous base due to its hydrophilic character (see section 3.4). The position of functional groups on the benzene ring, such as in the meta or para position, does not have any effect on resist sensitivity.

The film thickness loss after development is strongly affected by the number of hydroxyl groups in a molecule, because hydrogen bonds between phenolic hydroxyl groups of the novolak and hydroxyl groups of the phenylcarbinols capture the phenylcarbinol molecules in matrix resin. Large remaining film thickness loss was observed in the case of monofunctional compounds (BZ), probably due to their high volatility from surface of the resist film during the baking process although the baking temperature was much lower than boiling points of the phenylcarbinols (boiling points of BZ-1, BZ-2, and BZ-3 are 205 °C, 204 °C/745 mmHg and 202 °C, respectively).

3.2. Phenylcarbinol Reactivity with Acid. To clarify the difference of sensitivity among the primary, secondary, and tertiary phenylcarbinols, the reactivity of phenylcarbinols with acid in a novolak matrix was evaluated by using a pseudo-Arrhenius plot of the resist sensitivity. The PEB temperature was varied from 60 to 80 °C and baked for 2 min, while the prebaking conditions were kept constant at 80 °C for 2 min to obtain the pseudo-Arrhenius plots (Figure 3). The slopes of the plots give the activation energy of the insolubilization reaction of the phenylcarbinol resists. The tertiary phenylcarbinol (PDIOL-3) had the lowest activation energy, followed by the secondary, and then the primary phenylcarbinols had the highest. This order coincides with the order of the resist sensitivity; in other words, lower activation energy leads to higher resist sensitivity. And it is well-known that the order of stability of the benzyl cation is tertiary > secondary
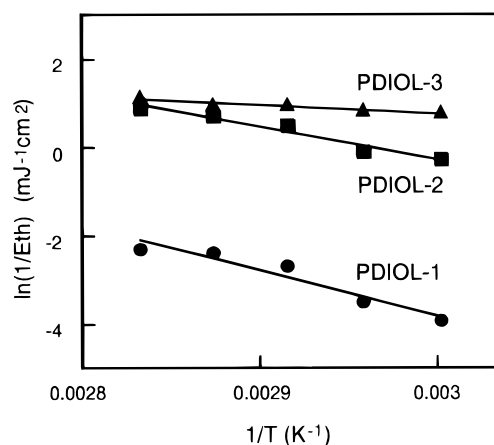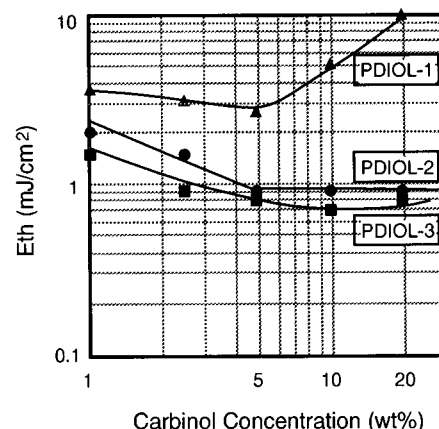
Figure 4. Effect of phenylcarbinol concentration on resist sensitivity.

> primary.[11] Presumably, the stability of the benzyl cation also affects the reactivity as well as resist sensitivity.

3.3. Effect of Phenylcarbinol Concentration on Resists Characteristics. To further clarify the insolubilization mechanism of the phenylcarbinol resists, we evaluated the dependence of resist sensitivity on the phenylcarbinol concentration. The phenylcarbinol (PDIOL-1, PDIOL-2, or PDIOL-3) concentration was varied from 1 to 20 wt % based on the novolak resin. Prebaking and PEB were done at 80 °C for 2 min. The sensitivity of the PDIOL-1 resist reaches a maximum at 5 wt % loading and then decreases sharply when the concentration exceeds 5 wt % as can be seen in Figure 4. These results indicate that the cross-linking reaction between novolak and PDIOL-1 plays a major role while the bimolecular condensation of PDIOL-1 plays a minor role in the PDIOL-1 resist insolubilization. On the other hand, the sensitivity of the PDIOL-2 and PDIOL-3 resists increased with the phenylcarbinol concentration before leveling off at about 10 wt % loading. These results suggest that intermolecular reactions of PDIOL-2 and PDIOL-3 play a dominant role in the insolubilization of the PDIOL-2 and PDIOL-3 resists.

The effect of phenylcarbinol (PDIOL) concentration on the dissolution rate of resist films is shown in Figure 5. In all three types of resist, phenylcarbinols promoted

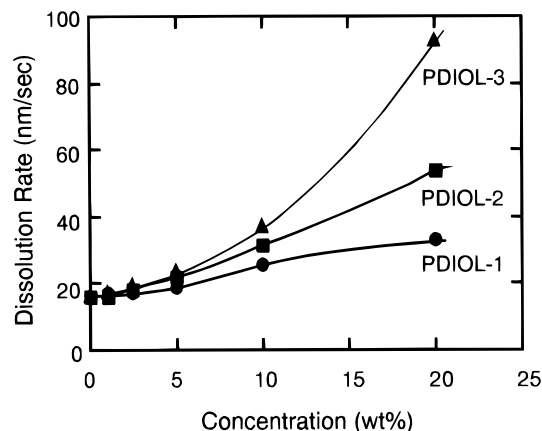(11) Morrison, R. T.; Boyd, R. N. *Organic Chemistry*; Allyn and Bacon, Inc.: 1983; p 234.

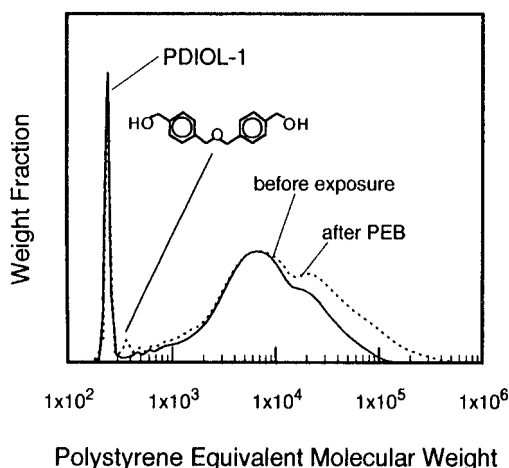**Figure 5.** Effect of phenylcarbinol concentration on dissolution rate of resist films.

Figure 6. Molecular weight distributions of PDIOL-1 resist before exposure and after PEB. Exposure dose: 1.5 J/cm^2.

Figure 7. IR difference spectrum of the PDIOL-1 resist before exposure and after PEB. Exposure dose: 64 mJ/cm^2.
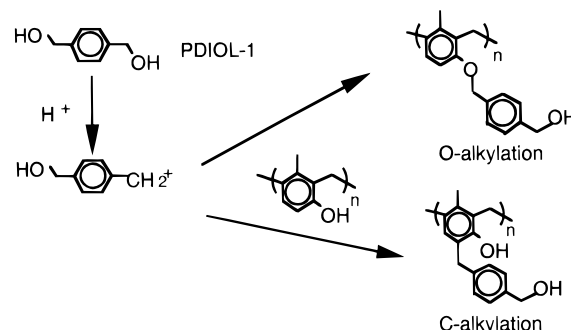
Figure 8. Possible scheme of reactions contributing to the insolubilization of the PDIOL-1 resist.

the dissolution rate of novolak resin. How much the dissolution rate is enhanced depends on the chemical structure of the phenylcarbinol. The tertiary carbinol acts as the strongest dissolution promoter, followed by the secondary and then primary carbinols. Because methyl groups of the secondary and tertiary phenylcarbinols strongly hinder hydrogen bond between novolak and the phenylcarbinols.

3.4. Carbinol Chemistry in the Novolak Resin Matrix. To elucidate the nature of the acid-catalyzed reaction of phenylcarbinols in the novolak resin matrix, GPC and IR spectra of the resists containing primary (PDIOL-1), secondary (PDIOL-2), and tertiary (PDIOL-3) phenylcarbinols were measured.

(1) Chemistry of Primary Phenylcarbinols (PDIOL-1). GPC spectra of the PDIOL-1 resist before exposure and after postexposure baking are shown in Figure 6. The sharp peak of PDIOL-1 decreased and the molecular weight of the novolak resin increased markedly after exposure and the subsequent baking. This prominent increase of the molecular weight is responsible for the acid-catalyzed cross-linking of novolak resin by PDIOL-1. The newly appeared peak ($M_w = 360$) was identified as that of dibenzyl ether.[5,6] The IR difference spectrum of the PDIOL-1 resist before exposure and after PEB is shown in Figure 7. Decreases in the hydroxyl group (3250 cm^{-1}) and C−OH (1004 cm^{-1}) absorption bands, which are attributable to the dehydration of PDIOL-1, can be seen. The increased bands at 1500 and 1170
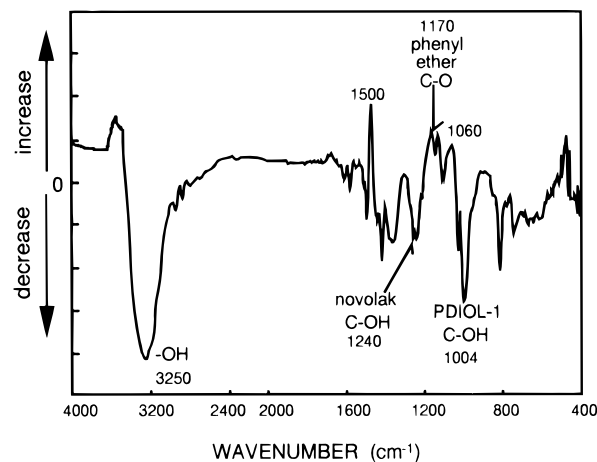
cm^{-1} are due to the C- and O-alkylation, respectively, between the novolak resin and the benzyl cation. On the basis of the results of GPC and IR measurements, a possible insolubilization scheme of the PDIOL-1 resist is illustrated in Figure 8. The PDIOL-1 reacts with acid to form a benzyl cation which cross-links the novolak resin by C- and O-alkylations. The bimolecular condensation of the PDIOL-1 generates dibenzyl ether (1060 cm^{-1}); however, dibenzyl ether acts as a weak dissolution inhibitor of novolak resin in an aqueous base. Therefore, the cross-linking reaction is responsible for the insolubilization of the primary phenylcarbinol resists.

(2) Chemistry of Tertiary Phenylcarbinols (PDIOL-3). In the case of the PDIOL-3 resist, the molecular weight of the novolak resin slightly increased, and the low molecular weight (below 2000) components were prominently increased after PEB (Figure 9). We believe the low molecular weight components were cationically polymerized compounds of olefinic compounds which were produced by intramolecular dehydration of the PDIOL-3. An IR difference spectrum of the PDIOL-3 resist before exposure and after PEB (Figure 10) supports this belief which indicates the formation of olefin compounds (893 cm^{-1}). On the basis of these results, a possible mechanism of the insolubilization of the PDIOL-3 resist is shown in Figure 11. The PDIOL-3 reacts with acid to form olefin compounds that subsequently is converted into polymeric compounds due to cationic polymerization. The polymeric compounds act as strong dissolution inhibitors of novolak resin.

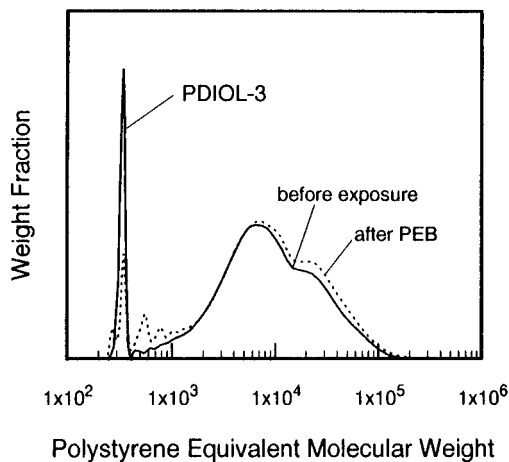*(3) Chemistry of Secondary Phenylcarbinols (PDIOL-2).* We found that the chemical reactivity of the

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Figure 9. Molecular weight distributions of PDIOL-3 resist before exposure and after PEB. Exposure dose: 225 mJ/cm^2.
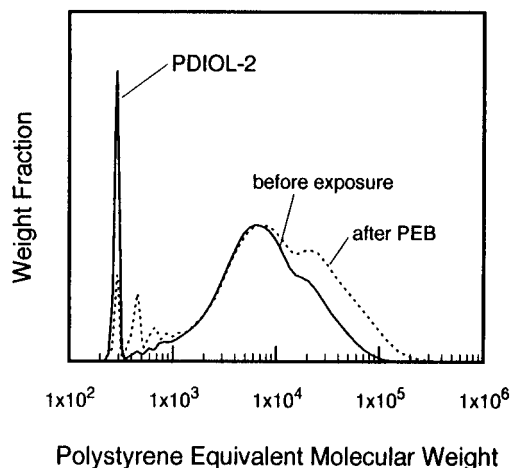

Figure 12. Molecular weight distributions of PDIOL-2 resist before exposure and after PEB. Exposure dose: 90 mJ/cm^2.
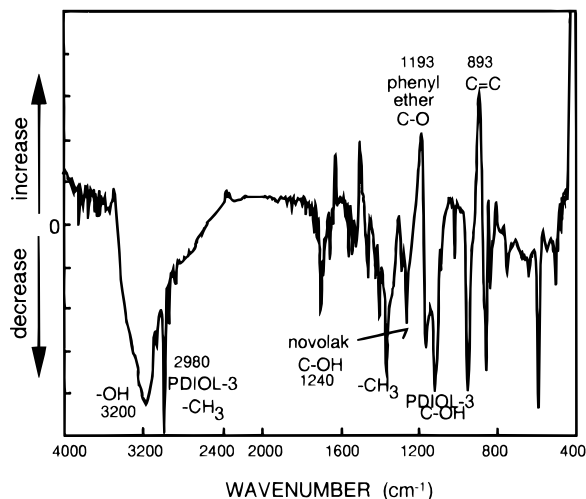

Figure 10. IR difference spectrum of the PDIOL-3 resist before exposure and after PEB. Exposure dose: 6.4 mJ/cm^2.

Figure 13. IR difference spectrum of the PDIOL-2 resist before exposure and after PEB. Exposure dose: 6.4 mJ/cm^2.

Figure 11. Possible scheme of reactions contributing to the insolubilization of the PDIOL-3 resist.
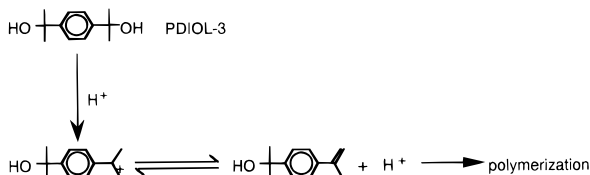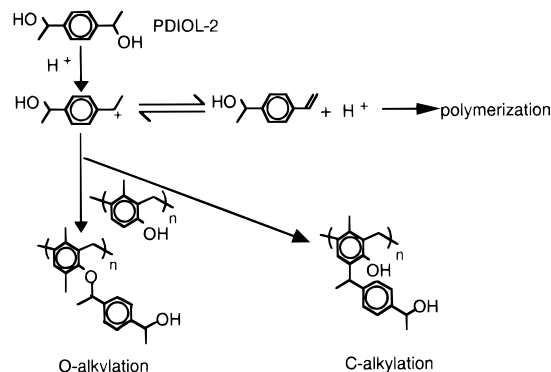

Figure 14. Possible scheme of reactions contributing to the insolubilization of the PDIOL-2 resist.

PDIOL-2 with acid in the novolak resin lies between that of PDIOL-1 and PDIOL-3 reactions as explained below. Gel permuation chromatograms of the PDIOL-2 resist are shown in Figure 12. The molecular weight of the PDIOL-2 resist increased upon exposure and baking, as did in the PDIOL-1 resist, and low molecular weight components were produced, as was observed in the PDIOL-3 resist (Figure 12). The increase in the molecular weight is probably the result of the cross-linking reactions (O- and/or C-alkylation) of novolak resin with the benzyl cation. The IR difference spectrum of the PDIOL-2 resist (Figure 13) indicates the formation of a phenyl alkyl ether (1170 cm^{-1}) as well as the substitution of hydrogen on aromatic ring by the benzyl cation (1505 cm^{-1}). The low molecular weight components appear to be ethers or polymeric compounds produced by cationic polymerization of the PDIOL-2.
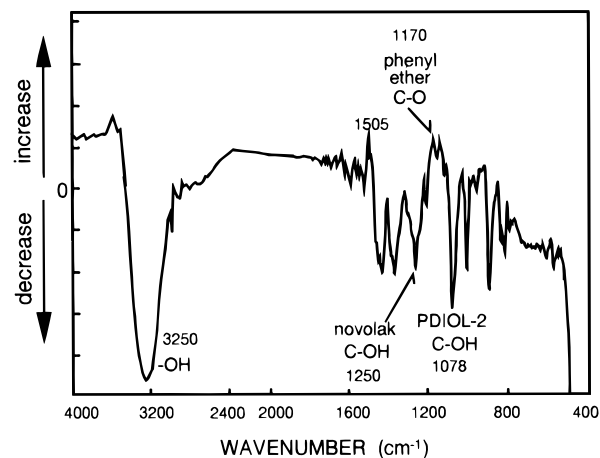
These products inhibit the dissolution of novolak in basic developers.

A possible mechanism of the insolubilization of the PDIOL-2 resist is shown in Figure 14. The PDIOL-2 reacts with acid to form the intermediate benzyl cation. The resultant benzyl cation cross-links the novolak resin by C- and O-alkylation. In addition, the benzyl cation is converted into olefin compounds which produce polymeric materials through cationic polymerization.

3.5. Lithographic Characterization of Carbinol Resist. Phenylcarbinols are suitable components of the resist system for KrF excimer laser lithography because they have very small extinction coefficient at 248 nm.
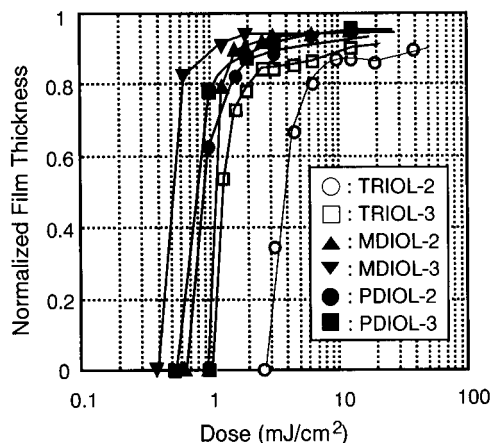
Figure 15. Exposure characteristic curves for resists using poly(4-hydroxystyrene) as a matrix resin.

To make the best use of phenylcarbinols in KrF lithography, poly(4-hydroxystyrene) was selected as the matrix resin because it also has a small extinction coefficient at the wavelength. We evaluated the resist sensitivity of resists made using several phenylcarbinols in the same composition as in section 3.1, except that poly(4-hydroxystyrene) was used instead of the novolak. A TMAH (1.19 wt %) aqueous solution was used for the development.

The sensitivity curves of the phenylcarbinol resists are shown in Figure 15. The resists containing monofunctional BZs and primary phenylcarbinols such as MDIOL-1 and PDIOL-1 did not work as negative resists. The resists using poly(4-hydroxystyrene) showed inferior properties, in terms of sensitivity and contrast, compared to the resists using novolak resin as a matrix resin. The difference in the resist properties between the poly(4-hydroxystyrene) and the novolak resists is presumably due to the higher solubility of poly(4-hydroxystyrene) compared to the novolak resin.

In terms of the contrast of the poly(4-hydroxystyrene) resists, MDIOL-2 was the best of the phenylcarbinols evaluated as can be seen in Figure 15. Patterning of a resist composed of poly(4-hydroxystyrene), MDIOL-2, and DIT was carried out with a Canon KrF excimer laser stepper (0.45 NA). The results are shown in Figure 16. Line-and-space patterns of 0.45 μm were resolved with a dose of 6.0 mJ/cm^2. The round shape of the fine patterns is probably caused by the volatility of the MDIOL-2 during the baking process and deactivation of photogenerated acid by basic components in air.
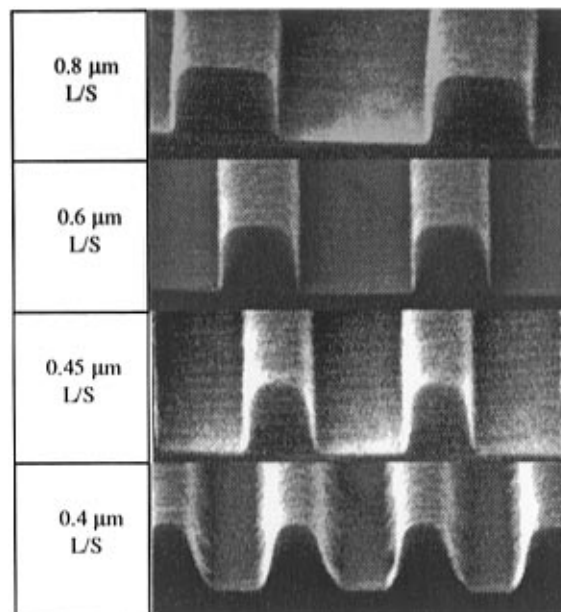

Figure 16. Scanning electron micrograph of line-and-space patterns made using a Canon KrF excimer laser stepper on a MDIOL-2 resist. Poly(4-hydroxystyrene)/MDIOL-2/DIT = 100/20/2 (weight ratio); exposure dose: 6.0 mJ/cm^2; PEB: 80 °C, 2 min; film thickness: 0.56 μm.

4. Conclusion

The relationship between the chemical structure of phenylcarbinols and the sensitivity of resists composed of a phenolic resin, a phenylcarbinol, and a photoacid generator were investigated. A resist using the tertiary phenylcarbinols had the highest sensitivity, and resists using the secondary and primary phenylcarbinols followed in turn. The resist containing the primary phenylcarbinol is insolubilized by cross-linking of the novolak resin. On the other hand, insolubilization of the resist using the tertiary phenylcarbinol is the result of olefin formation and cationic polymerization, rather than cross-linking. The resist containing secondary phenylcarbinols showed intermediate characteristics between the primary and tertiary phenylcarbinols resists.