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Photosensitive polyimide-precursor based on polyisoimide: dimensionally stable polyimide with a low dielectric constant

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Abstract

A positive-working photosensitive polyimide (PI) precursor based on fluorinated polyisoimide (FPII) and 2,3,4-tris(1-oxo-2-diazonaphthoquinone-5-sulfonyloxy)benzophenone (D5SB) as a photosensitive compound has been developed. FPII was prepared by ring-opening polyaddition of dianhydrides, pyromellitic dianhydride and biphenyltetracarboxylic dianhydride, with diamine, 2,2′-bis(trifluoromethyl)benzidine and followed by treatment with trifluoroacetic anhydride–triethylamine in *N*-methyl-2-pyrrolidinone. The FPII film showed a good solubility in a wide range of organic solvents. The dissolution behaviour of FPII containing 30 wt% of D5SB after exposure was studied and it was found that the difference of dissolution rate between the exposed and the unexposed parts was enough to get a positive pattern due to photochemical reaction of D5SB in the polymer film. The photosensitive fluorinated polyimide (FPI) precursor containing 30 wt% of D5SB showed a sensitivity of 250 mJ cm^{-2} and a contrast of 1.5 with 436 nm light, when it was developed with a mixture of 2.38% aqueous tetramethylammonium hydroxide solution and 2-propanol at room temperature. The FPI film cured up to 360°C had a low coefficient of thermal expansion of 10.8 ppm $°C^{-1}$ and a low dielectric constant of 2.89. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Polyisoimide; Highly dimensional stability; Photosensitive polyimide precursor

1. Introduction

Since the first research of photosensitive polyimide (PSPI) was reported by Rubner et al. in 1971 [1], PSPIs are attracting increasing attention in the microelectronic industry because they greatly simplify the complex, multistep processing required when conventional non-PSPIs are used in photolithographic processes.

Most of the negative-type PSPIs are prepared from poly(amic acid)s (PAAs), where cross-linking sites are introduced to amic acids through ester [1] and ammonium salt [2] linkages. On the other hand, the positive-type PSPIs consist of PAAs and *o*-diazonaphthoquinone (DNQ) [3] or 1,4-dihydropyridine [4] derivatives, polyimide (PI) containing hydroxyl groups and DNQ [5], and *o*-nitrobenzyl esters of PAAs [6]. The latter positive-type PSPIs are consistent with the trend of using aqueous base solutions as developers for the photoresist processing technology.

Recently, PIs with low dielectric constants and coefficients of thermal expansion (CTE) are required to increase circuit speed and minimize the stresses between the films and the substrates.

In the preceding paper [7], we reported the preparation and properties of polyisoimides (PIIs) as a highly dimensionally stable polyimide precursor with a low dielectric constant. The PIIs have a high solubility and are easily converted to the corresponding PIs by thermal treatment. Furthermore, migration of copper in the PI film is hardly observed during the thermal isomerization reaction. We also reported that the resist consisting of PII and DNQ acts as a positive-working alkaline-developable PSPI precursor [8]. These findings prompted us to develop a new PSPI with the lower dielectric constant and the higher dimensional stability based on a PII.

In this paper, we report the development of positive-working photosensitive alkaline-developable PI-precursor based on PII using DNQ as a photosensitive compound. The PII was converted to PI with the higher dimensional stability and the low dielectric constant by thermal treatment.

2. Experimental

2.1. Materials

N-Methyl-2-pyrrolidinone (NMP), *N*,*N*-dimethyl-

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acetamide (DMAc) and triethylamine (TEA) were purified by vacuum distillation. Pyromellitic dianhydride (PMDA), biphenyltetracarboxylic dianhydride (BPDA) were recrystallized from acetic anhydride. 2,2′-Bis(trifluoromethyl)benzidine (BTFB) was recrystallized from water–methanol. Trifluoroacetic anhydride was used without further purification. Other reagents and solvents were obtained commercially and used as received. The 2,3,4-tris(1-oxo-2-diazonaphthoquinone-5-sulfonyloxy) benzophenone (D5SB) used in this study was kindly donated by Toyo Gosei Kogyou Co. Ltd and was used without further purification.

2.2. Polymer synthesis

2.2.1. FPII from PMDA, BPDA and BTFB

PMDA (0.436 g, 2.0 mmol) and BPDA (0.588 g, 2.0 mmol) were added to a solution of BTFB (1.28 g, 4.0 mmol) in NMP (9.2 ml). This solution was stirred at room temperature for 48 h. Phthalic anhydride (0.07 g, 0.5 mmol) was then added to this solution. After stirring at room temperature for 6 h, the viscous solution was diluted with NMP (30.0 ml), and TEA (1.68 ml, 12.0 mmol) was added dropwise with stirring. The reaction mixture was cooled with an ice-water bath, and trifluoroacetic anhydride (2.52 ml, 18.0 mmol) was then added dropwise with stirring. The mixture was stirred at room temperature for 4 h and then poured into 2-propanol (800 ml). The precipitated polymer was filtered off and dried in vacuo at 80°C [yield = 2.16 g (99%)]. The inherent viscosity of the polymer in NMP was 0.42 dl g^{-1} at a concentration of 0.5 dl g^{-1} at 30°C. I.r. (KBr), ν (cm^{-1}): 1810 and 1700 (C=O) and 930 (C–O). Elemental analysis, calculated for $C_{54}H_{20}F_{12}N_4O_8 \cdot 1.2H_2O$:C, 58.68; H, 2.03; N, 5.08. Found: C, 58.77; H, 2.38; N, 5.23.

2.2.2. FPI from FPII and photosensitive compound

To the solution of the obtained FPII (2.0 g) in DMAc (8.0 ml) was added D5SB (0.6 g). Film cast on glass plate was heated on the hot-plate in the following steps: 100°C, 2 h; 150°C, 2 h; 200°C, 0.5 h; 250°C, 0.5 h; 300°C, 0.5 h; 360°C, 2 h.

2.3. Dissolution rate

FPII was dissolved in cyclohexanone at a concentration of 20 wt%, to which was added D5SB (10–30 wt%, of the total solid). Films spin-cast on silicone wafers, were prebaked at 80°C for 10 min, and then exposed to a filtered super-high-pressure mercury lamp SH-200 (Toshiba Lighting and Technology Corporation). Imagewise exposure was carried out in a contact mode. The exposed films were developed with the mixture of 2.38% aqueous tetramethylammonium hydroxide (TMAH) solution and 2-propanol in the ratio of 1:1 at room temperature.

2.4. Photosensitivity

The 3.5 μm thick FPII film on a silicone wafer was exposed at a wavelength of 436 nm to the filtered super-high-pressure mercury lamp, developed in the mixture of 2.38% aqueous TMAH solution and 2-propanol at room temperature and rinsed in water. The characteristic curve was obtained by a plot of normalized film thickness against exposure energy.

2.5. Measurements

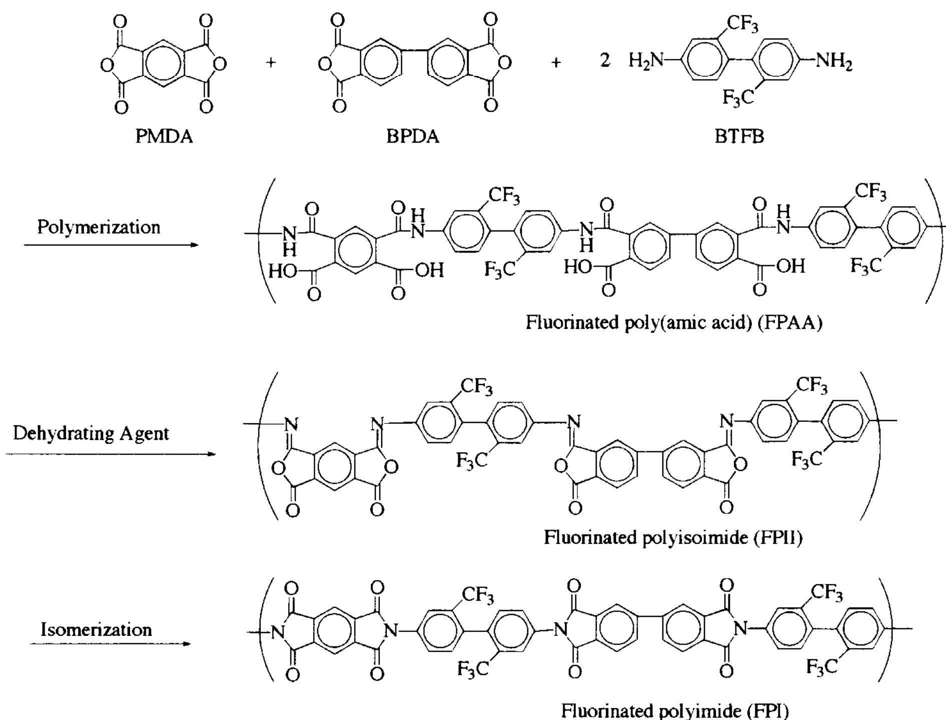
Fourier transform infrared absorption spectroscopy (*FT*i.r.) spectra were recorded on a Jasco *FT*i.r.-230 *FT*i.r. spectrophotometer under the following conditions: Spectral width 4000–400 cm^{-1}, 16 accumulations, resolution 16 cm^{-1}, signal processed by cosine apodization. Depending on their physical state, samples were recorded as a film, or potassium bromide pellet. Thermal analyses were performed on a Seiko SSS 5000-t.g.–d.t.a. 200 instrument at a heating rate of 10°C min^{-1} for thermogravimetric analysis (t.g.a.) and a Seiko SSS 5000 DSC 220 at a heating rate of 20°C min^{-1} for differential scanning calorimetry (d.s.c.) under nitrogen. Viscosity measurements were carried out by using an Ostwald viscometer at 30°C. The film thickness was measured by surface texture measuring instrument with Dektak 3030 system (Veeco Instrument Inc.) and Surfcom (Tokyo seimitsu). The CTEs were measured by the thermomechanical analysis (t.m.a.) with a Seiko SSS 560M at a heating rate of 10°C min^{-1}. The dielectric constants were measured by a Hewlett Packard 4284A Precision LCR meter at a frequency of 1 MHz and a temperature at 25°C. Specimens for samples were subjected to drying at 120°C for 30 min to eliminate absorbed water. Moisture sorption was determined by measuring film weight after exposure to 85°C–85%RH for 168 h. Scanning electron micrographs were obtained by field emission scanning electron microscope (Hitachi, S-4000 at 3 kV of accelerating voltage).

3. Results and discussion

3.1. Synthesis of fluorinated polyisoimide (FPII)

Based on the preceding work [7], the fluorinated polyisoimide (FPII) was prepared by copolymerization of a rigid dianhydride and a flexible dianhydride, such as pyromellitic dianhydride (PMDA) and biphenyltetracarboxylic dianhydride (BPDA), in the molar ratio of 1:1 with a rigid diamine, 2,2′-bis(trifluoromethyl)benzidine (BTFB), and followed by treatment with trifluoroacetic anhydride–triethylamine in NMP (Scheme 1). The polymer was produced in excellent yield with an inherent viscosity of 0.42 dl g^{-1}.

This polymer was identified as the expected FPII by *FT*i.r. and elemental analysis. The i.r. spectrum showed characteristic absorptions at 1700 and 1810 cm^{-1} due to isoimide



Scheme 1. Synthesis of fluorinated polyimide (FPI).

carbonyl group. The elemental analysis also supported the formation of the expected polymer. The polymer was a yellow powder and a transparent flexible film was cast from the polymer solution. Table 1 summarized the results of qualitative solubility of FPII and the corresponding fluorinated polyimide (FPI). FPII was soluble in acetone, THF, cyclohexanone and aprotic solvents, such as DMAc and NMP. However, FPI was insoluble in almost all organic solvents.

Table 1
Solubilities of FPII and FPI

Solvent	Solubility	
	FPII	FPI
Acetone	±	–
Methanol	±	–
2-Propanol	–	–
Acetonitrile	–	–
Dioxane	+	–
Cyclohexanone	+	–
2-Butanone	+	–
m-Cresol	+	–
2-Methoxyethanol	+	–
THF	+	–
DMF	+	–
DMAc	+	–
DMSO	+	–
NMP	+	–
H_2SO_4	+	±

Key: +, soluble at room temperature; ±, partially soluble or swelling; and –, insoluble

3.2. Lithographic evaluation

The selection of a photosensitive compound is very important for the accomplishment of a good pattern image. Fig. 1 shows the u.v. visible spectrum of the 2 μm thick FPII, which has a transmittance about 90% at 436 nm. Therefore, DNQ derivative 2,3,4-tris(1-oxo-2-diazonaphthoquinone-5-sulfonyloxy)benzophenone (D5SB), having a strong absorption in the range 320–450 nm, was selected as the photosensitive compound.

Fig. 2 shows changes in the u.v. visible spectra of the FPII film containing 30 wt% of D5SB upon 436 nm u.v. (g-line) irradiation. The intensity of characteristic absorption band in the range of about 400–450 nm gradually decreased, and this absorption band disappeared completely when 400 mJ cm^{-2} of g-line was irradiated. Therefore, the resist consisting of FPII and D5SB as a matrix and a photoactive compound would be expected to work as the g-line sensitive PSPI system.

The solubility of the exposed part (436 nm) for the PSPI resist toward an aqueous base solution was investigated. This film, however, did not dissolve in 2.38%–10% aqueous TMAH solutions. Then, a mixed developer of 2.38% aqueous TMAH solution and 2-propanol (IPA) was employed. The effect of IPA content on the dissolution rate between the exposed (450 mJ cm^{-2}) and unexposed films at 25°C and 45°C was studied and the results are shown in Figs 3 and 4, respectively. The dissolution rate was estimated by measuring the film thickness after development. Both the dissolution rates of the exposed part and the dissolution rate

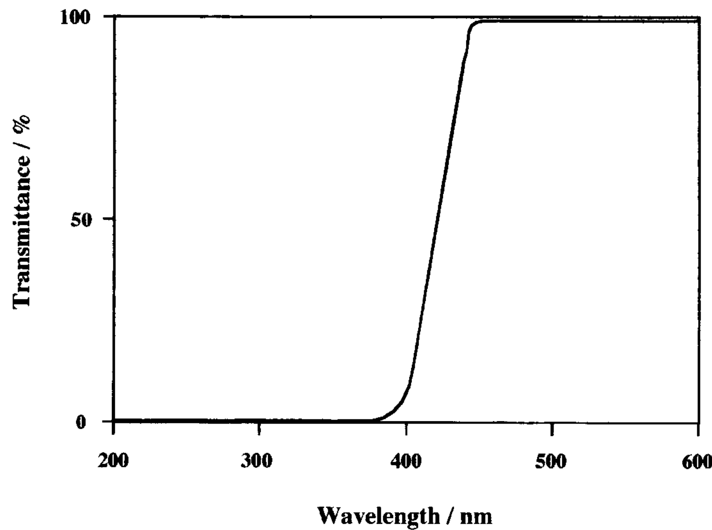


Fig. 1. U.v. visible spectrum of the FPII film.

difference between the exposed and unexposed parts increased with increasing the IPA content at both temperatures. Since the loss of film thickness was lower at 25°C compared with that at 45°C, it was decided to perform development at 25°C.

The contents of DNQ influence to therdissolution rate of exposed and unexposed parts as a dissolution promoter and an inhibitor, respectively. Then, the influence of D5SB content on the dissolution rate in the mixed developer of 2.38% TMAH and IPA (vol%, 1:1) solution after exposure (450 mJ cm^{-2}) was studied (Fig. 5). In the exposed part, the dissolution rate increased with increasing D5SB contents. On the other hand, the solubility of unexposed part was almost unchanged. These results indicate that D5SB acts as a dissolution promoter in the exposed part, but it does not act as a dissolution inhibitor probably because of a high hydrophobicity of FPII in the unexposed part. 30 wt% loading of D5SB is necessary to achieve a good dissolution contrast.

Fig. 6 shows the relationship between the prebake

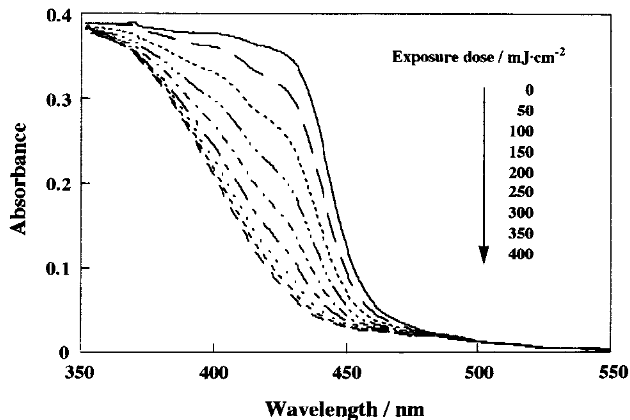


Fig. 2. U.v. visible spectra of FPII film containing 30 wt% of D5SB after exposure to the u.v. light.

temperature (PB) and the dissolution rate of FPII containing 30 wt% of D5SB. The exposed (450 mJ cm^{-1}) film dissolved faster than the corresponding unexposed film, and the its dissolution rate toward to the developer gradually decreased with increasing the PB temperature. This behaviour is explained by the decrease of the residual solvent. On the other hand, the dissolution rate of unexposed part was constant probably because the slow dissolution rate due to high hydrophobic property of matrix and D5SB made unclear the effect of residual solvent on the dissolution rate.

At 120°C, the dissolution rate of both areas was drastically decreased due to partially imidization and decomposition of D5SB. Moss et al. reported the thermal degradation of DNQs in a PAA matrix; the half-life of the decomposition is 8 min at 130°C and an insoluble film is produced due to crosslinking [9]. It is assumed that the same thermal degradation occurred in the FPII matrix. Therefore, PB temperature was decided below partially imidization temperature of FPII and degradation temperature of D5SB.

The dissolution mechanism of FPII film in the TMAH-IPA developer is considered as follows. Although the FPII matrix is insoluble in the developer, PII is susceptible to hydrolysis, giving alkaline-soluble PAA. In the exposed part, the hydrolysis of FPII occurs by the action of TMAH solution because the developer can penetrate easily into FPII film due to the existence of carboxylic acids produced by photochemical transformation of D5SB.

After preliminary optical optimization studies involving D5SB loading, prebaking temperature and concentration of developer, we prepared a PSPI precursor system consisting of FPII and 30 wt% of D5SB. The sensitivity curve for a 3.5 μm thick PII film shown in Fig. 7 was consistent with the dissolution behaviour studied above, indicating that the sensitivity (D^0) and contrast (γ^0) were 250 mJ cm^{-2} and 1.5, with 436 nm light, respectively.

Fig. 8 showed a scanning electron micrograph of the contact-printed image after exposure of 450 mJ cm^{-2}. This

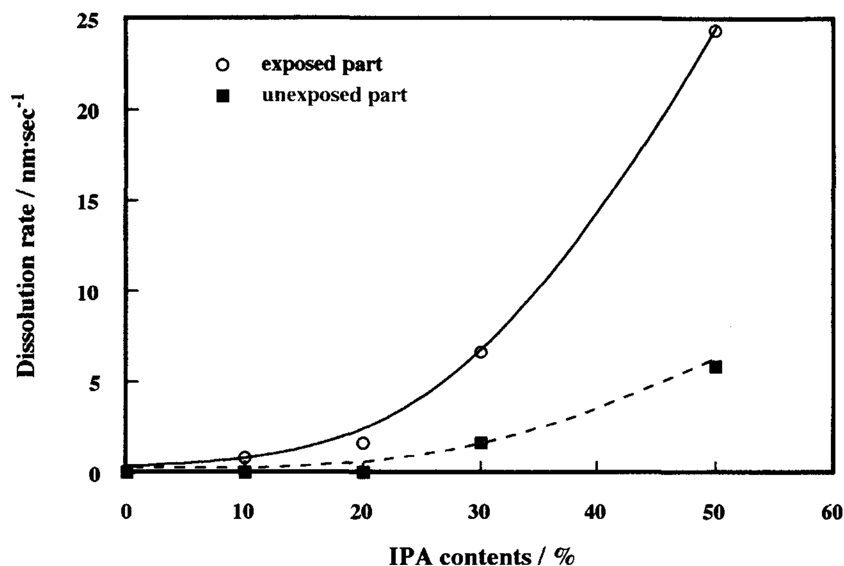


Fig. 3. Effect of 2-propanol content at 25°C on the dissolution rate of FPII film containing 30 wt% of D5SB.

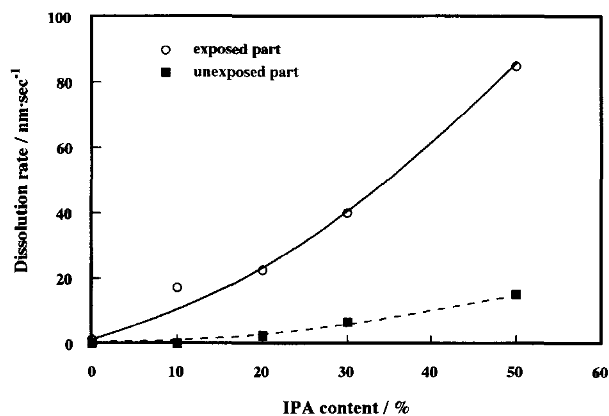


Fig. 4. Effect of 2-propanol content at 45°C on the dissolution rate of FPII film containing 30 wt% of D5SB.

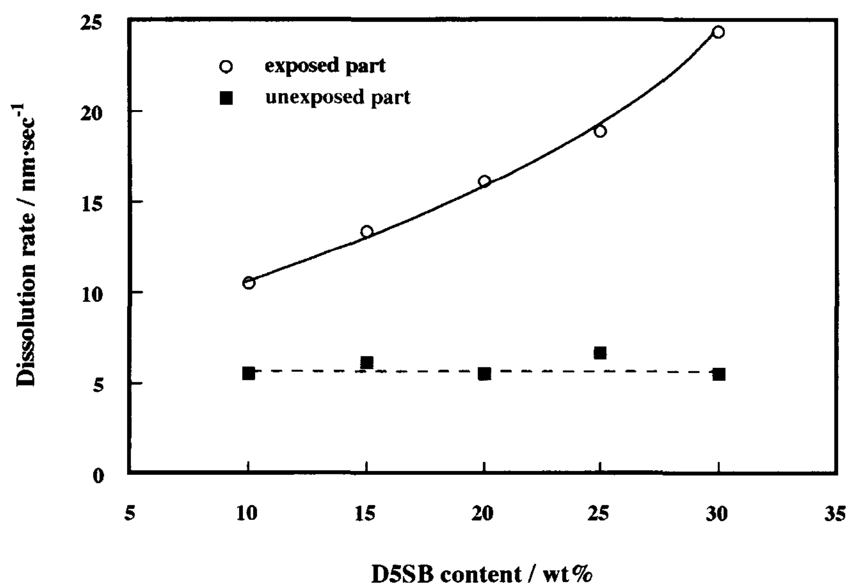


Fig. 5. Effect of D5SB content of the FPII film on the dissolution rate.

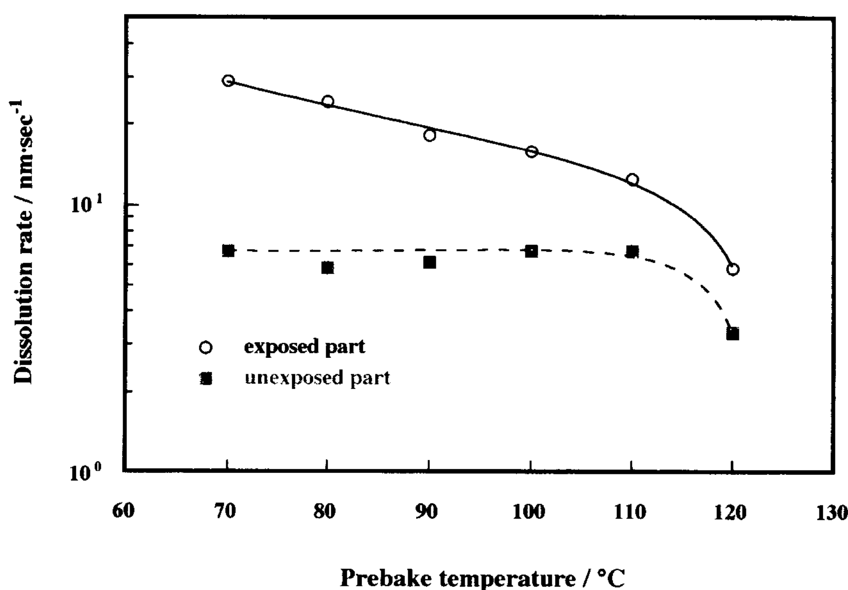


Fig. 6. Effect of prebake temperature on the dissolution rate of FPII film containing 30 wt% of D5SB.

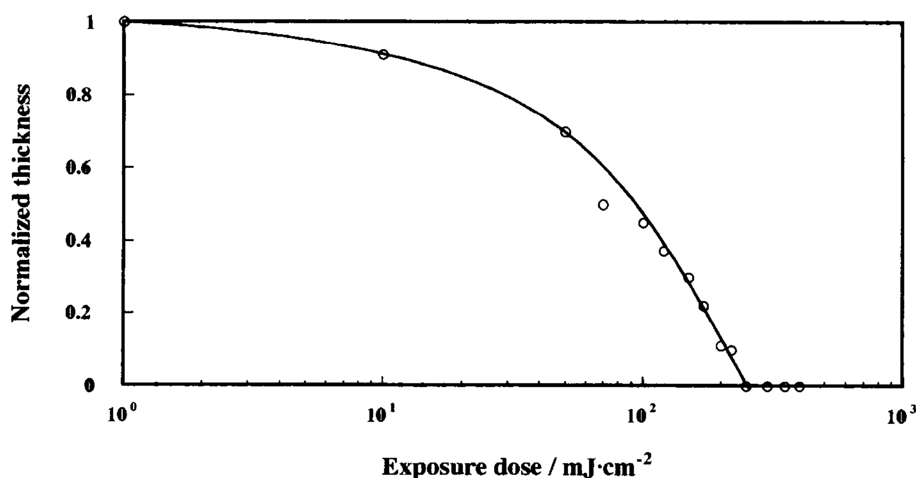


Fig. 7. Characteristic exposure curve for the FPII–D5SB system.

resist is capable of resolving 3 μm feature when 10 μm thick film is used. Further, this positive image in the FPII film was converted to the positive image in the FPI film by high temperature treatment (curing steps; 150°C, 0.5 h; 200°C, 2 h; 250°C, 0.5 h; 300°C, 0.5 h; and 360°C, 2 h) without any deformation (Fig. 9).

3.3. Physical properties of polymer films

Table 2 showed comparison of physical properties between two kinds of PI films, FPI-1 and FPI-2 prepared by thermal treatment of FPII and FPII containing 30 wt% of D5SB, respectively. The coefficient of thermal expansion (CTE) of FPI-2 showed a little larger value compared to that of FPI-1, but was still low value. Dielectric constant at 1 MHz and moisture sorption of FPI-2 were small and almost same as those of FPI-1.

Fig. 10 shows t.g.–d.t.a. curves of films after development with the mixed developer at 25°C (dashed line) and curing in the following steps: 150°C, 0.5 h; 200°C, 0.5 h; 250°C, 0.5 h; 300°C, 0.5 h; 360°C, 1 h (solid line). The dashed line exhibited slopes with three steps being evidence. The first weight loss in the range of 100°C–200°C was attributed to vapourization of primary D5SB degraded products, residual solvents and water produced by thermal imidization. The second weight loss continued up to at around 350°C due to the degradation of non-vapourized residual of primary degraded D5SB. The decomposition of polyimide occurred at a temperature higher than 500°C. On the other hand, the solid line shows no weight loss below 400°C and the 10% weight loss temperature was 565°C. These results indicate that D5SB as the photosensitive compound can be removed by high-temperature treatment after the development process, and that physical and thermal properties of the resulting FPI have not damaged such as degradation at low temperature by the addition of D5SB.

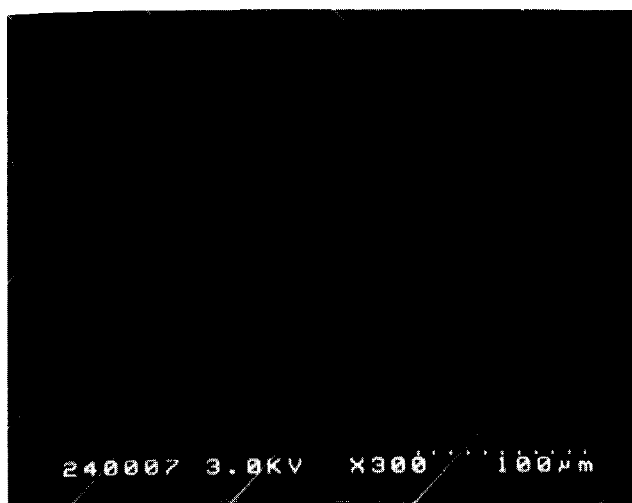


Fig. 8. Scanning electron micrograph of positive pattern printed in the FPII film containing D5SB (after development).

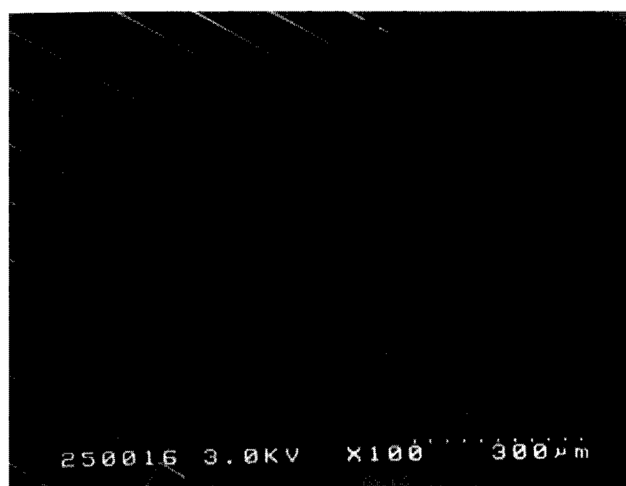


Fig. 9. Scanning electron micrograph of positive pattern heated up to 360°C.

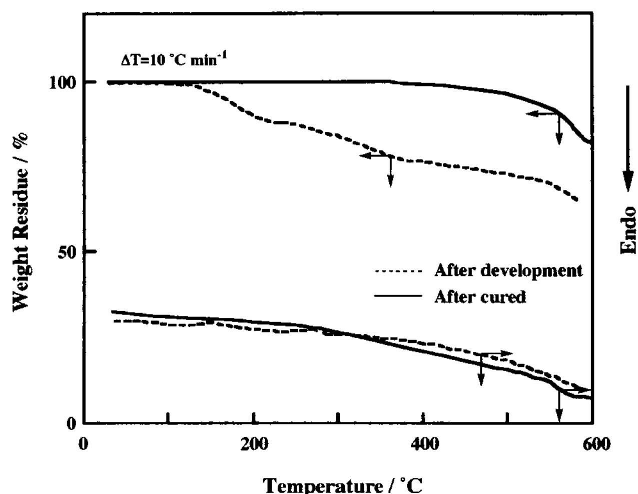


Fig. 10. T.g.–d.t.a. curves of FPII and FPI films in nitrogen.

Table 2
Physical properties of PIs

Polymer	CTE (ppm °C^{-1})[a]	Dielectric constant[b]	Moisture sorption[c] (%)	TG[d] (°C)
FPI-1[e]	7.8	2.98	0.9	580
FP1-2[f]	10.8	2.89	0.8	565

[a]Measured by thermomechanical analysis at a heating rate of 10°C min^{-1}
[b]Taken at 1 MHz at 25°C
[c]Determined by measuring film weight after exposure to 85°C–85%RH for 168 h
[d]Temperature at 10% weight loss recorded with t.g. at heating rate of 10°C min^{-1} in nitrogen
[e]Polyimide made by thermal cure of PII
[f]Polyimide made by thermal cure of PII containing 30 wt% of D5SB

4. Conclusions

A fluorinated polyisoimide (FPII) was synthesized from PMDA and BPDA and BTFB, followed by treatment with trifluoroacetic anhydride–triethylamine. FPII containing 30 wt% of D5SB was found to be a positive-type photosensitive polyimide precursor, in which D5SB acts as the dissolution promoter. This resist system could be developed with the mixture of aqueous alkaline solution and IPA. Its sensitivity and contrast were 250 mJ cm^{-2} and 1.5, respectively, when using 436 nm light. The PSPI film after development and curing had the low CTE, dielectric constant and moisture sorption, and these physical properties were almost same as those of the original PI.

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