

Novel Positive-Working Aqueous-Base Developable Photosensitive Polyimide Precursors Based on Diazonaphthoquinone-Capped Polyamic Esters

Steve Lien-Chung Hsu,¹ Po-I Lee,¹ Jinn-Shing King,² Jyh-Long Jeng²

¹Department of Materials Science and Engineering, National Cheng-Kung University, Tainan, 701-01, Taiwan, Republic of China

²Industrial Materials Research Labs, Industrial Technology Research Institute, Hsinchu, Taiwan, Republic of China

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ABSTRACT: Novel positive-working aqueous-base developable photosensitive polyimide (PSPI) precursors based on partially diazonaphthoquinone (DNQ)-capped polyamic esters bearing phenolic hydroxyl groups and a DNQ photosensitive compound (PIC-3) were developed. The partially DNQ capped polyamic esters were prepared from an esterification reaction of 1,2-naphthoquinone diazide-5-sulfonyl chloride with the polyamic esters. The partially DNQ capped polyamic esters decreased the dark film loss effectively in the aqueous-base developer and were able to make thicker film resists compared to the uncapped polyamic esters. The 25 mol % DNQ-capped BisAPAF-PMDA poly-

amic ester and BisAPAF-ODPA polyamic ester containing 25 wt % PIC-3 photosensitive compound showed a sensitivity of 176 and 185 mJ/cm², and a contrast of 1.68 and 1.02, respectively, in a 3- μ m film with 1.25 wt % tetramethylammonium hydroxide developer. A pattern with a resolution of 5 μ m was obtained from both PSPI precursor compositions. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2293–2300, 2003

Key words: polyimides; synthesis; photoresists; positive-working; diazonaphthoquinone

INTRODUCTION

Despite their high cost, photosensitive polyimides (PSPIs) have been widely used in microelectronic devices such as buffer coatings, passivation layers, alpha particle barriers, interlayer insulations, and wafer scale packages because they simplify processing steps and allow avoidance of the use of a photoresist to obtain the desired patterns.^{1,2} Currently, most of the PSPIs used in microelectronic industry are negative-working, organic solvent developable types. In addition to the swelling problem of the negative-type resist, the growing concerns of environmental and safety issues about using organic solvents as developers have greatly accelerated the development of positive-working aqueous-base developable PSPIs.

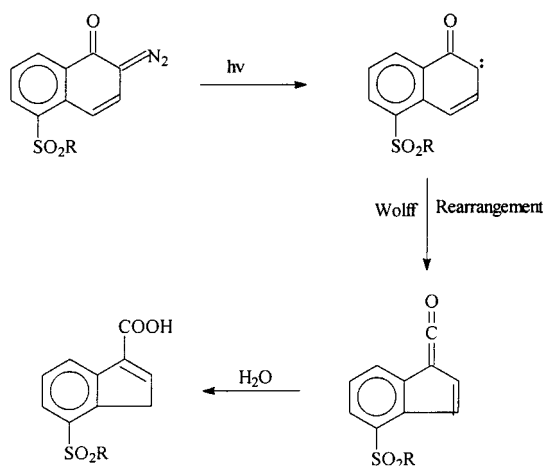
In the past decade, several approaches have been proposed to prepare positive-working, aqueous-base developable PSPIs.^{3–14} Thus far, only just a few of them have actually been introduced into the market. The research and development of this type of PSPIs are still ongoing. In our previous study¹⁵ we reported the preparation of a positive-working, aqueous-base

developable PSPI formulation based on a polyamic ester bearing phenolic hydroxyl groups and a diazonaphthoquinone (DNQ) photoactive compound as the dissolution inhibitor. The polyamic ester has good solubility in organic solvents and is able to prepare a high solids content formulation. Compared to other polyamic acid- or polyamide-based PSPIs, it can be totally dissolved in aqueous-base developers without residue after development, and has high sensitivity and resolution. However, this PSPI system has the common problem of most DNQ-added aqueous-base developable PSPIs, which is the high dark film loss during development. The drawback arises from the fact that the DNQ photoactive compound cannot completely inhibit the aqueous-base solubility of the polymer. It will prevent the PSPI from obtaining a thick film resist.

In this study we report a method to improve the drawback of that PSPI system. Here the DNQ group was used to partially protect the phenolic hydroxyl groups in the polyamic ester through the esterification of 1,2-naphthoquinone diazide-5-sulfonyl chloride with the polyamic ester to reduce its aqueous-base solubility. After exposure to UV light, the DNQ undergoes photolysis and converts to indenecarboxylic acid, as shown in Scheme 1, which promotes the aqueous solubility of the polyamic ester.^{16,17} In this way, novel low dark film loss positive-working aqueous-base developable PSPIs can be prepared.

Correspondence to: S. Hsu (lchsu@mail.ncku.edu.tw).

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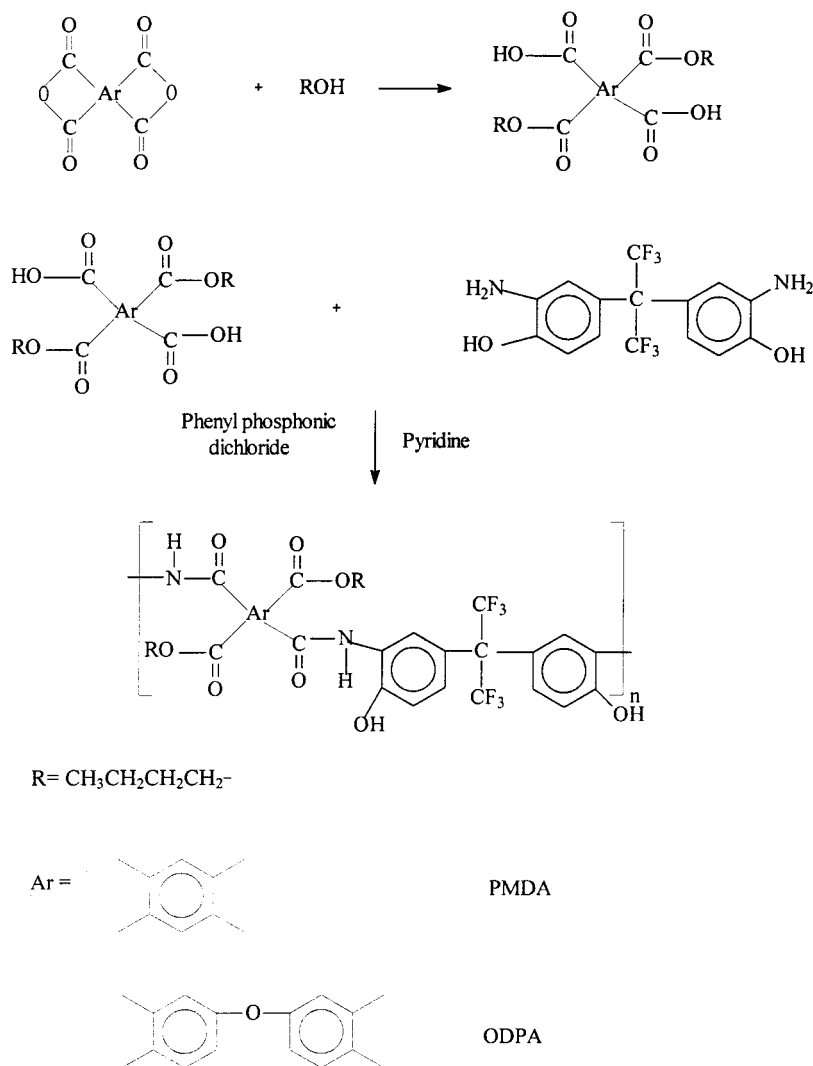


Scheme 1

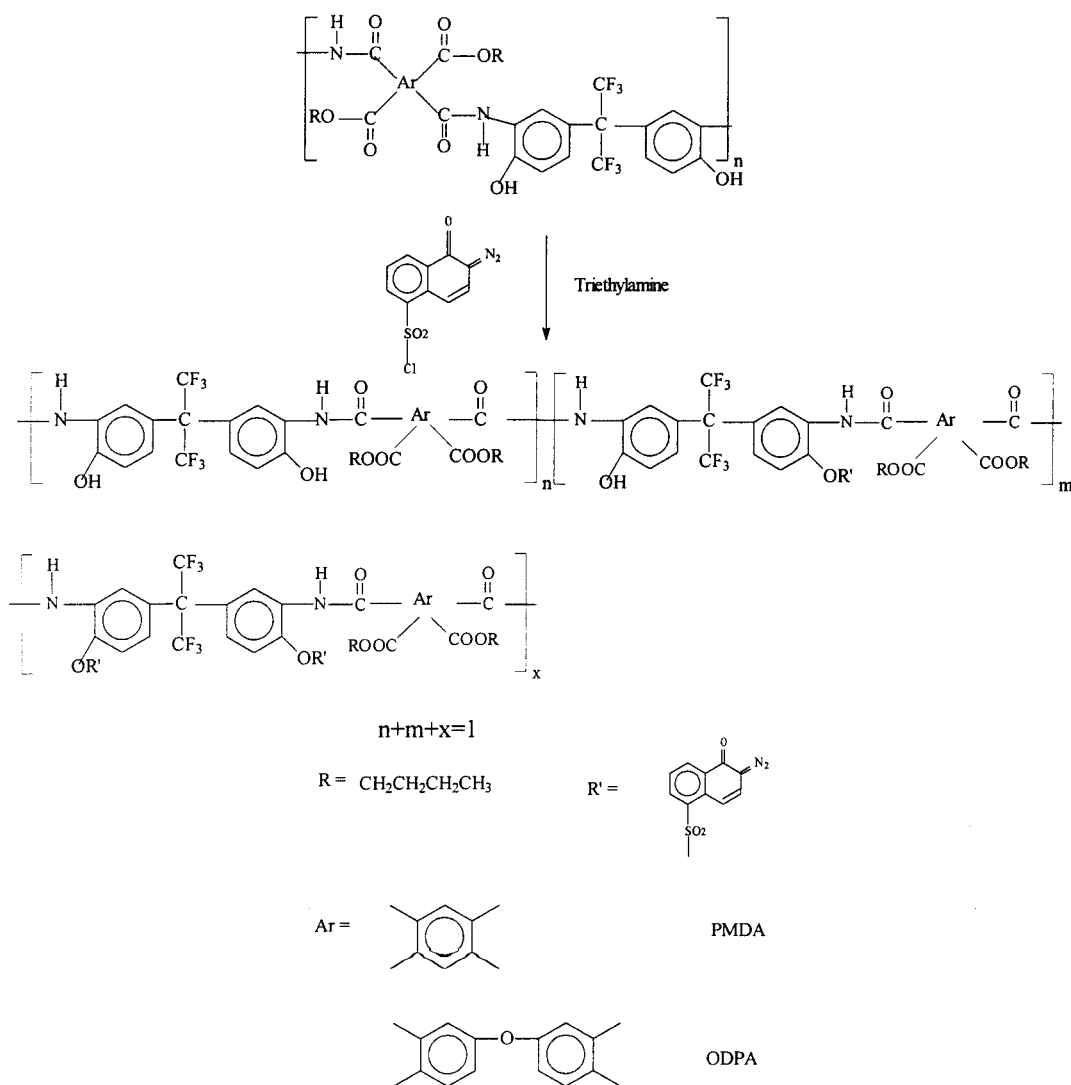
EXPERIMENTAL

Materials

Oxydiphthalic anhydride (ODPA), pyromellitic dianhydride (PMDA), and 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (BisAPAF) were purchased from Chriskev (Leawood, KS). Anhydrous *N*-methyl-2-pyrrolidone (NMP) and pyridine were obtained from Aldrich (St. Louis, MO) and used without further purification. 2,3,4-Tris(1-oxo-2-diazonaphthoquinone-5-sulfonyloxy)-benzophenone (PIC-3) photosensitive compound was obtained from Koyo Chemicals (Osaka, Japan). 1,2-Naphthoquinone diazide-5-sulfonyl chloride was obtained from TCI Co. (Tokyo, Japan). Other chemicals were used as received. Tetramethylammonium hydroxide (TMAH) in 25 wt % solution was obtained from Lancaster (Morecambe, UK) and diluted to the desired concentration with deionized water.



Scheme 2



Scheme 3

Synthesis of polyamic ester

The synthesis of BisAPAF-PMDA polyamic acid *n*-butyl ester is described in the previous study.¹⁵ The same procedure was used to prepare the BisAPAF-ODPA polyamic acid *n*-butyl ester. The synthesis steps are illustrated in Scheme 2.

Synthesis of DNQ-capped polyamic esters

A representative example of 10 mol % DNQ-capped BisAPAF-PMDA polyamic acid *n*-butyl ester is as follows: To a 250-mL three-neck round-bottom flask equipped with a mechanical stirrer and a condenser, 6.96 g (10 mmol) of BisAPAF-PMDA polyamic acid *n*-butyl ester and 50 mL THF were added. The solution was stirred until the polymer was totally dissolved, and then 0.53 g (2 mmol) of 1,2-naphthoquinone diazide-5-sulfonyl chloride was added. After being stirred for 10 min, 0.2 g (2 mmol) of triethylamine

was added dropwise to the solution, and the reaction mixture was stirred for 5 h. The solution was precipitated in 1000 mL of deionized water. The polymer was collected by filtration and washed with deionized water five times. Finally, the polymer was dried under vacuum at 45°C for 24 h. The actual concentration of DNQ in each polyamic ester was determined by the absorption ratio of 2119 cm^{-1} (N=N) versus 1660 cm^{-1} (amide C=O) in the IR spectrum. The 100 mol % DNQ-capped BisAPAF-PMDA polyamic acid *n*-butyl ester was obtained from the reaction of BisAPAF-PMDA polyamic acid *n*-butyl ester with an excess amount of 1,2-naphthoquinone diazide-5-sulfonyl chloride. The synthesis steps are illustrated in Scheme 3.

Preparation of DNQ-capped polyamic ester film and thermal conversion to polyimide

Five grams of 25 mol % DNQ-capped BisAPAF-PMDA or BisAPAF-ODPA polyamic ester powder was dis-

TABLE I
Inherent Viscosities of Polyamic Esters

Polyamic ester	Inherent viscosity ^a (dL/g)
BisAPAF-PMDA polyamic acid <i>n</i> -butyl ester	0.23
BisAPAF-ODPA polyamic acid <i>n</i> -butyl ester	0.16

^a Measured at a concentration of 0.5 g/dL in NMP at 30°C.

solved in 20 g of dimethylacetamide (DMAC) to make a 20% (w/w) solution. A film was cast from the viscous solution onto a glass plate by use of a doctor's knife. The film was dried at 100°C for 1 h, 200°C for 1 h, and 300°C for 2 h in a heating oven to convert the polyamic ester to a polyimide.

Characterization

The IR spectra were recorded on a Jasco (Tokyo, Japan) 460 FTIR spectrometer. ¹H-NMR spectra were recorded on a Bruker (Rheinstetten, Germany) Advance 600 spectrometer. Inherent viscosity was measured using a Cannon-Ubbelohde (State College, PA) No. 100 viscometer at a concentration of 0.5 g/dL in NMP at 30°C. Thermal stability was analyzed using a TA Instruments (New Castle, DE) thermogravimetric analyzer (TGA Model Q500) at a heating rate of 10°C/min under nitrogen. The glass-transition temperature (T_g) and the in-plane coefficient of thermal expansion (CTE) of cured polyimide film were determined using a TA Instruments thermal mechanical analyzer (TMA Model 2940) with an extension probe under 0.05-N tension force on the film, at a heating rate of 5°C/min under nitrogen. The UV-visible spectrum was obtained on a Varian Cary (Palo Alto, CA) 100 UV-vis spectrophotometer.

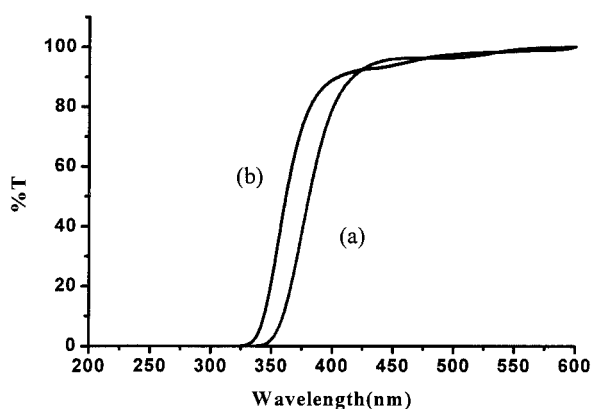


Figure 1 UV-visible spectra of BisAPAF-PMDA polyamic ester (a) and BisAPAF-ODPA polyamic ester (b).

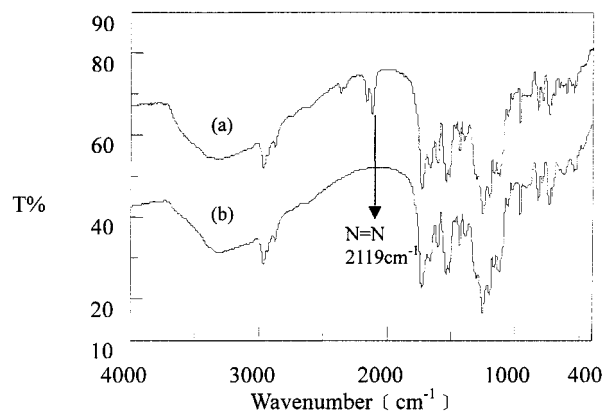


Figure 2 FTIR spectra of 100 mol % DNQ-capped BisAPAF-PMDA polyamic acid *n*-butyl ester before and after exposure to UV light.

Preparation of photoresist formulation and lithographic evaluation

A representative example of a photoresist formulation of 25 mol % DNQ-capped BisAPAF-PMDA polyamic acid *n*-butyl ester is as follows: Five grams of the 25 mol % DNQ-capped BisAPAF-PMDA polyamic acid *n*-butyl ester was dissolved in 20 g of γ -butyrolactone (GBL) and 1.25 g of a DNQ photoactive compound (PIC-3) was added to prepare the photoresist solution. The solution was filtered through a 5- μ m Teflon filter. It was then spin-coated onto a silicon wafer, and soft-baked in an airflow clean room oven at 105°C for 40 min to obtain a film of about 3 μ m thickness. The film was exposed to an unfiltered mercury arc lamp measured at 250–400 nm. The wafer was developed in a 1.25 wt % TMAH developer followed by a deionized water rinse. The film thickness was measured with a Tenco (San Jose, CA) α -step instrument. The characteristic curve was obtained by plotting the normalized film thickness against the exposure energy. The dark film loss of the photoresist formulation was measured by the ratio of the film thickness of the unexposed area

TABLE II
Dissolution Rates of Different DNQ Capping Level BisAPAF-PMDA Polyamic Esters

Polymer	DNQ capping level ^a (mol %)	DNQ capping level ^b (mol %)	Dissolution rate (μ m/min) ^c
1	0	0	2.44
2	10	17	2.18
3	25	22	0.71
4	50	54	0.44
5	75	79	0.22
6	100	100	0.09

^a Theoretical value (according to the amount of 1,2-naphthoquinone diazide-5-sulfonyl chloride added).

^b Determined by the absorption ratio of 2119 cm^{-1} (N=N) versus 1660 cm^{-1} (amide C=O) in the IR spectra.

^c Dissolved in 1.25 wt % TMAH solution.

TABLE III
Solubilities of 25 mol % DNQ-Capped Polyamic Esters and Polyimides

Solvent	25 mol % DNQ-capped BisAPAF-PMDA polyamic ester	25 mol % DNQ-capped BisAPAF-ODPA polyamic ester	BisAPAF-PMDA polyimide	BisAPAF-ODPA polyimide
NMP	+ ^a	+	– ^b	–
DMAC ^c	+	+	–	–
DMF ^d	+	+	–	–
THF ^e	+	+	–	–
Acetone	+	+	–	–
Ethanol	–	–	–	–

^a +, Soluble.

^b –, Insoluble.

^c DMAC, dimethylacetamide.

^d DMF, dimethylformamide.

^e THF, tetrahydrofuran.

after development to the film thickness of the same area before development.

RESULTS AND DISCUSSION

Synthesis of polyamic esters

As described in the previous study,¹⁵ the polyamic ester can be prepared from the direct polymerization of diacid diester and diamine with an activator, phenyl phosphonic dichloride. The diamine used in this study was 2,2-bis(3-amino-4-hydroxyphenol)hexafluoropropane (BisAPAF). The diacid diester was prepared from the nucleophilic substitution reaction of dianhydride and *n*-butanol. Two dianhydrides were used in the preparation of polyamic esters. They were oxydiphthalic anhydride (ODPA) and pyromellitic dianhydride (PMDA). The inherent viscosities of these two polyamic esters are shown in Table I. The IR spectra of the polyamic esters showed a broad absorption band at 3400–3100 cm⁻¹ attributed to the amino (N–H) and hydroxyl (OH) groups, and an amide carbonyl absorption at 1660 cm⁻¹. The ¹H-NMR spectra of the polyamic esters exhibited the signals of hydroxyl proton (10.3 ppm), amino proton (9.8 ppm), and the *n*-butyl protons (0.8, 1.3, 1.5, and 4.2 ppm). The UV-visible spectra of polyamic esters in tetrahydrofuran (THF) with a concentration of 1 mg/L are shown in Figure 1. Because of the presence of the oxygen atom in the ODPA molecule, which can separate the chromophore groups (benzene and imide rings), the BisAPAF-OPDA polyamic ester is more transparent than the BisAPAF-PMDA polyamic ester. The transmittance of BisAPAF-OPDA polyamic ester at 365 nm (I-line) is over 70% compared to that of BisAPAF-PMDA polyamic ester, which is only 30%. Thus BisAPAF-OPDA polyamic ester-based PSPI can be exposed by an I-line stepper but BisAPAF-PMDA polyamic ester-based PSPI can be exposed only by a G-line (436 nm) stepper or broadband source.

Synthesis of DNQ-capped polyamic esters

One drawback of the positive tone photoresist is the high dark film loss, which is attributed to the fact that the DNQ photoactive compound cannot completely inhibit the aqueous-base solubility of the polymer through the hydrogen bonding between the diazo groups of DNQ and the phenolic hydroxyl groups in the polymer. One way to improve the dark film loss is through the protection of the phenolic hydroxyl groups before exposure to light to reduce their solubility and to restore the solubility after exposure to light. In this research, we tried to use DNQ to protect the polyamic esters (Scheme 3). The IR spectrum of 100% protected BisAPAF-PMDA polyamic ester is shown in Figure 2(a). The appearance of N=N absorption at 2119 cm⁻¹ and S=O absorption at 1380 cm⁻¹ indicated that the DNQ was attached to the polymer.⁹ After exposure to light, the N=N absorption disappeared, as shown in Figure 2(b). By using different amounts (based on the molar amount of phenolic hydroxyl groups in the polymer repeating units) of 1,2-naphthoquinone diazide-5-sulfonyl chloride, we were able to synthesize polyamic esters with different DNQ capping levels. The dissolution rates of BisAPAF-PMDA polyamic esters with different DNQ capping levels in 1.25 wt % TMAH solution are shown in Table II. The decrease of dissolution rate in aqueous base with the increase of DNQ capping level indicates that

TABLE IV
Thermal Properties of Cured Polyimides

Polyimide	CTE (μm m ⁻¹ °C ⁻¹) ^a	T _g (°C) ^a	T ₅ (°C) ^b
BisAPAF-PMDA	47	355	455
BisAPAF-ODPA	56	341	444

^a Measured by TMA at a heating rate of 5°C/min.

^b 5% weight loss temperature in nitrogen.

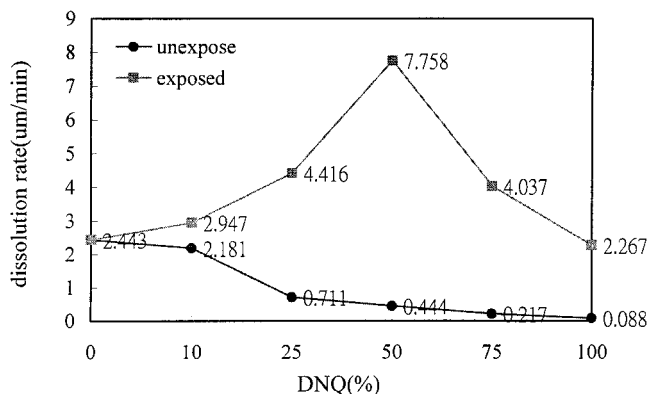


Figure 3 Dissolution rates versus DNQ capping levels of DNQ-capped BisAPAF-PMDA polyamic ester.

different amounts of DNQ were attached to the polyamic esters.

Polymer characterization

Table III summarizes the qualitative solubilities of the 25 mol % DNQ-capped BisAPAF-PMDA polyamic acid *n*-butyl ester, 25 mol % DNQ-capped BisAPAF-ODPA polyamic acid *n*-butyl ester, and the corresponding BisAPAF-PMDA polyimide and BisAPAF-ODPA polyimide. Both of the polyamic esters were soluble in several organic solvents but neither of the polyimides dissolved in any organic solvents. The

thermal properties of cured polyimides are shown in Table IV. Because of the more rigid structure, the BisAPAF-PMDA polyimide showed a higher T_g and lower CTE than those of the BisAPAF-ODPA polyimide from TMA analyses. The cured 25 mol % capped BisAPAF-PMDA polyimide also showed better thermal stability than that of the 25 mol % capped BisAPAF-ODPA polyimide. Their 5% weight loss temperatures in nitrogen are 455 and 444°C, respectively.

Lithographic evaluation

To determine the effect of DNQ capping level on the solubility of the polymer, five batches of different DNQ-capped polyamic esters ranging from 10 to 100 mol % were synthesized. Their dissolution rates of unexposed and exposed films measured in 1.25 wt % TMAH solution versus the DNQ capping levels are shown in Figure 3. The dissolution rates of the unexposed films decreased as the capping level increased. For the 100 mol % DNQ-capped polyamic ester, the dissolution rate approached zero. The results indicated that DNQ capping could effectively reduce the dark film loss. However, the dissolution rates of the exposed films increased as the capping level increased, as expected, up to 50 mol % DNQ capping, and then decreased abruptly as the capping level increased. In addition, we also found that the undissolved portion of the films with DNQ capping level

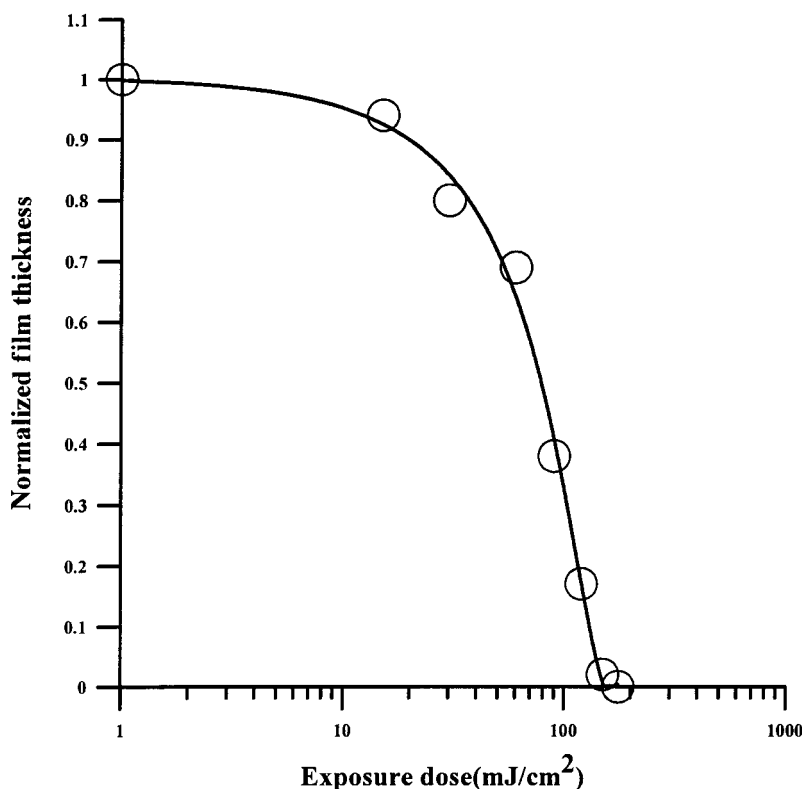


Figure 4 Characteristic exposure curve of 25 mol % DNQ-capped BisAPAF-PMDA polyamic ester/25 wt % PIC-3 system.

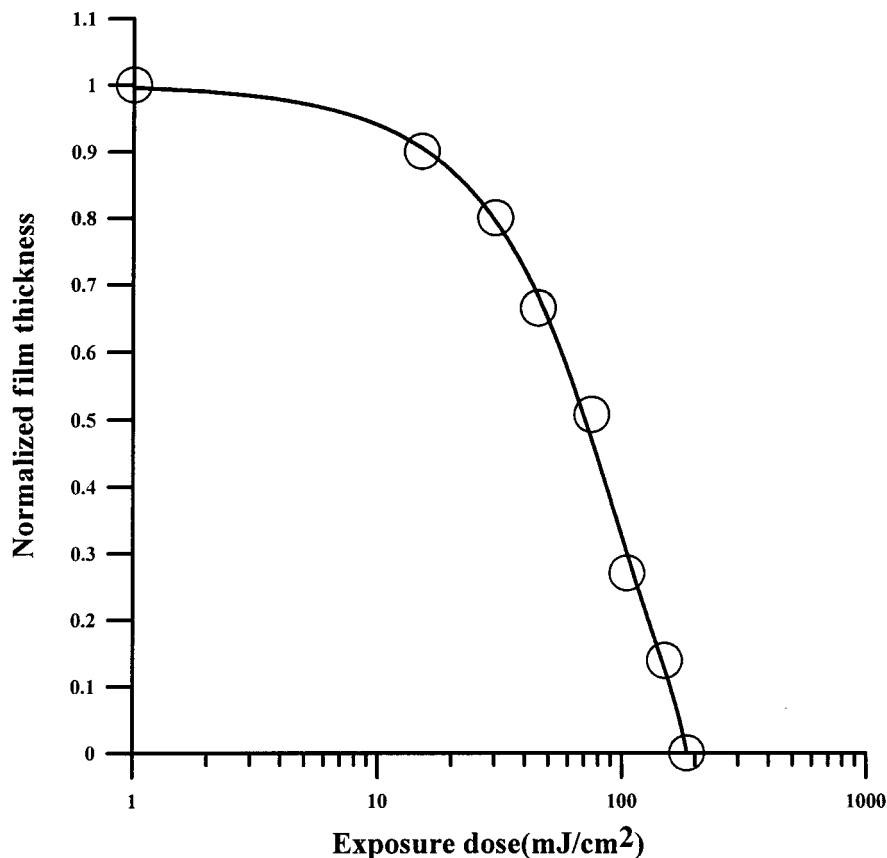


Figure 5 Characteristic exposure curve of 25 mol % DNQ-capped BisAPAF-ODPA polyamic ester/25 wt % PIC-3 system.

over 50 mol % was swelling, which indicated the occurrence of crosslinking between DNQ moieties after exposure when the capping level was too high. Omote et al.⁹ reported the same situation in their DNQ-capped polyimide system. Therefore, in our PSPI formulations, we chose 25 mol % capping level polyamic esters as the base materials.

A photosensitive polyamic ester composition was prepared from 25 mol % DNQ-capped BisAPAF-ODPA polyamic esters with 25 wt % PIC-3 photosensitizer in GBL. The exposure characteristic curves of a 3- μ m film of the compositions developed by a 1.25 wt % TMAH solution are shown in Figures 4 and 5. The

sensitivity of the BisAPAF-PMDA system is 176 mJ/cm² and the contrast is 1.68; the sensitivity of the BisAPAF-ODPA system is 185 mJ/cm² and the contrast is 1.02. A 5- μ m resolution line/space pattern can be obtained in a 3- μ m film from both systems, as shown in Figures 6 and 7. Their resolutions are better than that of the previously reported uncapped BisAPAF-PMDA polyamic ester.¹⁵ The dark film losses of the capped and uncapped polyamic esters are shown in Table V. The DNQ-capped BisAPAF-PMDA polyamic ester is 6%, which is much lower than that of the uncapped polymer. A similar situation was also found in the capped and uncapped BisAPAF-ODPA

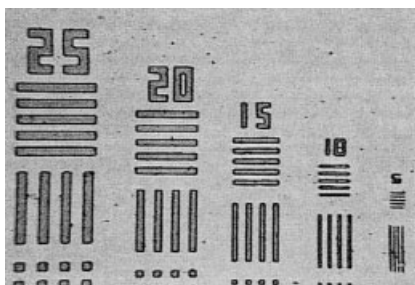


Figure 6 Optical micrograph of a pattern from 25 mol % DNQ-capped BisAPAF-PMDA polyamic ester/25 wt % PIC-3 system after development and cured at 300°C for 2 h.

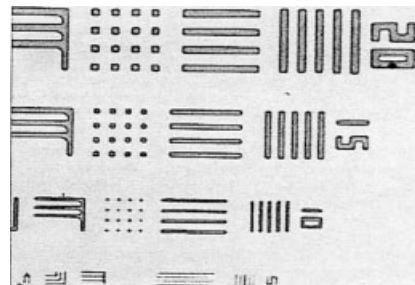


Figure 7 Optical micrograph of a pattern from 25 mol % DNQ-capped BisAPAF-ODPA polyamic ester/25 wt % PIC-3 system after development and cured at 300°C for 2 h.

TABLE V
Dark Film Losses of DNQ Capped and
Uncapped Polyamic Esters

Formulation ^a	Dark film loss (%) ^b
BisAPAF-PMDA polyamic ester	22
25 mol % DNQ-capped BisAPAF-PMDA polyamic ester	6
BisAPAF-ODPA polyamic ester	35
25 mol % DNQ-capped BisAPAF-ODPA polyamic ester	14

^a All formulations contained 25 wt % PIC-3.

^b Measured at 1.25 wt % TMAH developer.

polyamic ester. The result showed that the capping of hydroxyl groups did increase the film retention, and the capped polyamic ester was able to obtain a thicker film resist than the uncapped polyamic ester.

CONCLUSIONS

Through the esterification reaction of 1,2-naphthoquinone diazide-5-sulfonyl chloride and the polyamic esters containing phenolic hydroxyl groups, partially DNQ capped polyamic esters were synthesized. The partially DNQ capped polyamic esters decreased the dark film loss effectively in the aqueous-base developer and were able to make thicker film resists compared to the uncapped polyamic esters. The 25 mol % DNQ-capped BisAPAF-PMDA polyamic ester and BisAPAF-ODPA polyamic ester containing 25 wt % PIC-3 photosensitive compound showed a sensitivity of 176 and 185 mJ/cm², and a contrast of 1.68 and 1.02, respectively, in a 3- μ m film with 1.25 wt % tetramethylammonium hydroxide developer. A pattern with a

resolution of 5 μ m was obtained from both PSPI precursor compositions.

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