New Negative Type Photosensitive Polyimide Based on Poly(hydroxyimide), Cross-linker, and Photoacid Generator

Mitsuru Ueda * and Tomonari Nakayama

Department of Materials Science and Engineering, Faculty of Engineering, Yamagata University, Yonezawa 992, JAPAN

ABSTRACT: A negative working photosensitive polyimide based on polyhydroxyimide (PHI), 2,6-bis(hydroxylmethyl)-4-methylphenol (BHMP) as cross-linker, and a photo acid-generator diphenyliodonium 9,10-dimethoxyanthracene (DIAS) has been developed. The PHI was prepared by the ring-opening polyaddition of 4,4'-hexafluoroisopropylidenebis(phthalic anhydride)(6FDA) and 4,4'-diamino-4"-hydroxytriphenylmethane (DHTM), followed by thermal cyclization in refluxing xylene. The PHI film showed excellent transparency to UV light. The photosensitive polyimide containing 70 wt% of PHI, 20 wt% of BHMP, and 10 wt% of DIAS showed a sensitivity of 70 mJ/cm^2 and a contrast of 3.8 when it was exposed to 365 nm light and postbaked at 120 °C, followed by developing with a 2.5 % aqueous teramethylammonium hydroxide (TMAH) solution at 40 °C.

Introduction

Photosensitive polyimides (PSPI)s are widely used as protection and insulation layers in semiconductor manufacturing. They are very attractive since the number of processing steps is reduced by avoiding the use of classical photo resists.

Most of the negative type-PSPIs is prepared from poly(amic acid)s, where cross-linking sites are introduced to amic acids through ester and acid amine ion linkages. [1-2] On the other hand, the positive type-PSPIs consist of polyamic acid and o-diazonaphthoquinone (DNQ)[3] or 1,4-dihydropyridine derivatives,[4] polyimide containing hydroxyl groups and DNQ, [5] or o-nitrobenzyl esters of polyamic acid. [6]

In the previous paper, [7] we reported the new positive-working alkaline-developable PSPI based on poly(hydroxyimide) (PHI) and 2,3,4-tris[1-oxo-2-diazonaphthoquinone-4-sulfonyloxy] benzophenone. This is consistent with the trend using aqueous base solutions as a developer for the photoresist processing technology in the microelectronics industry.

Recently, Frechet et al. studied several three components resist systems containing poly(4-hydroxystyrene), polyfunctional benzylic alcohols, and photoacid generators, and found that polyfunctional benzylic alcohols act as excellent cross-linkers in the presence of acid and showed high lithographic sensitivities. [8] This finding prompted us to employ the approach to the development of a new PSPI using the PHI. Because the PHI contains p-hydroxyphenyl unit that reacts easily with electrophilic reagent benzylic carbocation.

This paper describes the development of a novel approach to the negative type PSPI that is based chemically on the propensity for the PHI to cross-link rapidly with 2,6-bis(hydroxylmethyl)-4-methylphenol (BHMP) in the presence of a catalytic quantity of acids.

Experimental Section

Materials. 4,4'-Hexafluoroisopropylidenebis(phthalic anhydride) (6FDA) was obtained from American Hoechst Co. Ltd. 2,6-Bis(hydroxylmethyl)-4-methylphenol (BHMP) was prepared by hydroxymethylation of p-cresol according to the reported

procedure.[9] Diphenyliodonium 9,10-dimethoxyanthracene (DIAS) was prepared by the reaction of diphenyliodonium with sodium 9,10-dimethoxyanthracene-2-sulfonate that was obtained by the reduction of sodium anthraquinone-2-sulfonate with zinc, followed by the methylation with dimethyl sulfate.[10] N-Methyl-2-pyrrolidinone (NMP) was stirred over powdered calcium hydride overnight, then distilled under reduced pressure, and stored over 4 A molecular sieves. Other reagents and solvents were obtained commercially and used as received. 4,4'-Diamino-4''-hydroxtriphenylmethane (DHTM) was prepared by the reaction 4-hydroxybenzaldehyde (1.22 g, 10.0 mmol), aniline (3.14 g, 34.5 mmol) and aniline hydrochloride (0.08 g, 0.59 mmol) according to the reported procedure.[11] The yield was 1.17 g (40%).; m.p=200-202 °C. (lit. [11] 195 °C) ^{1}H NMR (DMSO-d_6): 9.2 (s, OH, 1H), 6.9-6.4 (m, PhH, 12H), 5.1 (8s, CH, 1H), 4.9 (s, NH$_2$, 4H). Anal. Calcd for $C_{19}H_{18}N_2O$: C, 78.60; H, 6.25; N, 9.65. Found: C, 78.66; H,6.34; N, 9.52.

Preparation of polyhydroxyimide (PHI)

A solution of DHTM (0.290 g, 1.0 mmol) in NMP (2.8 mL) was cooled with an ice-water bath. To this solution was added with stirring 6FDA (0.444 g, 1.0 mmol). The mixture was stirred at room temperature for 3 h. The resulting viscous solution was diluted with NMP (10 mL) and poured into 50 % methanol aqueous solution (200 mL). The polyamic acid (PAA) precipitated was filtered off and dried *in vacuo* at 50 °C for 12 h. The resulting PAA was dispersed in xylene and then refluxed for 90 min and the precipitate was collected and washed with hexane and dried at 50 °C for 12 h *in vacuo* . The polymer was purified by reprecipitation by pouring polymer solution (NMP) into 50 % methanol aqueous solution (200 mL). The precipitated polymer was finally dried at 200 °C for 12 h *in vacuo* . The yield was 0.509 g (73 %). The inherent viscosity of the polymer in NMP was 0.48 dL/g at a concentration of 0.5 g/dL at 30°C. IR(KBr), v (cm^{-1}) 3430 (O-H) and 1780, 1720 cm^{-1} (C=O). Anal. Calcd for $(C_{38}H_{20}F_6N_2O_5$ 3/2 H$_2$O)$_n$: C, 62.90; H, 3.19; N, 9.65. Found: C, 62.91; H, 3.15; N, 3.88.

Photosensitivity

The 3 μm PHI films on a silicone wafer were exposed at 365 nm wavelength to the filtered super high-pressure mercury lamp, developed in 2.5 % tetramethylammonium hydroxide (TMAH) aqueous solution at 40 °C, and rinsed in water. The characteristic curve was obtained by a normalized film thickness against exposure energy.

Measurement

The infrared spectra were recorded on a Hitachi I-5020 FT-IR spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL EX 270 spectrometer. Viscosity measurements were carried out by using an Ostwald viscometer at 30 °C. Thermal analyses were performed on a Seiko SSS 5000-TG/DTA 220 instrument at a heating rate of 10 °C/min for (TGA) and a Seiko SSS 5000-DSC220 at a heating rate of 20 °C/min for differential scanning calorimetry (DSC) under nitrogen. Molecular weights were determined by a gel permeation chromatograph (GPC) with polystyrene calibration using JASCO HPLC system equipped with Shodex KD-80M column at 40 °C in DMF containing 10 mmol/L of LiBr. The film thickness was measured by Dektak 3030 system (Veeco Instruments Inc.).

Results and Discussion

Synthesis of polyhydroxyimide (PHI)

Polyimides generally exhibit low optical transparency to UV-light and have a yellow color due to its charge transfer complex, and the coloration limits the formation of thick film patterns. Therefore, several methods have been employed to obtain less colored polyimides, e.g., introducing fluoroalkyl groups, separating chromophoric groups, and reducing the electronic interaction between color-causing centers. In particular, introducing the fluoroalkyl group into the main polymer chain is considered to be more versatile technique both in the transparency and solubility of polyimide. Therefore, we chose 4,4'-hexafluoroisopropylidenebis(phthalic anhydride)

(6FDA) as a candidate of tetracarboxylic anhydride. On the other hand, a diamine monomer having hydroxyphenyl moiety, 4,4'-diamino-4"-hydroxtriphenylmethane (DHTM) was prepared by the reaction of 4-hydroxybenzaldehyde with aniline in the presence of aniline hydrochloride.

The synthesis of PHI was carried out by the ring-opening polyaddition of 6FDA, and DHTM in NMP.

DIAS

PHI

BHMP

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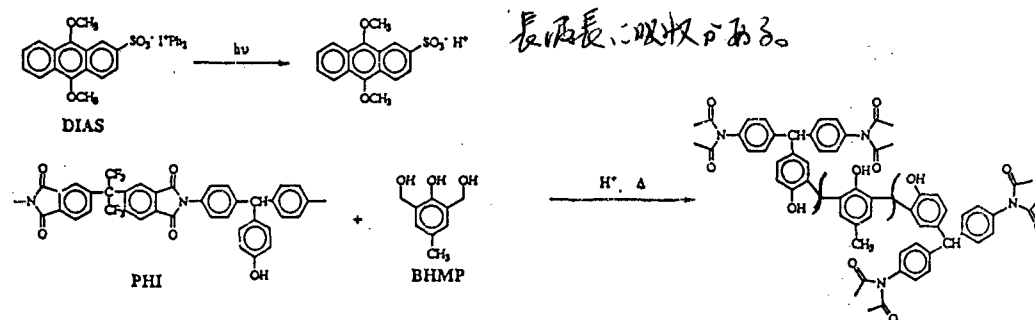
The polycondensation proceeded in homogeneous solution and gave a quantitative yield of polyamic acid (PAA) with the inherent viscosity of 0.48 dL/g. Subsequently, the PAA was converted to PHI by refluxing in xylene for 90 min.

The polymer was confirmed to be the corresponding PHI by infrared spectroscopy and elemental analysis. The IR spectrum exhibited characteristic absorptions at 1780 and 1720 cm^{-1} due to the imide carbonyl. Elemental analysis also supported the formation of the expected polymer.

The PHI was reddish powders and soluble in dipolar aprotic solvents at room temperature, 2-methoxyethanol, bis(2-methoxyethyl) ether, and 1-methoxy-2-acetoxypropane at room temperature. A transparent film was cast from the solution of the PHI in these solvents.

The molecular weight of the PHI with the inherent viscosity of 0.48 dL/g was determined by GPC. The GPC trace was unimodal with the polydispersity of 1.7. The chromatogram indicated that the relative Mn and Mw are 61,000 and 104, 000, respectively.

The thermal behavior of the PHI was studied by thermogravimetry (TG). The PHI showed a 10 % weight loss at 480 and 490 °C in air and in nitrogen, respectively. Differential scanning calorimetry on powders did not show any clear endotherms.

Lithographic Evaluation

The UV-visible spectrum of 1μm thick PHI film shows strong absorption with a cutoff between 300 and 400 nm. The transmittance of the PHI film at 365 nm was 85 %. As described in the introduction, polyfunctional benzylic alcohols act as good cross-linkers for poly(4-hydroxystyrene) in the presence of acid.[8] This acid-catalyzed cross-linking reaction was studied in detail, and this reaction was proposed to proceed via a direct C-alkylation as well as an initial O-alkylation followed by a subsequent acid-catalyzed rearrangement to the final alkylated product. Furthermore, both a thermal cross-linking and an acid-catalyzed cross-linking process were proposed for this alkylation. [12] We decided to use 2,6-bis(hydroxylmethyl)-4-methylphenol (BHMP) as a cross-linker on the basis of the availability and the sensitivity.

Many onium salts such as diaryliodonium and triarylsulfonium salts are well known as photoacid generators. [13] However, onium salts that have the absorption band in the wavelengths longer than 300 nm were few. Recently, diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate (DIAS) having the absorption longer than 300 nm was developed and shown to produce 9,10-dimethoxyanthracene-2-sulfonic acid by the irradiation with 365 nm light. [14] Furthermore, the DIAS as a photoacid generator was successfully applied to the formulation of positive photoresist

composed of bisphenol A protected with tert-butoxycarbonyl group and a novolak resist matrix. [16] Therefore, we decided to use the DIAS as the photoacid generator.

The changes of electronic absorption spectrum of PHI film containing 10 wt % DIAS upon photo irradiation were investigated. The absorption bands at 370, 386, and 408 nm were decreased by irradiation with 365 nm light. The final spectrum was analogous to that of 9,10-dimethoxyanthracene-2-sulfonic acid.

In order to investigate the dissolution behavior of exposed and unexposed areas, the effects of the post exposure bake (PEB) temperature and PEB time on the dissolution rate was studied. The dissolution rate was estimated by measuring the film thickness after the development. The results in the case of the resist formulated by mixing the PHI (70wt%), BHMP (20 wt%), and DIAS (10 wt%) in 2-methoxyethanol is shown in Figure 1, where the film was exposed 200 mJ/cm^2 to 365 nm UV radiation, post baked at 120°C, and developed with 2.5 % tetramethylammonium hydroxide (TMAH) aqueous solution at 40°C. The dissolution rate of the exposed part decreased rapidly with increasing PEB time. On the other hand, the solubility of the unexposed part was almost unchanged. The difference of the dissolution rate between exposed and unexposed parts reached about 70 times after PEB at 120 °C for 5 min. These results indicate that the cross-linking reaction is promoted effectively by PEB treatment. The probable cross linking process via electrophilic aromatic substitution will be discussed at the later section.

The effect of the BHMP loading on the dissolution rate in 2.5 % TMAH aqueous solution after the exposure of 200 mJ/cm^2 and PEB at 120 °C for 5 min was studied and the results are shown in Figure 2. It was found that the 20 wt% of BHMP loading was necessary to achieve the enough dissolution contrast.

After these preliminary optimization studies involving BHMP and DIAS loading, and developing temperature, we prepared a photosensitive polyimide system consisting of PHI (70 wt%), BHMP (20 wt%), and DIAS (10 wt%). The sensitivity curve for a 2 μm thick film shown in Figure 3 was consistent with the dissolution behavior studied above, indicating that the sensitivity (D$^{0.5}$) and contrast (γ 0.5) were 70 mJ/cm^2 and 3.8, with 365 nm light, respectively, after PEB treatment at 120°C for 5 min. followed by developing with 2.5 % TMAH aqueous solution at 40 °C.

In Figure 4 is presented scanning electron micrographs of the contact printed image that was obtained using a resist composed of the PHI (70 wt %), bis(hydroxylmethyl)-4-methylphenol (20 wt %), and DIAS (10 wt %), post baked at 120°C for 5 min after exposure to 150 mJ/cm^2, and developed with 2.5 % TMAH aqueous solution. The resist is capable of resolving 8 μm feature when 4 μm thick films are used.

4. Conclusions

The new PHI was prepared by the ring-opening polyaddition of 6FDA, and DHTM. The photochemical reaction of DIAS in the PHI film was occurred smoothly because PHI has an excellent transparency in UV-region. The new PSPI was formulated by mixing the PHI (70 wt%), bis(hydroxylmethyl)-4-methylphenol (20 wt%), and DIAS (10 wt%) in 2-methoxyethanol, and was found to be an alkaline developable negative-type PSPI. The thermal stability after the high thermal treatment of developed film is almost the same as the neat resin of PHI.

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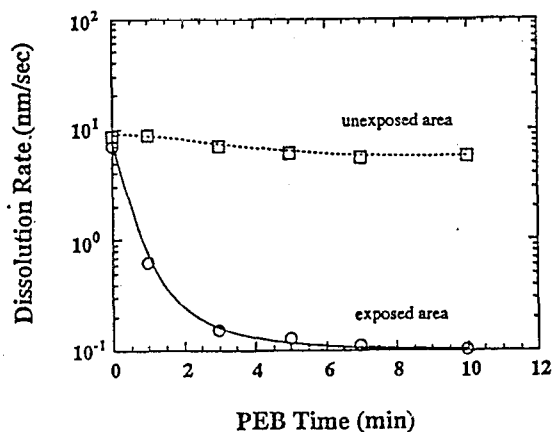
Figure 1. Relationship between PEB time and dissolution rate of PHI containing BHMP and DIAS.
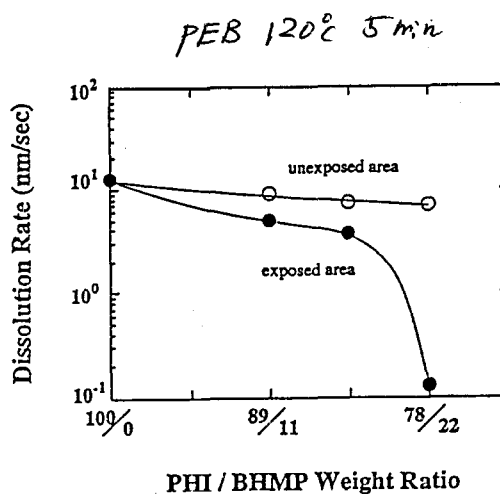

Figure 2. Relationship between DIAS content and dissolution rate of PHI containing BHMP.
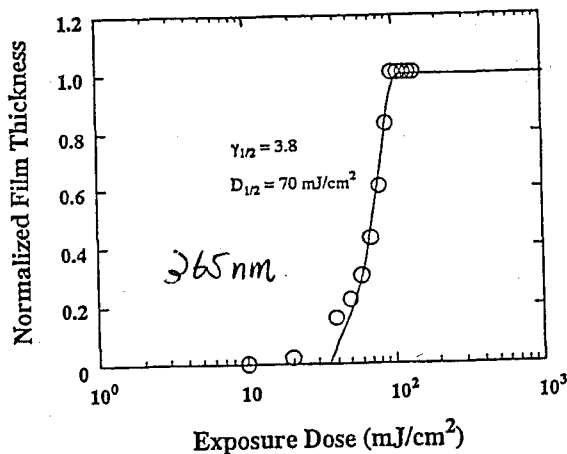

Figure 3. Exposure characteristic curves for the system of PHI, BHMP, and DIAS.
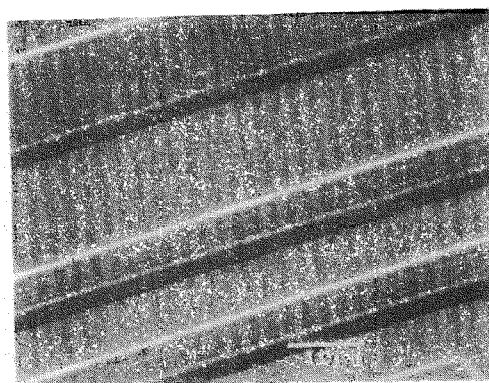

Figure 4. Scanning electron micrograph of the negative image printed in the PHI system.

Figure Caption

Figure 1. Relationship between PEB time and dissolution rate of PHI containing BHMP and DIAS.

Figure 2. Relationship between DIAS content and dissolution rate of PHI containing BHMP.

Figure 3. Exposure characteristic curves for the system of PHI, BHMP, and DIAS.

Figure 4. Scanning electron micrograph of the negative image printed in the PHI system.

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