Alkaline-Developable, Chemically Amplified, Negative-Type Photosensitive Polyimide Based on Polyhydroxyimide, a Crosslinker, and a Photoacid Generator

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ABSTRACT: A chemically amplified photosensitive polyimide based on polyhydroxyimide (PHI) from cyclobutanetetracarboxylic dianhydride and 4,4′-(hexafluoroisopropylidene)bis(2-aminophenol), 4,4′-methylenebis[2,6-bis(hydroxymethyl)phenol] (MBHP) as a crosslinker, and (5-propylsulfonyloxyimino-5*H*-thiophen-2-ylidene)-(2-methylphenyl)acetonitrile (PTMA) as a photoacid generator was developed to obtain the abilities of low temperature patterning, low dielectric constant, and high sensitivity. The chemically amplified photosensitive polyimide, consisting of PHI (70 wt %), MBHP (20 wt %), and PTMA (10 wt %), showed a high sensitivity ($D_{0.5}$) of 5.9 mJ/cm^2 and a good contrast ($\gamma_{0.5}$) of 3.9, respectively, producing a clear negative-tone line-and-space pattern with 6-μm resolution. Furthermore, the chemically amplified photosensitive polyimide showed a high transparency in the *i*-line region and a low dielectric constant of 2.54. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 3605–3611, 2009

Key words: photoresists; polyimides; dielectric properties

INTRODUCTION

Polyimides (PIs) are used as insulation materials in microelectronics because of their excellent thermal stability and mechanical properties, solution processability, and reasonably low dielectric constants.[1–3] The fabrication of electronic devices containing metal wiring embedded in PIs is simplified with photosensitive polyimides (PSPIs).[4–8] Otherwise, extra processes are required for the patterning of PI films. The creation of alkaline-developable PSPIs is particularly beneficial in terms of the environment.

Most negative-type PSPIs are prepared from poly(amic acid)s (PAAs), where crosslinking sites are introduced into PAAs through esters,[4,5] acid amine ion interactions,[6] or direct attachment to aromatic rings in PAAs.[7] Moreover, chemically amplified PSPIs with crosslinkers have been developed.[8,9] However, in most cases with PAAs, high-temperature thermal treatment is required to convert the patterns of PAAs to those of corresponding PIs. This high-temperature process is not applicable to electronic devices because the thickness of silicon wafers is less than 100 μm, and thus, less thermal stress is required. To remedy these problems, a low-temperature process is currently required in industry.

In previous articles,[10,11] we reported the direct formulation of PSPIs based on PAAs and a photobase generator as the catalyst for low-temperature imidization below 200°C. However, an even lower temperature process, such as at 150°C, is required for high stacking of microelectronic devices.

The introduction of soluble PIs can eliminate the high-temperature curing step in the patterning process. Moreover, alkaline-developable soluble polyhydroxyimides (PHIs) can be obtained by the introduction of phenolic hydroxyl groups, as reported in previous articles.[8,12–14]

We recently reported various photosensitive thermally stable polymers having phenolic hydroxyl groups combined with a crosslinker, 4,4′-methylenebis[2,6-bis(hydroxymethyl)phenol] (MBHP), and they showed very high sensitivity.[15–17] These findings prompted us to develop a novel photosensitive PHI [chemically amplified photosensitive polyhydroxyimide (PSPHI)] containing MBHP as the crosslinker that would provide higher sensitivity in comparison with previous PSPHIs.

Herein, to realize low-temperature patterning, a low dielectric constant, and high sensitivity, we report a chemically amplified PSPHI based on PHI from cyclobutanetetracarboxylic dianhydride (CBDA) and 4,4′-(hexafluoroisopropylidene)bis(2-aminophenol)

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(6FAP) with MBHP as the crosslinker and (5-propylsulfonyloxyimino-5*H*-thiophen-2-ylidene)-(2-methylphenyl)acetonitrile (PTMA) as the photoacid generator (PAG). PIs having low dielectric constants are required to increase the circuit speed. Alicyclic and semialicyclic PIs are particularly interesting as optoelectronic and interlayer dielectric materials.[18–21] Thus, the PHI from CBDA and 6FAP was selected as a matrix polymer to obtain high solubility, high transparency at the *i*-line, a low dielectric constant that was attributed to the hexafluoroisopropylidine group, and alicyclic units in the polymer.

EXPERIMENTAL

Materials

N-Methyl-2-pyrrolidone (NMP) was purified by vacuum distillation. CBDA and PTMA, kindly donated by JSR Corp. (Tokyo, Japan) and Ciba Specialty Chemicals Co., Ltd. (Basel, Switzerland), respectively, were used without further purification. MBHP was prepared according to a previous report.[22] A 2.38 wt % aqueous tetramethylammonium hydroxide (TMAH) solution was used as a standard developer. Other reagents and solvents were used as received.

Synthesis of PHI

To a solution of 6FAP (2.000 g, 5.46 mmol) in NMP (9.0 mL) was added CBDA (1.071 g, 5.46 mmol) in one portion with stirring. The mixture was stirred at room temperature for 24 h to give a viscous clear solution. The inherent viscosity of the PAA in NMP was 0.39 dL/g at a concentration of 0.5 g/dL in NMP at 30°C. The polymer solution was diluted to 15 wt % with NMP, and then, *o*-xylene was added to the polymer solution. The resulting mixture was heated at 180°C for 12 h for thermal cyclization. During this step, the water generated by a ring-closure reaction was separated as the *o*-xylene azeotrope. After the reaction was complete, CBDA–6FAP was precipitated from the NMP solution with water three times and dried overnight at 80°C under reduced pressure.

UV measurement

The PHI film, with a thickness of 2.6 μm, was formed by spin coating on a quartz substrate and then baked at 100°C for 5 min. The reference PHI film from 4,4′-oxydiphthalic anhydride (ODPA) and 6FAP, with a thickness of 2.6 μm, was prepared by the thermal imidization of poly(hydroxy amic acid) (PHAA) on a quartz substrate. The PHAA film was heated at 200°C for 0.5 h, 250°C for 0.5 h, and 300°C for 1 h. Ultraviolet–visible (UV–vis) spectra were measured by a Jasco V-560 spectrophotometer (Tokyo, Japan).

PI film preparation and refractive-index measurements

PHI and PSPHI solutions in *N*,*N*-dimethylacetamide were spin-coated on the quartz substrate followed by baking at 140°C for 5 min. The wholly aromatic PHI film from ODPA and 6FAP was prepared by a method similar to that used for the preparation for the UV measurement. The film thicknesses of PHI, PSPHI, and ODPA/6FAP-type PHI were 6.4, 4.8, and 8.1 μm, respectively. The refractive indices of PHI films were measured at a wavelength of 1320 nm at room temperature with a Metricon model PC-2000 prism coupler. With linearly polarized laser light with parallel [transverse electric (TE)] and perpendicular [transverse magnetic (TM)] polarization to the film plane, the in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices and the film thicknesses of the samples were determined. The average refractive index (n_{AV}) values were calculated from the following equation:

$$n_{AV} = \sqrt{(2n_{TE}^2 + n_{TM}^2)/3}$$

Dissolution rate

The PHI was dissolved in 2-methoxyethanol (2ME); then, MBHP and PTMA were added (the total solid content was 17 wt %). The resist films, with 1.0-μm thicknesses, were obtained via spin casting from the solutions on silicon wafers. These films were prebaked at 80°C for 3 min and then exposed to a filtered super-high-pressure mercury lamp at 365 nm; this was followed by postexposure baking (PEB) at a temperature of 100–150°C for a definite time. The dissolution rate (Å/s) of the film thickness was determined from changes in the film thickness before and after development with 2.38 wt % aqueous TMAH.

Photosensitivity

The photosensitive polymer film, with a 1.0-μm thickness, on a silicon wafer was prepared by the dissolution of PHI, MBHP, and PTMA in 2ME; this was followed by spin casting on the silicon wafer, prebaking at 80°C for 3 min, exposure to irradiation at a wavelength of 365 nm (*i*-line) with various exposure doses, PEB at 140°C for 3 min, and then developing with 2.38 wt % aqueous TMAH for 3 s at room temperature. A characteristic photosensitive curve was obtained by the plotting of a normalized film thickness against the exposure dose (mJ/cm^2). Image-wise exposure through a mask was carried out in contact-printing mode.

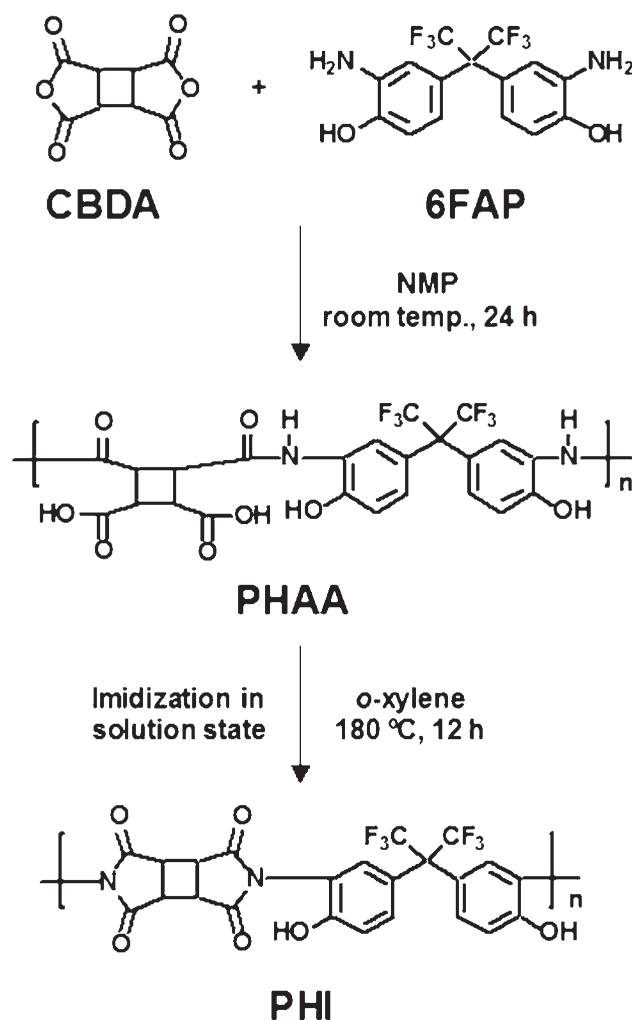
Measurements

Viscosity measurements were carried out with an Ostwald viscometer (SIBATA Scientific Technology Ltd., Tokyo, Japan) at 30°C in NMP. Fourier transform infrared spectra were recorded on a Horiba FT-720 instrument (Kyoto, Japan). Thermogravimetry (TG) was performed with a Seiko TG/DTA 6300 instrument (Chiba, Japan). The film was spin-coated on a silicon wafer from a polymer solution in 2ME, and the film thickness was measured by Veeco Instrument Dektak^3 surface profiler (USA). Field emission scanning electron micrographs were taken with a Technex Lab Tiny 1540 scanning electron microscope (Tokyo, Japan) with a 15-kV acceleration voltage for imaging. Pt/Pd was sputtered on the film before the scanning electron microscopy (SEM) measurements.

RESULTS AND DISCUSSION

Synthesis of PHI from CBDA and 6FAP

The ring-opening polyaddition of CBDA with 6FAP was carried out in NMP at room temperature for 24 h (Scheme 1); this produced PAA with an inherent viscosity of 0.39 dL/g. This was followed by a thermal ring-closing reaction in the solution state. The characterization of the obtained PHI was confirmed by IR spectroscopy, as shown in Figure 1. The IR spectrum showed characteristic absorptions at 1780 and 1720 cm^{-1} due to the imide carbonyl groups. Furthermore, characteristic absorption of O—H stretching was observed at 3400 cm^{-1}, whereas no amide signals were observed at 1660 cm^{-1} in PAA.



Scheme 1 Synthesis of PHI from CBDA and 6FAP.

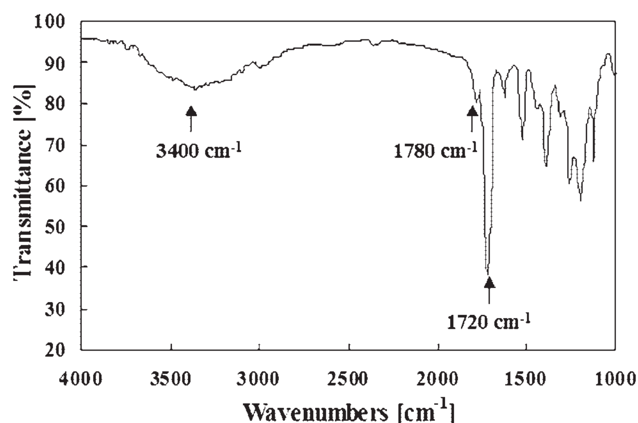


Figure 1 IR spectrum of PHI.

The thermal stability of PHI was measured by TG. The TG curves of PHIs are shown in Figure 2. The PHI resulted in a 5% weight loss at 414°C under nitrogen. This decomposition temperature was lower than that of the wholly aromatic PHIs, such as the PHI from OPDA and 6FAP. It was, however, high enough for microelectronic applications.

Transparency of PHI

The UV–vis spectra of the PHI film with a thickness of 2.6 μm is shown in Figure 3 with that of the reference PHI film (thickness = 2.6 μm) from ODPA and 6FAP

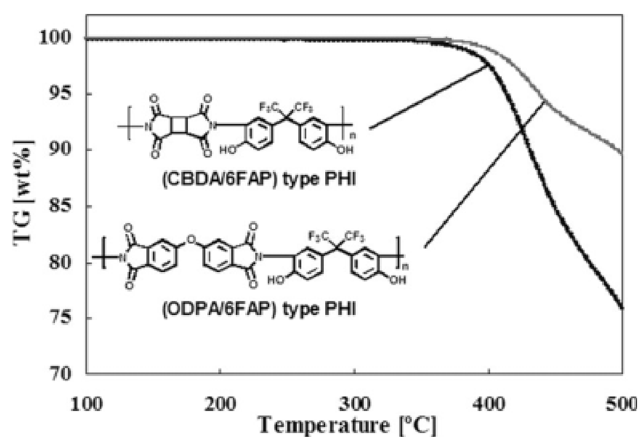


Figure 2 TG curves of CBDA/6FAP-type PHI and ODPA/6FAP-type PHI.

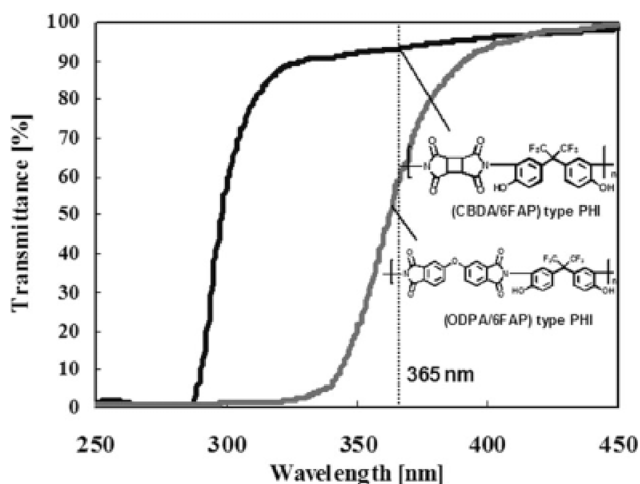


Figure 3 UV spectra of CBDA/6FAP-type PHI and ODPA/6FAP-type PHI.

because the introduction of an electron-withdrawing group in a diamine unit is effective at lowering the highest occupied molecular orbital levels and thus increasing the band gaps, which causes hypochromic shifts of the absorptions originating from the highest occupied molecular orbital to the lowest unoccupied molecular orbital transitions. As expected, in the case of the semiaromatic PI structures, which hardly formed intermolecular and intramolecular charge-transfer complexes, the transmittance of the PHI CBDA/6FAP film measured at 365 nm was 93%, which was much higher than that of the reference PHI (56%).

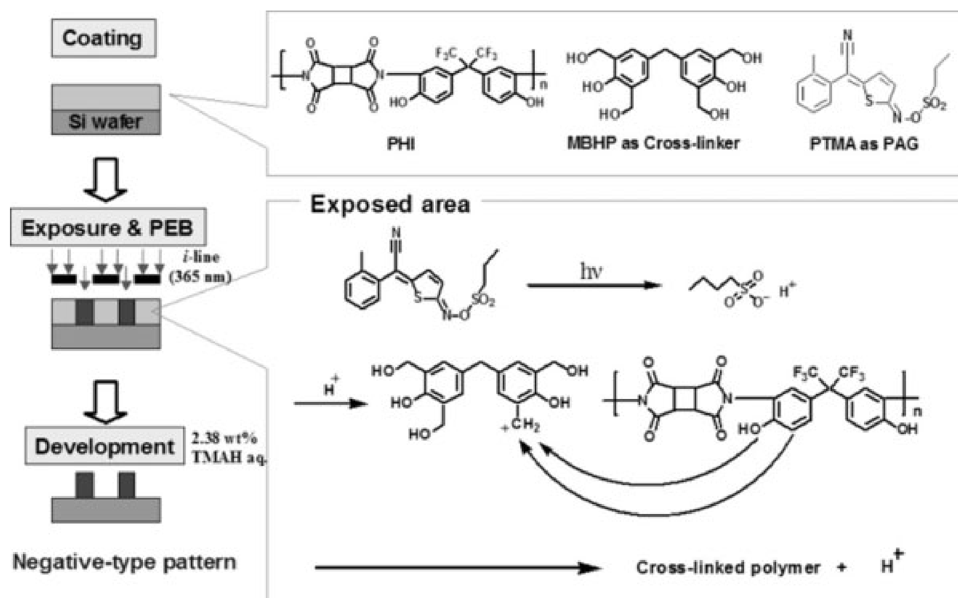
Dielectric constants

The n_{AV} values of PHI and PSPHI, which consisted of PHI (70 wt %), MBHP (20 wt %), and PTMA (10 wt %), were determined as 1.519 and 1.546, respectively. The dielectric constant of a material at optical frequencies can be estimated from the refractive index according to Maxwell's equation ($\varepsilon = n^2$, where ε is the dielectric constant and n is the refractive index). The dielectric constant around 1 MHz was evaluated to be $1.10n_{AV}^2$, which included an additional contribution of approximately 10% from the infrared absorption. The n_{AV} values of 1.519 and 1.546 could be translated into dielectric constants of 2.54 and 2.63, respectively. These values were considerably lower than the optically estimated dielectric constant of the other wholly aromatic PHI and ODPA/6FAP-type PHI (dielectric constant = 2.73) because of the introduction of an alicyclic unit, a cyclobutane ring, in the polymer structure.

Lithographic evaluation

The patterning process is shown in Scheme 2. It was assumed that the sulfonic acids generated in the exposure area catalyzed the formation of benzylic carbocation species, which underwent electrophilic substitution on the aromatic rings and hydroxyl groups to produce C- and O-alkylated polymers. The O-alkylated polymers were arranged into C-alkylated ones by heating. These reactions converted an alkaline soluble PHI into a crosslinked polymer, as shown in Scheme 2.[8,23]

The PEB temperature is crucial in a chemically amplified resist system because the diffusion of generated acids from PAG after *i*-line exposure in the films is an important key factor. Thus, the effect of the PEB temperature on the dissolution rate in 2.38 wt % aqueous TMAH was studied. The results



Scheme 2 Patterning process of PSPHI.

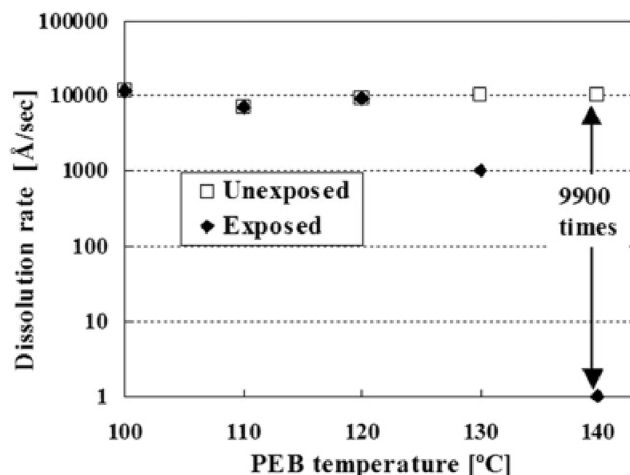


Figure 4 Effect of the PEB temperature on the dissolution rate of exposed and unexposed 1.0-μm films (PHI/MBHP/PTMA = 70/20/10 wt %). The *i*-line exposure and PEB time were fixed at 100 mJ/cm^2 and 1 min, respectively.

in the case of the resist formulated by the mixture of the PHI (70 wt %), MBHP (20 wt %), and PTMA (10 wt %) in 2ME are shown in Figure 4. A very high dissolution contrast (DC; 9900×) was obtained at a PEB temperature of 140°C.

The diffusion length of photogenerated acid was also influenced by the PEB time. Figure 5 shows the effect of the PEB time on the dissolution rate of the films post-exposure-baked at 140°C. A very high DC was obtained at a PEB time of 1 min. When the PEB time was decreased to 30 s, a sufficient DC was not obtained. These results clearly indicate that the photogenerated acid effectively diffused in the film under the condition of PEB at a temperature of 140°C for 1 min.

To obtain contrasting pattern profiles from the exposed and unexposed areas, the effects of PAG and crosslinker composition were investigated. The film was irradiated at 100 mJ/cm^2, post-exposure-baked at 140°C for 1 min, and developed with 2.38 wt % aqueous TMAH. The results shown in Figure 6 indicate that a 10 wt % loading was necessary to achieve a high DC.

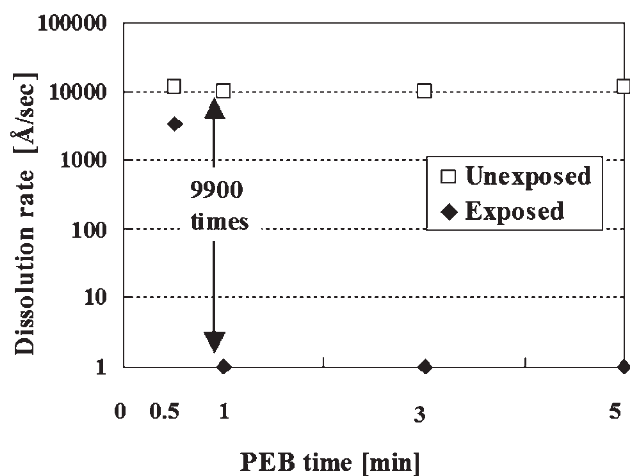


Figure 5 Effect of the PEB time at 140°C on the dissolution rate of exposed and unexposed 1.0-μm films (PHI/MBHP/PTMA = 70/20/10 wt %). The *i*-line exposure was fixed at 100 mJ/cm^2.

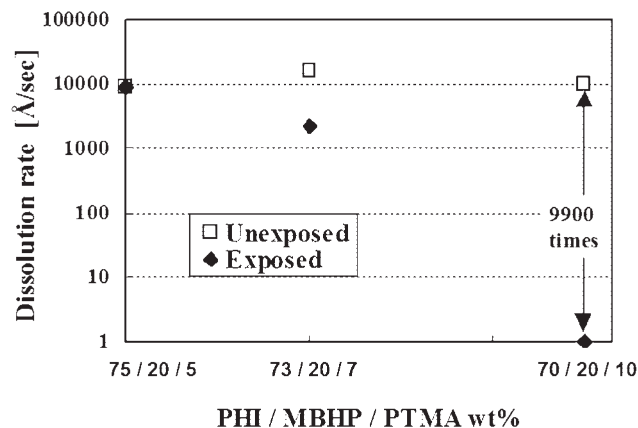


Figure 6 Effect of the PTMA composition on the dissolution rate of exposed and unexposed 1.0-μm films. The *i*-line exposure and PEB were fixed at 100 mJ/cm^2 and 140°C for 1 min, respectively.

Next, the effect of the MBHP composition on the dissolution rate in 2.38 wt % aqueous TMAH after exposure to 100 mJ/cm^2 and PEB at 140°C for 1 min was studied, and the results are shown in Figure 7. These results indicate that a 20 wt % MBHP loading was required to obtain a large DC at 10 wt % PAG loading.

On the basis of these preliminary optimization studies, a resist consisting of novolac resin (70 wt %), MBHP (20 wt %), and PTMA (10 wt %) was formulated. The sensitivity curve for the 1-μm film thickness shown in Figure 8 indicated a high sensitivity ($D_{0.5}$) of 5.3 mJ/cm^2 and a good contrast ($\gamma_{0.5}$) of 3.9 after PEB treatment at 140°C for 3 min followed

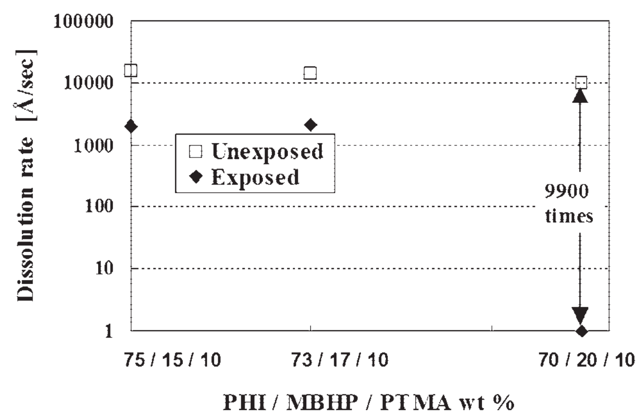


Figure 7 Effect of the MBHP composition on the dissolution rate of exposed and unexposed 1.0-μm films. The *i*-line exposure and PEB were fixed at 100 mJ/cm^2 and 140°C for 1 min, respectively.

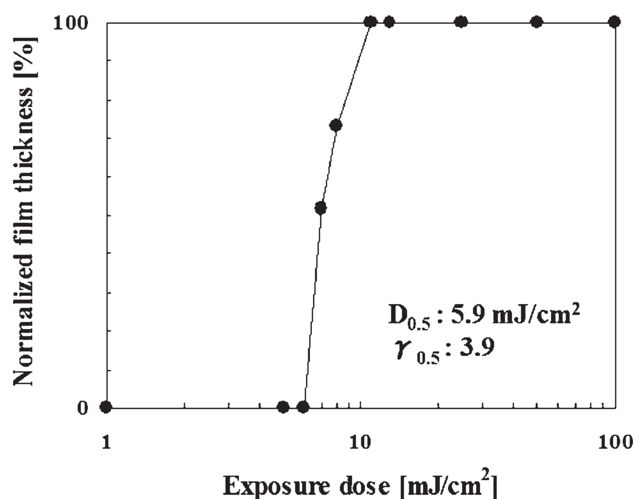


Figure 8 Characteristic photosensitivity curve of PSPHI (PHI/MBHP/PTMA = 70/20/10 wt %) in a 1.0-μm film. The PEB temperature, PEB time, and development time were fixed at 140°C, 1 min, and 3 s, respectively.

by development with 2.38 wt % aqueous TMAH at room temperature. In this case, the PEB time was increased to 3 min to accurately measure the sensitivity.

Figure 9 presents an SEM micrograph image of a contact-printed pattern after exposure to the *i*-line at 50 mJ/cm^2 through a photomask followed by development with 2.38 wt % aqueous TMAH at room temperature. A clear negative pattern with a 6-μm feature could be observed when a 2.0 μm thick film was used. This resist system was further applied to produce a thick pattern. A 20-μm image was made in an 8.4 μm thick film by PEB at 140°C for 3 min after exposure to the *i*-line at 50 mJ/cm^2 followed by developing with 2.38 wt % aqueous TMAH at room temperature for 11 s. Adequate resolution and edge sharpness are shown in Figure 10.

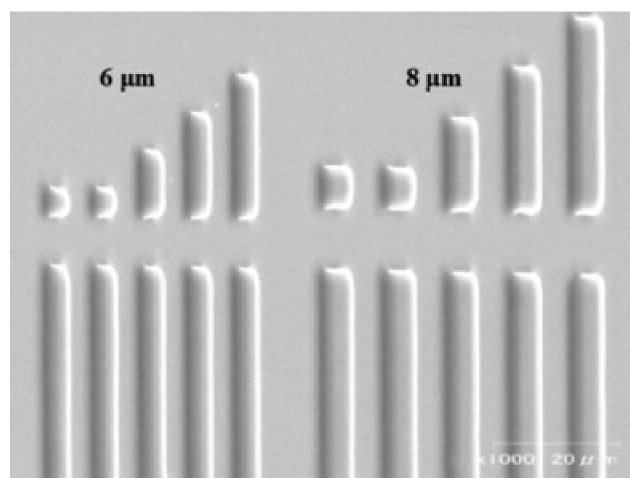


Figure 9 SEM image of the negative pattern in a 2.1-μm-thick film (PHI/MBHP/PTMA = 70/20/10 wt %). The prebaking, *i*-line exposure, and PEB were fixed at 80°C for 3 min, 40 mJ/cm^2, and 140°C for 1 min, respectively.

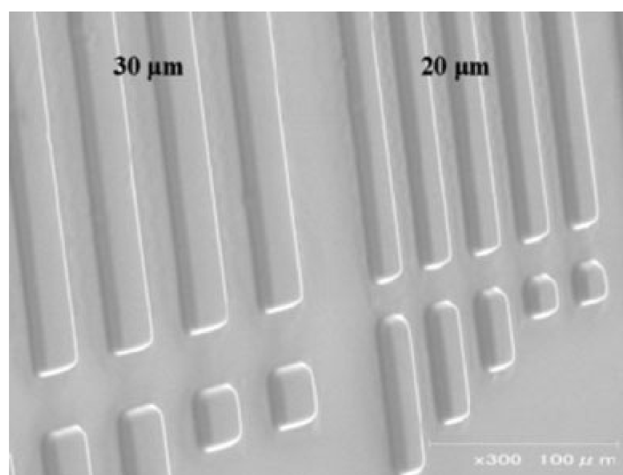


Figure 10 SEM image of the negative pattern in an 8.4-μm-thick film (PHI/MBHP/PTMA = 70/20/10 wt %). The prebaking, *i*-line exposure, and PEB were fixed at 100°C for 3 min, 50 mJ/cm^2, and 140°C for 3 min, respectively.

CONCLUSIONS

A new negative-type PSPHI for low-temperature patterning with an alkaline developer was produced. The matrix polymer made from CBDA and 6FAP showed high transparency in the *i*-line region and a low dielectric constant of 2.54. PSPHI, consisting of PHI (70 wt %), MBHP (20 wt %), and PTMA (10 wt %), showed a high sensitivity ($D_{0.5}$) of 5.9 mJ/cm^2 and a good contrast ($\gamma_{0.5}$) of 3.9, respectively; this produced a clear negative-tone line-and-space pattern with 6-μm resolution. A thick pattern was also depicted with this PSPHI system. This PSPHI can be applied to insulators, buffer coatings, and passivation layers in high-stacking microelectronic devices because this PSPHI showed good patterning performance in low-temperature processes, such as those at 140°C.

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