A Positive-Working Photosensitive Polyimide Based on Thermal Cross-Linking and Acidolytic Cleavage

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ABSTRACT: A novel positive-working photosensitive polyimide (PSPI) based on a poly(hydroxyimide) (PHI), a crosslinking agent having vinyl ether groups, and a photoacid generator (PAG) was prepared. The PHI as a base resin of the three-component PSPI was synthesized from 4,4′-oxydiphthalic anhydride and 2,2′-bis(3-amino-4-hydroxyphenyl)hexafluoropropane through ring-opening polymerization and subsequent thermal cyclization. 2,2′-bis(4-(2-(vinyloxy)ethoxy)phenyl)propane (BPA-DEVE) was used as a vinylether compound and diphenyliodonium 5-hydroxynaphthalene-1-sulfonate was used as a PAG. The phenolic hydroxyl groups of the PHI and the vinyl ether groups of BPA-DEVE are thermally crosslinked with acetal structures during prebake step, and the crosslinked PHI becomes completely insoluble in an aqueous basic solution. Upon exposure to UV light (365 nm) and subsequent postexposure bake (PEB), a strong acid generated from the PAG cleaves the crosslinked structures, and the exposed area is effectively solubilized in the alkaline developer. The dissolution behavior of the PSPI containing each 11.5 wt % of BPA-DEVE and of the PAG was studied after UV exposure (365 nm) and PEB. It was found that the difference in dissolution rates between exposed and unexposed areas was enough to get high resolution. A fine positive pattern with a resolution of 5 μm in a 3.7-μm-thick film was obtained from the three-component PSPI. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 2632–2637, 2008

Key words: photosensitive polyimide; poly(hydroxyimide); lithography; chemical amplification

INTRODUCTION

In recent years, PSPIs are widely used as protection and insulation layers in semiconductor manufacturing in the place of conventional polyimides because their use in the fabrication of microelectronic devices can reduce the number of processing steps required to obtain the desired photolithographic pattern.[1–3]

Negative-working PSPIs are quite common and commercially available. Most of them are prepared from poly(amic acid)s where crosslinking sites are introduced amic acids through ester and acid-amine ion linkage.[4,5] However, the use of positive-working PSPIs rather than negative-working PSPIs is preferred in lithography because of many advantages such as lower sensitivity to dust particles, better suited shapes for the pattern profiles in multilayer systems, developability with alkaline aqueous solutions, and reduced impact on the environment.[2,3] There are many reports on the alkaline-developable positive-working PSPI, which are mainly prepared from polyimide precursor and dissolution inhibitor such as diazonaphtoquinone (DNQ).[6,7] Reaction developable PSPI based on soluble polyimide and DNQ,[8,9] and the direct attachment of DNQ to the PI precursors[10,11] have also been reported. On the other hand, very few studies have explored the use of chemical amplification mechanism, which is an effective method for obtaining high resolution and sensitivity.[12–14]

As an advanced design of chemically amplified photoresist, Yamaoka and coworkers reported several photoresist systems based on the thermal cross-linking and acidolytic de-*cross*-linking of vinyl ether groups.[15–17] The vinyl ether groups react with the phenolic hydroxyl groups at high temperature to form crosslinked networks with acetal structures. Upon exposure to UV light and subsequent PEB, a strong acid generated from a PAG cleaves these crosslinked structures. Such chemistry of the vinyl ether group can be usefully utilized not only for the advanced design of chemically amplified photoresist but also for that of PSPI. In this article, we report the preparation and properties of a positive-working PSPI system using the chemistry of the vinyl ether groups. The PSPI system consists of a PHI used as a base polymer having phenolic hydroxyl groups, a crosslinking agent having vinyl ether groups, and a PAG.

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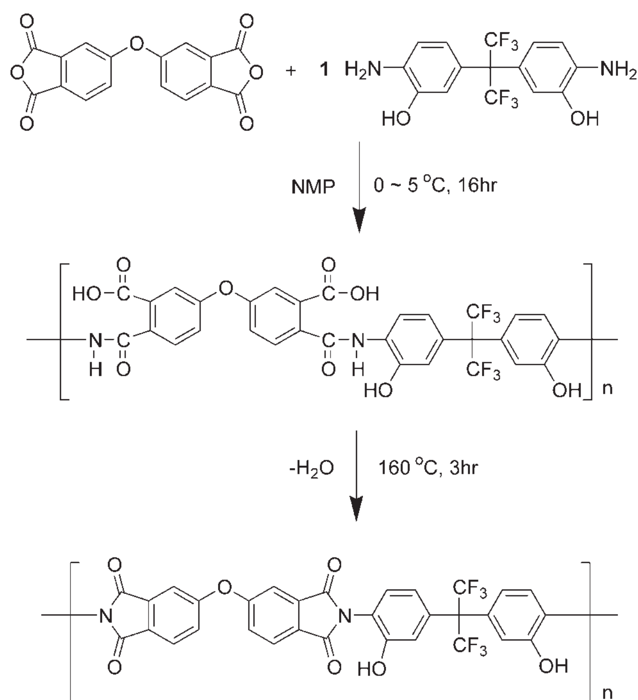


Scheme 1 Synthesis of PHI.

EXPERIMENTAL

Materials

4,4′-Oxydiphthalic anhydride (ODPA) was obtained from Shanghai Research Institute (Shanghai, China) and used after vacuum-drying at 130 °C for 5 h. 2,2′-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (BAPAF; Central glass, Tokyo, Japan) was used as received. Anhydrous 1-methyl-2-pyrrolidinone (NMP) was obtained from Aldrich Chemical Co. (St. Louis, MO) and dehydrated with 4 Å molecular sieves prior to use. BPA-DEVE was synthesized by reacting 2-chloroethyl vinyl ether with bisphenol A in the presence of sodium hydroxide, as reported previously.[15,18] Diphenyliodonium 5-hydroxynaphthalene-1-sulfonate (DINS) was prepared with the method described in our previous report.[19] Tetramethyl ammonium hydroxide (TMAH; 2.38 wt %) aqueous solution was purchased from Clariant Korea Ltd. (Seoul, Korea).

Synthesis of PHI

In a 250 mL round-bottom flask, 18.31 g (0.05 mol) of BAPAF was dissolved in 80 mL of NMP. While keeping the flask at 0 ~ 5°C, 15.51 g (0.045 mol) of ODPA was slowly added and stirred at 0–5°C for 16 h. After polymerization, 80 mL of NMP and 50 mL of toluene was added to the flask. The obtained poly(amic acid) was thermally imidized at 160°C for 3 h. Meanwhile, the water generated from its ring-closure reaction was separated as toluene azeotrope. After the reaction was completed, the solution was slowly poured into an ethanol-water mixture to obtain precipitate. The precipitate was filtered and dried in a vacuum oven at 40°C for 48 h.

Characterization

The infrared (IR) spectra were recorded on a Bio-Rad FTS-375C FT-IR spectrometer with attenuated total reflectance method. ^{1}H NMR spectrum was measured on a Bruker DRX-500 NMR spectrometer. Dimethyl sulfoxide-d_6 was used as a solvent. The UV–visible spectra were obtained on a JASCO V-560 UV–visible spectrophotometer. Gel permeation chromatography (GPC; GPCmax, Viscotek) for molecular weight determination was performed at 40°C in tetrahydrofuran. The number-average and weight-average molecular weights were calculated with respect to polystyrene standards.

Preparation and lithographic evaluation of the PSPI composition

Three grams of PHI was dissolved in 7 g of NMP. BPA-DEVE (0.45 g), the same amount of DINS, and 0.04 g of 3-aminopropyltriethoxysilane solution (10 wt % in NMP) as an adhesion promoter were added to the PHI solution and dissolved. The resulting solution was then filtrated through a 1-μm poly(tetrafluoroethylene) filter to provide a PSPI composition. It was then spin-coated on a Si wafer and prebaked at 90°C for 2 min and at 130°C for 2 min to obtain a film of about 5-μm thickness. A photomask was vacuum-pressed against the coated silicon wafer, which was then irradiated with filtered UV light with a wavelength of 365 nm from a high-pressure mercury lamp (ORIEL Instruments). The wafer was then post-exposure baked at 130°C for 1.5 min, developed with a 2.38 wt % TMAH aqueous solution for 4 min, and washed with distilled water to give a clear-patterned film. The thickness of the patterned PSPI film was 5 μm after development, as measured with a

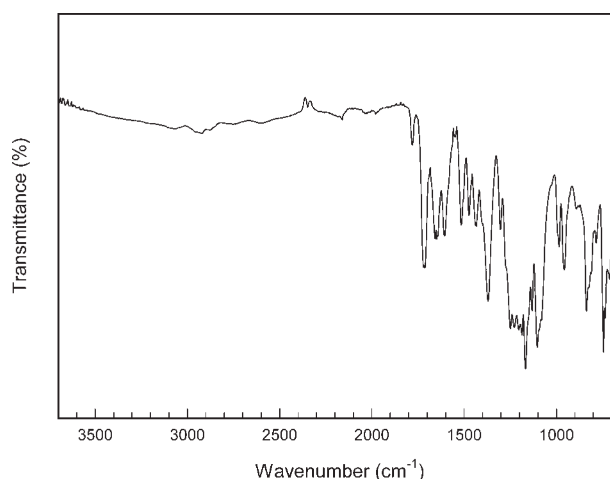


Figure 1 FT-IR spectrum of PHI.

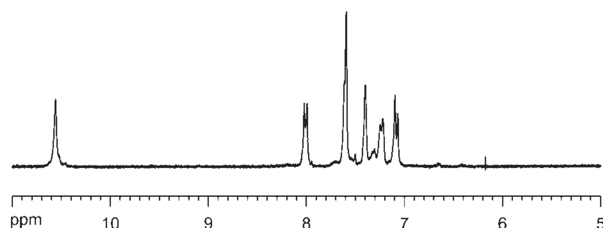


Figure 2 ^{1}H NMR spectrum of PHI.

surface profiler (TENCOR® P-10). The dissolution rate was determined by dividing the change in thickness of the developed film by the developing time, and a characteristic curve was obtained by plotting the normalized film thickness against the exposure energy. The pattern profiles were obtained with scanning electron microscopy (SEM; JEOL JSM-5600).

RESULTS AND DISCUSSION

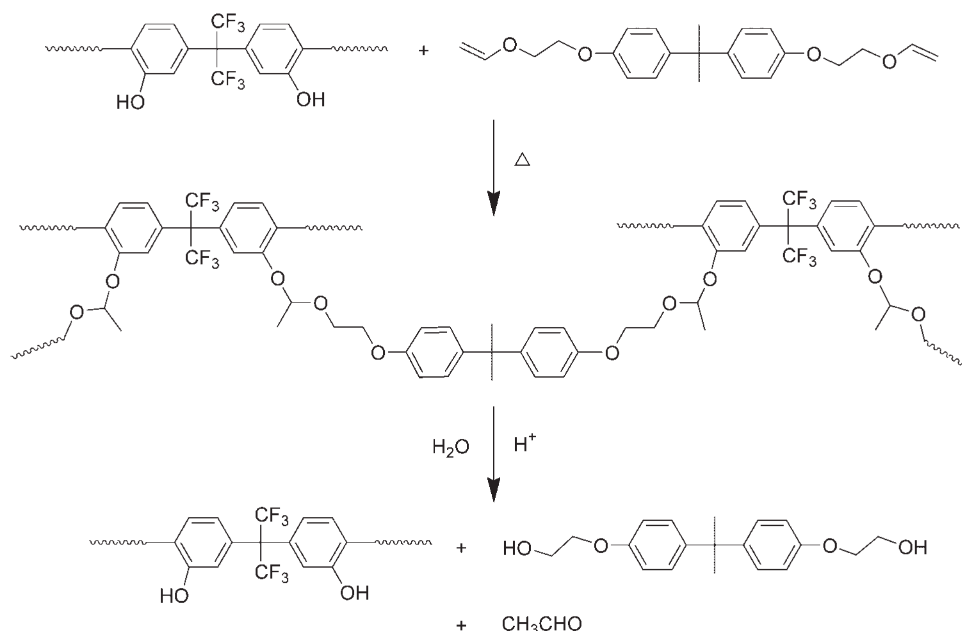
Synthesis and characterization of PHI

PHI, used as a base polymer of the three-component PSPI, was synthesized with a standard two-step procedure as shown in Scheme 1. In the first step, poly(amic acid) was synthesized via the ring-opening polymerization of ODPA and BAPAF. The poly(amic acid) was then thermally imidized to produce the PHI. The structure of the PHI was confirmed by IR spectroscopy (Fig. 1). Strong bands at 1780 and 1720 cm^{-1} are commonly attributed to the symmetrical and asymmetrical stretching vibrations of imides. The broad absorption band from 3000 to 3600 is due to hydroxyl group and the absorption band at 1374 cm^{-1} is due to C—N stretching. Structure of the PHI was also determined by ^{1}H NMR (Fig. 2). The peak at 10.5 ppm is due to a proton of hydroxyl group, and the peaks at 7.1–8.0 ppm are due to the protons of phenyl groups. From the results of IR and ^{1}H NMR spectroscopies, the conversion of poly(amic acid) into the PHI was confirmed.

The molecular weights of the PHI were determined by GPC. The number and weight average molecular weights of the PHI were found to be 11,253 and 54,300, respectively, (M_w/M_n = 4.82). The PHI based in ODPA and BAPAF has good solubility in most polar organic solvents such as acetone, THF, NMP, DMF, and DMAc, as reported previously.[20] Such good solubility is due to a flexible linkage of hexafluoroisopropylidene groups and polar substituents of hydroxyl groups in polymer backbone.

Photolithographic evaluation

Our positive-working PSPI system is consisted with a PHI, a crosslinking agent having vinyl ether groups, and an *i*-line (365 nm) PAG. On the basis of the previous reports,[15–17] the resist chemistry of the present three-component system is recognized as shown in Scheme 2. In prebake step, the crosslinked networks of the polyimide with acetal structures occur through electrophilic addition between the phenolic hydroxyl groups of the PHI and the vinyl ether groups of BPA-DEVE. Upon UV exposure and subsequent PEB, these crosslinks are cleaved by a photogenerated acid through acid-catalyzed reaction to give PHI, alcohol, and acetaldehyde. The de-*cross*-linked PHI in the exposed region can be then removed with a basic aqueous solution.



Scheme 2 Thermal crosslinking and de-*cross*-linking mechanism.

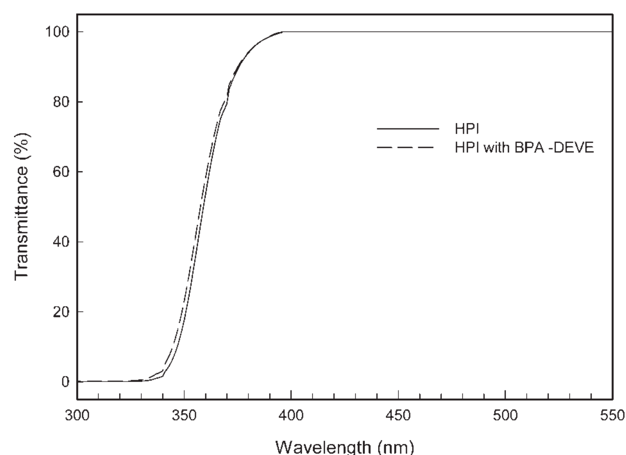


Figure 3 UV–visible transmittance spectra of PHI and PHI with 13 wt % BPA-DEVE.

UV–visible spectra of 5-μm-thick film of the PHI and its blend with BPA-DEVE were shown in Figure 3. The spectrum indicates that the PHI film based on ODPA and BAPAF is transparent in the region around 365 nm. The transmittance at 365 nm is 70%, which is not so high but adequate level for the microlevel patterning. By the addition of 15 wt % BPA-DEVE, the transmittance is not significantly varied because the BPA-DEVE has no absorption at around 365 nm.

Figure 4 shows the changes in FT-IR spectra for a PHI film containing 30 wt % BPA-DEVE. The film was prebaked at 130°C for 15 min. After prebake, the absorption bands at 1201 and 982 cm^{-1} due to C—O—C asymmetrical stretching and —H stretching in vinyl ether group were decreased. The absorption band at 1607 cm^{-1} due to C=C stretching of vinyl ether overlapped with C—C stretching of benzene ring was also decreased after the prebake. In addition, the weak absorption at 1040 cm^{-1} due to the symmetrical stretching of acetal group appeared after prebake. These results indicate that the vinyl ether groups react with the hydroxyl groups to form crosslinked networks with acetal structure during the prebake.

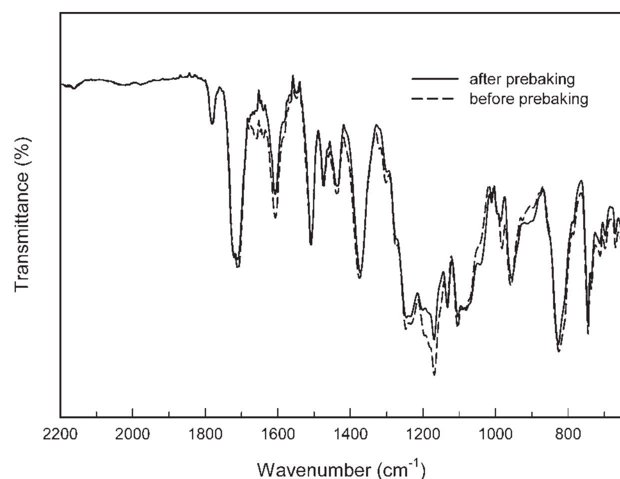


Figure 4 FT-IR spectra of the PHI film containing BPA-DEVE before and after prebake.

TABLE I
Effect of BPA-DEVE Content on the Dissolution Rate

BPA-DEVE content (wt %)	0	4.8	9.1	10.7	13.0	15.0
Dissolution rate (nm/s)	712	325	23	13	0	0

The effect of BPA-DEVE content on the dissolution rate of the three-component PSPI was studied. Table I shows the relationship between the addition ratio of BPA-DEVE and the dissolution rate after prebake at 130°C for 2 min. The dissolution rate was estimated by the measurement of the film thickness after development. A PHI film without vinyl ether compound dissolved in a 2.38% TMAH aqueous solution at a rate of 720 nm/s. However, the dissolution rate of the PHI was significantly decreased with the addition of BPA-DEVE. The PHI becomes completely insoluble in the alkaline developer with a BPA-DEVE content of 13 wt %. It is due to the thermal crosslinking reaction as well as the dissolution inhibition effect of BPA-DEVE. Thus, the optimum content of BPA-DEVE is considered to be about 13 wt %, which maximizes the difference in dissolution rates between the exposed and unexposed areas.

To investigate the PEB temperature effect on the dissolution behavior of the PSPI composition, the dissolution rates of exposed areas at various PEB temperatures were measured. The PHI film containing each 11.5 wt % of PAG and of BPA-DEVE was prebaked at 130°C for 2 min, exposed to 365 nm light with 1000 mJ/cm^2, (postexposure) baked at various temperatures ranging from 100 to 130°C for 3 min, and developed with 2.38 wt % TMAH aqueous solution at 25°C for 1 min. The results shown in Figure 5 indicate that the dissolution rate of the exposed region increases with an increase in PEB temperature on the basis of the cleavage of the crosslinked networks. The PEB time effect on the dissolution rate at 130°C was also investigated, and the results were shown in the inset of Figure 5. Although the dissolution rate is slightly increased with an increase of PEB time, the variation of PEB time does not significantly affect the dissolution rate of exposed area.

To clarify the difference of dissolution behavior between the exposed and unexposed areas, the effect of varying the PAG content on the dissolution rate in the TMAH developer was studied. The DINS was used as an *i*-line PAG, which is highly soluble in NMP due to its hydroxyl groups. The UV–visible

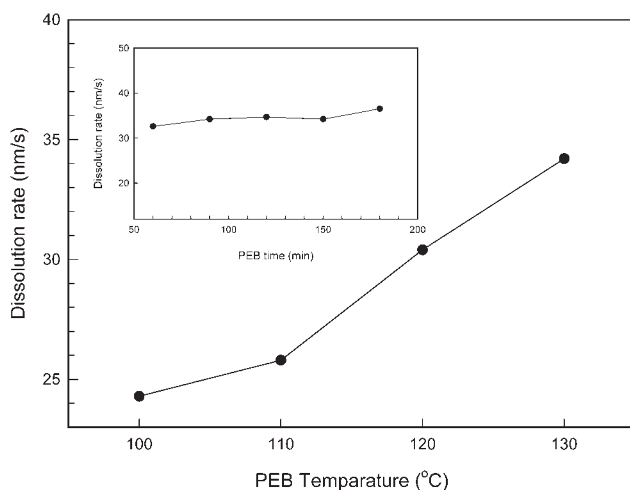


Figure 5 Effect of varying the PEB temperature on the dissolution rate of the PHI film containing each 11.5 wt % of PAG and of BPA-DEVE.

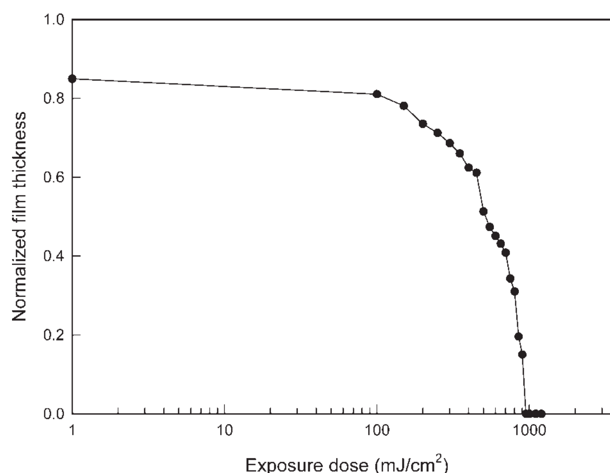


Figure 7 Exposure Characteristic curve of the PHI film containing each 11.5 wt % of PAG and of BPA-DEVE.

spectrum and photochemical reactions of this PAG was described in our previous report.[13] The PHI and BPA-DEVE were formulated with the ratio of 1 : 0.15 (*wt* : *wt*) in NMP, and then DINS was added to the solution with various content for the solid in solution from 4 to 21 wt %. The PSPI films spin-coated on silicon wafers were prebaked at 130°C for 2 min, exposed to UV light (365 nm, 1000 mJ/cm^2), and then postexposure baked at 130°C for 3 min. As shown in Figure 6, the dissolution rate of exposed area gradually increased with an increase in the content of DINS on the basis of the cleavage of the crosslinked networks by the photogenerated acid. However, unexposed area starts to dissolve slightly in the developer at a DINS content of 11.5 wt %, although the crosslinked PHI film without DINS is completely insoluble. This is due to the hydroxyl group of DINS, which increases the solubility of the crosslinked PHI film in the alkaline developer. Considering the ratio of the dissolution rates between the exposed and unexposed areas, 11.5 wt % was chosen as an optimum content for the DINS.

After these preliminary optimization studies, we prepared a PSPI composition based on the PHI with each 11.5 wt % of BPA-DEVE and of PAG. The sensitivity curve for a 5-μm-thick film of the composition developed by a 2.38 wt % aqueous TMAH solution is shown in Figure 7. The sensitivity (D^o) of the composition is 900 mJ/cm^2, and contrast (γ^o) is 3.02. Such sensitivity of the PSPI system is relatively low compared to that of regular chemically amplified deep UV photoresists. This is largely due to low transmittance of the base polymer and ~ 10 times thick PHI films. The residual basic solvent (NMP) also contributes to lower the sensitivity of the PSPI system by capturing photogenerated acid through

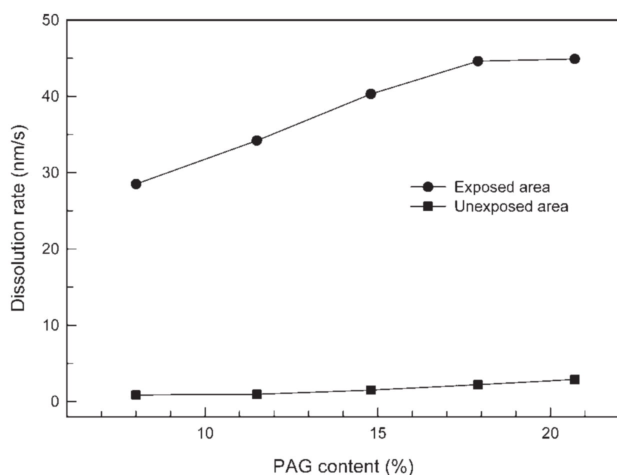


Figure 6 Effect of varying the DINS content on the dissolution rate of the PHI film containing 13 wt % BPA-DEVE.

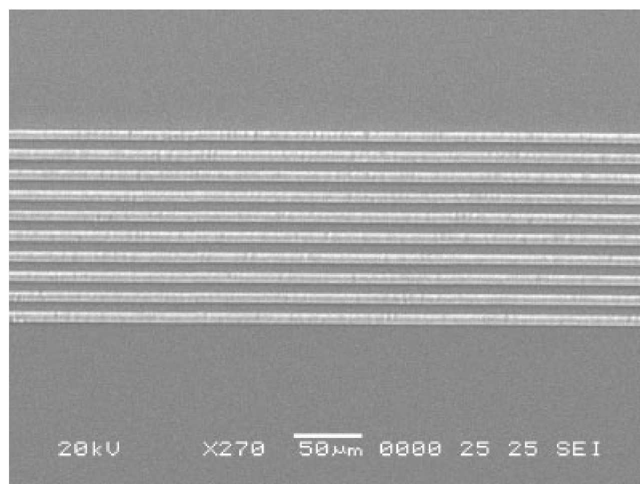


Figure 8 SEM image of 5 μm lines/spaces PHI pattern after development.

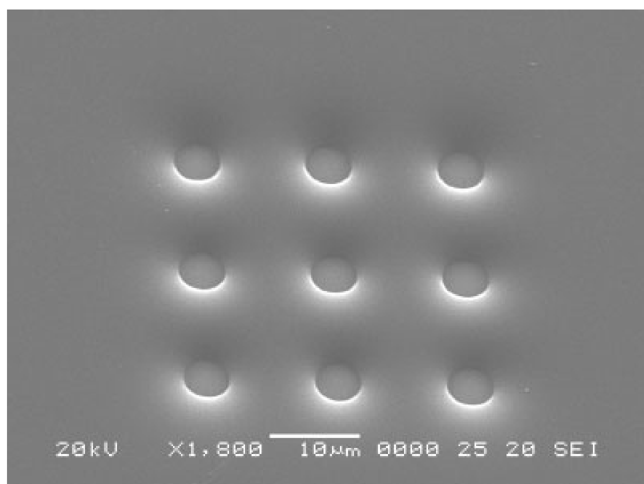


Figure 9 SEM image of hole pattern with 5 μm diameter in the PHI film after thermal treatment at 300°C.

acid–base reaction. Figure 8 shows a SEM image of a positive pattern in a 3.7-μm-thick film of the PSPI composition. It was processed with PEB at 130°C for 3 min after the exposure of the film to 1000 mJ/cm^2. Clear positive patterns with 5-μm resolution were obtained.

Figure 9 shows hole patterns with 5 μm diameter of the PHI film after thermal curing at 300 °C. The film thickness was reduced to about 32% compared with that of the developed film by the thermal curing process. The shrinkage is probably due to the decomposition of BPA-DEVE and DINS. However, no distortion or deformation of the pattern was observed after the thermal treatment. Further studies onto the physical and dielectric properties of the three-component PSPI are in progress, particularly with respect to the practical use of the dielectric layer in semiconductor packaging.

CONCLUSIONS

A novel positive-working PSPI based on the thermal crosslinking and acidolytic de-*cross*-linking reaction of vinyl ether groups was prepared from a PHI, a BPA-DEVE, and a PAG. The PHI was synthesized from the polymerization and cyclization of ODPA and BAPAF, which was quite soluble in a 2.38 wt % TMAH aqueous solution. However, it becomes completely insoluble through the thermal crosslinking with 13 wt % BPA-DEVE in the alkaline developer. Through chemical amplification mechanism, a strong acid generated from DINS successively cleaves the crosslinked PHI with an aid of thermal energy. After the optimizations of photolithographic processes, a pattern with a resolution of 5 μm was obtained from the three-component PSPI.

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