New Positive-Type Photosensitive Poly(phenylene ether): Poly(2-hydroxy-6-methylphenol-*co*-2,6-dimethylphenol) with Diazonaphthoquinone

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A positive working thermally stable and photosensitive polymer based on poly(2-hydroxy-6-methylphenol-*co*-2,6-dimethyl phenol) (PHP-MP) and 2,3,4-tris[2-diazo-1(2H)-naphthalenone-4-sulfonyloxy] benzophenone (D4SB) as a photoreactive compound has been developed. The copolymer. PHP-MP was prepared by oxidative coupling polymerization of 2-(tetrahydropyran-2-yl)oxy-6-methylphenol with 2,6-dimethylphenol, followed by acid treatment. The PHP-MP film showed excellent transparency above 300 nm. A clear positive pattern was obtained when it was exposed to 365 nm light, followed by developing with a 2.38% aqueous tetramethyl-ammonium hydroxide (TMAH) solution at 25 ℃.

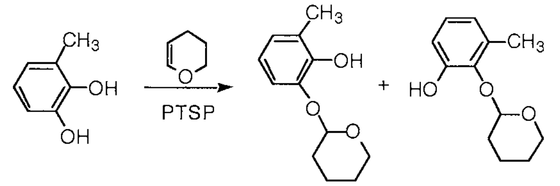
Photosensitive polyimides (PSPIs) are widely used as protection and insulation layers of very large scale integrated circuit (VLSI), multi-chip modules for computers, telecommunications and thermal-heads because they simplify processing and do not need a photoresist used in the microlithograpy or a toxic etchant such as hydrazine. Most PSPIs reported so far are a negative working type and need organic solvents as a developer.[1-3] However, negative PSPIs swell during development, because a developer is an organic solvent. Thus, it limits the pattern resolution. In order to overcome these problems, positive working PSPIs that can be developed with water-based solutions have been attracting great interest. Therefore, several groups[4-6] have reported resists consisting of polyamic acids (PAAs) and 2-diazo-1(2H)-naphthalenone (DNQ). However, dissolution rates of PAAs toward a 2.38% aqueous TMAH solution are essentially too high to get sufficient dissolution contrast. So, the dissolution rates of PAAs have to be reduced by prebaking, or post exposure bake (PEB). Other DNQ sensitized approaches were made by introducing DNQ, and phenol moieties into PAA through sulfonic ester and ester linkages, respectively.[7,8] By controlling the contents of these groups to obtain good dissolution contrast, these PSPI-precursors have also been found to provide excellent positive images.

On the other hand, most of the standard resist materials used in semiconductor manufacturing are positive type resist based on novolac resin with DNQ, where DNQ acts as the dissolution inhibitor for aqueous base development of the novolac resin.

We were interested in a hydroxy-substituted poly(phenylene ether) as a candidate of alkaline developable thermally stable and photosensitive polymer. Because poly(phenylene ether)s are well known thermally stable polymers and phenol units are responsible for alkaline development.

In this paper, we report the new positive working alkaline developable thermally stable and photosensitive polymer based on poly(2-hydroxy-6-methylphenol-*co*-2,6-dimethylphenol) (PHP-MP) and 2,3,4-tris[2-diazo-1(2H)-naphthalenone-4-sulfonyloxy] benzophenone (D4SB) as a photoreactive compound.

Monomer, 2-(tetrahydropyran-2-yl)oxy-6-methylphenol (1) was synthesized by tetrahydropyranylation of 3-methyl catechol in the presence of *p*-toluenesulfonic acid pyridinium salt (PTSP). (Eq.1) This reaction produced a mixture of 1 and 2-(tetrahydropyran-2-yl)oxy-3-methylphenol (2). Monomer 1 was isolated by using column chromatography (toluene as an eluent).[9]



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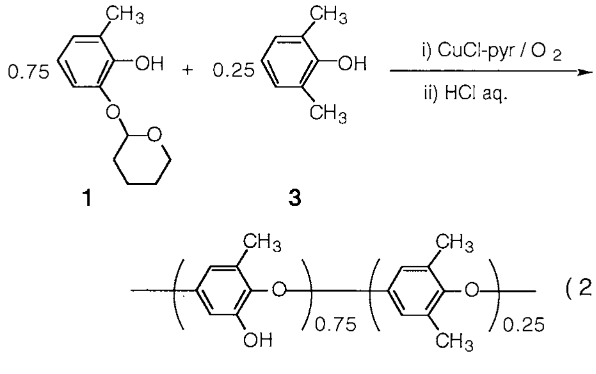
PHP-MP was prepared by oxidative coupling polymerization of 1 with 2, 6-dimethylphenol (3) in the presence of copper (I) chloride and pyridine in toluene,



1 3

(2)

PHP-MP

followed by acid cleavage of the protecting group.(Eq.2) The yield was quantitative. The structure of PHP-MP was identified as the corresponding poly(hydroxyphenylene ether) by IR and ^{1}H- and ^{13}C-NMR spectroscopies. The IR spectrum exhibited a characteristic OH stretching absorption at 3415 cm^{-1}. The ^{1}H-NMR spectrum showed a methyl singlet at 2.0 ppm, the OH signal at 9.5 ppm, and aromatic signals at 6.0-6.5 ppm. The molar ratio of comonomers 1 (0.75 mol%) and 3 (0.25 mol%) incorporated in polymer was also confirmed by the intensities of the signals at 2.0 (CH_3) and 9.5 (OH). The ^{13}C-NMR spectrum is shown in Figure 1, together with assignments of the observed resonance. No extra peaks were found, clearly indicating the formation of the expected polymer.

The molecular weight of the polymer was determined by gel permeation chromatography (GPC) in THF. The GPC trace was unimodal with a polydispersity of 2.3. The chromatogram indicates that the relative Mn and Mw were 10,200 and 23,700, respectively, based on polystyrene standard.

The UV-visible spectrum of a 1 μm thick film of the PHP-MP

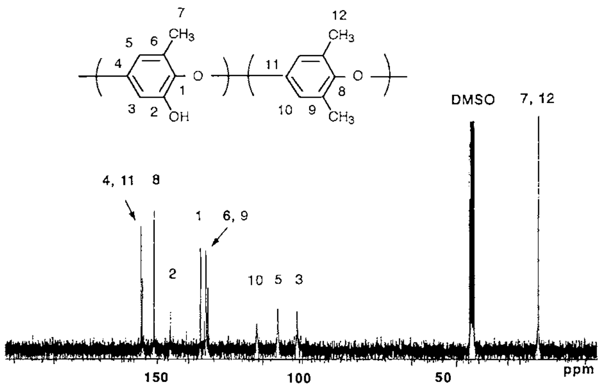


Figure 1. ^{13}C-NMR spectra of PHM-MP in DMSO-d_6.

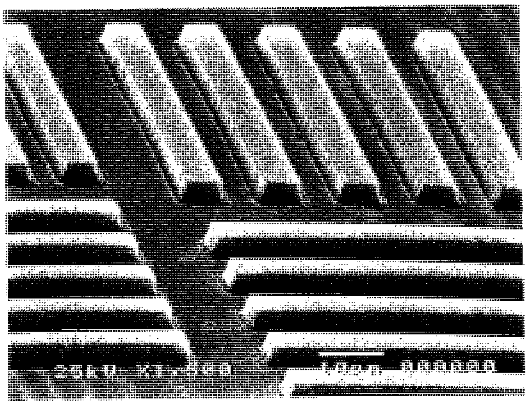


Figure 2 . Scanning electron micrograph of positive image printed from PHP-MP containning D4SB.

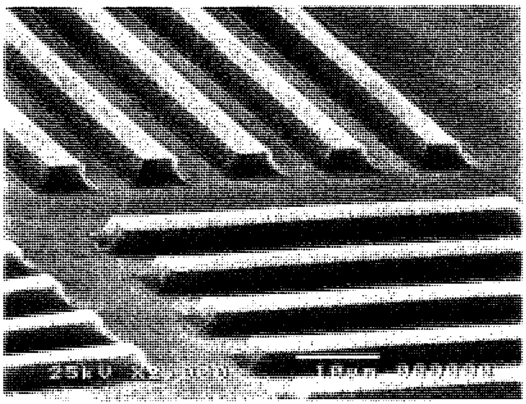


Figure 3 . Scanning electron micrograph of thermally treated patterns.

indicates that polymer is almost transparent above 300 nm. The polymer was dissolved in 15 wt% in ethyl lactate at room temperature, to which was added D4SB(25 wt%). Films spin-cast on silicon wafers were prebaked at 80 ℃ for 10 min, exposed 190 mJ/cm^2 to UV light, developed with a 2.38 % aqueous TMAH, and rinsed with water. Figure 2 shows a scanning electron micrograph of positive image. This resist is capable of resolving 5 µm features when 4-5 µm thick film is used. A scanning electron micrograph of positive image heated at 300 ℃ for 60 min is presented in Figure 3. The heat-treated positive image does not show any distortion and clearly reveals the high thermal stability of the resist. To achieve an excellent resolution, a more detailed optimization study involving D4SB and irradiation dose is in progress.

References and Notes

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9 The yield was 45%. IR (NaCl): ν 3540, 2950, 1610, 1481, 1265 cm^{-1}. ^{1}H-NMR($CDCl_3$): δ 1.6-2.0 (m, CH_2 of pyran, 6H), 2.5 (s, CH_3, 3H) 3.6-3.7 (m, CH_2 of pyran, 1H), 3.9-4.1 (m, CH_2 of pyran, 1H), 5.1-5.2 (m, CH of pyran, 1H), 6.5 (s, OH, 1H), 6.67-6.75 (m, ArH, 1H), 6.80-6.85 (m, ArH, 1H), 6.90-6.96 (m, Ar-H, 1H). ^{13}C-NMR($CDCl_3$): δ 15.4, 19.4, 24.7, 30.5, 63.4, 100.0, 115.0, 119.2, 125.0, 125.1, 144.2, 145.5. MS (FAB): m/z = 208 (M^+).