Positive Photosensitive Polyimides Using Polyamic Acid Esters with Phenol Moieties

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SYNOPSIS

Polyimide resists developable with basic aqueous solutions were realized by polyamic acid esters with phenol moieties (PPh's) and naphthoquinone diazides. The polyimide precursors (PPh's) were synthesized from diamines and dicarboxylic acids that have phenol moieties through ester linkage. A selective reaction of alcohol groups with acid dianhydride groups made the synthesis of the PPh's possible, even if the phenol groups were in the reaction mixtures. The PPh's were soluble in basic aqueous developer, but their dissolution rates were too low for use as resists. To increase the resist dissolution rate, polyamic acids were added to the PPh's. By adjusting the dissolution rates in basic aqueous developers, fine patterns could be realized. The polyimide resists had high thermal stability and reliable adhesive property to silicon substrate. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Among the properties of polyimides used in the microelectronics industry, the desirable is ease of application, excellent planarization capability, and good electrical insulating properties.

Photosensitive polyimide simplifies processing and does not need a toxic etchant, such as hydrazine. Most photosensitive polyimides consist of polyamic acids whose carboxylic acid groups have been replaced by esters[1] or ions[2] capable of cross-linking. They need organic solvents as developers. This is incompatible with existing photoresist processing technology in the microelectronics industry that uses aqueous solution containing dilute organic bases.[3]

Positive photosensitive polyimides, developable with base aqueous solution, have been attracting great interest. Kubota et al. described the synthesis *o*-nitrobenzyl esters of polyamic acid.[4] Khanna and Mueller reported polyimides bearing hydroxy groups for positive working naphthoquinone diazide sensitized resists.[5] Positive polyimide resists, in which naphthoquinone diazides are bonded partially to the hydroxy groups on the polyimide backbone, have also been reported.[6] Although these resist systems provide excellent resist patterns, specific diamines and acid dianhydrides were necessary for the syntheses, which has imposed a limitation on the polymer structures.

Other approaches were made by using polyamic acids themselves. The resists consist of the polyamic acids and naphthoquinone diazides. Polyamic acids are usually too soluble in basic aqueous solutions. Therefore, the dissolution rates had to be reduced by prebaking[7] or postexposure baking.[8,9]

The authors' goal was to prepare novel polyimide resists developable with basic aqueous solutions and sensitive to the g-line (436 nm) of a mercury lamp. Considering that polyimides absorb UV light up to about 400 nm, the irradiation should be g-line. Naphthoquinone diazides are the best candidates for the photoactive compound, because they are sensitive to the g-line.

Preparation of polyimide precursors with adequate dissolution rates in basic aqueous developers is essential for the realization. To achieve the purpose, the phenol moieties were introduced into polyamic acids through ester linkage, because the phenol moieties have the potentiality to control the dissolution rates.[5,6] The resists consist of PPh and naph-

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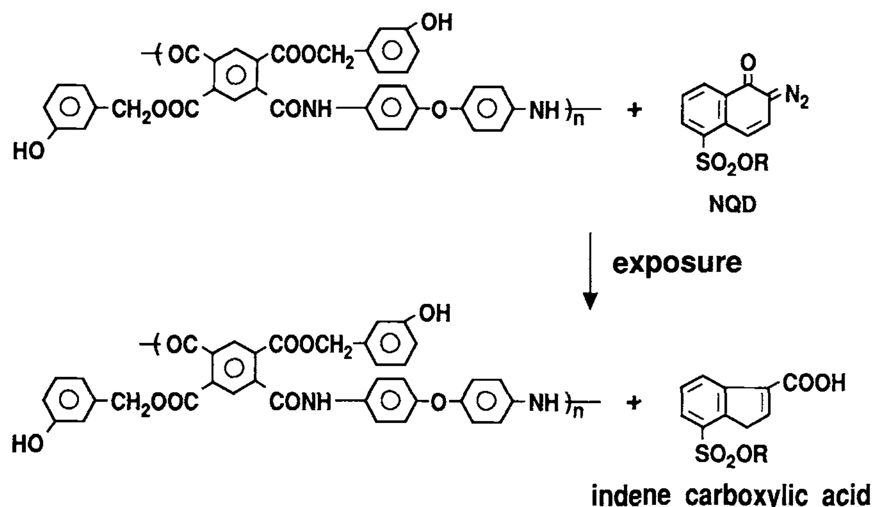


Figure 1 Resist compositions and mechanism of photolithography.

thoquinone diazide (NQD). When the resists are exposed to the g-line, NQDs are changed to indenecarboxylic acids. Because of this, the solubility of the resist to a basic aqueous developer increases, which makes it possible to develop the resist by using a basic developer (Fig. 1). The mechanisms are assumed to be similar to those for typical positive photoresists containing NQDs and novolac resins.[3]

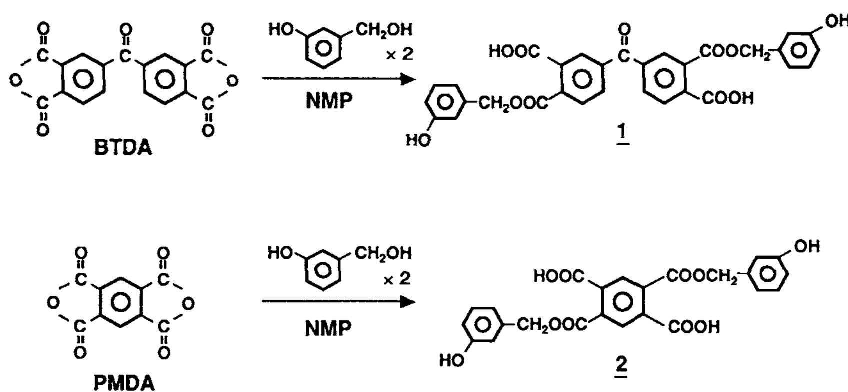
The reason why the phenol groups are bonded to the side-chain ester groups is that the ester groups might be removed during high-temperature processes for the imidization. The polyimide structures having phenol groups in the main chains have been reported in other articles[5,6]; however, the OH groups remaining in the main chains sometimes cause some trouble in electrical insulations. This article reports the synthesis of polyimide precursors and the resist properties.

EXPERIMENTAL

All syntheses were conducted under a nitrogen atmosphere. All solvents were dried with molecular sieves before use.

Syntheses of Dicarboxylic Acid with Phenol Moieties

3,3′,4,4′-Benzophenone tetracarboxylic acid dianhydride (BTDA, 32.22 g) was reacted with *m*-hydroxybenzyl alcohol (24.83 g) in *N*-methyl-2-pyrrolidinone (NMP, 100 mL) at 100°C for 3 h to form dicarboxylic acid diester with phenol moiety **1** (Scheme 1). ^{1}H-NMR (acetone-d_6, ppm) 5.29 (s, CH_2), 6.77–7.30, 7.82–8.30 (m, Ar H), 8.20–8.30 (OH); IR (KBr disk, cm^{-1}) 3410 (OH, carboxylic



Scheme 1. Synthesis route of diesters with phenol moieties.

acid, phenol) 1730 (C=O, ester), 1670 (C=O, ketone).

In the same manner, pyromellitic acid dianhydride (PMDA, 2.18 g) was reacted with *m*-hydroxybenzyl alcohol (2.48 g) to form **2.** ^{1}H-NMR (acetone-d_6, ppm) 5.30 (s, CH_2), 6.79–7.22, 8.00–8.30 (m, Ar H), 8.20–8.30 (OH); IR (KBr disk, cm^{-1}) 3420 (OH, carboxylic acid, phenol) 1730, (C=O, ester).

These diesters were exclusively benzyl esters. Phenyl esters were not observed by ^{1}H-NMR spectroscopy. The resultant solutions were used for the following polymerization without isolation of the monomers.

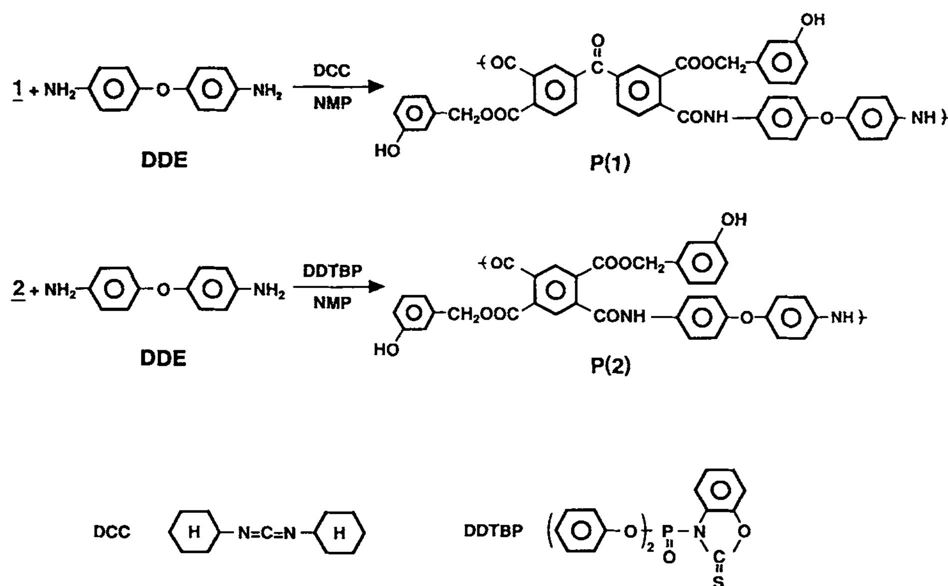
Syntheses of Copolyamic Acid Esters with Phenol Moieties PPhs

P(1)

The synthesis route of polyamic acid esters bearing phenol moieties is shown in Scheme 2. The solution of **1** was cooled with an ice bath. 4,4′-Diaminodiphenyl ether (DDE, 19.02 g), 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyl disiloxane (APDS, 1.24 g), and 80 mL of NMP were added to the solution **1.** APDS was added to improve adhesion to substrates. The molar ratio for the dicarboxylic acid diester **1** and these diamines was **1** : DDE : APDS = 1.00 : 0.95 : 0.05. Dicyclohexylcarbodiimide (DCC, 41.67 g) was dissolved in NMP (80 mL). The DCC solution was added to the mixture dropwise for 20 min. The mixture was stirred at 1–5°C for 1 h and at room temperature for 8 h. The reaction mixture was filtered and poured into 2000 mL of methanol. The precipitated polymer was washed with water several times. The polymer P(1) was dried *in vacuo* at 50°C for 20 h. Yield 67%; inherent viscosity 0.22 dL/g (0.50 g in 100 mL of NMP at 30°C); IR (KBr disk, cm^{-1}) 3300 (OH, phenol, NH, amide), 1720 (C=O, ester), 1660 (C=O, ketone, amide), 1540 (NH, amide).

P(2)

Diphenyl(2,3-dihydro-2-thioxo-3-benzoxazo-lyl) phosphonate (DDTBP) was synthesized in the method described in the literature.[10] DDE (1.90 g), APDS (0.12 g), triethylamine (2.02 g), DDTBP (12.65 g), and 10 mL of NMP were added in solution **2.** The molar ratio for the dicarboxylic acid diester **2** and the diamines was **2** : DDE:APDS = 1.00 : 0.95 : 0.05. The mixture was stirred at room temperature, until DDTBP was dissolved, and then stirred at 50–60°C for 10 h. The solution was poured into 1 wt % of $NaHCO_3$ aqueous solution (1000 mL) and the precipitated polymer was washed with water several times. The polymer was dissolved in NMP (30 mL) and the polymer solution was poured into methanol (1000 mL). The precipitated polymer P(2) was filtered and dried *in vacuo* at 50°C for 20 h. Yield 38%; inherent viscosity 0.56 dL/g (0.50 g in 100 mL of NMP at 30°C); IR (KBr disk, cm^{-1}) 3300 (OH, phenol, NH, amide), 1730 (C=O, ester), 1660 (C=O, amide); 1540 (NH, amide).



Scheme 2. Synthesis route of polyamic acid esters with phenol moieties (PPh's).

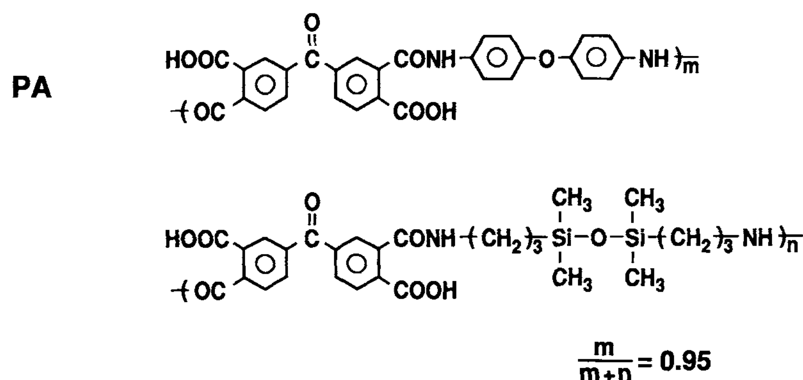


Figure 2 Polyamic acid (PA).

Polyamic Acid (PA)

BTDA, 32.22 g, was mixed with 130 mL of NMP. The suspension was cooled with an ice bath. The solution containing DDE (19.02 g), APDS (1.24 g), and NMP (80 mL) was added dropwise for 15 min. The mixture was stirred at 1–5°C for 8 h. The resultant polyamic acid (PA) solution was used without further purification. Inherent viscosity was 0.65 dL/g (0.50 g in 100 mL of NMP at 30°C). The structure of PA is shown in Figure 2.

Naphthoquinone Diazide (NQD)

1,2-Naphthoquinone diazide-5-sulfonic acid ester with 2,3,4,4′-tetrahydroxybenzophenone (esterified ratio: 75%) was purchased from Toyo Gosei Kogyo and used without any purification.

Dissolution Rates for Polymers

Synthesized polymers were dissolved in NMP. After filtration, the polymer solutions were coated onto silicon wafers and baked on a hot plate at 110°C for 3 min. Dissolution rates for polymers were calculated from the film thickness before and after immersing in NMD3 (positive resist developer, Tokyo Oka Kogyo, 2.38% tetramethylammonium hydroxide aqueous solution), by dividing the decreased thickness by the time involved.

Lithographic Evaluation

Resist compositions are shown in Table I. The resists were prepared as follows: P(1) and P(2) was added to PA solution, followed by adding NQD. To adjust the dissolution rate in the developer, PA was added to the resists. The NQD content was 20 wt % to the solid body. NMP was added to the mixture to adjust the concentration. The concentration of solid ingredients was 25 wt %. The mixture was stirred at room temperature to form the clear solution, which was filtered through a 0.50 micron filter to provide the resist solution. After filtration, resists were coated onto silicon wafers and baked on a hot plate at 110°C for 3 min. Resist thickness was about 5 μm. The wafers were exposed with a Cobilt CA-800 contact printer. The exposure was made in the 400–436 nm range. The resists were developed with NMD3 or diluted NMD3 with water, followed by

Table I Resist Compositions and Their Characteristics

Resist	Polymer		Developer TMAH[a] aq (wt %)	Development Time (s)	Sensitivity (mJ/cm^2)
R1-25	P (1)/PA	75/25[b]	2.38	60	115
R1-50		50/50	2.38	20	90
R1-75		25/75	0.40	30	—
R2-25	P (2)/PA	75/25	2.38	90	110

[a] TMAH, tetramethylammonium hydroxide.
[b] Weight ratio. Polymer/NQD/NMP = 80/20/300 (weight ratio).

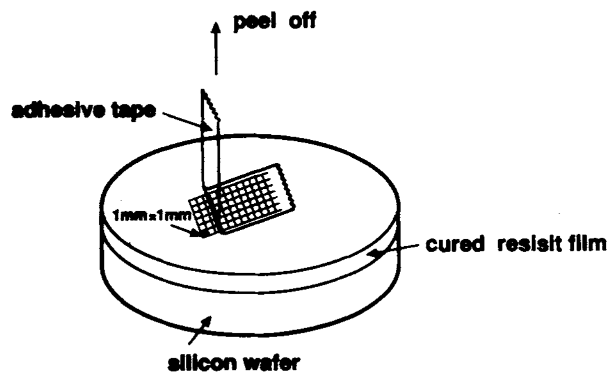


Figure 3 Method of adhesive strength test.

rinsing them in water. The resist film was baked for imidization at 90°C for 30 min, 150°C for 60 min, and 250 and 350°C for 30 min using a TABAI Super Temp Oven STPH-100 in a N_2 atmosphere.

Thermal Stability

TGA thermographs of P(1), P(2), and fully cured resist film were measured by a Seiko Denshi Kogyo TG-DTA SSC/560 GH in a N_2 atmosphere. The temperature was increased at the rate of 10°C/min.

Adhesive Strength

To estimate the adhesive strength of the resist film, the following experiment was carried out (Fig. 3). Resists were coated onto silicon wafers and heated up to 350°C. One hundred 1 mm squares were drawn on the cured film by a razor. An adhesive tape was stuck onto these square lattices. The tape was peeled off, and the number of squares removed with the tape was counted. Afterward, a pressure cooker test (PCT) was carried out and changes in the adhesive strength were examined. For the PCT treatment, wafers were exposed to high-temperature water vapor (120°C, 2 atm) for 24 h and the peeling test was repeated.

RESULTS AND DISCUSSION

The reaction of PMDA or BTDA with *m*-hydroxybenzyl alcohol was exclusively selective. It was easy to distinguish the alcoholic diesters from the phenolic diesters, measuring the ^{1}H-NMR chemical shift of the CH_2. If the acid anhydrides react with the alcohol groups to give Ph—CO—O—CH_2—Ph—OH, the NMR chemical shift for the benzyl protons should be around 5.2 ppm. However, if the acid anhydrides react with the phenol groups to give Ph—CO—O—Ph—CH_2—OH, the chemical shift for the benzyl protons should be around 4.6 ppm. In this reaction mixture, only the 5.3 ppm peak was observed, suggesting that the acid anhydride reacted with the alcohol groups exclusively even if phenolic OH groups were in the reaction system. A peak that sifted when the D_2O was added to the mixture was observed at 8.20–8.30 ppm. This was assigned to phenolic OH groups and carboxylic acid OH's. However, it was impossible to distinguish the phenolic OH groups from the carboxylic acid OH. These selective reactions made the syntheses of P(1) and P(2) possible.

The inherent viscosities for P(1) and P(2) were 0.22 and 0.56 dL/g (0.50 g in 100 mL of NMP), respectively. It has been reported that a phenol reacts with benzoic acid to form the ester at low yield by using DCC.[11] The side reaction involved in carboxylic acid and phenol of the dicarboxylic acid diester **1** may decrease the molecular weight of P(1). On the other hand, Ueda et al. reported that in the case of DDTBP, reactions between NH_2 and COOH occurred selectively, even if phenols existed.[10] Because of this, higher molecular weight polymer could be obtained by using DDTBP.

Preparation of polyimide precursors having adequate dissolution rates in basic aqueous developers is essential for the realization of polyimide resists. Dissolution rates for the synthesized polymers were measured in basic aqueous solution. The alkaline developer NMD3 contains 2.38 wt % tetramethylammonium hydroxide (TMAH). Both P(1) and P(2) were soluble in the developer, but their dissolution rates were too low for use as resists. Roughly speaking, the dissolution rates of novolac resins available for positive resists have to be from 10 to

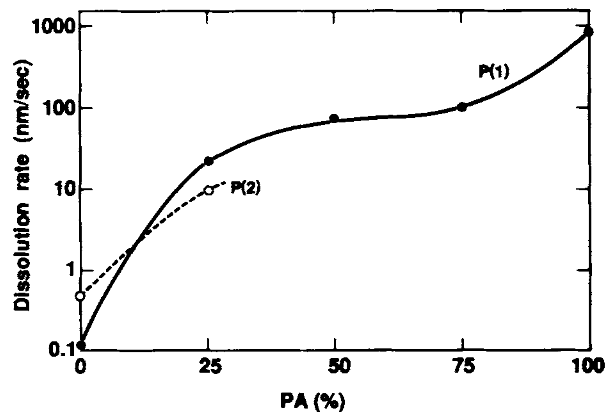


Figure 4 Dissolution rates of polymers in 2.38% TMAH aq solution.

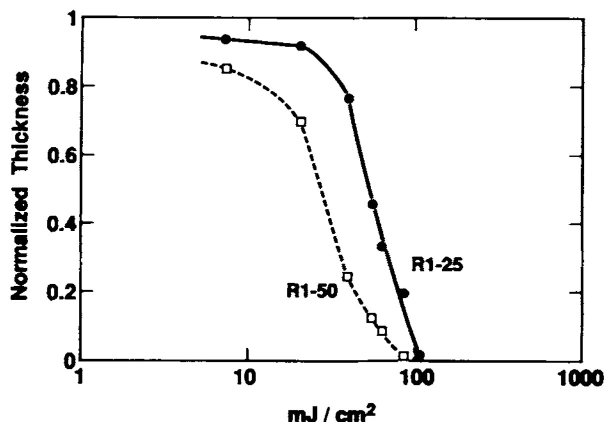


Figure 5 Contrast curves of the resists containing P(1) and PA.

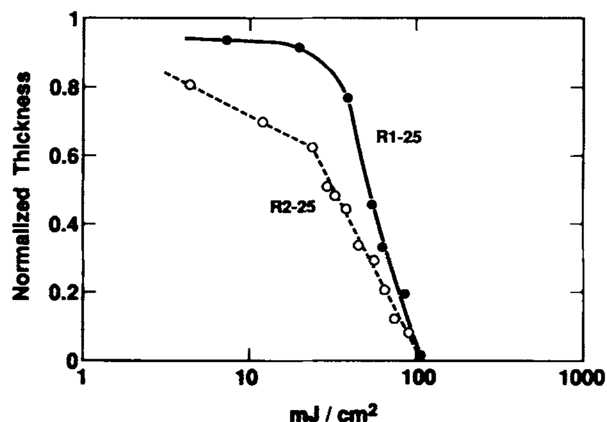


Figure 7 Contrast curves of the resists R1-25 and R2-25.

30 nm/s. However, the dissolution rates for P(1) and P(2) were less than 1 nm/s. To increase the dissolution rate, polyamic acid PA was added. PA is assumed to be more soluble in an alkaline developer. Figure 4 shows the change of the dissolution rates when PA was added to P(1) or P(2). As the PA was added, the dissolution rate was increased considerably. When 25 wt % of PA was added, the dissolution rates for P(1) and P(2) were around 20 and 10 nm/s, respectively. These were about the same as those for the novolac resins.

Resists were made from P(1) or P(2), PA, and NQD. The NQD seems to present in the resist solution as a separate entity, because the NQD peaks were still observed in GPC curves even after the

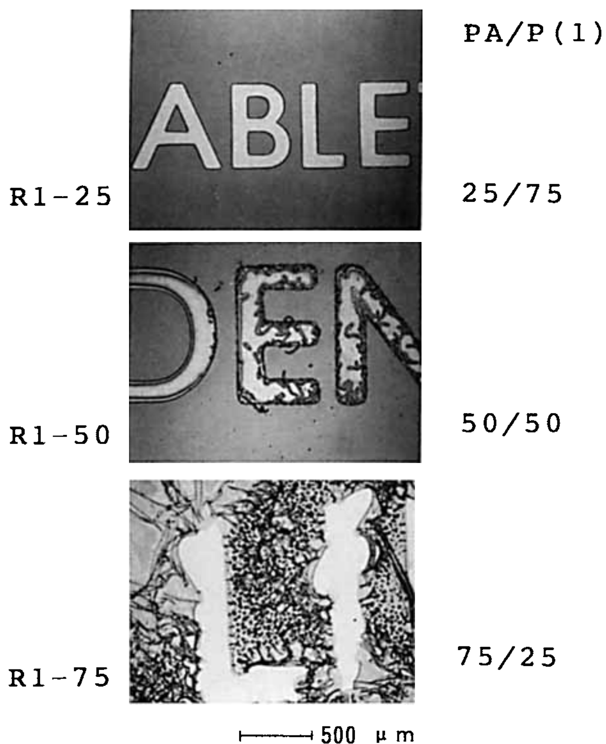


Figure 6 Patterns fabricated by the resists containing P(1) and PA.

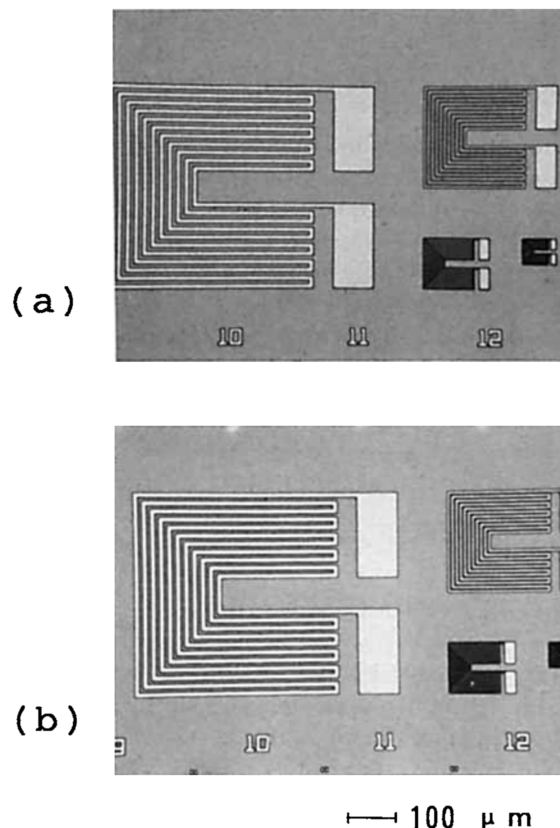


Figure 8 Patterns fabricated by the resist R2-25: (a) after development, (b) after cured up to 350°C.

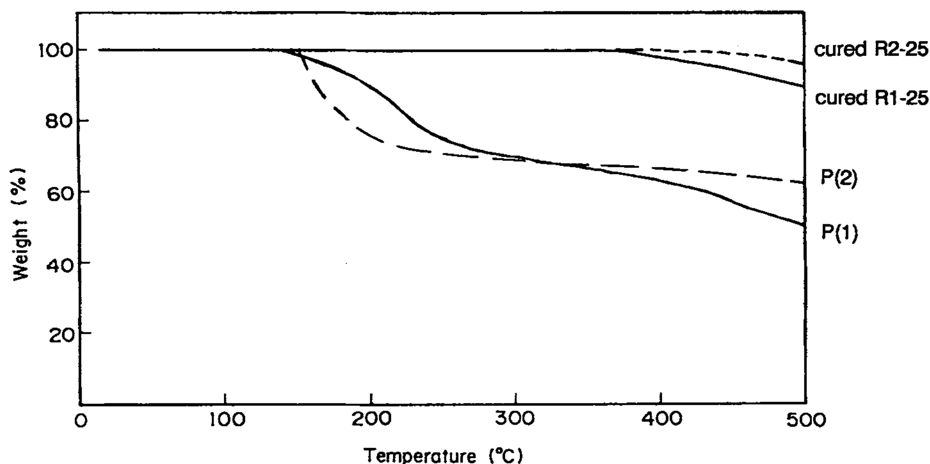


Figure 9 TGA curves of P(1) and P(2) and cured R1-25 and R2-25.

resist film was prebaked. Characteristics of the resists are shown in Table I. Figure 5 shows contrast curves of the resists that consist of P(1) and PA. R1-25 and R1-50 contained P(1) and PA at the weight ratio of P(1):PA = 75 : 25 and 50 : 50, respectively. Their sensitivities were around 100 mJ/cm^2. Figure 6 shows patterns fabricated by the resists containing P(1) and PA. R1-25 gave the best patterns. As the PA content increased, the resolution deteriorated. R1-75, which contained P(1) and PA at the weight ratio of P(1):PA = 25 : 75, did not give patterns even when diluted developers were used. These results show that adjusting of dissolution rates of polymers in basic aqueous developers is essential for realizing fine resist patterns.

Figure 7 shows contrast curves of the resists R1-25 and R2-25 containing P(1) and P(2), respectively. The γ value of R1-25 seems to be superior to that of the R2-25. This is probably because the molecular weight of P(1) is lower than that for P(2).

Figure 8 shows patterns fabricated by R2-25. Less than 10 micron line and space patterns were resolved [Fig. 8(a)]. To imidize the resist, the wafer was heated to 350°C. There was no deformation observed [Fig. 8(b)]. The resist thickness was decreased to 65% by curing.

Figure 9 gives TGA curves of these polymers and the cured resists R1-25 and R2-25. P(2) was imidized at lower temperature than was P(1). After imidization, P(2) was more stable than was P(1). The temperature at which the weight losses of the cured R1-25 and R2-25 reach 5% was 440 and 500°C, respectively, indicating the high thermal stability of the polymers. The thermal stability of R2-25 was higher than that of R1-25. This is probably because the thermal stability of P(2) was better than that of P(1).

When devices are molded in plastics, high reliability for polyimide adhesion to LSI surfaces is required under high-temperature and high-humidity conditions. Results of the peeling test for polyimide resists are shown in Table II. No square lattices were removed for both R1-25 and R2-25 films after curing. Afterward, the wafers were exposed to high-temperature water vapors at 120°C for 24 h and the peeling tests were repeated. R1-25 was partly peeled off with the adhesive tape. On the other hand, R2-25 film was not removed at all. The adhesive property for R2-25 with higher molecular weight was superior to that of R1-25.

Table II Adhesive Properties of Resists

	Removed Squares	
Resist	Before PCT[a]	After PCT
R1-25	0/100	22/100
R2-25	0/100	0/100

[a] PCT: pressure cooker test, 120°C, 2 atm, 24 h.

CONCLUSION

We have found a novel way to synthesize polyamic acid esters with phenol moieties (PPh's). The selective reaction between acid anhydride groups and alcohols made the synthesis possible. Positive acting, aqueous base developable photoresists were made

from PPh, polyamic acids, and naphthoquinone diazides (NQDs). The polyimide resists had high thermal stability and reliable adhesive properties to silicon substrates.

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