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Positive-working alkaline-developable photosensitive polyimide precursor based on polyisoimide using diazonaphthoquinone as a dissolution inhibitor

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A positive-working photosensitive polyimide precursor based on polyisoimide (PII) and 2,3,4-tris(1-oxo-2-diazonaphthoquinone-4-sulfonyloxy) benzophenone (D4SB) as a photoreactive compound has been developed. The polyisoimide was prepared by the ring-opening polyaddition reaction of 4,4′-hexafluoroisopropylidenebis(phthalic anhydride) (6FDA) and 3,3′-diaminodiphenylsulfone (3,3′-DDS), followed by treatment with trifluoroacetic anhydride–triethylamine in *N*-methyl-2-pyrrolidone (NMP). The polyisoimide film showed excellent transparency to u.v. light, and good solubility in a wide range of organic solvents. The dissolution behaviour of the polyisoimide film containing 20 wt% of D4SB after exposure and post-exposure bake (PEB) has been studied and it has been found that the dissolution rate of an exposed area was ~80 times faster than that of an unexposed area, due to the photochemical reaction of D4SB in the polymer film. The photosensitive polyimide precursor containing 20 wt% of D4SB showed a sensitivity of 250 mJ cm^{-2} and a contrast of 2.4 with 435 nm light, when it was post-baked at 150°C for 10 min, followed by developing with 5% tetramethylammonium hydroxide solution at 45°C.

(Keywords: polyisoimide; polyimide precursor; dissolution behaviour)

INTRODUCTION

For applications in the microelectronics industry, aromatic polyimides are useful polymers because of their good thermal stabilities, relatively low dielectric constants and excellent mechanical properties. In recent years, there has been an increased interest in polyimide dielectrics that can be imaged by u.v. lithographic techniques. A photosensitive polyimide simplifies processing and does not need a photoresist to be used in the microlithography stage, nor a toxic etchant such as hydrazine. Most photosensitive polyimides are prepared from poly(amic acid)s (polyimide precursors), in which crosslinking sites are introduced into the amic acids through ester[1] and acid–amine ion linkages[2]. In these cases, organic solvents are usually necessary in the development process.

Recently, positive photosensitive polyimides which can be developed using aqueous base solutions have been attracting great interest. Omote and Yamaoka reported that nifedipine (1,4-dihydro-2,6-dimethyl-4-(nitrophenyl)-3,5-pyridinedicarboxylic acid dimethylester) acts as a dissolution inhibitor in poly(amic acid) after a post-exposure bake (PEB)[3]. This system is positive-working and developable with tetramethylammonium hydroxide (TMAH) aqueous solution and exhibits a good sensitivity and contrast.

On the other hand, diazonaphthoquinone (NQD) is a typical photoreactive compound for the formation of positive photoresists. Upon exposure to u.v. light, NQD is converted to indene carboxylic acid, which is extremely soluble in aqueous base solutions by virtue of the carboxylic acid functionality. Several groups[4–6] have reported the preparation of resists consisting of poly(amic acid)s and NQD. However, the dissolution rates of the poly(amic acid)s are essentially too high to get a sufficient dissolution contrast. Therefore, the dissolution rates of the poly(amic acid)s have to be reduced either by prebaking, or by a post-exposure bake.

We have been interested in polyisoimide as a polyimide precursor[7]. Polyisoimide has excellent solubility when compared to that of the corresponding polyimide and is easily converted to polyimide without elimination of any volatile compounds. This finding prompted us to employ a new approach for the development of a positive photosensitive polyimide precursor. This article

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describes the preparation and properties of a positive-working photosensitive polyimide precursor, consisting of polyisoimide and NQD as the polymer matrix and photosensitive compound, respectively.

EXPERIMENTAL

Materials

Cyclohexanone, *N*-methyl-2-pyrrolidone (NMP), and triethylamine (TEA) were purified by vacuum distillation. 4,4′-Hexafluoroisopropylidenebis(phthalic anhydride) (6FDA) was obtained from American Hoechst Co. Other reagents and solvents were obtained commercially and were used as received. The 2,3,4-tris(1-oxo-2-diazonaphthoquinone-4-sulfonyloxy) benzophenone (D4SB) used in this study was kindly donated by Toyo Gosei Kogyou Co., Ltd and was used without further purification.

Synthesis of polyisoimide (PII)

A solution of 3,3′-diaminodiphenylsulfone (3,3′-DDS) (1.24 g, 5.0 mmol) in NMP (10.0 ml) was cooled with an ice–water bath. To this solution was added, with stirring, 6FDA (2.22 g, 5.0 mmol). The mixture was stirred at room temperature for 6 h. The resulting viscous solution was then diluted with NMP (32.0 ml), and TEA (1.4 ml, 10.0 mmol) was added dropwise with stirring. The reaction mixture was cooled with an ice–water bath, and trifluoroacetic anhydride (2.1 ml, 15.0 mmol) was added dropwise with stirring. The mixture was stirred at room temperature for 4 h and then poured into 2-propanol (800 ml). The polymer that precipitated was filtered off and dried *in vacuo* at 40°C (yield = 3.34 g (96%)). The intrinsic viscosity of the polymer in *N*,*N*-dimethyl acetamide (DMAc) was 0.40 dl g^{-1}, at a concentration of 0.5 g dl^{-1} at 30°C. I.r. (KBr), ν (cm^{-1}): 1810 (C=O) and 925 cm^{-1} (C–O). Elemental analysis, calculated for $C_{31}H_{14}F_6N_2O_6S$: C, 56.72; H, 2.15; N, 4.27. Found: C, 56.20; H, 2.51; N, 4.31.

Dissolution rate

PII was dissolved in cyclohexanone at a concentration of 20 wt%, to which was added D4SB (5–30 wt% of the total solid). Films, spin-cast on NaCl plates or Si wafers, were prebaked at 60°C for 10 min, and then exposed to a filtered super-high-pressure mercury lamp (Toshiba Lighting and Technology Corporation; Model SH-200). Imagewise exposure was carried out in a contact mode. The exposed films were post-baked at 80–170°C for 10 min, and were then subjected to i.r. spectroscopic measurement, or were developed with 5% tetramethylammonium hydroxide (TMAH) aqueous solution at 45°C.

Photosensitivity

The 5 μm PII films on silicone wafers were exposed to the filtered super-high-pressure mercury lamp at wavelengths of 365 and 436 nm, developed in 5% TMAH aqueous solution at 45°C, and rinsed in water and 2-propanol. The characteristic exposure curve was obtained by plotting the normalized film thickness against exposure energy.

Measurements

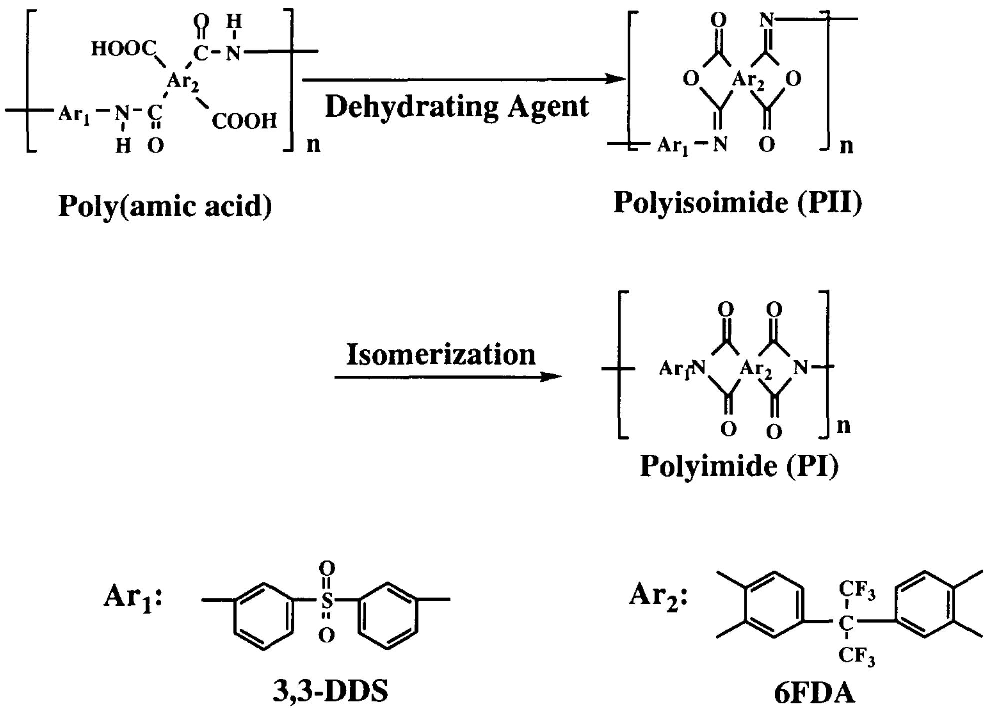
The infra-red spectra were recorded on a Hitachi I-5020 FT-IR spectrophotometer. Viscosity measurements were carried out by using an Ostwald viscometer at 30°C. Thermal analyses were performed on a Seiko SSS 5000-TG/DTA 200 instrument at a heating rate of 10°C min^{-1} for thermogravimetric analysis (t.g.a.) and on a Seiko SSS 5000-DSC220 at a heating rate of 10°C min^{-1} for differential scanning calorimetry (d.s.c.) under nitrogen. Molecular weights were determined by gel permeation chromatography (g.p.c.) with polystyrene standards, by using a JASCO HPLC system equipped with a Shodex KD-80M column at 40°C in DMF. The film thickness was measured by a Dektak 3030 system (Veeco Instruments Inc.).

RESULTS AND DISCUSSION

Synthesis of polyisoimide (PII)

Viable polyisoimide as a candidate precursor for photosensitive polyimides must possess excellent solubility and good transmission in the u.v. region, as well as good film properties. However, polyisoimides generally exhibit lower optical transparencies than the corresponding polyimides, and have intense yellow colours. Therefore, it is very important to design a matrix polymer having high optical transparency. Less coloured polyimides can be prepared by modifying the molecular structures. In particular, diamines containing sulfone groups are effective in preparing transparent polyimides because they hinder the charge transfer interaction between the colour-causing centres by reducing the electron density of the amine[8–11]. In addition, the 3,3′-linkage prevents conjugation between the aromatic moieties. On the other hand, introducing a fluoroalkyl group into the main polymer chain is considered to be a more versatile technique, both from the point of view of transparency and solubility of the resulting polyimide.

Therefore, we chose the polyisoimide (PII) derived from 4,4′-hexafluoroisopropylidenebis(phthalic anhydride) (6FDA) and 3,3′-diaminodiphenylsulfone (3,3′-DDS) as a candidate for the polymer matrix. The polyisoimide was prepared by the ring-opening polyaddition of 6FDA and 3,3′-DDS, followed by treatment with trifluoroacetic anhydride–TEA in NMP (*Scheme 1*). This polymer was identified as the required PII by means of infra-red spectroscopy and elemental analysis. The i.r. spectra showed a characteristic absorption at 1810 cm^{-1} due to the isoimide carbonyl group. Imide contents as determined by i.r. spectroscopy were less than 5%. Elemental analysis also supported the formation of the expected polymer. The molecular weight of the polymer having an intrinsic viscosity of 0.40 dl g^{-1} was determined by g.p.c. The g.p.c. trace was unimodal with a polydispersity of 2.0, and indicated that the relative $\bar{M}_n$ and $\bar{M}_w$ values were 72 000 and 149 000, respectively, based on polystyrene standards. The polymer was obtained in the form of a white powder and a transparent flexible film was produced by casting the polymer solution. *Table 1* shows (qualitative) solubility results both for PII and the corresponding polyimide (PI). For comparison, the latter was prepared by chemical cyclization of poly(amic acid), using an acetic anhydride–



Scheme 1

Table 1 Solubility of polyisoimide (PII) and polyimide (PI)

Solvent	Solubility	
	PII	PI
Acetone	+ +	+
Methyl ethyl ketone	+ +	±
Cyclohexanone	+ +	−
Isoamyl acetate	±	−
Dioxane	+ +	−
Chloroform	+ +	±
1,2-Dichloroethane	+ +	+
1,1,2,2-Tetrachloroethane	+ +	−
N,N-Dimethyl formamide	+ +	±
N,N-Dimethyl acetamide	+ +	+ +
Methanol	−	−
2-Propanol	−	−
2-Methoxy ethanol	−	−

+ +, soluble at room temperature; +, soluble by heating; ±, partially soluble or swelling; −, insoluble

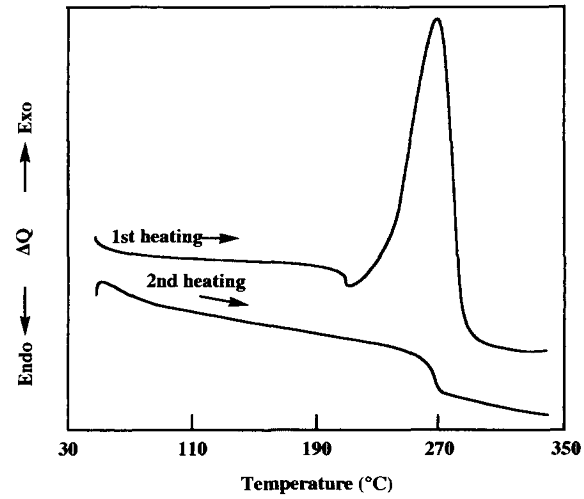


Figure 1 D.s.c. curves of polyisoimide in nitrogen

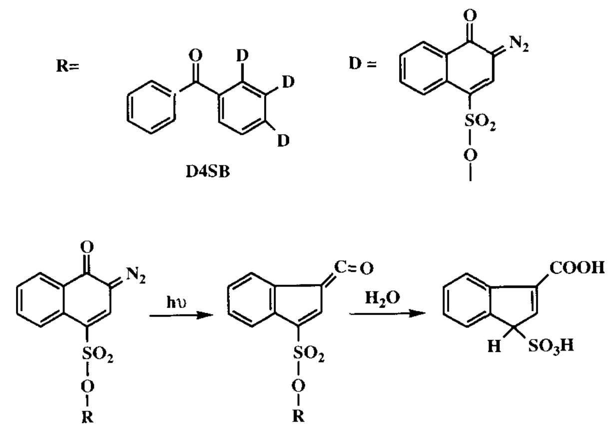
pyridine dehydrating agent. The polyisoimide exhibited excellent solubility toward various solvents when compared to that observed for the corresponding polyimide.

Thermal properties of PII

Differential scanning calorimetry (d.s.c.) measurements were made on the PII powder and the results are shown in *Figure 1*. The PII exhibited an endotherm at 203°C and a large exothermic peak at around 260°C in the first heating cycle. In the second heating cycle, these peaks were not observed and a new endothermic peak appeared at 258°C. The i.r. spectrum after the first heating showed strong imide carbonyl absorptions at 1780 and 1725 cm^{-1}. Based on these data, the first endotherm at 203°C and the large exothermic peak at around 260°C, which were observed in the first heating cycle, are assigned to the glass transition temperature (T_g) and the thermal isomerization temperature of the PII, respectively. Moreover, the endothermic peak observed at 258°C in the second heating cycle represents the T_g of the corresponding PI which had been isomerized from the PII. The thermal stability of the PII was examined by thermogravimetric analysis (t.g.a.), showing a 10% weight loss at 520°C in nitrogen (*Figure 2*). Furthermore, no weight loss was observed at around 260°C.

Lithographic evaluation

The selection of a photoreactive compound is very important for the accomplishment of a good pattern image when using an aqueous base developer. A typical positive photoresist consists of a novolac resin with an NQD photoreactive compound as a dissolution inhibitor. Upon irradiation, the NQD undergoes a Wolff



Scheme 2

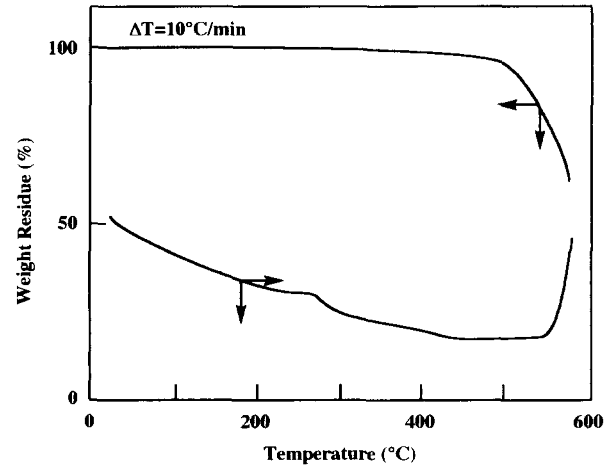


Figure 2 T.g.a. curve of polyisoimide in nitrogen

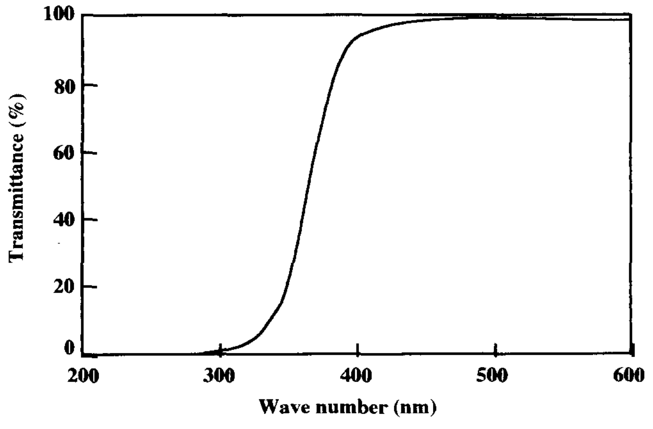


Figure 3 U.v.-visible spectrum of polyisoimide

rearrangement, followed by hydrolysis, to generate a base-soluble indene carboxylic acid. Furthermore, the diazonaphthoquinone sulfates also yield sulfonic acids by u.v. irradiation. These significant polarity changes would be expected to generate a large solubility-difference for the aqueous base developer. Thus, we have chosen 2,3,4-tris(1-oxo-2-diazonaphthoquinone-4-sulfonyloxy) benzophenone (D4SB) (*Scheme 2*) as our photoreactive material. The u.v.-visible spectrum of a 1 μm thick film of the PII (*Figure 3*) indicates that the film is transparent in the region around 360 nm. The transmittance of the PII film at 436 nm was more than 95%. *Figure 4* shows changes in the u.v.-visible spectrum of D4SB in THF and the change upon u.v. irradiation. The intensity of the absorption band at 375 nm was decreased rapidly as a result of the irradiation. Therefore, the resist consisting of PII and D4SB as a matrix and photoreactive compound would be expected to show the high sensitivity toward g-line.

In order to investigate the dissolution behaviour of an exposed (500 mJ cm^{-2}) and an unexposed area, the effect of the D4SB loading on the dissolution rate in a developer after PEB (at 150°C for 10 min) was studied and the results are shown in *Figure 5*. The dissolution rate was estimated by measuring the film thickness after development; this was performed at 45°C by using 5% TMAH solution as a developer. The dissolution rate of the exposed part clearly increased with increasing D4SB contents, and the exposed film dissolved faster than the unexposed film at all D4SB content levels. Furthermore, the dissolution rates of the unexposed films for each D4SB content level were almost identical. This result indicates that for D4SB to act as a dissolution promoter in PII film then 20 wt% of D4SB was necessary in order to achieve a good dissolution contrast.

Figure 6 shows the relationship between the post-exposure bake (PEB) temperature and the dissolution rate of PII containing 20 wt% of D4SB. The exposed (500 mJ cm^{-2}) film containing 20 wt% of D4SB dissolved

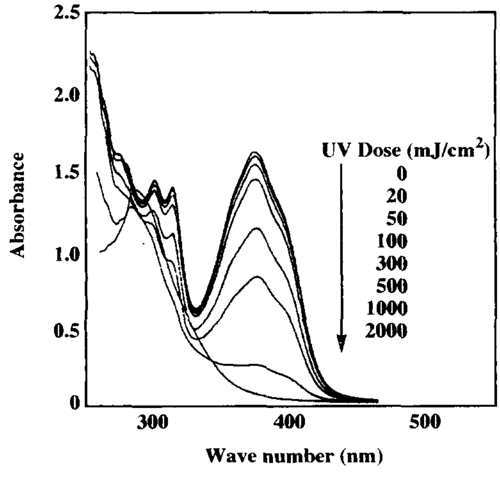


Figure 4 U.v.-visible spectra of D4SB

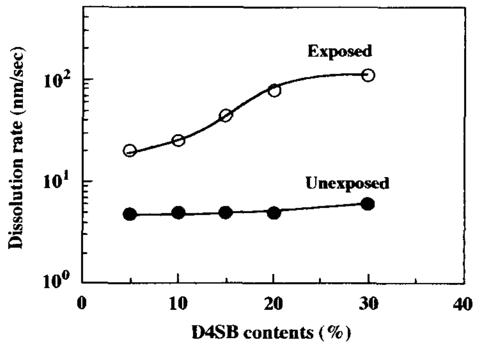


Figure 5 Relationship between dissolution rate and D4SB content of the polyisoimide film

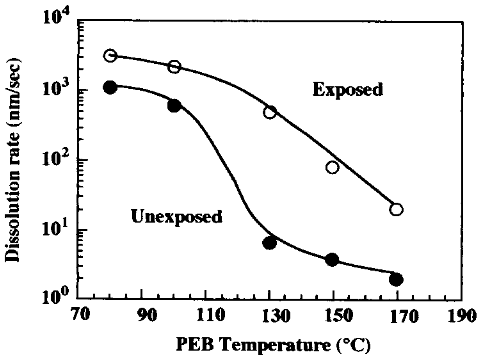


Figure 6 Relationship between the PEB temperature and dissolution rate of a polyisoimide containing 20 wt% D4SB

faster than the corresponding unexposed film at all PEB temperatures examined. In the low-PEB-temperature regions, the dissolution rates of both the exposed and unexposed areas were too fast to achieve good patterns. However, at PEB temperatures over 130°C, the dissolution contrasts between the exposed and unexposed parts were enough to obtain a good pattern image. Moss *et al.*[5] reported the thermal degradation of NQDs in a poly(amic acid) matrix; the half-life of the decomposition is 8 min at 130°C and 89 s at 150°C, and an insoluble film is produced due to crosslinking. In our case, the dissolution rates of the unexposed part were drastically reduced above the PEB temperature of 130°C, whereas the dissolution rates of the exposed part were gradually decreased with increasing PEB temperature. These results indicate that D4SB might be decomposed at higher PEB temperatures, thus resulting in the formation of an insoluble film.

The most widely used positive resists are generally two-component materials, consisting of an alkaline-soluble matrix resin that is rendered insoluble in aqueous alkaline solutions through the addition of hydrophobic radiation-sensitive materials. In our case, although the PII matrix is insoluble in aqueous alkaline solutions, the polyisoimide is susceptible to hydrolysis, giving alkaline-soluble poly(amic acid). In the exposed areas, the hydrolysis of PII might occur by the action of aqueous alkaline because the developer can penetrate easily into the PII film due to the existence of hydrophilic groups such as hydroxyl, carboxylic acid or sulfonic acid, which have diffused sufficiently into the exposed area during the PEB process. Therefore, this dissolution-accelerating behaviour in an exposed film was considered to result from the polarity change of PII due to the photochemical reaction of the D4SB and the hydrolysis of PII in the development process.

After a preliminary optimization study involving D4SB loading, post-baking temperature, and developing temperature, we prepared a photosensitive polyimide precursor system consisting of PII and 20 wt% of D4SB. The sensitivity curve for a 5 μm thick PII film shown in *Figure 7* was consistent with the dissolution behaviour studied above, indicating that the sensitivity (D^0) and contrast (γ^0) were 300 mJ cm^{-2} and 4.5, with 365 nm light, respectively, after PEB treatment at 150°C for 10 min. Furthermore, with 436 nm light the values of D^0 and γ^0 were 250 mJ cm^{-2} and 2.4, respectively. *Figure 8* shows the scanning electron micrograph of a positive-image projection 'printed' from PII by post-baking at 150°C for 10 min after exposure of the film to 400 mJ cm^{-2}. This resist is capable of resolving a 2.5 μm feature when 5 μm thick films are used.

Thermal stability of polymer films

Figure 9 shows t.g.a. curves of films after development with 5% TMAH solution at 45°C (dashed line), and after curing at 400°C for 30 min (solid line). The former curves (dashed lines) exhibited slopes with two steps being evident. The first weight loss starts at around 150°C, indicating that both vaporization of residual solvent and degradation of the D4SB begins at this temperature.

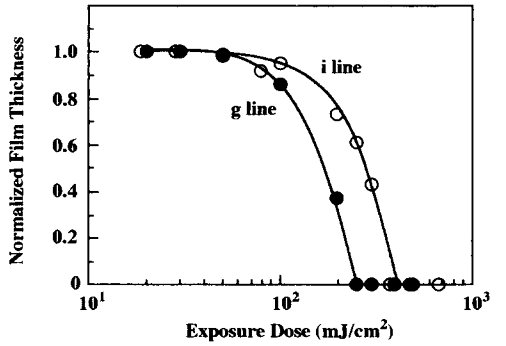


Figure 7 Characteristic exposure curves for the PII/D4SB system

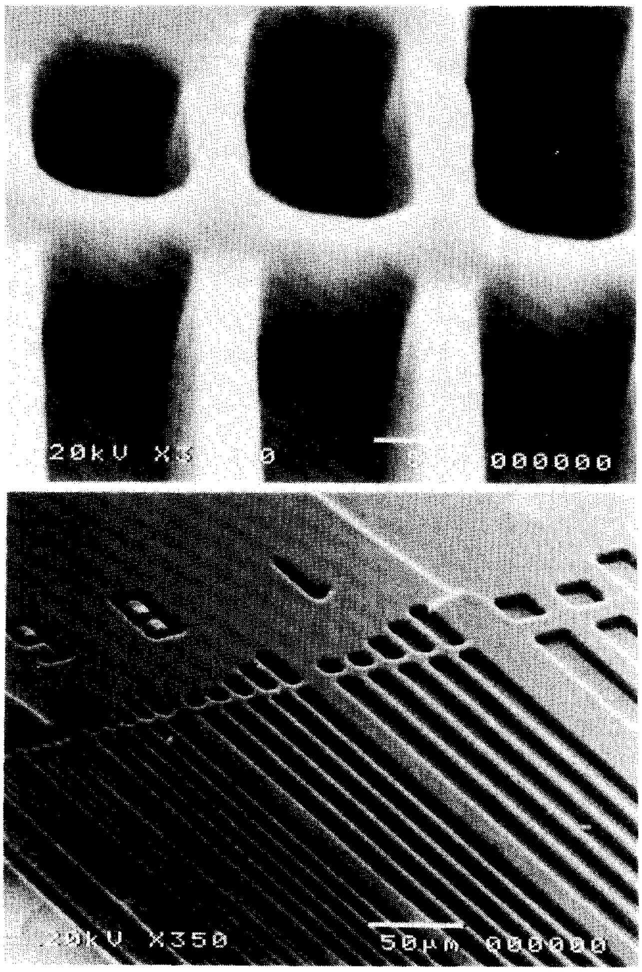


Figure 8 Scanning electron micrograph of a pattern printed from polyisoimide containing D4SB, after development with 5% TMAH solution

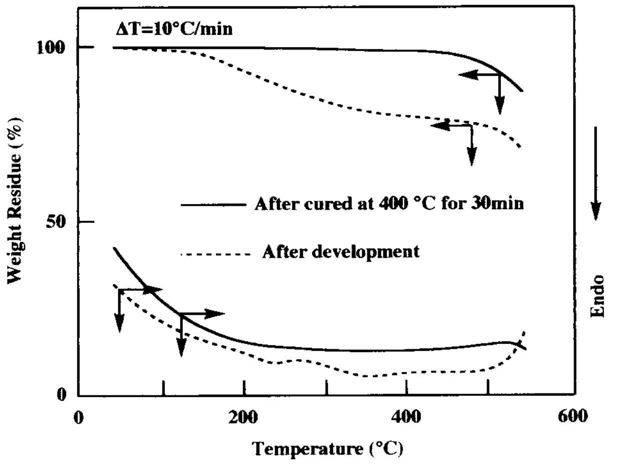


Figure 9 T.g.a. curves of polyisoimide films in nitrogen

The weight loss continues up to 350°C, while the decomposition of the polyimide occurs at temperature higher than 500°C. On the other hand, the solid line shows no weight loss below 450°C, with the 10% weight loss temperature being 510°C. These results indicate that D4SB as the photoreactive compound can be removed by high-temperature treatment after the development process, and that the thermal properties of the resulting polyimide were not damaged by the addition of D4SB.

CONCLUSIONS

A polyisoimide (PII) with high optical transparency above 300 nm was synthesized from 4,4′-hexafluoroisopropylidenebis(phthalic anhydride) (6FDA) and 3,3′-diaminodiphenylsulfone (3,3′-DDS). The PII containing 20 wt% of D4SB was found to be a positive-type photosensitive polyimide precursor, in which D4SB acts as the dissolution controller. This resist system is capable of being developed with aqueous alkaline solution. The sensitivity and contrast of the PI with D4SB were 250 mJ cm^{-2} and 2.4, respectively, when using 436 nm light. The thermal stability after development is almost the same as that of the neat polyisoimide resin. The excellent solubilities of the PIIs, compared to those of the corresponding PIs, is particularly advantageous in potential applications of such polymer matrices.

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