

Negative-type Chemically Amplified Photosensitive Semi-alicyclic Polybenzoxazole *via* Acid-catalyzed Electrophilic Substitution

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ABSTRACT: A negative-type photosensitive semi-alicyclic polybenzoxazole (Nega-PSPABO) based on poly(*o*-hydroxy amide) containing an adamantyl unit (PAHA) and oxybis(3,4-dihydroxymethyl)benzene (OBHB) as a cross-linker, and a photoacid generator, (5-propylsulfonyloxyimino-5*H*-thiophen-2-ylidene)-(2-methylphenyl)acetonitrile (PTMA) has been developed. PAHA with a weight average molecular weight of 24,100 was prepared from 1,3-adamantanedicarbonyl chloride (ADC) and 4,4'-(hexafluoroisopropylidene)bis(*o*-aminophenol) (6FAP) in the presence of lithium chloride in *N*-methyl pyrrolidinone (NMP) at 0 °C for 12 h. The photosensitive polymer based on 85 wt % PAHA, 10 wt % OBHB, and 5 wt % PTMA showed a sensitivity of $D_{0.5} = 14.4 \text{ mJ/cm}^2$ and a contrast of 2.4 when it was exposed to a 365 nm light (i-line) and developed with a 2.38 wt % aqueous tetramethylammonium hydroxide solution (TMAHaq) at 25 °C. A fine negative image of 7 μm line-and-space pattern was also printed in the film which was exposed to 80 mJ/cm² of i-line by contact-printing mode. The negative image in PAHA was converted to the corresponding PABO pattern image by thermal treatment without pattern deformation. The average refractive index of Nega-PSPABO was 1.542 from which the dielectric constant estimated was 2.62 at 1 MHz.

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KEY WORDS Chemically Amplified Photosensitive Polymer / Semi-aromatic Polybenzoxazole / Photoresist / Cross-linker / Electrophilic Substitution / Negative Image / Low Dielectric Constant /

Photosensitive polybenzoxazoles (PSPBOs)^{1–11} have been used as protection and insulation layers for very large scale integration circuits (VLSIs) and multichip modules for computers owing to their high thermal stability and excellent mechanical and electrical properties.¹² Up to now PSPBO based on poly(*o*-hydroxy amide) (PHA) derived from 4,4'-(hexafluoroisopropylidene)bis(*o*-aminophenol) (6FAP) and 4,4'-oxybis(benzoic acid) derivatives with a photosensitive compound is widely used. However, PSPBO having a lower dielectric constant and higher transparency is required to increase the circuit speed and to maximize the throughput of wafers in exposure tools.

In a preceding paper,¹³ we reported the synthesis of semi-alicyclic PHA (PAHA) with high transparency (99% T @ 365 nm) and the corresponding PBO (PABO) having the low dielectric constant ($\epsilon = 2.55$). PAHA was then employed as a new positive-type photosensitive PABO (Posi-PSPABO) consisting of PAHA, 1,3,5-tris[(2-vinyloxy)ethoxy]benzene (TVEB) as an acidolytic de-cross-linker, and diphenyliodonium-9,10-dimethoxyanthracene-2-sulfonate (DIAS) as a photoacid generator in chemical amplification system. Posi-PSPABO shows high photosensitivity (40 mJ/cm²) because of the introduction of an adamantyl unit, which is effective in decreasing both

molecular density and conjugation in the main chain due to the bulkiness and the *sp*³ character of carbons, respectively. The next target is to develop a negative-type chemically amplified PSPABO (Nega-PSPABO) using PAHA for expanding the image formation and improving the sensitivity.

As a cross-linker, 4,4'-methylenebis[2,6-di(hydroxymethyl)]phenol (MBHP, the structure is shown in Scheme 4) has been used extensively for negative-tone chemically amplified photosensitive materials so far.^{14–16} Since the remained phenolic hydroxyl group in MBHP may increase dielectric constants of the films after the thermal treatment, a new cross-linker without phenol units are more desirable.

This article reports the development of a three-component Nega-PSPABO with high transparency and a low dielectric constant based on PAHA, oxybis(3,4-dihydroxymethyl)benzene (OBHB) as a novel cross-linker, and (5-propylsulfonyloxyimino-5*H*-thiophen-2-ylidene)-(2-methylphenyl)acetonitrile (PTMA) as a photoacid generator.

EXPERIMENTAL

Materials

Tetrahydrofuran (THF) was distilled from sodium

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metal and benzophenone ketyl. *N*-Methyl-2-pyrrolydione (NMP) was dried over calcium hydride, distilled under reduced pressure, and stored over 4-Å molecular sieves. 6FAP was purified by recrystallization from THF. ADC was prepared by reaction of 1,3-adamantenedicarboxylic acid with excess amounts of thionyl chloride, followed by recrystallization from *n*-hexane. A photoacid generator, PTMA,¹⁷ was kindly donated by Ciba Specialty Chemicals Co., Ltd. and was used without further purification. A cross-linker, MBHP, was prepared according to a reported procedure.¹⁸ The other reagents and solvents were used as received.

Synthesis of Oxybis(3,4-phthalic acid dimethyl ester) (2)

A solution of 4,4'-oxydiphthalic anhydride **1** (7.82 g, 25.2 mmol) and sulfuric acid (2 mL) in methanol (260 mL) was refluxed for 24 h. The solution was concentrated with a rotary evaporator, and then poured into water. After the aqueous solution was decanted, the precipitate was dissolved in THF (80 mL) and then added saturated aqueous sodium bicarbonate solution with stirring. The organic layer was separated with a separatory funnel, while the aqueous layer was extracted with THF/ether (2/1, v/v) (20 mL \times 3 times). The combined organic solution was dried over magnesium sulfate anhydride, followed by evaporation. The residue was purified by recrystallization from isopropyl alcohol/hexane to give white crystals. The yield was 6.34 g (63%). Mp: 71–72 °C. IR (KBr, ν , cm^{-1}): 2954 (CH_3), 1720 ($\text{C}=\text{O}$), 1292 (Ph–O–Ph). ¹H NMR (CDCl_3 , δ , ppm): 7.83 (d, $J = 8.4$ Hz, 2H, Ar–H), 7.27 (d, $J = 2.7$ Hz, 2H, Ar–H), 7.16 (dd, $J = 8.4, 2.7$ Hz, 2H, Ar–H), 3.91 (s, 12H, CH_3). ¹³C NMR ($\text{DMSO}-d_6$, δ , ppm): 167.9, 167.2, 158.8, 135.8, 132.1, 127.0, 121.3, 119.4, 53.3, 53.1. *Elemental anal.* Calcd for $\text{C}_{20}\text{H}_{18}\text{O}_9$: C, 59.70; H, 4.51; O, 35.79; Found C, 60.03; H, 4.54; O, 35.43.

Synthesis of Oxybis(3,4-dihydroxymethyl)benzene (OBHB)

A solution of **2** (10.5 g, 26.1 mmol) in dry THF (180 mL) was cooled with an ice–water bath. To this solution was added dropwise a solution of lithium aluminum hydride (LAH; 3.49 g, 92.0 mmol) in dry THF (90 mL) for 20 min. The mixture was stirred for 24 h at room temperature. Ethyl acetate (350 mL) was added to the reaction mixture slowly to quench excess amount of LAH, and the mixture was poured into water. Aqueous hydrochloric acid solution (2N) was then added with stirring until the solution was slightly acidic. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (60 mL \times 3 times). Then, the combined organic layer was washed with an aqueous sodium bicarbonate solution and

dried over magnesium sulfate anhydride. The solvent was removed with a rotary evaporator and the solid residue was purified by column chromatography (ethyl acetate/THF = 6/1 in volume), followed by recrystallization from THF/hexane to give white crystals. The yield was 3.88 g (51%). Mp: 104.2–104.5 °C. IR (KBr, ν , cm^{-1}): 3278 (OH), 2877 (CH_2), 1604 (Ar), 1245 (Ph–O–Ph). ¹H NMR ($\text{DMSO}-d_6$, δ , ppm): 7.34 (d, $J = 8.4$ Hz, 2H, Ar–H), 7.05 (d, $J = 2.4$ Hz, 2H, Ar–H), 6.83 (dd, $J = 8.4, 2.4$ Hz, 2H, Ar–H), 4.99 (dt, $J = 13.8, 5.4$ Hz, 4H, OH), 4.50 (dd, $J = 15.6, 5.1$ Hz, CH_2). ¹³C NMR ($\text{DMSO}-d_6$, δ , ppm): 156.8, 142.8, 134.7, 129.5, 117.3, 117.1, 60.9, 60.7. *Elemental anal.* Calcd for $\text{C}_{16}\text{H}_{18}\text{O}_5$: C, 66.19; H, 6.25; O, 27.56; Found C, 66.50; H, 6.36; O, 27.14.

Synthesis of Adamantane-containing Poly(o-hydroxyamide) (PAHA) and the Corresponding Polybenzoxazole (PABO)

PAHA was prepared by low temperature solution polycondensation of 6FAP and ADC in the presence of lithium chloride as reported in our previous paper.^{13,19} Number- and weight-average molecular weights (M_n , M_w) were measured by GPC (DMF, polystyrene standards) to be 12,600 and 22,100, respectively ($M_w/M_n = 1.8$). PABO was prepared from PAHA by thermal curing at elevated temperature up to 350 °C under nitrogen.

Dissolution Rate

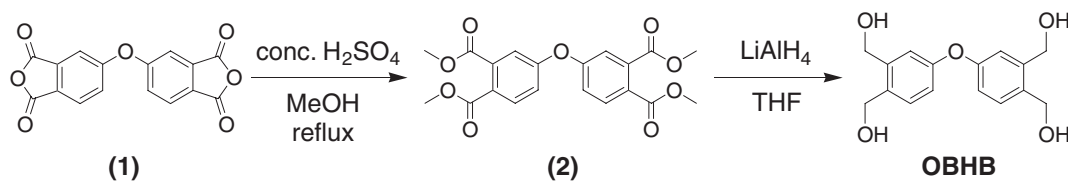
PAHA was dissolved in cyclohexanone at a concentration of 15 wt % to which was added OBHB (5–10 wt % of the total solid) and PTMA (5 wt % of the total solid). This photosensitive polymer film spin-cast from the solution on a silicon wafer was pre-baked at 100 °C for 2 min, and then exposed to a filtered super-high-pressure mercury lamp at 365 nm (i-line), followed by post-exposure baking at a temperature (120–140 °C) for 5–10 min. The exposed film was developed with 2.38 wt % of tetramethylammonium hydroxide (TMAHaq) solution at 25 °C. Dissolution rate ($\text{\AA}/\text{s}$) of the film was determined from changes in the film thickness before and after the development.

Photosensitivity

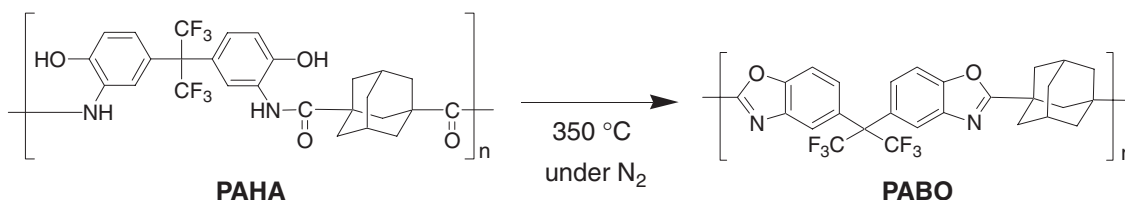
A 2.2- μm -thick photosensitive polymer film on a silicon wafer was exposed to i-line and then developed with 2.38 wt % of TMAHaq at 25 °C for 10 s, followed by rinsing with water. A characteristic curve was obtained by plotting a normalized film thickness as a function of exposure dose (mJ/cm^2).

Model Reaction for Cross-linking

PAHA, *p*-methoxy benzyl alcohol (two equiv of a PAHA repeat unit) and *p*-toluenesulfonic acid mono-



Scheme 1. Synthesis of OBHB.



Scheme 2. Structure of PAHA and PABO.

hydrate (pTS; 10 wt % of PAHA) were dissolved in THF (as 15 wt % of PAHA solution). A film cast from the solution onto a laboratory dish was heated at 100 °C and then 140 °C for 10 min each, followed by vacuum drying at 50 °C for 2 h. A film without pTS was also prepared in the same procedure. Each sample was dissolved in DMSO-*d*₆ for the measurement of ¹H NMR spectroscopy.

Measurements

Fourier transferred infrared spectra (IR) were taken with a Horiba FT-210 spectrophotometer. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a BRUKER GPX300 (¹H at 300 MHz and ¹³C at 75 MHz) spectrometer. Thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) were performed on a Seiko TG/DTA 6300 and DSC 6200, respectively at a heating rate 5 °C/min under nitrogen stream. Number- and weight-average molecular weights (*M_n*, *M_w*) were determined by a gel permeation chromatography (GPC) with a Tosoh HLC-8120 GPC system equipped with polystyrene gel columns (TSK GELS; GMH_{HR}-M, and GMH_{HR}-L) at 40 °C in DMF (containing 0.01 M of LiBr) at a flow rate of 1.0 mL/min, calibrated with polystyrene standards. Film thickness on silicon wafers was measured by Veeco Instrument Dektak³ surface profiler. The field emission scanning electron microscope (SEM) was taken with a HITACHI S-800 scanning electron microscope with 15 kV accelerating voltage for imaging. Refractive indices of photosensitive PABO films formed on quartz substrates were measured at a wavelength of 1.320 μm at room temperature with a Metricon model PC-2000 prism coupler. Using linearly-polarized laser with parallel (TE: transverse electric) and perpendicular (TM: transverse magnetic) polarization to the film plane, the in-plane (*n*_{TE}) and

out-of-plane (*n*_{TM}) refractive indices and the film thickness of the samples were determined. The dielectric constant (ϵ) at 1.0 MHz frequency was calculated from the following equation: $\epsilon = 1.10 n_{AV}^2$, where *n*_{AV} is average refractive index (*i.e.*, $n_{AV} = (2n_{TE} + n_{TM})/3$).

RESULTS AND DISCUSSION

Synthesis of Cross-linker, OBHB

The phenolic hydroxyl unit in MBHP increases moisture absorption that induces a high dielectric constant (ϵ) of materials. To overcome this problem, MBHP should be replaced with a cross-linker without a phenol unit. A novel cross-linker, OBHB consisting of tetrafunctional benzylic alcohol moieties was designed and prepared as shown in Scheme 1. 4,4'-Oxydiphthalic anhydride (**1**) was treated with methanol and a catalytic amount of sulfuric acid to produce the corresponding tetramethyl ester derivative (**2**), which was converted to OBHB by reduction with LAH in dry THF in good yield.

Synthesis of PAHA and PABO

PAHA was synthesized by low temperature solution polycondensation, according to the previous paper.¹³ Such modification of PAHA by the insertion of bulky alicyclic moiety in the polymer backbone realizes a shift of the absorption to lower wavelength and lower dielectric constant, compared to wholly aromatic PHAs. The obtained PAHA showed 22,100 of *M_w* and 1.8 of polydispersity (*M_w*/*M_n*) in GPC (DMF at 40 °C, calculated with polystyrene standards). PABO was prepared by thermal treatment at elevated temperature up to 350 °C for 1 h under nitrogen as shown in Scheme 2. The satisfactory conversion from PAHA to PABO was confirmed by IR spectrum.

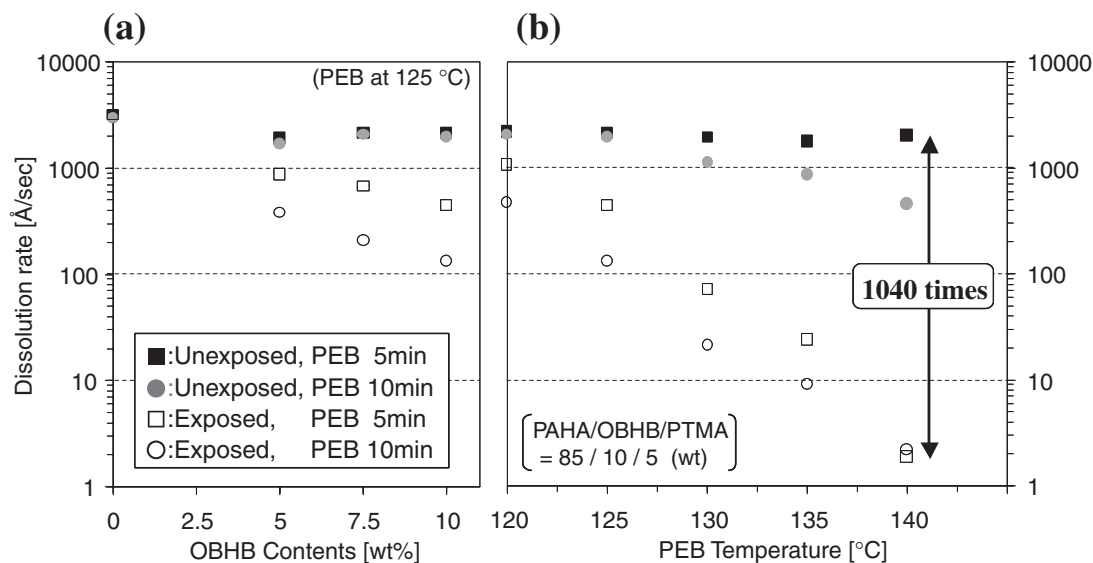


Figure 1. Dissolution rate of PSPABO as function of (a) OBHB contents and (b) post-exposure-bake-temperature. Other lithographic conditions were fixed as follows: (a) PAHA/PTMA = 85/5 in weight, PEB at 125 °C; (b) PAHA/OBHB/PTMA = 85/10/5 in weight; both (a) and (b) 40 mJ/cm² of exposure to i-line, development with 2.38 wt % TMAHaq at 25 °C.

Lithographic Evaluation in Negative-tone Chemically Amplification with OBHB

As no absorption in the UV–vis spectrum of PAHA was observed above 320 nm, PTMA having an absorption band extending to 450 nm was selected as a photoacid generator for photolithographic evaluation with i-line exposure (365 nm).¹⁷ PTMA is more soluble in organic solvents such as cyclohexanone than DIAS which was used as a photoacid generator for the Posi-PSPABO. The film was obtained from the solution of PAHA, OBHB and PTMA in cyclohexanone by spin-cast on a silicon wafer, and then pre-baked at 100 °C for 2 min in air. To the photosensitive polymer film, a UV light at 365 nm (i-line) by a filtered super-high-pressure mercury lamp was irradiated, followed by post-exposure bake (PEB) and development with 2.38 wt % of TMAHaq at 25 °C.

To clarify dissolution behaviors of the exposed and unexposed areas toward 2.38 wt % TMAHaq, the effects of OBHB loading and PEB temperature were studied and the results are shown in Figure 1. The dissolution rate was estimated from the change of the film thickness before and after the development. As shown in Figure 1a, the dissolution rate in the exposed area decreases with increasing the contents of OBHB up to 10 wt % both for 5 min and 10 min in PEB time. However, the dissolution difference between the exposed and unexposed areas is about 14 times at the 10 wt % OBHB loading. This dissolution contrast is not enough to obtain a clear pattern.

Cross-linking reactions between PAHA and OBHB are also promoted by PEB treatment in the chemical amplification resists. Thus, the effect of the PEB tem-

perature was studied as shown in Figure 1b. Baking at 140 °C for 5 min effectively reduces the dissolution rate of the exposed area, and the dissolution difference between the two areas reaches over 1000 times.

Based on these preliminary optimization studies, a photosensitive polymer system consisting of PAHA (85 wt %), OBHB (10 wt %), and PTMA (5 wt %) was formulated. The photosensitivity curve of the formulated resist film in 2.2 μm thickness is shown in Figure 2, where the PEB treatment was carried out

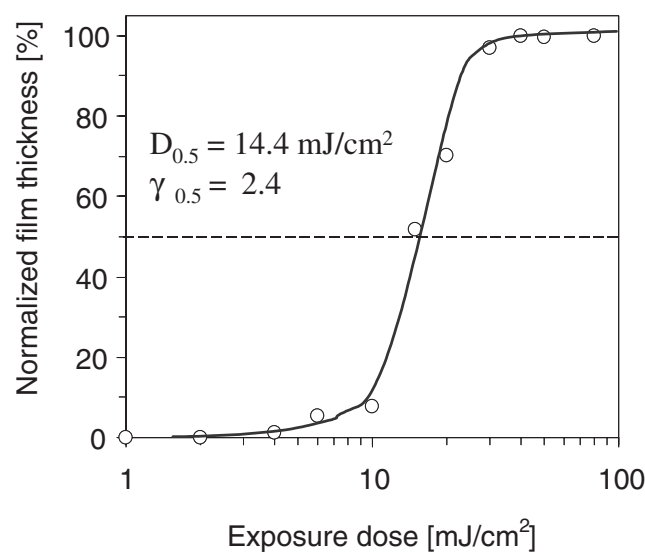


Figure 2. Characteristic sensitivity curve of Nega-PSPABO film (2.2 μm thickness) consisting of PAHA (85 wt %), OBHB (10 wt %) and PTMA (5 wt %). The film was pre-baked at 100 °C for 2 min, post-exposure baked at 140 °C for 5 min, and developed with 2.38 wt % TMAHaq at 25 °C for 10 s.

at 140 °C for 5 min. This resist system shows the high sensitivity ($D_{0.5} = 14.4 \text{ mJ/cm}^2$) and contrast ($\epsilon_{0.5} = 2.4$) with 365 nm wavelength of light.

Figure 3 depicts a SEM image of a contact-printed pattern obtained with the 2.5- μm -thick resist film under the optimized conditions. A clear negative-tone

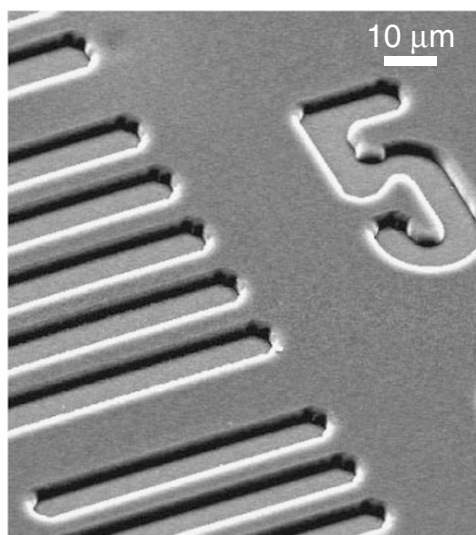


Figure 3. SEM image of the contact-printed film consisting of PAHA (85 wt %), OBHB (10 wt %) and PTMA (5 wt %) on a silicon wafer. In lithographic evaluation, the 2.5- μm -thick film was exposed to 80 mJ/cm² of i-line, developed with 2.38 wt % TMAHq at 25 °C for 14 s.

image with a 7 μm line-and-space resolution can be observed.

Mechanism of Cross-linking with OBHB

To make clear the mechanism of the acid-catalyzed cross-linking, a model reaction was carried out using PAHA, *p*-methoxybenzyl alcohol (two equiv of PAHA) and *p*-toluenesulfonic acid monohydrate (pTS; 10 wt % of PAHA). The mixture of PAHA, *p*-methoxybenzyl alcohol and pTS in THF was cast on a laboratory dish, followed by heating at 100 °C for 10 min and then at 140 °C for 10 min to mimic the pre-baking and post-baking steps in the resist processing. Finally, vacuum drying at 50 °C for 2 h was carried out to remove the remained solvent. Figure 4 shows ¹H NMR spectra obtained after the baking steps with and without pTS. Without pTS, almost no change of the signals in the spectrum is observed (Figure 4a). In the presence of pTS, the characteristic methylene protons of the benzyl alcohol and phenolic hydroxyl protons of PAHA at 4.4 and 10.3 ppm, respectively (signal *m* and *e* in Figure 4a), disappear completely and C-alkylated methylene protons at 3.7 ppm are formed (signal *y* in Figure 4b).

These results indicate that a photogenerated acid catalyzes the formation of benzylic cation species, which undergo electrophilic substitution on the aromatic rings and the hydroxyl groups to produce C- and O-alkylated polymers. The O-alkylated polymers

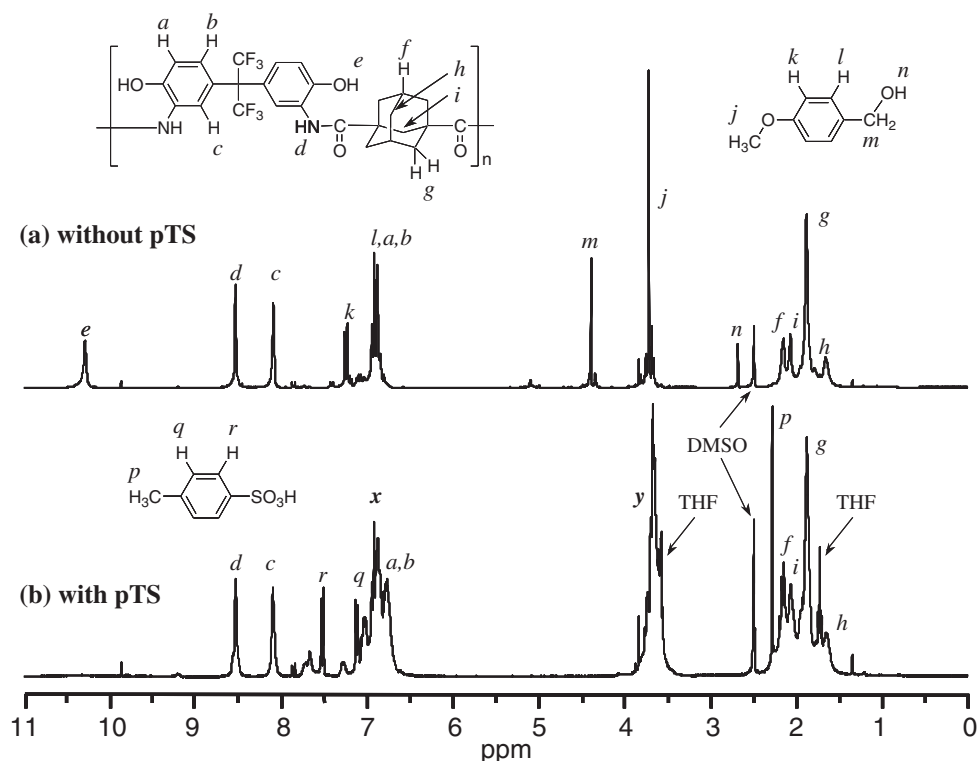
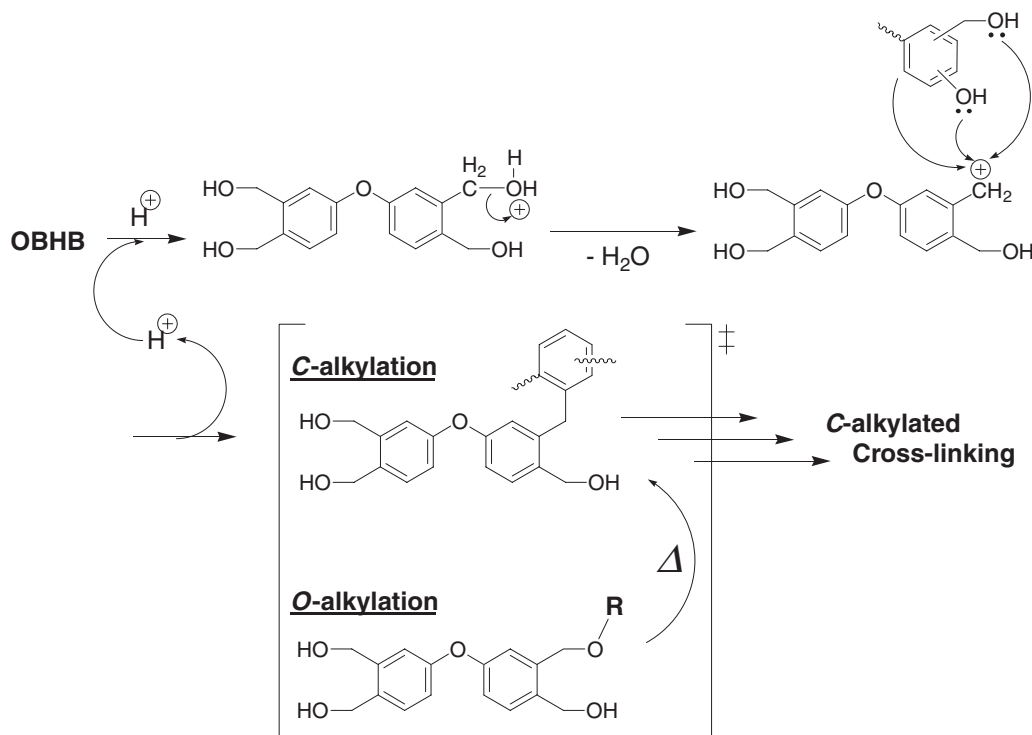


Figure 4. ¹H NMR spectra of PAHA film consisting of (a) *p*-methoxy benzyl alcohol, (b) *p*-methoxy benzyl alcohol and pTS in DMSO-*d*₆. Each film was baked at 100 °C for 10 min and then 140 °C for 10 min, followed by vacuum drying at 50 °C for 2 h.



Scheme 3. Mechanism of acid-catalyzed cross-link reaction of OBHB.

are rearranged into the C-alkylated ones by heating.^{20,21} These reactions convert soluble PAHA into insoluble cross-linked polymers as shown in Scheme 3. Unlike MBHP in which the phenolic hydroxyl group is effective for the formation of benzylic cation as an electron-donating group, a promotion of the electrophilic substitution with OBHB may be attributed to the oxygen atom of ether linkage in OBHB as suggested by Lee *et al.*²²

Thermal Stability of Photosensitive PABO

The thermal stability of the patterned PABO was evaluated by thermogravimetry (TG). To convert PAHA into PABO, the cross-linked resist film was heated up to 350 °C, held at that temperature for 1 h under nitrogen and cooled down to 50 °C, where the characteristic absorptions of hydroxyl and amide groups at 3400 and 1650 cm^{-1} , respectively, disappeared in the IR spectrum. Figure 5a shows a TG curve of PSPABO. A 5% weight loss temperature (T_{d5}) is observed at 468 °C which is 50 K lower than that of the additive-free PABO (518 °C, Figure 5b).¹³ The lower T_{d5} is attributed to remained additives such as OBHB and PTMA in the film, however, thermal stability over 450 °C is enough high for the application to protector or insulator for VLSIs. Figure 6 shows a SEM image of PABO pattern after the thermal treatment up to 350 °C under nitrogen. No deformation of 7- μm -featured patterns was observed (Figure 3), where the final film thickness was shrunk

from 4.7 to 4.1 μm after the cure.

Dielectric Constants of PABO Resist Films

Refractive indices (n_{TE} : in-plane, n_{TM} : out-of-plane) of a series of photosensitive PABO films on quartz plates were measured by using prism-coupler. From the refractive index (n), dielectric constant of each resist film at 1 MHz was estimated according to a modified Maxwell's equation ($\epsilon \approx 1.1 \times n^2$). The films of the PSPABOs were prepared by spin-cast

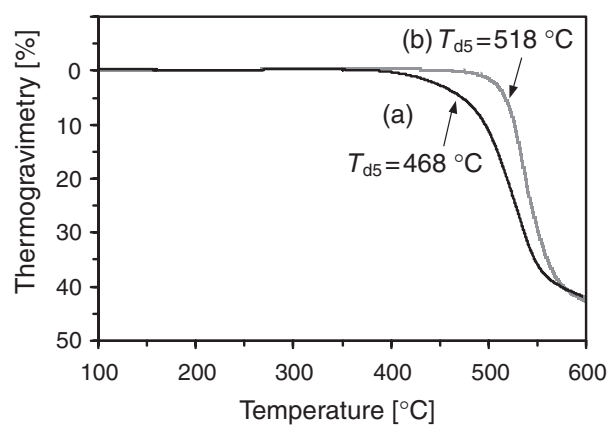


Figure 5. Thermogravimetry of (a) PSPABO film consisting of PAHA (85 wt %), OBHB (10 wt %) and PTMA (5 wt %), and (b) PABO film (ref 13). Each film was cured up to 350 °C for 1 h under nitrogen. 5% weight loss temperatures (T_{d5} s) are indicated beside each curve.

from cyclohexanone solution on quartz plates, pre-bake (100 °C, 2 min), exposure to i-line (100 mJ/cm²) and PEB (140 °C, 5 min), followed by the thermal treatment (350 °C, 1 h, under nitrogen) as a similar

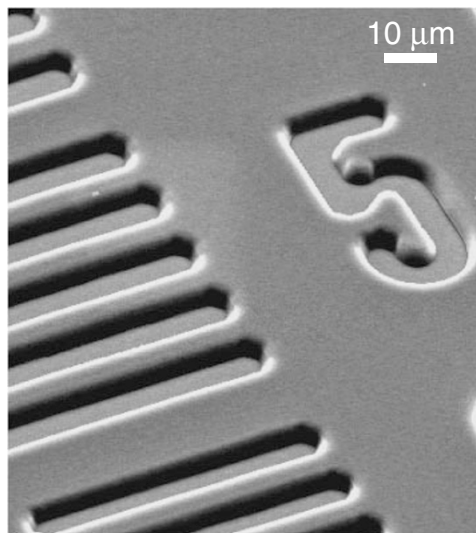


Figure 6. SEM image of cured PABO pattern on a silicon wafer. In lithographic evaluation, the film consisting of PAHA (85 wt %), OBHB (10 wt %) and PTMA (5 wt %) was exposed to 80 mJ/cm² of i-line in contact-printing, developed with 2.38 wt % TMAHaq at 25 °C for 14 s. The patterned film was then cured at the elevated temperature up to 350 °C and then hold at the temperature for 1 h under nitrogen, providing 4.1-μm-thick PABO film.

way to lithographic evaluation investigated above.

Table I summarizes the measured refractive indices and the estimated dielectric constants of the PSPABO resist films compared with those of additive-free PABO and wholly aromatic PSPBO (Scheme 4) that were referred from the previous reports.^{13,16} As expected, the ϵ value for Nega-PSPABO consisting of PAHA/OBHB/PTMA ($\epsilon = 2.62$) is lower than that for Nega-PSPABO based on PAHA/MBHP/PTMA ($\epsilon = 2.67$) because of no phenolic hydroxyl groups in OBHB.

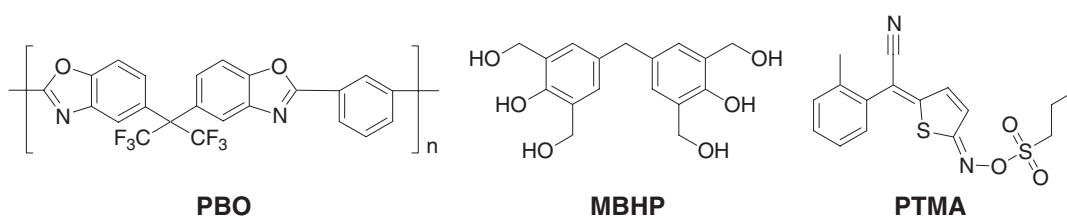
CONCLUSIONS

Nega-PSPABO was formulated by mixing PAHA (85 wt %), OBHB (10 wt %) and PTMA (5 wt %) in cyclohexanone, and functioned as an alkaline-developable chemically amplified PSPABO. Incorporation of the novel acid-catalyzed cross-linker based on benzylic alcohol, OBHB, into the Nega-PSPABO resist system induces not only high photosensitivity ($D_{0.5} = 14$ mJ/cm² of i-line), but also the lower dielectric constant of the matrix polymer (optically estimated $\epsilon = 2.62$) due to the absence of phenolic hydroxyl groups in OBHB. The cross-link reaction employed with OBHB undergoes through electrophilic substitution on the matrix polymer and itself based on the ¹H NMR study. The negative image was converted into the corresponding PABO image by the thermal treatment with clear 7-μm-featured patterns.

Table I. Refractive indices and optically estimated dielectric constant of photosensitive polybenzoxazoles

Film	Thickness (μm)	Refractive index			Dielectric constant
		n_{TE}^a	n_{TM}^b	n_{AV}^c	ϵ^d
PABO	6.5	1.5244	1.5211	1.5233	2.55
Nega-PSPABO-I ^e	6.5	1.5436	1.5394	1.5422	2.62
Nega-PSPABO-II ^f	4.6	1.5705	1.5334	1.5581	2.67
Nega-PSPBO ^g	4.1	1.5828	1.5738	1.5798	2.75

^aIn-plane refractive index measured by prism coupler. ^bOut-of-plane refractive index by prism coupler. ^cAverage refractive index calculated as following equation: $n_{AV} = (2n_{TE} + n_{TM})/3$. ^ddielectric constant calculated optically as following equation: $\epsilon = 1.1 \times n_{AV}^2$. ^ePhotosensitive PABO derived from PAHA (85 wt %), OBHB (10 wt %) and PTMA (5 wt %). The film on a quartz was exposed to i-line and post-exposure baked at 140 °C for 10 min, followed by cure at 350 °C for 1 h under nitrogen. ^fPhotosensitive PABO derived from PAHA (85 wt %), MBHP (10 wt %) and PTMA (5 wt %). The film preparation was similar to above (e). ^gPhotosensitive wholly aromatic PBO referred from ref 16.



Scheme 4. Components for previous negative-tone PSPBO with wholly aromatic polymer (ref 16).

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