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A New Negative-Type Photosensitive Polyimide Based on Poly(hydroxyimide), a Cross-Linker, and a Photoacid Generator

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ABSTRACT: A negative working photosensitive polyimide based on poly(hydroxyimide) (PHI), 2,6-bis-(hydroxymethyl)-4-methylphenol (BHMP) as cross-linker, and photoacid generator diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate (DIAS) has been developed. The PHI was prepared by the ring-opening polyaddition of 4,4′-hexafluoroisopropylidenebis(phthalic anhydride) and 4,4′-diamino-4″-hydroxytriphenylmethane, followed by thermal cyclization in refluxing xylene. The PHI film showed excellent transparency to UV light. The photosensitive polyimide containing 70 wt % PHI, 20 wt % BHMP, and 10 wt % DIAS showed a sensitivity of 70 mJ/cm^2 and a contrast of 3.8 when it was exposed to 365 nm light and postbaked at 120 °C, followed by developing with a 2.5% aqueous tetramethylammonium hydroxide solution at 40 °C. The mechanistic study on the formation of images is also discussed.

Introduction

Photosensitive polyimides (PSPIs) are widely used as protection and insulation layers in semiconductor manufacturing. They are very attractive since the number of processing steps is reduced by avoiding the use of classical photoresists.

Most of the negative-type PSPIs are prepared from poly(amic acid)s, where cross-linking sites are introduced to amic acids through ester and acid amine ion linkages.[1,2] On the other hand, the positive-type PSPIs consist of poly(amic acid) and *o*-diazonaphthoquinone (DNQ)[3] or 1,4-dihydropyridine derivatives,[4] polyimide containing hydroxyl groups and DNQ,[5] or *o*-nitrobenzyl esters of polyamic acid.[6]

In a previous paper,[7] we reported a new positive working alkaline-developable PSPI based on poly(hydroxyimide) (PHI) and 2,3,4-tris[(1-oxo-2-diazonaphthoquinone-4-sulfonyl)oxy]benzophenone. This is consistent with the trend of using aqueous base solutions as developers for the photoresist processing technology in the microelectronics industry.

Recently, Frechet et al. studied several three-component resist systems containing poly(4-hydroxystyrene), polyfunctional benzylic alcohols, and photoacid generators, and they found that polyfunctional benzylic alcohols act as excellent cross-linkers in the presence of acid and show high lithographic sensitivities.[8] This finding prompted us to employ the approach for the development of a new PSPI using the PHI, because the PHI contains a *p*-hydroxyphenyl unit that reacts easily with the electrophilic benzylic carbocation.

This paper describes the development of a novel approach to a negative-type PSPI that is based chemically on the propensity for the PHI to cross-link rapidly with 2,6-bis(hydroxymethyl)-4-methylphenol in the presence of a catalytic quantity of acids.

Experimental Section

Materials. 4,4′-Hexafluoroisopropylidenebis(phthalic anhydride) (6FDA) was obtained from American Hoechst Co. Ltd. 2,6-Bis(hydroxymethyl)-4-methylphenol (BHMP) was prepared by hydroxymethylation of *p*-cresol according to a reported procedure.[9] Diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate (DIAS) was prepared by the reaction of diphenyliodonium chloride with sodium 9,10-dimethoxyanthracene-2-sulfonate, which was obtained by the reduction of sodium anthraquinone-2-sulfonate with zinc and aqueous sodium hydroxide solution, followed by the methylation with dimethyl sulfate.[10] *N*-Methyl-2-pyrrolidinone (NMP) was stirred over powdered calcium hydride overnight and then distilled under reduced pressure and stored over 4 Å molecular sieves. Other reagents and solvents were obtained commercially and used as received.

Preparation of 4,4′-Diamino-4″-hydroxtriphenylmethane (DHTM). 4-Hydroxybenzaldehyde (1.22 g, 10.0 mmol), aniline (3.14 g, 34.5 mmol), and aniline hydrochloride (0.08 g, 0.59 mmol) were dissolved at 110 °C under nitrogen atmosphere. The mixture was heated at 150 °C for 1.5 h. The reaction mixture was then cooled to room temperature, and the excess aniline was distilled *in vacuo*. The residue was dissolved in 1 M aqueous hydrochloric acid solution and treated with 10 wt % aqueous sodium hydroxide solution until the precipitate dissolved, and then this solution was washed with three 100 mL portions of ether. Subsequently, the aqueous phase was neutralized with 1 M hydrochloric acid aqueous solution, and the precipitate was collected by filtration and dried. The product was purified by flash column chromatography (methylene chloride/ethyl acetate/methanol 80:18:2) and recrystallized from ethanol to give purple red needles. The yield was 1.17 g (40%): mp = 200−202 °C. (lit.[11] mp 195 °C); ^{1}H NMR (DMSO-d_6) δ 9.2 (s, OH, 1H), 6.9−6.4 (m, PhH, 12H), 5.1 (s, CH, 1H), 4.9 (s, NH$_2$, 4H). Anal. Calcd for $C_{19}H_{18}N_2O$: C, 78.60; H, 6.25; N, 9.65. Found: C, 78.66; H,6.34; N, 9.52.

Preparation of Poly(hydroxyimide) (PHI). A solution of DHTM (0.290 g, 1.0 mmol) in NMP (2.8 mL) was cooled with an ice−water bath. To this solution was added with stirring 6FDA (0.444 g, 1.0 mmol). The mixture was stirred at room temperature for 3 h. The resulting viscous solution was diluted with NMP (10 mL) and poured into 50% aqueous methanol solution (200 mL). The poly(amic acid) (PAA) that precipitated was filtered off and dried *in vacuo* at 50 °C for 12 h. The resulting PAA was dispersed in xylene and then refluxed for 90 min, and the precipitate was collected and washed with hexane and dried at 50 °C for 12 h *in vacuo*. The polymer was purified by reprecipitation by pouring polymer solution (NMP) into 50% aqueous methanol solution (200 mL). The precipitated polymer was finally dried at 200 °C for 12 h *in vacuo*. The yield was 0.509 g (73%). The inherent viscosity of the polymer in NMP was 0.48 dL/g at a concentration of 0.5 g/dL at 30 °C: IR(KBr) ν (cm^{-1}) 3430 (O−H) and 1780, 1720 cm^{-1} (C=O). Anal. Calcd for $(C_{38}H_{20}F_6N_2O_5\cdot{}^3/_2H_2O)_n$: C, 62.90; H, 3.19; N, 9.65. Found: C, 62.91; H, 3.15; N, 3.88.

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Photosensitivity. PHI was dissolved in 20 wt % in 2-methoxyethanol at room temperature, and to this solution were added BHMP and DIAS. Films spin-cast on silicon wafers were prebaked at 80 °C for 10 min and exposed through a filtered super-high-pressure mercury lamp (Ushio USH-200DP). Imagewise exposure through a mask was carried out in a contact-printing mode.

Dissolution Rate. The 3 μm PHI films on a silicon wafer were exposed at 365 nm wavelength to the filtered super-high-pressure mercury lamp, developed in 2.5% tetramethylammonium hydroxide (TMAH) aqueous solution at 40 °C, and rinsed in water. The characteristic curve of the normalized film thickness against exposure energy was obtained.

Model Reaction. PHI (78 wt %), 2,4-dimethyl-6-(hydroxymethyl)phenol (DHMP) (22 wt %), and *p*-toluenesulfonic acid monohydrate (10 mol % to DHMP) are dissolved in 2-methoxyethanol. The solution was spin-coated onto a silicon wafer, followed by heating at 55 °C for 5 min, and then at 120 °C for 10 min. The sample was dissolved in DMSO-d_6 and analyzed by ^{1}H NMR spectroscopy.

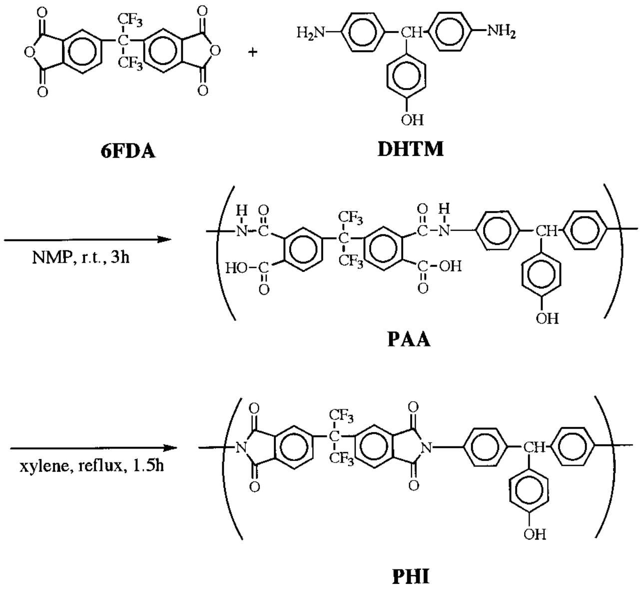
Measurement. The infrared spectra were recorded on a Hitachi I-5020 FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL EX 270 spectrometer. Viscosity measurements were carried out by using an Ostwald viscometer at 30 °C. Thermal analyses were performed on a Seiko SSS 5000-TG/DTA 220 instrument at a heating rate of 10 °C/min for thermogravimetric analysis (TGA) and a Seiko SSS 5000-DSC220 at a heating rate of 20 °C/min for differential scanning calorimetry (DSC) under nitrogen. Molecular weights were determined by gel permeation chromatography (GPC) with polystyrene standard using a JASCO HPLC system equipped with a Shodex KD-80M column at 40 °C in DMF containing 10 mmol/L LiBr. The film thicknesses were measured by a Dektak 3030 system (Veeco Instruments Inc.).

Results and Discussion

Synthesis of Poly(hydroxyimide) (PHI). Polyimides generally exhibit low optical transparency to UV light and have a yellow color due to charge transfer complex formation, and the coloration limits the formation of thick-film patterns. Therefore, several methods have been employed to obtain less colored polyimides, e.g., introducing fluoroalkyl groups, separating chromophoric groups, and reducing the electronic interaction between color-causing centers. In particular, introducing the fluoroalkyl group into the main polymer chain is considered to be a more versatile technique with respect to both the transparency and the solubility of the polyimide. Therefore, we chose 4,4′-hexafluoroisopropylidenebis(phthalic anhydride) (6FDA) as a candidate tetracarboxylic anhydride. On the other hand, a diamine monomer having a hydroxyphenyl moiety, 4,4′-diamino-4″-hydroxtriphenylmethane (DHTM), was prepared by the reaction of 4-hydroxybenzaldehyde with aniline in the presence of aniline hydrochloride.

The synthesis of PHI was carried out by the ring-opening polyaddition of 6FDA and DHTM in NMP. The polycondensation proceeded in a homogeneous solution and gave a quantitative yield of poly(amic acid) (PAA) with an inherent viscosity of 0.48 dL/g. Subsequently, the PAA was converted to PHI by refluxing in xylene for 90 min.

The polymer was confirmed to be the corresponding PHI by infrared spectroscopy and elemental analysis. The IR spectrum exhibited characteristic absorptions at 1780 and 1720 cm^{-1} due to the imide carbonyl. Elemental analysis also supported the formation of the expected polymer.



The PHI was a reddish powder, soluble in dipolar aprotic solvents at room temperature and in 2-methoxyethanol, bis(2-methoxyethyl) ether, and 1-methoxy-2-acetoxypropane at room temperature. A transparent film was cast from the solution of the PHI in these solvents.

The molecular weight of the PHI with the inherent viscosity of 0.48 dL/g was determined by GPC. The GPC trace was unimodal with a polydispersity of 1.7. The chromatogram indicated that the relative M_n and M_w are 61 000 and 104 000, respectively.

The thermal behavior of PHI was studied by thermogravimetry (TG). A typical trace for the PHI is shown Figure 1. The PHI gave a 10% weight loss at 480 and 490 °C in air and nitrogen, respectively. Differential scanning calorimetry on powders did not show any clear endotherms.

Lithographic Evaluation. The transmission UV−visible spectrum of a 1 μm thick PHI film is shown in Figure 2. The PHI film shows strong absorption with a cutoff between 300 and 400 nm. The transmittance of the PHI film at 365 nm was 85%.

As described in the Introduction, polyfunctional benzylic alcohols act as good cross-linkers for poly(4-hydroxystyrene) in the presence of acid.[8] This acid-catalyzed cross-linking reaction was studied in detail, and the reaction was proposed to proceed via a direct C-alkylation as well as an initial O-alkylation, followed by a subsequent acid-catalyzed rearrangement to the final alkylated product. Furthermore, both a thermal cross-linking and an acid-catalyzed cross-linking process were proposed for this alkylation.[12] We decided to use 2,6-bis(hydroxymethyl)-4-methylphenol (BHMP) as a cross-linker on the basis of its availability and the sensitivity.

Many onium salts, such as diaryliodonium and triarylsulfonium salts, are well known as photoacid generators.[13] However, there are few onium salts that have an absorption band at wavelengths longer than 300 nm.[14] Recently, diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate (DIAS) having an absorption higher than 300 nm was developed and shown to produce 9,10-dimethoxyanthracene-2-sulfonic acid upon irradiation with 365 nm light.[10] Furthermore, DIAS as a photoacid generator was successfully applied to the formulation of positive photoresist composed of bisphenol A protected with a *tert*-butoxycarbonyl group and a novolak resist matrix.[15] Therefore, we decided to use DIAS as the photoacid generator.

The electronic absorption spectrum of PHI film containing 10 wt % DIAS, and its changes upon photoir-

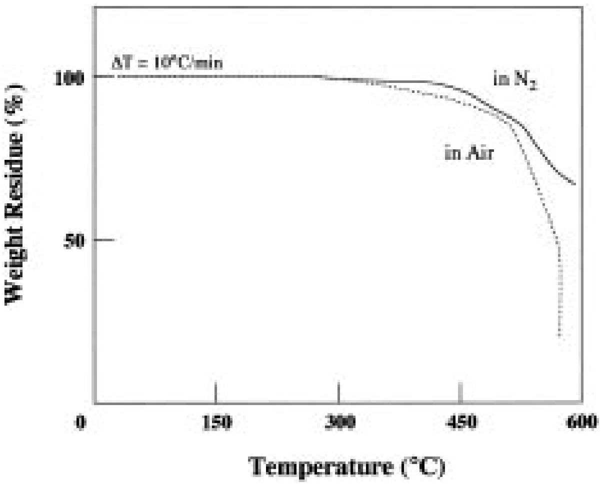


Figure 1. TG curves of PHI (---) in air and (—) in nitrogen.

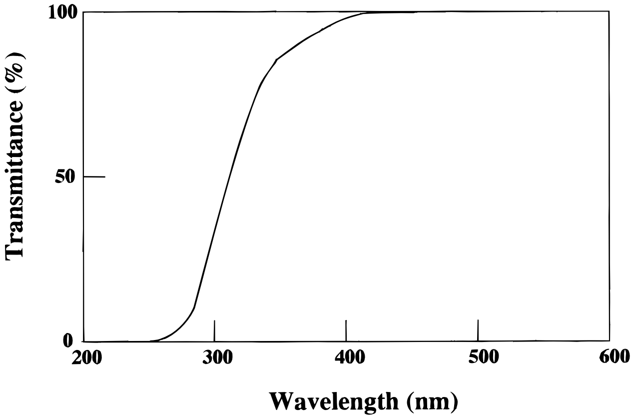


Figure 2. UV−visible spectrum of PHI film.

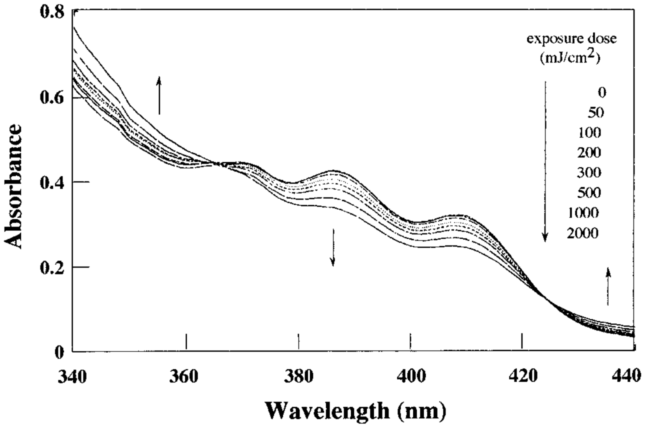


Figure 3. Change of UV−visible spectrum of DIAS (10 wt % relative to PHI) in PHI film due to 365 nm light irradiation.

radiation, are shown in Figure 3. The absorption bands at 370, 386, and 408 nm were decreased upon irradiation with 365 nm light. The final spectrum was analogous to that of 9,10-dimethoxyanthracene-2-sulfonic acid.

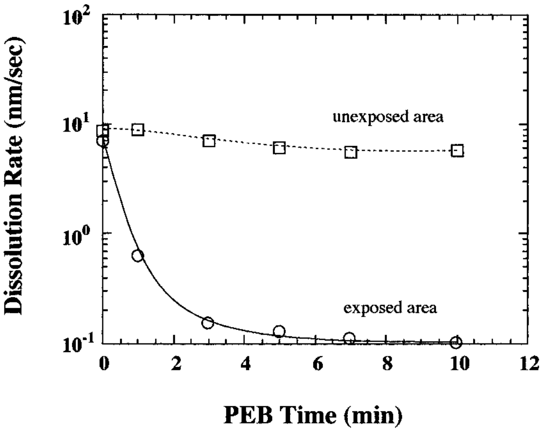


Figure 4. Relationship between PEB time and dissolution rate of PHI containing BHMP and DIAS.

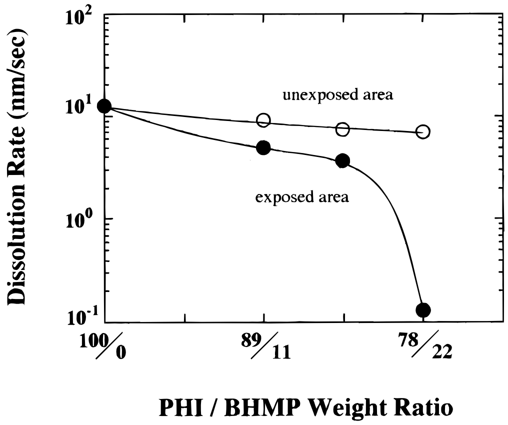


Figure 5. Relationship between DIAS content and dissolution rate of PHI containing BHMP.

To investigate the dissolution behavior of exposed and unexposed areas, the effects of the post-exposure bake (PEB) temperature and PEB time on the dissolution rate were studied. The dissolution rate was estimated by measuring the film thickness after the development. The results in the case of the resist formulated by mixing the PHI (70 wt %), BHMP (20 wt %), and DIAS (10 wt %) in 2-methoxyethanol is shown in Figure 4, where the film was exposed 200 mJ/cm^2 to 365 nm UV radiation, postbaked at 120 °C, and developed with 2.5% tetramethylammonium hydroxide (TMAH) aqueous solution at 40 °C. The dissolution rate of the exposed part decreased rapidly with increasing PEB time. On the other hand, the solubility of the unexposed part was almost unchanged. The difference of the dissolution rates between exposed and unexposed parts reached about 70 times after PEB at 120 °C for 5 min. These results indicate that the cross-linking reaction is promoted effectively by PEB treatment. The probable cross-linking process via electrophilic aromatic substitution will be discussed in a later section.

The effect of the BHMP loading on the dissolution rate in 2.5% TMAH aqueous solution after the exposure of 200 mJ/cm^2 and PEB at 120 °C for 5 min was studied, and the results are shown in Figure 5. It was found that a 20 wt % BHMP loading was necessary to achieve adequate dissolution contrast.

After these preliminary optimization studies involving BHMP and DIAS loading and developing temperature, we prepared a photosensitive polyimide system consisting of PHI (70 wt %), BHMP (20 wt %), and DIAS (10 wt %). The sensitivity curve for a 2 μm thick film, shown in Figure 6, was consistent with the dissolution behavior studied above, indicating that the sensitivity ($D^{0.5}$) and contrast ($\gamma^{0.5}$) were 70 mJ/cm^2 and 3.8, with 365 nm light, respectively, after PEB treatment at 120 °C for 5 min, followed by development with 2.5% TMAH aqueous solution at 40 °C.

In Figure 7 is presented a scanning electron micrograph of the contact-printed image that was obtained using a resist composed of PHI (70 wt %), BHMP (20 wt %), and DIAS (10 wt %), postbaked at 120 °C for 5 min after exposure to 150 mJ/cm^2, and developed with

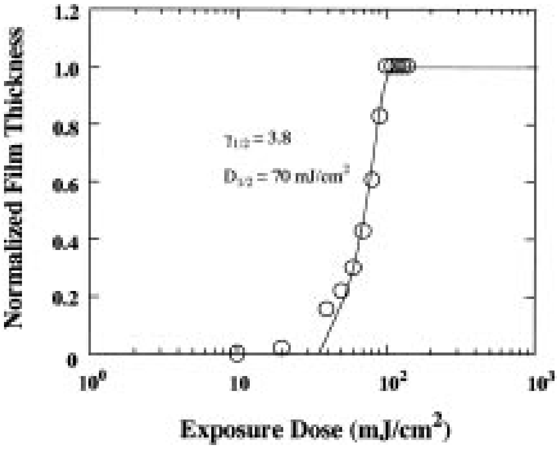


Figure 6. Exposure characteristic curves for the system of PHI, BHMP, and DIAS.

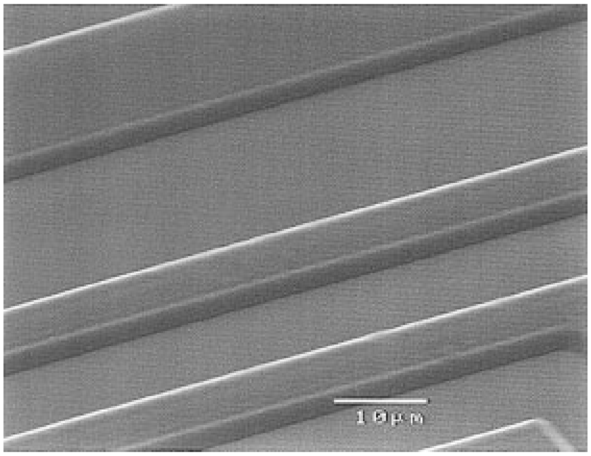


Figure 7. Scanning electron micrograph of the negative image printed in the PHI system.

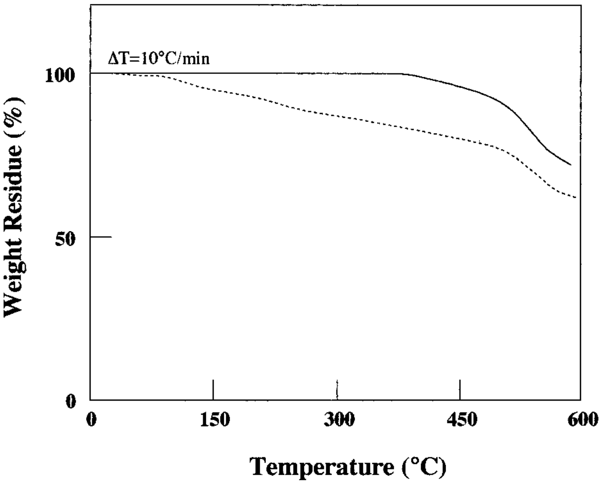


Figure 8. TG curves of the PHI system in nitrogen.

2.5% TMAH aqueous solution. The resist is capable of resolving 8 μm features when 4 μm thick films are used.

Thermal Stability of Polymer Films. Figure 8 shows TGA curves of films after postbaking at 120 °C for 5 min and then developing with 2.5% TMAH aqueous solution at 40 °C (dashed line) and curing at 350 °C for 30 min (solid line). The dashed line exhibited slopes with two steps. The first weight loss started around 120 °C, indicating that vaporization of residual solvent began at this temperature, followed by vaporization of BHMP and degradation of DIAS around 160 °C. The weight loss continued up to 300 °C, and the decomposition of polyimide occurred at temperatures higher than 500 °C. On the other hand, the solid line showed no weight loss below 400 °C, and the 10% weight loss temperature was 510 °C. These results indicate that DIAS can be removed by high-temperature treatment after the development process, and the thermal properties of the resulting polyimide are not damaged by the addition of DIAS.

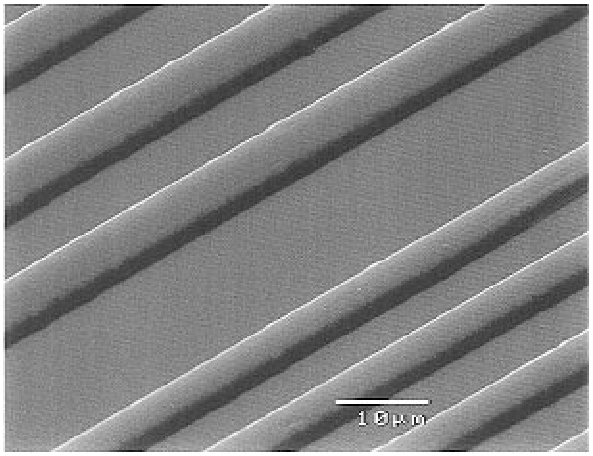


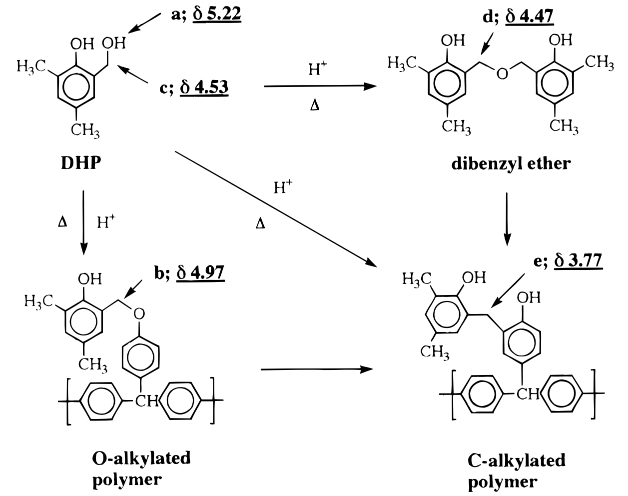
Figure 9. Scanning electron micrograph of the negative image heated at 300 °C for 30 min.

The commercially available negative-type PSPIs have a high percentage of shrinkage on final cure that induces patterned image distortion. A scanning electron micrograph of the negative image heated at 300 °C for 30 min is presented in Figure 9. The heat-treated negative image does not show any distortion and clearly reveals the high thermal stability of the resist.

Mechanism of the Acid-Catalyzed Cross-Linking. To clarify the mechanism of the acid-catalyzed cross-linking, a model reaction was carried out using PHI, a monofunctional benzyl alcohol, 2,4-dimethyl-6-(hydroxymethyl)phenol (DHP), and *p*-toluenesulfonic acid. This mixture in 2-methoxyethanol was spin-coated onto a silicon wafer, followed by heating at 55 °C for 5 min and then at 120 °C for 10 min to mimic the prebaking and postbaking steps in resist processing. Figure 10 shows the ^{1}H NMR spectra obtained for the prebaking and postbaking steps. In the prebaked film, new peaks were observed at 4.97, 4.47, and 3.77 ppm, except for the resonance peak due to DHP. These peaks were assigned to the methylene protons in the O-alkylated product, the dibenzyl ether formed by self-condensation of DHP, and the C-alkylated polymer, respectively, on the basis of a previous paper.[12]

The appearance of these new peaks was accompanied by a decrease in the amount of starting materials, indicating that a reaction occurred at the prebake step in the presence of *p*-toluenesulfonic acid. On the other hand, the methylene protons in DHP after postbaking disappeared completely, and the amount of dibenzyl ether also decreased rapidly. Furthermore, a significant quantity of C-alkylated product was formed.

On the basis of the above results, the model reaction using DIAS in place of *p*-toluenesulfonic acid was carried out by spin-coating the solution of PHI (70 wt %), DHP (20 wt %), and DIAS (10 wt %) in 2-methoxyethanol onto a silicon wafer. The resist sample was prebaked at 80 °C for 10 min and then irradiated at 365 nm with the exposure dosage of 500 mJ/cm^2. The exposed sample was then heated at 120 °C for 10 min, and the resulting resist was analyzed by ^{1}H NMR spectroscopy (Figure 11). The unexposed sample showed two peaks due to the hydroxy and methylene protons



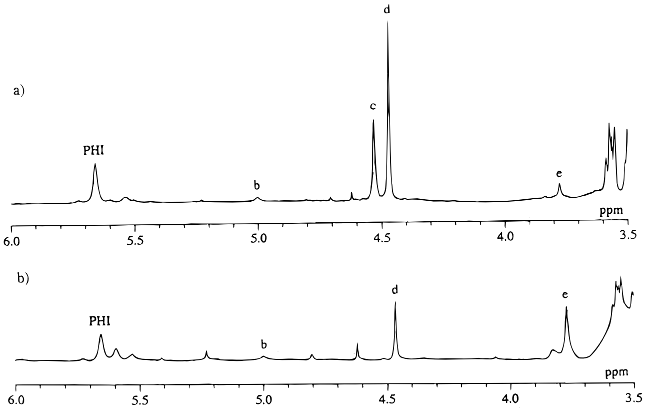


Figure 10. ^{1}H NMR spectra of model study with PHI, DHMP, and *p*-toluenesulfonic acid: (a) prebaked sample and (b) postbaked sample.

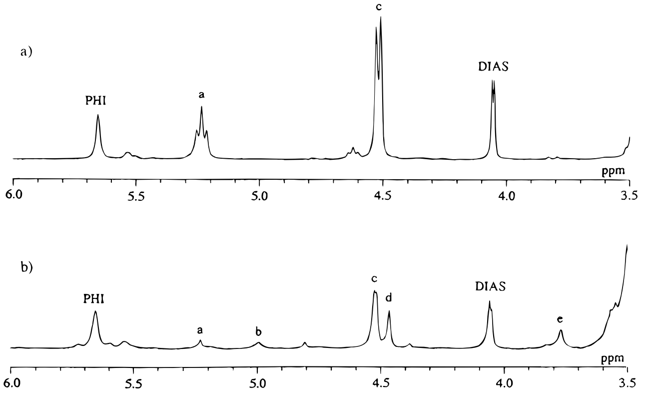
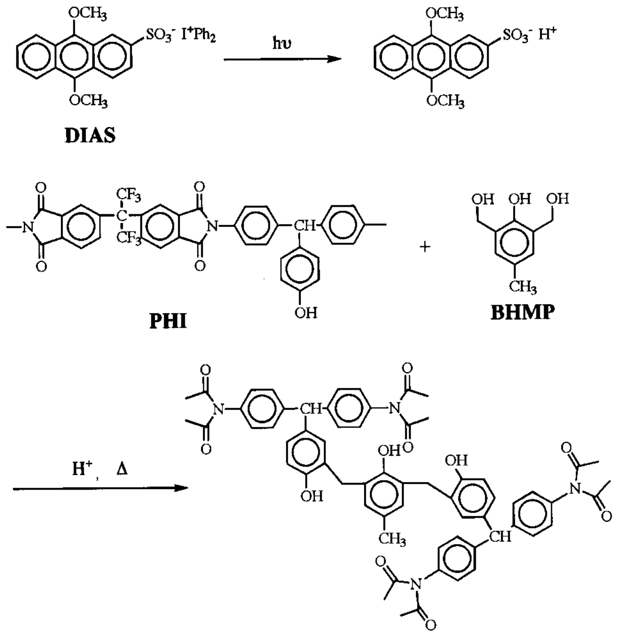


Figure 11. ^{1}H NMR spectra of model study with PHI, DHMP, and DIAS: (a) prebaked sample and (b) exposed and postbaked sample.

of the benzylic alcohol, and the formation of dibenzyl ether and alkylated polymers was not observed. In the sample exposed at 365 nm and heated at 120 °C, the peaks derived from DHP decreased rapidly, and the peaks due to dibenzyl ether and alkylated polymers increased significantly. These experiments showed that a photogenerated acid catalyzes the formation of benzylic carbocation species, which undergo electrophilic aromatic substitution to produce a C- and O-alkylated polymers. This reaction converts the soluble linear polymer to the insoluble cross-linked polymer.



Conclusions

The PHI was prepared by the ring-opening polyaddition of 6FDA and DHTM. The photochemical reaction of DIAS in the PHI film occurred smoothly because PHI has an excellent transparency in the UV region. The new PSPI was formulated by mixing the PHI (70 wt %), bis(hydroxymethyl)-4-methylphenol (20 wt %), and DIAS (10 wt %) in 2-methoxyethanol and was found to be an alkaline-developable negative-type PSPI. The thermal stability after the high thermal treatment of developed film is almost the same as that of the neat resin of PHI.

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