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A novel positive photosensitive polybenzoxazole precursor for microelectronic applications

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Abstract

A positive working, aqueous base developable photosensitive polybenzoxazole (PBO) precursor composition based on a partially trimethylsilyl (TMS) protected PBO precursor and a bisphenol A based 1,2-naphthoquinone diazide-4-sulfonate (DNQ-4) photosensitive compound has been developed. The polymer was prepared from a low temperature polymerization of 2,2′-bis(3-amino-4-hydroxyphenyl) hexafluoropropane (BisAPAF) and isophthaloyl chloride (IC), followed by reacting with trimethylchlorosilane. Subsequently, thermal cyclization of the PBO precursor at 350 °C produced the corresponding thermally stable PBO. The inherent viscosity of the precursor polymer was 0.35 dl/g. The cyclized PBO showed a glass transition temperature (T_g) at 309 °C and a 5% weight loss at 550 °C in nitrogen. The structure of the precursor polymer and the fully cyclized polymer were characterized by FTIR and ^{1}H NMR. The photosensitive PBO precursor containing 20 wt% DNQ-4 photosensitive compound showed a sensitivity of 172 mJ/cm^2 and a contrast of 1.33 in a 3-μm film with a 0.6 wt% tetramethylammonium hydroxide (TMAH) developer. A pattern with a resolution of 5 μm was obtained from this composition. The novel PBO precursor photosensitive composition showed a significant improvement in dark film loss after development and could be used to make a thick film resist. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Polybenzoxazole; Photosensitive; Positive working

1. Introduction

Several high temperature polymers have been used in microelectronic devices, such as buffer coating, passivation layers, alpha particle barrier, interlayer dielectrics, and wafer scale packages, etc. Among them, polyimides are the most popular material being used in the semiconductor industry [1,2]. However, polyimides contain polar carbonyl groups in the polymer backbone, and inherently have higher water absorption and dielectric constant than other less polar polymers. The polybenzoxazoles (PBOs) are another high temperature polymers, which have no polar groups in the polymer backbone and have lower water absorption and dielectric constant. They are well suitable for microelectronic applications and have received increasing interest in recent years for its use in the semiconductor industry [3–6]. Besides these characteristics, the precursor of PBO, polyhydroxyamide (PHA), bears phenolic hydroxyl groups in the polymer backbone, which render the polymer soluble in the aqueous base and make it suitable to be used as base resin for aqueous base developable photoresist. The conventional g-line (436 nm) and i-line (365 nm) photoresists are based on the novolac/diazonaphthoquinone (DNQ) systems. The phenolic hydroxyl groups in the novolac resin render the resin aqueous base solubility. Though a molecular interaction, probably a hydrogen bond between the diazo group of DNQ and the novolac resin, the aqueous base solubility of novolac can be inhibited by DNQ. After exposure with UV light, DNQ is converted to indenecarboxylic compounds which promote dissolution [7]. Similar to the novolac resin used in the commercial g-line or i-line photoresists, the aqueous base solubility of the PBO precursor can be inhibited by the addition of DNQ photoactive compound and can be restored after exposure to UV light. Based on the same principle and the special molecular structure in its backbone, the PBO precursor can be used to prepare a positive working photosensitive material for microelectronic applications [8,9].

Although the conventional photosensitive PBO has good lithographic performance, its dark film loss is high due to

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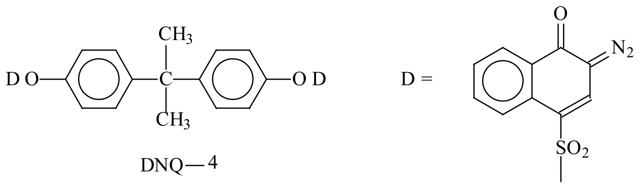


Scheme 1. Structure of DNQ-4.

the fact that PBO precursor has high solubility in the aqueous base developer. In the present study, we report the use of a trimethylsilyl (TMS) group to partially protect the phenolic hydroxyl groups in the PBO precursor to reduce its aqueous base solubility. The protected PBO precursor can be deprotected by acid from a DNQ photoactive compound after exposure to UV light. In this way, a novel low dark film loss photosensitive PBO precursor composition can be prepared.

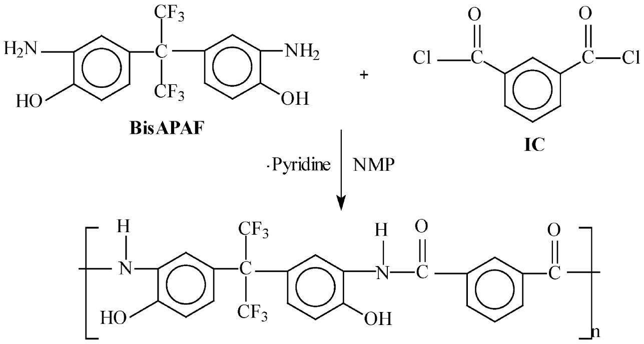
2. Experimental

2.1. Materials

2,2-Bis(3-amino-4-hydroxyphenyl)hexafluoropropane (BisAPAF) was purchased from Chriskev Company (USA). Isophthaloyl chloride (IC) was obtained from Aldrich and dried under vacuum at 60 °C for 24 h before use. Anhydrous *N*-methylpyrrolidine (NMP), tetrahydrofuran (THF), triethylamine, bisphenol A and pyridine were obtained from Aldrich and used without further purification. Naphthoquinone-1,2-diazide-4-sulfonic acid chloride (S-214) was purchased from TCI Co. (Japan). Trimethylchlorosilane (TMS) and tetramethylammonium hydroxide (TMAH) in 25 wt% solution were obtained from Lancaster. The bisphenol A based 1,2-naphthoquinone diazide-4-sulfonate (DNQ-4) photoacid generator was synthesized by reacting bisphenol A with S-214 according to the literature [10]. Its structure is shown in Scheme 1.

2.2. Synthesis of PBO precursor

A typical preparation of BisAPAF-IC PHA precursor proceeds as follows. To a dry 250 ml three-necked flask equipped with a nitrogen inlet and mechanical stirrer were added 5.21 g (14.24 mmol) of BisAPAF, 2.25 g (28.48 mmol) of pyridine and 50 g of anhydrous NMP. After the BisAPAF completely dissolved, the solution was cooled to 5 °C with ice water, and 2.89 g (14.24 mmol) of IC was added slowly into the solution. After complete addition, the reaction mixture was stirred at room temperature for 16 h. The resulting viscous solution was added drop wise to 1 l of stirring water. The precipitated polymer was collected by filtration, washed with methanol, and then dried in a vacuum oven at 80 °C for 24 h. The synthesis procedure is shown in Scheme 2.



Scheme 2. BisAPAF-IC PBO precursor synthesis.

2.3. Synthesis of PBO precursor partially protected by a trimethylsilyl (TMS) group

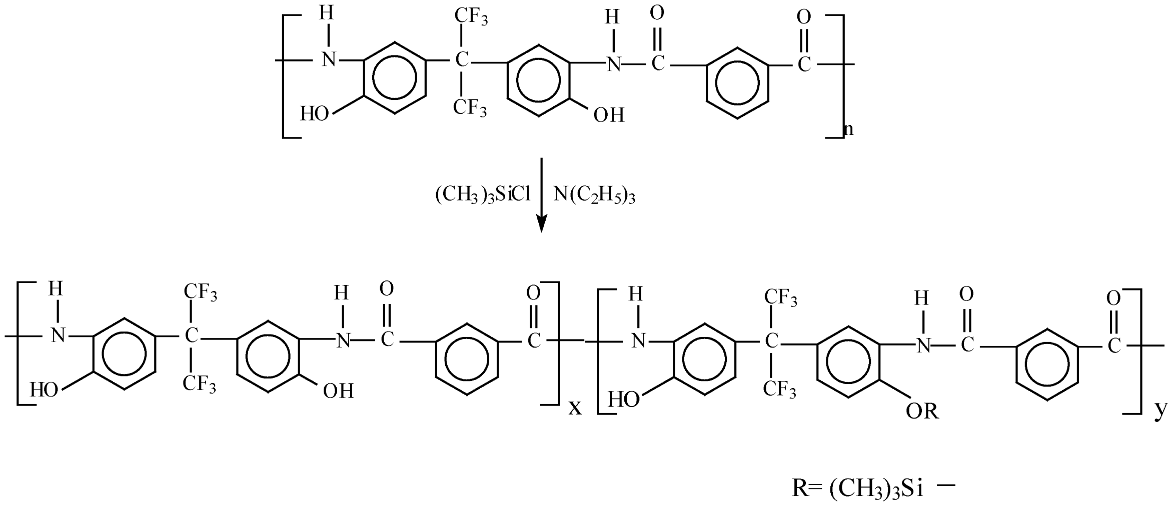
A 20% TMS protected BisAPAF-IC PBO precursor was prepared as follows. To a 250 ml three-necked round bottom flask equipped with a mechanical stirrer and a nitrogen inlet, 3.00 g (6 mmol) of BisAPAF-IC PHA and 18 g of THF were added. The mixture was cooled to 0–5 °C by using an ice-bath and then 0.26 g (2.4 mmol) of TMS was added. After stirring for 5 min, 0.282 g (2.76 mmol) of triethylamine in 5.64 g of THF was added slowly using an addition funnel. The reaction mixture was stirred at room temperature for 24 h and then precipitated in 300 ml of ice water. The polymer was collected by filtration and dried under vacuum at 80 °C for 24 h. The synthesis procedure is shown in Scheme 3.

2.4. Preparation of TMS protected PBO precursor film and thermal conversion to PBO

Five grams of 20% TMS protected PBO precursor powder was dissolved in 20 g of dimethylacetamide (DMAC) to make a 20% (w/w) solution. A film was cast from the viscous solution on a glass plate by a doctor's knife. The film was dried at 100 °C for 1 h, 200 °C for 1 h, and 350 °C for 1 h in a heating oven to convert the TMS protected PBO precursor to a PBO as shown in Scheme 4. The film was transparent yellow.

2.5. Characterization

The IR spectra were recorded on a Jasco 460 FTIR Spectrometer. ^{1}H NMR spectra were recorded on a Brucker Advance 600 Spectrometer using dimethylsulfoxide-d_6 as solvent. The inherent viscosity of BisAPAF-IC PBO precursor was measured using a Cannon-Ubbelohde no. 100 viscometer at a concentration of 0.5 g/dl in NMP at 30 °C. Thermal stability was analyzed using a TA instrument thermogravimetric analyzer (TGA) 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 BisAPAF-IC PBO film were determined using a TA Instruments thermal mechanical



Scheme 3. Synthesis of partially TMS protected PBO precursor.

analyzer (TMA) 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–vis spectrum was obtained on a Hitachi U-2001 UV–vis spectrophotometer.

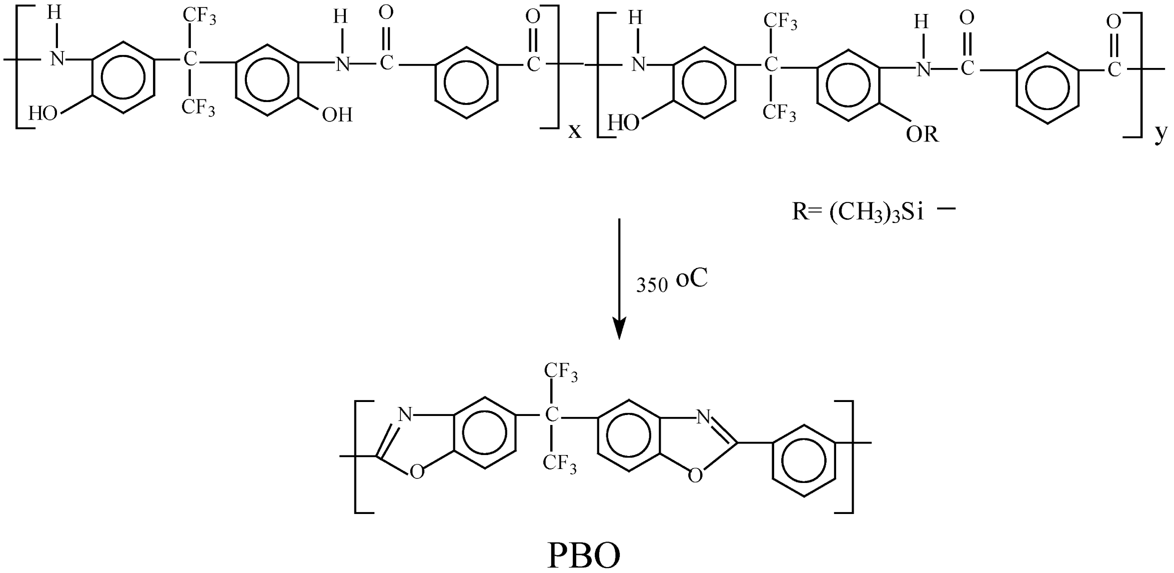
2.6. Preparation of photoresist formulation and lithographic evaluation

Two grams of 20% TMS protected BisAPAF-IC PBO precursor were dissolved in 10 g of NMP and 0.4 g of DNQ-4 photoactive compound was added to prepare the photoresist solution. The solution was filtered through a 1-μm Teflon filter. It was then spin-coated onto a silicon wafer and soft baked on an airflow clean room oven at 105 °C for 40 min to obtain a film around 3 μm thick. (The soft bake temperature was below the DNQ-4's decomposition temperature which was around 130 °C measured by TGA.) The film was exposed to an unfiltered mercury arc lamp measured at 250–400 nm. The wafer was developed in a 0.6 wt% TMAH developer. The film thickness was measured with a Tenco instrument Alpha-Step 200. The dissolution rates were calculated from the resist thickness before and after immersing in the TMAH solution, followed by dividing the decreased thickness by the immersing time. The characteristic curve was obtained by plotting the normalized film thickness against the exposure energy.

3. Results and discussion

3.1. Synthesis of PBO precursor

The soluble PHA was synthesized from the reaction of IC and BisAPAF at 5 °C in anhydrous NMP. The inherent



Scheme 4. Thermal cyclization of partially TMS protected PBO precursor.

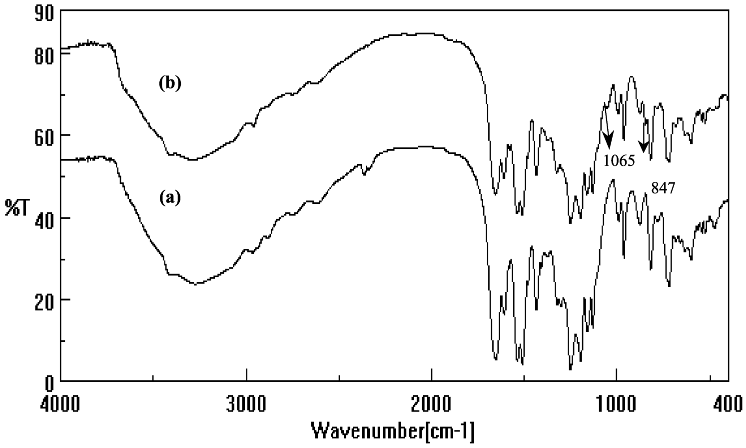


Fig. 1. IR spectra of (a) BisAPAF-IC PBO precursor and (b) 20% TMS protected BisAPAF-IC PBO precursor.

viscosity of the polymer was 0.35 dl/g measured at 30 °C in NMP at a concentration of 0.5 g/dl. The formation of PHA was confirmed by IR and ^{1}H NMR spectra as shown in Figs. 1 and 2. The polymer exhibited a broad absorption band at 3400–3100 cm^{-1} due to amino (N–H) and hydroxyl (OH) groups, and a strong carbonyl absorption at 1650 cm^{-1} in IR spectrum [11]. The ^{1}H NMR spectrum of the polymer also showed the hydroxyl (10.4 ppm) and amino (9.8 ppm) groups [12].

3.2. Synthesis of PBO precursor partially protected by a trimethylsilyl group

Yamaoka et al. have reported the use of trimethylsilyl (TMS) as the protecting group in the preparation of poly(*p*-hydroxystyrene) based deep UV resist because of its high rate of hydrolysis and good stability in the absence of acid [13]. Ho et al. [14] employed the same approach to prepare a photosensitive polyimide system. Due to the simplicity of the protecting reaction, we also chose the TMS protecting group in our photosensitive PBO system. The partially TMS protected PBO precursor was synthesized by reacting BisAPAF-IC PBO precursor with TMS in THF with a triethylamine catalyst at room temperature for 24 h. The amount of TMS added is 20% of the number of moles of the OH groups in the polymer. The FTIR and ^{1}H NMR spectra of the partially TMS protected PBO precursor were shown in Figs. 1 and 2. The appearance of a new $-Si-CH_3$ peak at 847 cm^{-1} and a $-Si-O-$ peak at 1065 cm^{-1} in IR spectrum indicated that the silylation of PBO precursor was successful [14]. The appearance of a TMS group at 0.20 ppm and the decrease of the intensity of the OH group in ^{1}H NMR spectrum further supported the finding. The protecting level was estimated from the integration of the OH peak, using the NH peak as an internal standard. ^{1}H NMR showed that about 20% of hydroxyl groups of the PBO precursor were protected, which was in good agreement with the amount of TMS added. We tried to prepare the TMS protected PBO precursor with a protecting level higher than 20%, but the

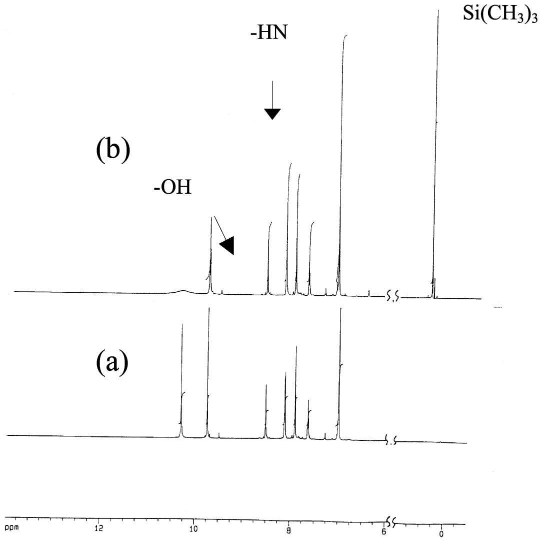


Fig. 2. ^{1}H NMR spectra of (a) BisAPAF-IC PBO and (b) 20% TMS protected BisAPAF-IC PBO precursors.

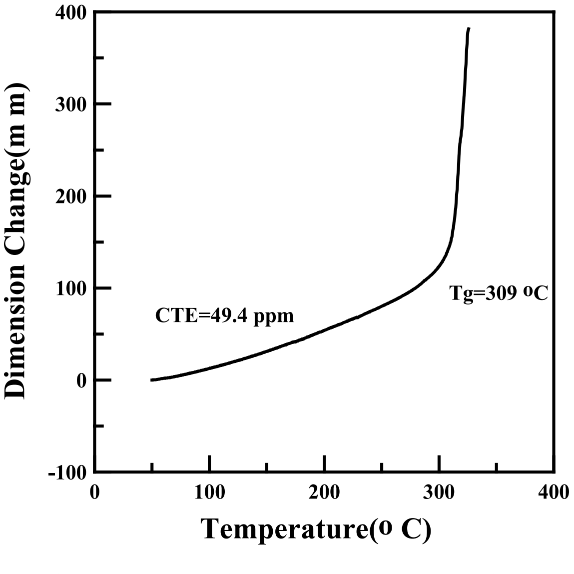


Fig. 3. TMA curve of the cured BisAPAF-IC PBO film.

Table 1
Solubility of BisAPAF-IC PBO precursor, 20% TMS protected BisAPAF-IC PBO precursor and cured PBO

Solvent	BisAPAF-IC PBO precursor	20% TMS protected BisAPAF-IC PBO precursor	Cured BisAPAF-IC PBO
NMP	+	+	−
DMAC	+	+	−
DMF	+	+	−
THF	+	+	−
Acetone	+	+	−
Ethanol	+	+	−

+ : soluble; − : insoluble; DMAC: *N*,*N*′-dimethylacetamide; DMF: *N*,*N*′-dimethylformamide; THF: tetrahydrofuran.

reaction mixture became cloudy, which could be due to the precipitation of the polymer. Higher the protecting level, lower is the dark film loss that can be obtained in the photoresist film. We chose the 20% TMS protecting PBO precursor as the base resin in our study, and did not try the resin with protecting level less than 20%.

3.3. Polymer characterization

Table 1 summarizes the qualitative solubility of the BisAPAF-IC PBO precursor, 20% TMS protected BisAPAF-IC PBO precursor, and the corresponding BisAPAF-IC PBO. The BisAPAF-IC PBO precursor and the 20 wt% TMS protected BisAPAF-IC PBO precursor were soluble in many solvents, but the cured PBO did not dissolve in any organic solvents. The TMA curve (Fig. 3) of the cured BisAPAF-IC PBO film shows a T_g at 309 °C and an in plane CTE of 49.4 ppm/°C. Fig. 4 shows the TGA thermograms of the BisAPAF-IC PBO precursor with 20% DNQ-4 film after development (a) and the cured BisAPAF-IC PBO film (b). The BisAPAF-IC PBO precursor with 20% DNQ-4 exhibits weight loss in two steps. The first step started around 140 °C which was attributed to the decomposition of DNQ-4 and the dehydration of the precursor due to thermal cyclization. The weight loss leveled off around 300 °C, and again started above 500 °C, which is due to the decomposition of PBO polymer. The cured BisAPAF-IC PBO film displayed good thermal stability. Its TGA thermogram, which was obtained at a heating rate of 10 °C/min, showed 5% weight loss at 550 °C in nitrogen. These results indicate that the DNQ-4 can be totally removed by high temperature curing at 350 °C, and will not affect the thermal stability of the cured PBO film. In the IR spectrum (Fig. 5) of the cured PBO film, a new characteristic absorption of benzoxazole ring appeared at 1620 cm^{-1} and the broad absorption disappeared at 3400–3100 cm^{-1} (OH groups) and 1650 cm^{-1} (carbonyl groups of PHA).

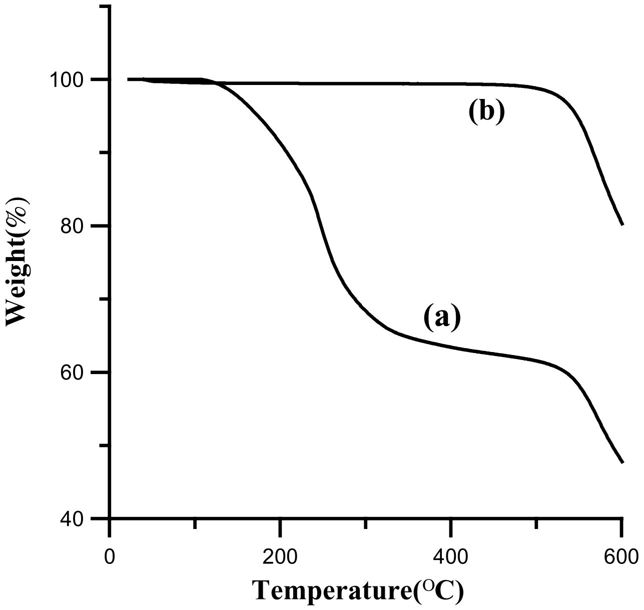


Fig. 4. TGA thermograms of (a) BisAPAF-IC PBO precursor with 20% DNQ-4 after development and (b) the cured BisAPAF-IC PBO film.

3.4. Lithographic evaluation

Many photoacid generators have been used in 254 nm and 193 nm photoresists, such as onium salts, nitro benzyl esters, halogenated organic compounds, etc. Most of them have absorption only in the deep UV area, and are transparent in the g-line and i-line area, which are unsuitable for use in photosensitive polyimides or PBO systems. The photoacid used in this study was bisphenol A based 1,2-naphthoquinone diazide-4-sulfonate (DNQ-4). Unlike the 1,2-naphthoquinone diazide-5-sulfonate (DNQ-5), which produces only a weak carboxylic acid after irradiation, the DNQ-4 generates both carboxylic acid and strong sulfonic

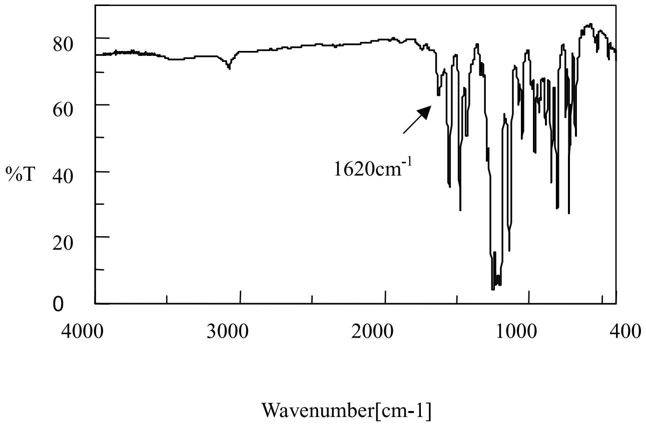
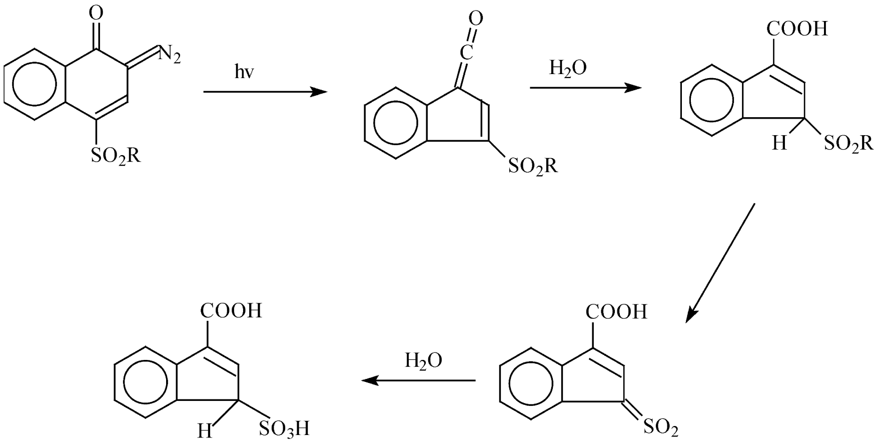
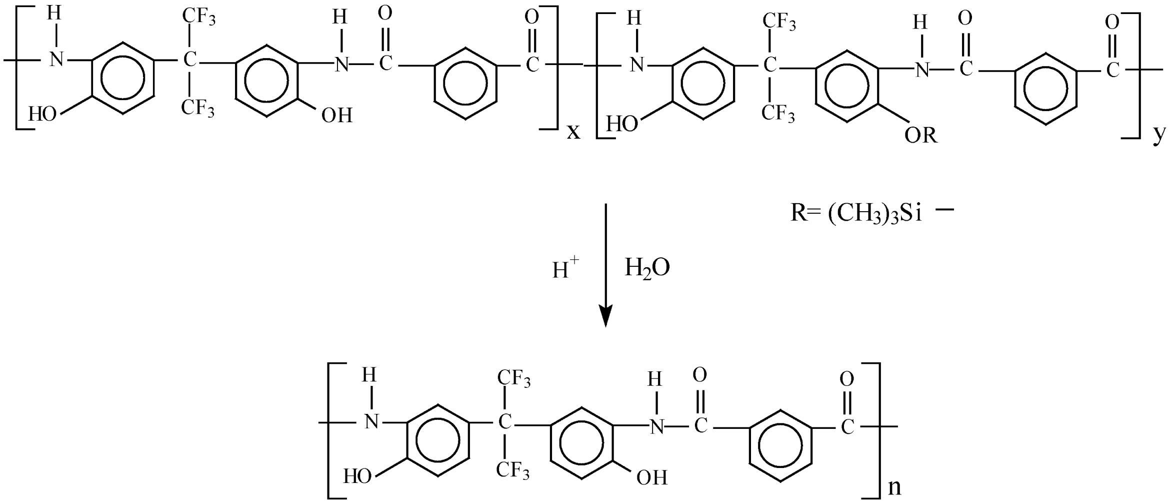


Fig. 5. IR spectrum of BisAPAF-IC PBO.



Scheme 5. Photoreaction mechanism of DNQ-4.



Scheme 6.

acid according to Scheme 5 [15]. It is suitable to use in the photosensitive TMS protected PBO precursor system to deblock the trimethylsilyl group as shown in Scheme 6, and to restore its aqueous base solubility.

The UV–vis spectrum of THF solution of 20% TMS protected BisAPAF-IC PBO precursor with a concentration of 1×10^{-3} mole/l in the 250–600 nm wavelength is shown in Fig. 6. Due to the presence of the hexafluoroisopropylidene (6F) group in the polymer backbone, which can separate chromophoric groups, the polymer has a high transmittance above 360 nm. Therefore the DNQ-4, having a strong absorption in the range of 320–450 nm (Fig. 7), can be used as the photosensitive compound in the resist formulation. Fig. 8 displays the absorption spectra of 20% TMS protected PBO precursor with 20% DNQ-4 before and after exposure. It is clear that the absorption peak at 365 nm of DNQ-4 is bleached.

The 20% TMS protected photosensitive PBO precursor composition consists of 20 wt% DNQ-4 in NMP. Using a 0.6 wt% TMAH solution as the developer, the dissolution rate was estimated by measuring the film thickness after development. The dissolution rates of the BisAPAF-IC

Table 2
Dissolution rates of BisAPAF-IC PBO precursor, 20% TMS protected BisAPAF-IC PBO precursor, 20% TMS protected BisAPAF-IC PBO precursor/20% DNQ-4 before and after exposure

Polymer	Dissolution rate (μm/s)
BisAPAF-IC PBO precursor	0.148
20% TMS protected BisAPAF-IC PBO precursor	0.036
20% TMS protected BisAPAF-IC PBO precursor + DNQ-4 (before exposure)	0.008
20% TMS protected BisAPAF-IC PBO precursor + DNQ-4 (after exposure)	0.181

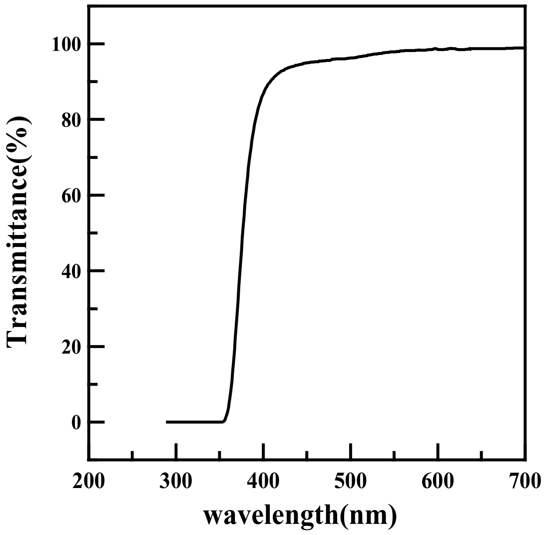


Fig. 6. UV–vis spectrum of THF solution of BisAPAF-PMDA polyamic acid *n*-butyl ester.

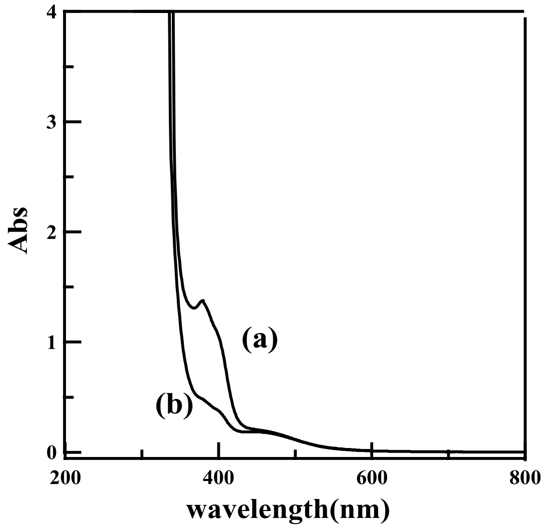


Fig. 8. UV–vis spectra of 20% TMS protected BisAPAF-IC PBO precursor film with 20 wt% DNQ-4 before and after exposure.

PBO precursor, the 20% TMS protected BisAPAF-IC PBO precursor, the 20% TMS protected BisAPAF-IC PBO precursor with 20% DNQ-4 before and after exposure, are shown in Table 2. Due to the TMS protecting groups, the dissolution rate of 20% TMS protected PBO precursor decreased from 0.148 to 0.036 μm/s. The high dissolution rate contrast between the exposed and unexposed areas is expected to have a high resolution. The exposure characteristic curve of 3-μm film for the 20% TMS protected BisAPAF-IC PBO precursor/DNQ-4 system developed by a 0.6 wt% TMAH solution is shown in Fig. 9. The system's sensitivity is 172 mJ/cm^2 and the contrast is 1.33. A resolution of 5-μm pattern can be obtained in a 3-μm film as shown in Fig. 10. The 20% TMS protected BisAPAF-IC PBO precursor was finally cured at 350 °C for 1 h to give the PBO pattern (Fig. 11). After thermal cure, the film thickness was reduced 29.6% compared to the precursor film. The reason for the film shrinkage is due to the release of water during the ring closure and the decomposition of DNQ-4 photosensitive compound. The most significant contribution of the TMS protected PBO precursor photosensitive composition is to reduce the dark film loss after development. Compared to the unprotected PBO precursor/DNQ-4 system, which has a high dark film loss of 36.5%, the TMS protected PBO precursor/ DNQ-4 system has only a 17.3% dark film loss after development that can be attributed to the considerable decrease in the dissolution rate of the 20% TMS protected PBO precursor. The decrease of dark film loss

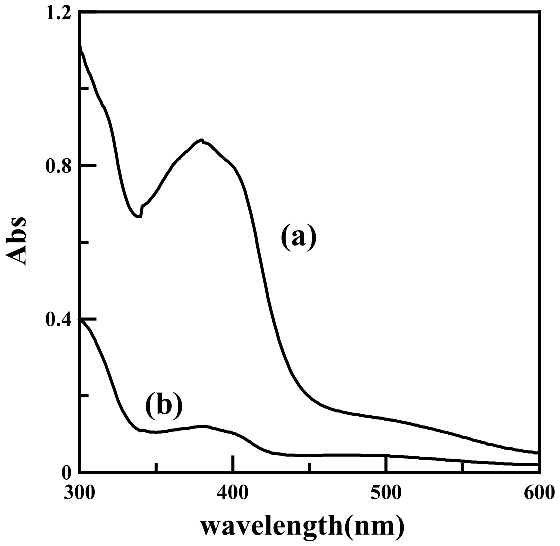


Fig. 7. UV–vis spectra of (a) DNQ-4 before exposure and (b) after exposure.

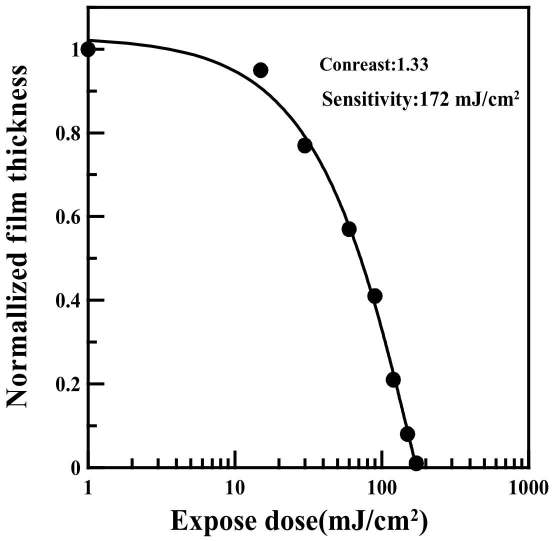


Fig. 9. Characteristic exposure curve of 20% TMS protected BisAPAF-IC with 20 wt% DNQ-4 system.

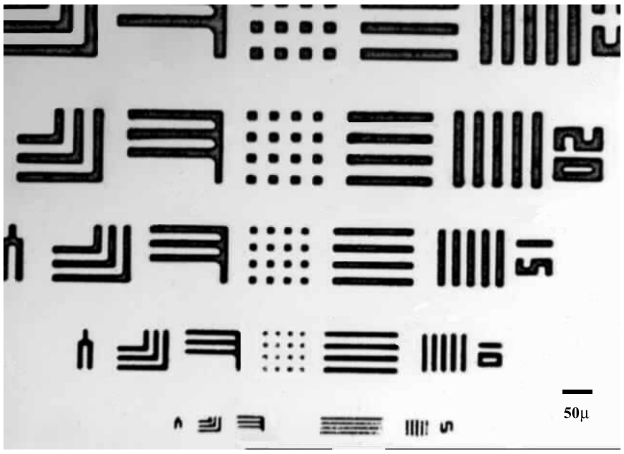


Fig. 10. Optical micrograph pattern of 20% TMS protected BisAPAF-IC/DNQ-4 system after development with 0.6 wt% TMAH solution.

helps in making thick films for use in microelectronic applications.

4. Conclusions

A partially TMS protected BisAPAF-IC PBO precursor was prepared from the low temperature polymerization of BisAPAF and IC followed by reacting with TMS. A novel positive working, aqueous base developable photosensitive resin composition was prepared from this polymer and from bisphenol A based 1,2-naphthoquinone diazide-4-sulfonate (DNQ-4) photoacid generator. The partially TMS protected photosensitive PBO precursor containing 20 wt% DNQ-4 photoacid generator showed a sensitivity of 172 mJ/cm^2 and a contrast of 1.33 in a 3-μm film. A pattern with a resolution of 5 μm was obtained from this composition. The novel PBO precursor photosensitive composition showed a significant improvement in dark film loss after development and could be used to make a thick film resist.

Acknowledgements

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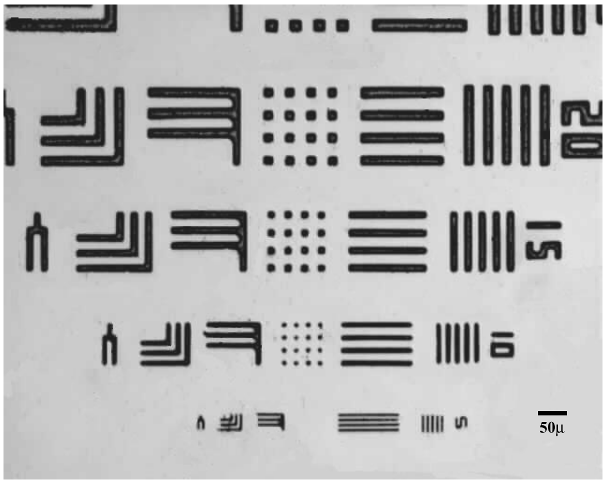

Fig. 11. Optical micrograph pattern of 20% TMS protected BisAPAF-IC/DNQ-4 system and cured at 350 °C for 1 h.

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