

Negative-Working Photosensitive Poly(phenylene ether) Based on Poly(2,6-dimethyl-1,4-phenylene ether), a Cross-Linker, and a Photoacid Generator

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ABSTRACT: A novel benzyl cation type cross-linker, hex-1,6-ylenebis[oxy(2,4,6-tris(acetyloxymethyl)-3,5dimethylbenzene)] (HOAD), that suppresses acid-catalyzed self-polycondensation has been developed. Furthermore, a negative-working, photosensitive poly(phenylene ether) (PSPPE) based on poly(2,6-dimethyl-1,4phenylene ether) (PPE), HOAD, and diphenylidonium 9,10-dimethoxyanthracene-2-sulfonate (DIAS) as a photoacid generator (PAG) has been developed. This resist system does not contain a high thermal curing process. The resist consisting of PPE (83 wt %), HOAD (10 wt %), and DIAS (7 wt %) showed excellent sensitivity ($D_{0.5}$) of 43 mJ/cm² and high contrast ($\gamma_{0.5}$) of 11 when it was exposed to 365 nm wavelength UV light (*i*-line), postexposure baked (PEB) at 190 °C for 5 min, and developed by dipping in toluene at 25 °C. A fine negative-type pattern having 6 μ m resolution on 2.4 μ m thick film on a silicon wafer was obtained by exposure to 300 mJ/cm² of the *i*-line by using a contact-printed mode. The resulting PSPPE film, cured at 220 °C for 1 h under nitrogen, had a low dielectric constant (ε : 2.61), good thermal stability, and low water absorption.

Introduction

Electronic devices such as personal computers, mobile phones, and their flash memories are rapidly becoming smaller and lighter, and their package substrates for semiconductor devices have higher density as assembling and smaller mounting areas. To match this quick trend, a recent three-dimensional assembly technology was realized to build up a multichip package (MCP)^{1,2} that consisted of highly stacked and different types of devices or a combination of thinner passive devices. Therefore, the thickness of the silicon wafer as a substrate has become thinner and thinner (less than $100 \,\mu$ m).³ Under these circumstances, the residual stress in the film due to mismatch of coefficient of thermal expansion (CTE) between insulating films (film thickness: $1-20 \ \mu m$) and thinner silicon wafers during thermal treatment of films induces warpage of thin silicon substrates coated with insulating films. Photosensitive polyimides (PSPIs)^{4,5} and poly(benzoxazole) (PSPBO)⁶⁻¹⁰ are typical insulators and positive or negative images of their precursors, poly(amic acid)s (PAAs) and poly-(o-hydroxyamide)s, are converted into polyimides (PIs) and poly(benzoxazole) (PBO) with elimination of H₂O, respectively, by thermal treatment at 300-350 °C. As a result, both high heat process and shrinkage because of dehydration from matrix polymer induce large warpage of thin silicon substrates coated by insulating films.

To remedy the warpage problem of thin silicon wafers, lowtemperature thermal treatment of photosensitive thermally stable polymers (PSTSPs) is desirable because of the reduction in thermal stress. We have reported a series of low-temperature cyclization methods of PSPIs and PSPBOs to produce more useful applications in the microelectronics industry.^{7,8,11–15} It is also important to develop PSTSP resists which do not require high-temperature curing treatment. Engineering plastics with

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high thermal stability and excellent mechanical properties such as PPE and poly(ether ether sulfone) (PEES) are excellent candidates for the matrices of PSTSP resists because there is no need for conversion from precursors of matrix polymers.^{16–18} In a preceding paper,¹⁸ we reported a negative-type PSPPE based on a matrix polymer PPE, a cross-linker 4,4'-methylenebis[2,6-bis-(methoxymethyl)phenol] (MBMP), and DIAS as a PAG.^{19,20} PSPPE consisting of PPE (73 wt %), MBMP (20 wt %), and DIAS (7 wt %) in 1,1,2,2-tetrachloroethane exhibited a high sensitivity $(D_{0.5})$ of 58 mJ/cm² and good contrast $(\gamma_{0.5})$ of 9.5 when it was exposed to the *i*-line. In addition, the film cured at 220 °C showed good thermal properties, a low dielectric characteristic, and low water absorption, the same as those of PPE film. However, large amounts of MBMP (20 wt %) as a crosslinker are required because acid-catalyzed self-polycondensation of MBMP mainly occurs between its phenolic hydroxyl groups or unsubstituted sites of its benzene rings and benzyl cations rather than a cross-linking reaction with polymer chains. To suppress the acid-catalyzed self-polycondensation of the cross-linker, a new benzyl cation-type cross-linker should be developed.

In this paper, we report the synthesis of a new cross-linker, HOAD, which reduces acid-catalyzed self-polycondensation, and the development of a negative-type PSPPE resist based on PPE, HOAD, and DIAS that provides a PSTSP resist system without high thermo-curing treatment as the insulator for nextgeneration microchips. Scheme 1 shows the photolithographic process of PSPPE. The PSPPE varnish solution is spin-coated on a silicon wafer and prebaked. Then, the film is exposed by the *i*-line through a photomask to produce anthracenesulfonic acid from DIAS. Upon PEB treatment of the PSPPE film, acids catalyze the alkylation reaction of PPE with HOAD to form cross-linked PPE. The dissolution rate of the exposed area to toluene as a developer decreases and a negative image is formed. Furthermore, the thermal stability, water absorption, dielectric characteristic, and residual stress of the resulting PSPPE film are also reported.





Experimental Section

Materials. The PPE and DIAS were purchased from Aldrich Co. Ltd. The number- and weight-average molecular weights $(M_n \text{ and } M_w)$ of PPE were 11 600 and 31 500, respectively. MBMP was synthesized by following the previous paper.¹⁸ *N*,*N*-Dimethylformamide (DMF) was distilled under reduced pressure after stirring over calcium hydride for 1 day and then stored over 4A molecular sieves. 3,5-Dimethylphenol, 1,3,5-trimethylbenzene, 1,6-dibromohexane, potassium carbonate (99.5%: K₂CO₃), tin(IV) chloride (SnCl₄), sodium acetate (98.5%: CH₃COONa), acetic acid (AcOH), 1,3,5-trioxane, chloromethyl methyl ether (ClCH₂OCH₃), dehydrated dichloromethane (CH₂Cl₂), hydrobromic acid (47%: HBr), 1,1,2,2-tetrachloroethane, methanesulfonic acid (CH₃SO₃H), toluene, and acetonitrile (CH₃CN) were obtained commercially and used as received.

Synthesis of 2,3,4,5,6-Pentamethylbenzyl Bromide (PBB). A solution of 2,3,4,5,6-pentamethylbenzene (2.00 g, 13.5 mmol), 1,3,5-trioxane (1.22 g, 13.5 mmol), and 47% HBr solution (20 mL) in AcOH (7 mL) was refluxed for 2.5 h under nitrogen.²¹ The reaction mixture was cooled to room temperature and then poured into water (300 mL) to afford a white beaded solid. The solid was filtrated and washed with water. The product was recrystallized from *n*-hexane to give a white solid. Yield: 3.22 g (99%); mp 82.2–82.5 °C. IR (KBr, ν , cm⁻¹): 2985–2870 (CH₃, –CH₂–), 1565 (Ar), 1435 and 1376 (CH₃, –CH₂–), 1203 cm⁻¹ (–CH₂Br). ¹H NMR (CDCl₃, δ , ppm): 2.22 (s, 6H, *CH*₃), 2.24 (s, 3H, *CH*₃), 2.34 (s, 6H, *CH*₃), 4.66 (s, 2H, *CH*₂Br). Anal. Calcd for C₁₂H₁₇Br: C, 59.76; H, 7.11. Found: C, 60.01; H, 7.01.

Synthesis of 2,3,4,5,6-Pentamethylbenzyl Acetate (PBA). A solution of PBB (1.50 g, 6.22 mmol) and sodium acetate (0.777 g, 9.33 mmol) in acetic acid (30 mL) was refluxed for 19 h under nitrogen.²² The reaction mixture was cooled to room temperature and then poured into water (300 mL) to afford a white solid. The solution was neutralized with 1 wt % sodium carbonate aqueous solution. The solid was filtrated and washed with water. The product was recrystallized from *n*-hexane to give a white solid.

Yield: 1.32 g (96%); mp 81.5–82.5 °C. IR (KBr, ν , cm⁻¹): 2989–2870 (CH₃, -CH₂-), 1732 (C=O), 1434 and 1381 (CH₃, -CH₂-), 1238 and 1025 cm⁻¹ (-O-). ¹H NMR (CDCl₃, δ , ppm): 2.07 (s, 3H, -COCH₃), 2.24 (s, 6H, -CH₃), 2.25 (s, 3H, -CH₃), 2.29 (s, 6H, -CH₃), 5.25 (s, 2H, -CH₂OC=O). Anal. Calcd for C₁₄H₂₀O₂: C, 76.33; H, 9.15. Found: C, 76.09; H, 9.02.

Synthesis of 1,3,5-Tris(chloromethyl)-2,4,6-trimethylbenzene (TCB). To a solution of 1,3,5-trimethylbenzene (1.00 g, 1.15 mL, 8.32 mmol), chloromethyl methyl ether (6.03 g, 5.64 mL, 74.9 mmol) in dehydrated CH₂Cl₂ (10 mL) was added dropwise over 20 min a solution of SnCl₄ (19.5 g, 8.77 mL, 74.9 mmol) in dehydrated CH₂Cl₂ (10 mL) under nitrogen in an ice bath $(0-5 \,^{\circ}\text{C})$.²³ The reaction mixture was stirred in an ice bath for 1 h and then at room temperature for 5 h. After that, unconverted SnCl₄ was quenched with water (100 mL). The solution was extracted three times with CH₂Cl₂ and washed with water. The separated organic layer was dried over magnesium sulfate, filtrated, and concentrated under reduced pressure. The crude product was purified by flash chromatography with CH₂Cl₂, giving a white solid. Yield: 2.08 g (94%); mp 175.5-176.0 °C. IR (KBr, v, cm⁻¹): 2990–2894 (CH₃, -CH₂-), 1567 (Ar), 1446, 1379 (CH₃, -CH₂-), 1253 cm⁻¹ (-CH₂Cl). ¹H NMR (CDCl₃, δ , ppm): 2.51 (s, 9H, $-CH_3$), 4.70 (s, 6H, $-CH_2$ Cl). Anal. Calcd for C12H15Cl3: C, 54.26; H, 5.69. Found: C, 54.20; H, 5.64.

Synthesis of 1,3,5-Tris(acetoxymethyl)-2,4,6-trimethylbenzene (TAB). A solution of TCB (1.49 g, 5.60 mmol) and sodium acetate (3.03 g, 36.4 mmol) in AcOH (50 mL) was refluxed for 20 h under nitrogen.²² The reaction mixture was cooled to room temperature and then poured into distilled water (300 mL) to afford a white solid. This was filtrated and washed with water. The product was recrystallized from ethyl acetate/*n*-hexane (1/7 volume ratio) to give a white needle. Yield: 1.86 g (99%); mp 155.0–155.5 °C. IR (KBr, ν , cm⁻¹): 2992–2931 (CH₃, -CH₂-), 1728 (C=O), 1581 (Ar), 1442 and 1377 (CH₃, -CH₂-), 1241 and 1034 cm⁻¹ (-O-). ¹H NMR (CDCl₃, δ , ppm): 2.07 (s, 9H, -COCH₃), 2.40 (s, 9H, -CH₃), 5.25 (s, 6H, -CH₂OC=O). Anal. Calcd for C₁₈H₂₄O₆: C, 64.27; H, 7.19. Found: C, 64.41; H, 7.09.

Synthesis of Hex-1,6-ylenebis[oxy(3,5-dimethylbenzene)] (HOD). To a solution of 3,5-dimethyllphenol (5.00 g, 40.9 mmol) and 1,6dibromohexane (4.65 g, 19.0 mmol) in DMF (35 mL) was added potassium carbonate (8.53 g, 61.4 mmol).²⁴ The mixture was stirred at 80 °C for 18 h under nitrogen. The reaction mixture was cooled to room temperature and poured into distilled water (500 mL) to afford a light ocher solid. The solid was filtrated and washed with water. The product was recrystallized from *n*-hexane to give a white solid. Yield: 5.53 g (89%); mp 69.4–70.3 °C. IR (KBr, ν , cm⁻¹): 3014–2854 (CH₃, -CH₂–), 1589 (Ar), 1463, 1427, and 1390 (CH₃, -CH₂–), 1294 and 1076 (-O–) cm⁻¹, ¹H NMR (CDCl₃, δ , ppm): 1.50–1.55 (m, 4H, -CH₂–), 1.75–1.85 (m, 4H, -CH₂–), 2.28 (s, 12H, -CH₃), 3.91–3.95 (t, 4H, -CH₂O–), 6.53 (s, 4H, *Ar*), 6.58 (s, 2H, *Ar*). Anal. Calcd for C₂₂H₃₀O₂: C, 80.94; H, 9.26. Found: C, 81.22; H, 9.18.

Synthesis of Hex-1,6-ylenebis[oxy(2,4,6-tris(chloromethylmethyl)-3,5-dimethylbenzene)] (HOCD). To a solution of HOD (0.500 g, 1.53 mmol), chloromethyl methyl ether (2.22 g, 2.07 mL, 27.6 mmol) in dehydrated CH₂Cl₂ (15 mL) was dropwised over 15 min a solution of SnCl₄ (7.19 g, 3.23 mL, 27.6 mmol) in dehydrated CH_2Cl_2 (5 mL) under nitrogen in ice bath (0-5 °C).²³ The reaction mixture was stirred for 1 h in an ice bath and then at room temperature for 7 h. After that, the unconverted SnCl₄ was quenched with distilled water (100 mL). The product was extracted three times with CH₂Cl₂ and washed with water. The separated organic layer was dried over magnesium sulfate, filtrated, and concentrated in vacuo. The crude product was purified by column chromatography with CH₂Cl₂, giving a white solid. Yield: 0.730 g (77%); mp 198.8–199.5 °C. IR (KBr, v, cm⁻¹): 2921–2856 (CH₃, -CH₂-), 1571 (Ar), 1452 and 1384 (CH₃, -CH₂-), 1255 and 1087 cm⁻¹ (-O-). ¹H NMR (CDCl₃, δ , ppm): 1.64–1.73 (m, 4H, – CH₂-), 1.94-2.03 (m, 4H, -CH₂-), 2.51 (s, 12H, -CH₃), 4.07-4.10 (t, 4H, -OCHH₂-), 4.68 (s, 4H, -CH₂Cl), 4.74 (s, 8H, -CH2Cl). Anal. Calcd for C28H36Cl6O2: C,54.48; H, 5.88. Found: C, 54.25; H, 5.76.

Synthesis of Hex-1,6-ylenebis[oxy(2,4,6-tris(acetyloxymethyl)-3,5-dimethylbenzene)] (HOAD). A solution of HOCD (0.500 g, 0.810 mmol) and sodium acetate (0.81 g, 9.72 mmol) in AcOH (35 mL) was refluxed for 33 h under nitrogen.²² The reaction mixture was cooled to room temperature and poured into distilled water (300 mL) to afford HOAD as a white solid. The product was recrystallized from ethyl acetate/n-hexane (7/11 volume ratio) to give a white solid. Yield: 0.570 g (93%); mp 163.8-164.5 °C. IR (KBr, v, cm⁻¹): 2931–2866 (CH₃, -CH₂-), 1736 (C=O), 1585 (Ar), 1442 and 1381 (CH₃, $-CH_2-$), 1246 and 1026 cm⁻¹ (-O-). ¹H NMR (CDCl₃, δ , ppm): 1.51–1.55 (m, 4H, -CH₂-), 1.80-1.89 (m, 4H, -CH₂-), 2.07 (s, 12H, -COCH₃), 2.09 (s, 6H, -COCH₃), 2.36 (s, 12H, -CH₃), 3.76-3.80 (t, 4H, -CH₂O-), 5.22 (s, 12H, -CH₂OC=O). ¹³C NMR (CDCl₃, *δ*, ppm): 16.10, 21.35, 26.37, 30.44, 59.55, 61.53, 126.1, 129.8, 142.0, 158.9, 171.3, 171.4, 171.6. Anal. Calcd for C₄₀H₅₄O₁₄: C, 63.31; H, 7.17. Found: C, 63.31; H, 7.10.

Acid-Catalyzed Model Cross-Linking Reaction. To PPE (45.0 mg, 0.375 mmol) and PBA (5.00 mg, 0.023 mmol) in deuterated chloroform (0.6 mL, CDCl₃) in a NMR glass tube was added CH₃SO₃H (0.0005 g, 0.005 mmol: 1.3 mol % to PPE).¹⁸ Nitrogen was charged to the glass tube, and the tube was heated at 60 °C for 1 h. To investigate the behavior of self-polycondensation of a cross-linker HOAD, CH₃SO₃H (0.0005 g, 0.0052 mmol: 10 mol % to PBA) was added to a solution of PBA (0.0113 g, 0.051 mmol) as a cross-linker model compound in deuterated chloroform (0.6 mL, CDCl₃) in the NMR glass tube. The glass tube was heated at 60 °C for 30 min under nitrogen. The ¹H NMR of the each sample was measured at 25 °C.

Dissolution Rate. PPE, each cross-linker (HOAD: 7, 10, and 20 wt %, TAB, MBMP, ¹⁸ CYMEL:²⁵ 10 wt %), and DIAS^{19,20} (5, 7, and 10 wt %) were dissolved in 1,1,2,2-tetrachloroethane (solid content: 6.5 wt %) at room temperature. Their polymer films (film thickness: ca. 1.2 μ m) were obtained by spin-casting from PSPPE varnish solution on a silicon wafer and prebaked at

80 °C for 30 s on the hot plate. After that, these films were exposed to 300 mJ/cm² of *i*-line through the photomask and followed by PEB on the hot plate at 160–200 °C for the set time. Those films were developed by dipping in toluene at 25 °C. The dissolution rate (Å/s) of the film was determined from both developing time and changes in the film thickness before and after the development.

Photosensitivity of PSPPE. The photosensitive polymer film with 1.2 μ m thickness on a silicon wafer was prepared by dissolving PPE, HOAD, and DIAS in 1,1,2,2-tetrachloroethane (total solid content: 6.5 wt %) at room temperature, followed by spin-casting on a silicon wafer and prebaking at 80 °C for 30 s on the hot plate, exposed to *i*-line irradiation with changing the exposure dose, PEB at 190 °C for 5 min on the hot plate, developed with dipping in toluene for 1 s at 25 °C. A characteristic photosensitive curve was obtained by plotting a normalized film thickness against exposure dose (unit: mJ/cm²). Image-wise exposure through a photomask was carried out in a contact-printing mode.

Preparation of Polymer Films for TGA, DSC, Water Absorption (WA), Dielectric Constant, and Residual Stress Measurement. To prepare the thick cured PSPPE films for TGA, DSC, and WA measurement, a negative-type PSPPE resist solution (PPE/HOAD/DIAS = 83/10/7 wt %) in 1,1,2,2-tetrachloroethane (total solid content: 18.6 wt %) was cast on a glass plate, kept at that room temperature for 6 h, prebaked at 80 °C for 10 min on the hot plate in air, and then the film was irradiated with *i*-line of 1000 mJ/cm², followed by PEB at 190 °C for 1 h under a flow of nitrogen, and finally cured at 220 °C for 1 h on the hot plate under a flow of nitrogen.¹⁸ The thick PPE film as a reference was prepared from 16.2 wt % 1,1,2,2-tetrachloroethane solution and followed by similar thermal treatment of the cured PSPPE film, without exposure. The cured PSPPE film (the rectangle-shaped film: length 40 mm, width 35 mm, thickness 45 μ m) and the PPE film (the rectangle-shaped film: length 40 mm, width 35 mm, thickness 43 μ m) were prepared for WA measurement, and those films were used for TGA and DSC. Whereas, to measure the refractive indices and optically estimated dielectric constants of a cured PSPPE and PPE film, the cured PSPPE film on a quartz substrate was prepared from a similar PSPPE solution by solvent-casting and prebaking at 80 °C for 1 min in air, irradiation with *i*-line of 1000 mJ/cm², PEB at 190 °C for 10 min, and curing at 220 °C for 1 h on the hot plate under a flow of nitrogen. As a reference, the PPE film was prepared from 16.2 wt % 1,1,2,2-tetrachloroethane solution and followed by similar thermal treatment for the cured PSPPE film, without exposure. The thickness of the cured PSPPE and PPE films were 4.8 and 4.2 μ m, respectively. In the case of direct measurement of dielectric constants and dissipation factors, both the 10.4 μ m thick PSPPE and the cured 9.8 μ m thick PPE film on each 50 mm \times 50 mm square silicon wafer (thickness: 712.5 μ m) were prepared following the above-mentioned preparation condition for refractive index. Moreover, in order to measure residual stress of each silicon wafer of the cured PSPPE and PPE film, the cured PSPPE film on an 8 in. silicon substrate (diameter: 200 mm; thickness: 712.5 μ m) was prepared from 10 wt % PSPPE solution in 1,1,2,2-tetrachloroethane, by spin-casting, and prebaking at 80 °C for 30 s on the hot plate in air, exposure with *i*-line of 300 mJ/cm², PEB at 190 °C for 5 min, and curing at 220 °C for 1 h in an oven under a flow of nitrogen. And also, the PPE film on an 8 in. silicon wafer was prepared from 10 wt % 1,1,2,2-tetrachloroethane solution and followed by same thermal treatment for the cured PSPPE film, without exposure. Those thickness of the cured PSPPE and PPE films on each 8 in. silicon wafer were 3.2 and 3.1 μ m, respectively.

Water Absorption. WA was measured by immersing the cured PSPPE film and PPE film into the distilled water at 25 °C for 6 h.¹⁸ After that, those films (the cured PSPPE film: length 40 mm, width 35 mm, thickness 45 μ m; PPE film: length 40 mm, width 35 mm, thickness 43 μ m) were taken out, wiped with tissue



Figure 1. ¹H NMR spectrum of the product obtained by an acid-catalyzed cross-linking reaction of PPE with PBA in the presence of CH₃SO₃H after heating at 60 °C for 1 h under nitrogen in CDCl₃.

paper, and quickly weighted on a microbalance. WA was estimated using the following equation

WA [wt %] =
$$(W_{\rm s} - W_{\rm d})/W_{\rm d} \times 100$$
 (1)

 $W_{\rm d}$ and $W_{\rm s}$ stand for the weight of film before and after immersing into the distilled water.

Measurements. The infrared spectroscopy (IR) was taken with a Horiba FT-210 spectrophotometer. The ¹H and ¹³C NMR spectra were obtained on a Bruker DPX-300S spectrometer (¹H at 300 MHz and ¹³C at 75 MHz). Deuterated chloroform (CDCl₃) was used as solvent with tetramethylsilane (TMS) as an internal standard. Elemental analyses were performed on a Yanaco MT-6 CHN CORDER with antipyrine as a standard sample. Number- and weight-average molecular weights $(M_n \text{ and } M_w)$ were estimated by gel permeation chromatography (GPC) on a Jasco GULLIVER 1500 system equipped with polystyrene gel columns (Plgel 5 mm MIXED-CT) eluted with CHCl₃ at a flow rate of 1.0 mL/min calibrated by standard polystyrene samples. Ultraviolet-visible spectroscopy (UV-vis) was performed on a Jasco V-650 spectrophotometer (solvent: CH₃CN). Thermogravimetric analysis (TGA) of the cured PSPPE and PPE films was performed on a Seiko TG/DTA 6300 at a heating rate of 10 °C/min under a flow of nitrogen. Differential scanning calorimetry (DSC) was recorded on a Seiko DSC 6300 at a heating rate of 10 °C/min under a flow of nitrogen. Glass transition temperature (T_g) was determined by DSC analysis. The film thickness was measured by Veeco Instrument Dektak³ surface profiler. The scanning electron microscopic image (SEM) was taken by a Technex Lab Tiny-SEM 1540 with 15 kV accelerating voltage for imagining. Refractive indices of PPE and the cured PSPPE resist films formed on quartz substrates were measured at a wavelength of 1320 nm at room temperature with a Metricon model PC-2000 prism coupler. Using linearly polarized laser light with parallel (TE: transverse electric) and perpendicular (TM: transverse magnetic) polarization to the film plane, the in-plane $(n_{\rm TE})$ and out-of-plane $(n_{\rm TM})$ refractive indices. The dielectric constant at 1 MHz frequency was calculated from the following equation as follows: $n_{\rm AV} = [(2n_{\rm TE}^2 + n_{\rm TM}^2)/3]^{1/2}$, $\varepsilon = 1.0 n_{\rm AV}^2$, where n_{AV} is an average refractive index. Dielectric constants

and dissipation factors with a load frequency of 1 MHz, of whose both the cured PSPPE and PPE films on each silicon wafer (50 mm \times 50 mm square, thickness: 712.5 μ m) were vacuum-deposited with aluminum by a JEOL JEL-420 vacuum evaporation system, were directly measured by Hewlett-Packard 4284A precision LCR meter with a 16085B terminal adapter. Residual stress of the cured PSPPE and PPE films on 8 in. silicon wafer (diameter: 200 mm; thickness: 712.5 μ m) was measured by Toho Technology Corp. thin film stress measurement system FLX-2320-S.

Results and Discussion

First, to clarify the mechanism of an acid-catalyzed crosslinking reaction, a model reaction was carried out using PPE, a monofunctional benzyl acetate (PBA), and CH₃SO₃H, ¹⁸ a mixture of which at a molar ratio of PPE/PBA/CH₃SO₃H: 1/0.061/ 0.013 was heated in CDCl₃ at 60 °C for 1 h.

Figure 1 shows the ¹H NMR spectrum of the resulting solution. The peak intensity of the acetoxymethyl protons of PBA at 5.25 ppm (singlet: a) decreases, and new peaks appear at 4.30-4.34 ppm (broad: g, i) and 6.41-6.45 ppm (h). These peaks are assigned to the methylene protons and aromatic protons of *C*-alkylated PPE, respectively. A small peak is also observed at 4.67 ppm (b) due to the methylene protons of the self-condensation product of PBA (see Supporting Information for details). The respective molar ratio of C-alkylated PPE and the selfcondensation product of PBA was estimated to be 43.6 and 1.2 mol % by the ratio of peak areas between the newly appearing methylene protons [(g + i), b] and the methylene proton (a) of unreacted PBA. These results indicate that C-alkylation between PPE and PBA mainly occurs and that the self-condensation reaction of PBA was greatly suppressed. Hence, this new HOAD is expected to be a good cross-linker to PPE with little selfcondensation.

Synthesis of Cross-Linker. On the basis of these findings, the new cross-linker, HOAD, was designed and prepared considering the following factors: (1) introduction of methyl groups to the benzene ring to suppress self-polycondensation of the cross-linker, (2) introduction of flexible aliphatic



chains to reduce the residual stress between the thinner silicon substrate and insulating film after cross-linking with a polymer and promote the cross-linking reaction to polymer chains by increasing mobility,^{9,10} and (3) introduction of many acetoxymethyl groups as a highly reactive functional group to generate benzyl cations.

The cross-linker, HOAD, was prepared in three steps, as shown in Scheme 2. The reaction of 1,6-dibromohexane with 3,5-dimethylphenol in the presence of K_2CO_3 afforded HOD, which was treated with chloromethyl methyl ether in the presence of SnCl₄ in CH₂Cl₂ to give HOCD in excellent yield. Finally, HOCD was quantitatively converted into HOAD by refluxing it in acetic acid in the presence of sodium acetate. The chemical structure of HOAD was confirmed by FT-IR, ¹H NMR and ¹³C NMR spectroscopy, and elemental analysis. The FT-IR spectrum showed characteristic absorptions at 1736 and 1246 cm⁻¹ which can be assigned to carbonyl and ether groups stretching, respectively. The ¹H and ¹³C NMR spectra can be fully assigned, as shown in Figures 2 and 3.

PSPPE Resist Formulation. A PSPPE resist was formulated by mixing PPE, HOAD, and DIAS in 1,1,2,2-tetrachloroethane, as shown in Scheme 1. HOAD is transparent above ca. 300 nm and does not prevent photoacid generation from DIAS having an absorption centered at ca. 345 nm.^{19,20} Moreover, HOAD has good solubility in general organic solvents. Thus, a transparent film on the silicon wafer was obtained after spin-coating a PSPPE resist solution on it, followed by prebaking. A cross-linker requires high thermal stability during the PEB process, so thermal stability of HOAD was evaluated by TG analysis. The 5 wt % weight loss temperature ($T_{d,5 wt \%}$) of HOAD was 305 °C, indicating its sufficiently high thermal stability.

Lithographic Evaluation. Preliminary optimization studies of the processing conditions were studied. The 1.2 μ m thick PSPPE films were obtained by spin-coating a solution of PSPPE resist in 1,1,2,2-tetrachloroethane on a silicon wafer, followed by prebaking at 80 °C for 30 s on a hot plate in an air atmosphere, exposing them to the *i*-line of 300 mJ/cm² through a photomask in a contact-printing mode, PEB at a set temperature for a prescribed period of time, and developing those treated films by dipping them in toluene at 25 °C. The dissolution rate of the resist film was calculated by measuring the change in thickness of the film on the silicon wafer before and after development. In a previous study, a large amount of the cross-linker MBMP (20 wt %) in a PSPPE resist was required.¹⁸ A half amount (10 wt %) of HOAD was first used because a higher reactivity was expected compared



Figure 2. ¹H NMR spectrum of a novel cross-linker HOAD.



Figure 3. ¹³C NMR spectrum of a new cross-linker HOAD.

to MBMP, as described above. A PSPPE resist composed of 83 wt % PPE, 10 wt % HOAD, and 7 wt % DIAS was formulated. To obtain a large dissolution contrast (DC) between exposed and unexposed areas in chemically amplified resists, the PEB temperature is the critical key factor for effective diffusion of an acid catalyst from a PAG after *i*-line exposure and also for the acceleration of an acid-catalyzed cross-linking reaction.

First, the effect of PEB temperature on the dissolution rate of the exposed and unexposed areas of the film was investigated, and the results are summarized in Figure 4. The dissolution rate in the exposed area decreases by increasing the PEB temperature. A PEB temperature at 190 °C gives a high DC (ca. 12000 times) between the exposed and unexposed areas, probably because of the high diffusion of a photogenerated anthracenesulfonic acid derivative. As the melting point of HOAD is ca.165 °C, the additive could work more effectively as a plasticizer of the film due to increase of mobility of polymer main chains by melting HOAD in the film during PEB treatment above 190 °C. PEB time is also an important factor for lithographic evaluation. As shown in Figure 5, PEB time of more than 5 min at 190 °C is necessary to obtain a large DC (ca. 12000 times).

Thus, the most effective PEB process condition was found to be 190 °C for 5 min after exposure of the PSPPE film to the *i*-line of 300 mJ/cm². Moreover, the effect of HOAD and



Figure 4. Effect of PEB temperature (PEB time: 5 min) on the dissolution rate for the PSPPE (PPE/HOAD/DIAS = 83/10/7 wt %) films in the exposed and unexposed areas.



Figure 5. Effect of PEB time (PEB temperature: 190 °C) on the dissolution rate for the PSPPE (PPE/HOAD/DIAS = 83/10/7 wt %) films in the exposed and unexposed areas.



Figure 6. Effect of loading HOAD as a cross-linker on PSPPE (DIAS: 7 wt %) resist on the dissolution rate for the PSPPE films in the exposed and unexposed areas.

DIAS loading was studied under the best PEB conditions (Figures 6 and 7). The dissolution rate in the exposed area decreases by increasing HOAD and DIAS loading and the DC reaches 12000-fold in the presence of 10 wt % HOAD and 7 wt % DIAS.

Under optimum conditions, the cross-linking performance of HOAD in the PSPPE resist was compared to other cross-linkers, such as TAB prepared in two steps, as shown in



Figure 7. Effect of loading DIAS as a PAG on PSPPE (HOAD: 10 wt %) resist on the dissolution rate for the PSPPE films in the exposed and unexposed areas.

Scheme 3. Synthesis of TAB as Another Cross-Linker To Suppress Self-Polycondensation



Scheme 4. Other Cross-Linkers (TAB, MBMP, and CYMEL)



Scheme 3, MBMP,¹⁸ and a melamine-type cross-linker (CYMEL),²⁵ as shown in Scheme 4.

HOAD exhibits the largest DC among them probably because of its excellent reactivity, multifunctional groups, and flexible aliphatic chains between cross-linking sites (see Figure 8). Meanwhile, as thermal decomposition of CYMEL starts at around 150 °C, the thermal cross-linking reaction may occur in the unexposed area of the film at 190 °C. Thereby, the effect of PEB temperature using CYMEL was investigated at lower PEB temperatures in the range of 150–190 °C. However, Figure 9 indicates that a large DC is not obtained at each PEB temperature.

On the basis of these preliminary optimizations, the PSPPE resist system consisting of PPE (83 wt %), HOAD (10 wt %), and DIAS (7 wt %) in 1,1,2,2-tetrachloroethane was formulated. The characteristic photosensitivity curve of a 1.2 μ m thick PSPPE resist film is shown in Figure 10. This PSPPE resist has high sensitivity ($D_{0.5}$) of 43 mJ/cm² and excellent contrast ($\gamma_{0.5}$) of 11 with the *i*-line. Figure 11 depicts an SEM image of a contact-printing pattern with 2.4 μ m thick film exposed to the *i*-line of 300 mJ/cm², PEB at 190 °C

Figure 8. Effect of kind of cross-linkers on PSPPE (DIAS: 7 wt %, loading of each cross-linker: 10 wt %) resist on the dissolution rate for the PSPPE films in the exposed and unexposed areas.

Figure 9. Effect of PEB temperature (PEB time: 5 min) on the dissolution rate for the PSPPE resist films (PPE/CYMEL/DIAS = 83/10/7 wt %) using CYMEL as a cross-linker in the exposed and unexposed areas.

Figure 10. Characteristic photosensitive curve of the PSPPE system (PPE/HOAD/DIAS: 83/10/7 wt %) using a new cross-linker HOAD. $D_{0.5}$ is the sensitivity, and $\gamma_{0.5}$ is the contrast.

for 5 min, and developed with toluene for 2 s. A clear negative-tone image with 6 μ m resolution was obtained. After curing at 220 °C in an oven for 1 h under a flow of nitrogen, thickness of the cured PSPPE film on a silicon wafer was 2.35 μ m. Thickness loss before and after curing was about 2% as same as that of the PSPPE resist using a previous cross-linker MBMP.

Thermal Stability and Water Absorption of Cured PSPPE Film. Table 1 summarizes the thermal property of the cured PSPPE and PPE films. The 10 wt % weight-loss temperatures ($T_{d,10 \text{ wt }\%}$) of the cured PSPPE and PPE are 418 and 441 °C, respectively.¹⁸ Although thermal stability of the

Figure 11. SEM image of the negative-working patterned 2.4 μ m thick PSPPE film (PPE/HOAD/DIAS: 83/10/7 wt %). The lithographic condition was as follows; the 10 wt % solid content solution in 1,1,2,2-tetrachloroethane was spin-coated on the silicone wafer, prebaked at 80 °C for 30 s on the hot plate, exposed to 300 mJ/cm² of *i*-line, PEB at 190 °C for 5 min on the hot plate, developed with dipping in toluene for 2 s at 25 °C (film thickness before and after development was not changed: 2.4 μ m).

Table 1. Thermal Property and WA of Both PPE and Cured PSPPE Films

polymer films	thickness (µm)	$T_{\mathrm{d},10 \mathrm{wt}\%}{}^{a}$ (°C)	T_g^b (°C)	WA ^c (wt %)
cured PSPPE	45	418	232	< 0.05
PPE	43	441	215	< 0.05
^a Measured by	TGA. ^b Measured	d by DSC. ^c Wate	er absorpt	ion.

cured PSPPE film decreases in comparison with that of the PPE film due to the residual HOAD and DIAS. On the other hand, T_g (232 °C) of the cured PSPPE is higher than that (215 °C) of the PPE film due to the acid-catalyzed cross-linking between main chains of polymer by thermal curing at 220 °C. Furthermore, T_g of the cured PSPPE film using HOAD is also higher than that (221 °C) of the PPE film using a previously reported MBMP despite the lower cross-linker loading.¹⁸

PPE shows low water absorption because there are no polar groups such as carbonyl or hydroxyl groups which impart a low dielectric constant. The water absorption of the cured PSPPE and PPE films cured at 220 °C for 1 h under nitrogen is summarized in Table 1. The cured PSPPE film shows low water absorption (less than 0.05%), the same as that of the PPE film.

Dielectric Constant of Cured PSPPE Film. PPE has an excellent advantage as a low-k material for stress buffer and insulation layers in microchips. The ε of the cured PSPPE and PPE films at 1 MHz can be estimated from the refractive index $(n_{\rm AV})$ of the film according to a modified version of Maxwell's equation, $\varepsilon = 1.0 n_{AV}^2$. Table 2 summarizes their refractive indices, optically estimated and directly measured dielectric constants of the cured PSPPE and PPE films. Their average refractive indices (n_{AV}) of those films are calculated as 1.5498 and 1.5460, which are translated to ε values as 2.40 and 2.39, respectively.¹⁸ Moreover, their dielectric constants and dissipation factors directly measured at 1 MHz of those films are 2.61, 2.54 and 0.0181, 0.0185, respectively. Although the dielectric constant of the cured PSPPE film is a little higher than that of the PPE film due to the additives such as the PAG and cross-linker in the film, it still shows sufficiently low dielectric constant.

Residual Stress of Cured PSPPE Film. Residual stress of both the cured PSPPE and PPE films are 28 and 25 MPa, respectively (Table 3). Residual stress is not low enough to suppress warpage of each silicon substrate coated insulating

 Table 2. Refractive Indices and Dielectric Constants of PPE and Cured PSPPE Films

polymer films	$d \ (\mu m)^a$	$n_{\rm TE}^{b}$	$n_{\rm TM}^{c}$	$n_{\rm AV}^{d}$	ε^{e}	$d (\mu m)^f$	ε^{g}	$ an \delta^h$
cured PSPPE PPE	4.8 4.2	1.5510 1.5472	1.5475 1.5435	1.5498 1.5460	2.40 2.39	10.4 9.8	2.61 2.54	0.0181 0.0185
^a Film thickness on the quartz substrate. ^b In-plane refractive indices. ^c Out-of-plane refractive indices. ^d Average refractive indices; $n_{AV} = [(2n_{TE}^2 + n_{TM}^2)/3]^{1/2}$. ^e Optically estimated dielectric constant; $\varepsilon = 1.0n_{AV}^2$. ^f Film thickness on the silicon substrate for the direct measurement of both ε and tan δ . ^g Dielectric constant directly measured at 1 MHz.								

Table 3. Residual Stress of PPE and Cured PSPPE Films on 8 in. Silicon Wafer

polymer films	cure (temp., time)	$d (\mu m)^a$	residual stress (MPa)
cured PSPPE	220 °C, 1 h, N ₂ flow	3.2	28
PPE	220 °C, 1 h, N ₂ flow	3.1	25

^a Film thickness on 8 in. silicon wafer after thermal curing in an oven.

film after cooling process from thermal treatment. This problem will be improved in the near future.

Conclusions

A novel benzyl cation type cross-linker, HOAD, that suppresses acid-catalyzed self-polycondensation has been developed. This new cross-linker has been successfully applied to develop a chemically amplified, negative-working PSPPE resist consisting of PPE, HOAD, and DIAS as the PAG. The PSPPE resist system exhibited excellent sensitivity ($D_{0.5}$) of 43 mJ/cm² and high contrast ($\gamma_{0.5}$) of 11. A clear negative-imaged line-and-space pattern with 6 μ m resolution was obtained in 2.4 μ m thick PSPPE film on a silicon wafer after development with toluene. The PSPPE film cured at 220 °C had a low dielectric constant, good thermal stability, and low water absorption, nearly the same as those of PPE film. This PSPPE resist system using HOAD can be one of the candidates of a PSTSP resist system for next-generation microchips.

Supporting Information Available: Synthetic routes for a cross-linker model compound, 2,3,4,5,6-pentamethylbenzyl

acetate (PBA), and ¹H NMR spectrum of the product obtained by acid-catalyzed self-condensation of PBA in the absence of PPE. This material is available free of charge via the Internet at http://pubs.acs.org.

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