

# Synthesis, Characterization, and Properties of a Novel Positive Photoresist Polyimide

BANG-CHEIN HO, JIAN-HONG CHEN, WEN-CHUNG PERNG, CHIN-LUNG LIN, LI-MEI CHEN

Union Chemical Laboratories, Industrial Technology Research Institute, Hsinchu, Taiwan 300, Republic of China

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**ABSTRACT:** An aqueous base-soluble polyimide (BAPAF/6FDA) was obtained from the polycondensation of 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (BAPAF) and 4,4'-(hexafluoroisopropylidene)-bis(phthalic anhydride) (6FDA). It exhibits high thermal stability and high transparency at 365 nm. A novel positive photoresist was prepared by protecting BAPAF/6FDA with a trimethylsilyl group while using diazonaphthoquinone as the photosensitizer. In addition, the silylated polyimide was converted to aqueous base-soluble polyimide in the presence of an acid and a slight amount of water. This photoresist yields a sensitivity of 110 mJ/cm<sup>2</sup> and a contrast of 3.24. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1313–1318, 1998

## INTRODUCTION

A positive photoresist based on novolac resin/diazonaphthoquinone photosensitizer systems has been extensively utilized due to its desirable combinations of availability and material properties, e.g., lithographic sensitivity and aqueous base solubility. The systems are the standard materials used in semiconductor manufacturing. However, the advancements in IC fabrication processes require the photoresist to withstand elevated temperatures and harsh environments during processing to maximize wafer throughput and device yields. Some of the processing steps include high current ion implantation, plasma etching, reactive ion etching, and metal deposition. Recent developments in photoresists include modification in materials as well as in the processing conditions, such as in the use of high molecular weight novolac, resin-bound sensitizer, silicone-modified novolac, and changes in processing parameters like the post-bake cycle and deep UV hardening<sup>1,2</sup> to enhance the resist's thermal stability.

Polyimides with a high thermal stability and

low dielectric constant have been important organic materials in the manufacturing of electronic devices. In recent years,<sup>3</sup> the applications of photoactive polyimides and their precursors to passivation layers, alpha particle barriers, stress buffers, and interlayer dielectrics are increasingly important in place of nonphotoactive polyimides. A number of photoactive polyimides<sup>4,5</sup> and their precursors<sup>6–8</sup> have been reported; however, most of them are not satisfactory for practical use. Novel photoactive polyimide precursors, having a hexafluoropropyl group within the chain structure, have been studied.<sup>9–12</sup> However, most photoactive polyimides and their precursors are negative-working and reports on positive-working photoactive polyimides or precursors are very limited. Positive-working polyimides<sup>13–17</sup> have received increasing interest in recent years, demonstrating improvements in transparency and solubility in common organic solvents. This article reports on the preparation and properties of a novel positive-working, photoactive polyimide with a trimethylsilyl group which can be deprotected by acid.

## EXPERIMENTAL

### Materials

2,2-Bis(3-amino-4-hydroxyphenyl)hexafluoropropane (BAPAF, Central Glass Co.) was purified

Correspondence to: B.-C. Ho.

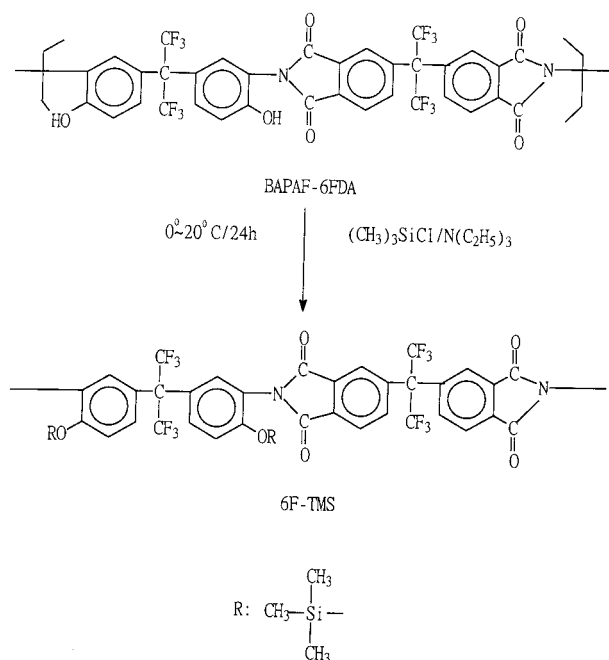
by recrystallization from methyl alcohol. 4,4'-(Hexafluoroisopropylidene)-bis(phthalic anhydride) (6FDA, Hoechst Celanese Co.) was used as received. Both *N,N*-dimethylacetamide (DMAc, Merck Co.) and tetrahydrofuran (THF, Aldrich Co.) were dried over a 4 Å molecular sieve and fractionally distilled under a vacuum from calcium hydride. Other materials from commercial sources were used as received.

### Synthesis of Polyimide Protected by a Trimethylsilyl Group

The soluble polyimide (BAPAF-6FDA) was prepared according to the following reaction: The polymerization was conducted in a closed vessel at room temperature at a concentration of 15% solids by weight in DMAc. A stoichiometric amount of 6FDA was added to a solution of the BAPAF in DMAc. The container was flushed with dry nitrogen and mechanically stirred overnight. The obtained polyamic acid was thermally cyclized at 150°C for 3 h. During this step, the water eliminated by its ring-closure reaction was separated as the *m*-xylene azeotrope at the same time. After the reaction was completed, BAPAF-6FDA was precipitated from the DMAc solution with water and dried at 50°C in a vacuum oven overnight. Five grams of BAPAF-6FDA was dissolved in 25 g of THF, and 1.4 g of trimethylchlorosilane was then added to the solution. After the solution was mechanically stirred for 5 min at 0°C, 1.5 g of triethylamine was added dropwise to the solution. The solution was reacted for 24 h at room temperature and then poured into an excess amount of ice water to precipitate the polymer. The precipitated polymer was filtered and dried rapidly in a vacuum oven. The preparation steps are illustrated in Scheme 1.

### Measurements

IR spectra were recorded on a Perkin-Elmer 842 spectrophotometer. <sup>1</sup>H-NMR spectra were obtained on a Bruker MSL-400 spectrometer, using DMSO-*d*<sub>6</sub> as a solvent. UV-visible spectra were obtained on a Hitachi 320 UV-vis spectrophotometer. The thermal behavior of polymer was examined using a DuPont 2100, equipped with 900 different scanning calorimetry (DSC) and 910 thermogravimetric analyzer (TGA) modules. All measurements were taken at a heating rate of 10°C/min in nitrogen with a flow rate of 50 mL/



**Scheme 1**

min. The dissolution rate was measured using interferometry.

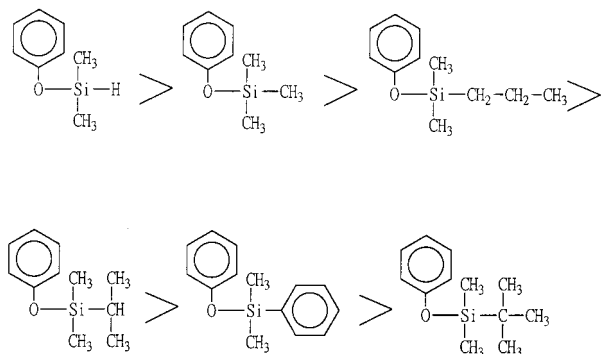
### Lithographic Evaluation

The polymer (1.0 g) was dissolved in DMAc and 0.2 g of a diazonaphthoquinone sensitizer was added to prepare the photoresist solution. The solution was filtered through a 0.45 μm filter. It was spread on a silicon wafer using a spincoater with a speed of 1500 rpm to form a photoresist layer and then prebaked at 90°C for 3 min. Approximately 1 μm of the photoactive polyimide film on a silicon wafer was exposed to a filtered high-pressure mercury lamp at a 365 nm wavelength, then developed in a 0.05N NaOH aqueous solution. A characteristic curve was obtained by the normalized film thickness against the exposure energy.

## RESULTS AND DISCUSSION

### Synthesis and Characterization of Polyimide Protected by a Trimethylsilyl Group

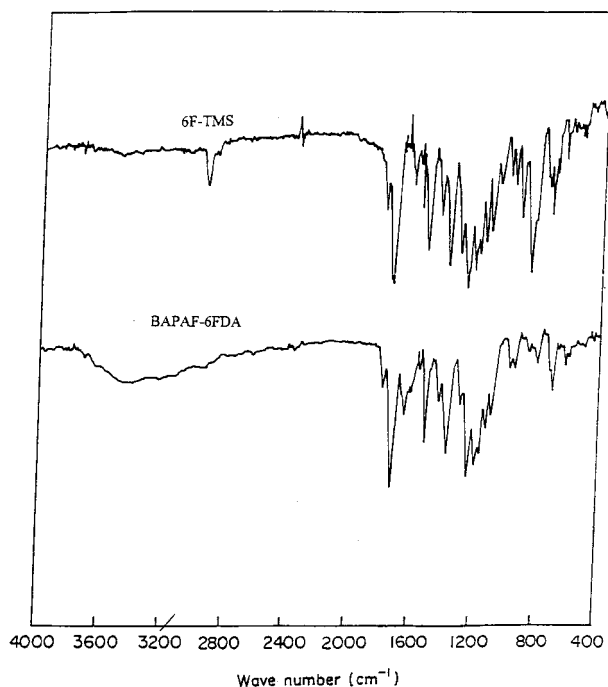
Polyimide BAPAF-6FDA exhibits high solubility not only in common organic solvents but also in aqueous bases. However, the solubility of BAPAF-6FDA in aqueous bases is diminished by protecting the hydroxyl group. The solubility dif-



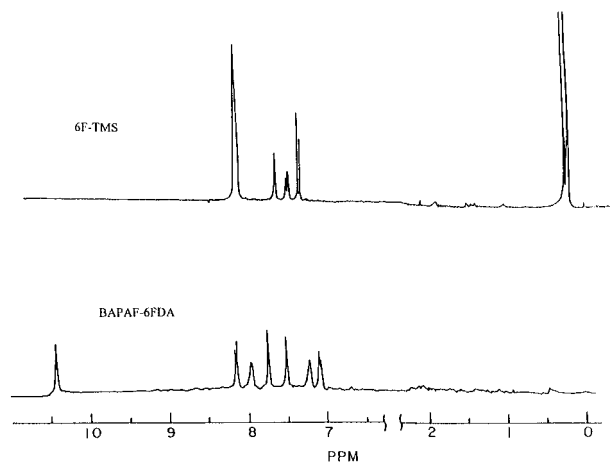
**Figure 1** The order of the hydrolysis rate.

ference owing to this polarity change suggests the potential design of a highly sensitive positive-working polyimide photoresist incorporating a chemical amplification process.

In 1989, Yamaoka et al.<sup>18</sup> examined the rate of acid-catalyzed hydrolysis which was carried out with a series of trialkylsilylated phenols and triarylsilylated phenols. The hydrolysis rate seems to be governed by the steric hindrance of the trisubstituted silyl group rather than by the electric induction effect since no obvious correlation between the rate of hydrolysis and Hammett's  $\sigma$  value of the silylating substituent was observed. In this report, trimethylsilyl was chosen as the protecting group in polyimide, because of its high



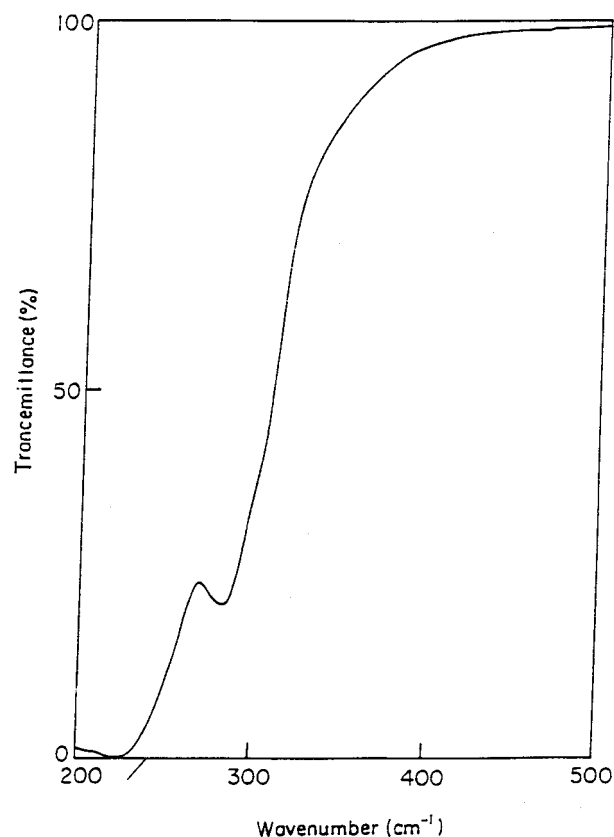
**Figure 2** IR spectrum of 6F-TMS and BAPAF-6FDA.



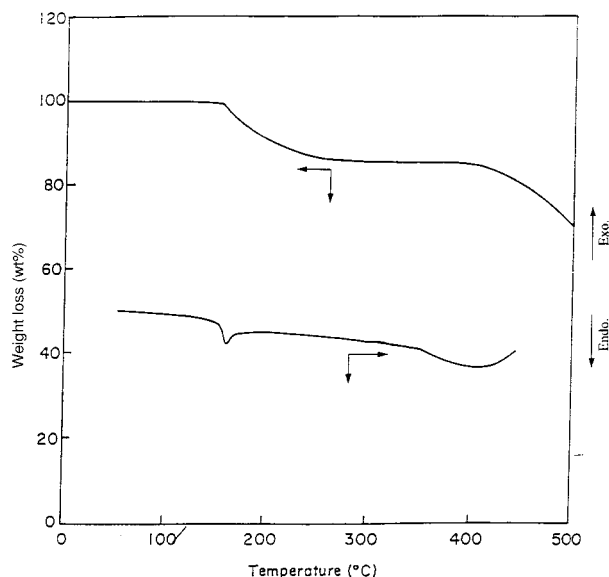
**Figure 3** <sup>1</sup>H-NMR spectrum of 6F-TMS and BAPAF-6FDA.

rate of hydrolysis and good stability in the absence of acid, in spite of the fact that dimethylsilyl exhibits the highest hydrolysis rate (Fig. 1).<sup>18</sup>

Polyimide protected by a trimethylsilyl group (6F-TMS) was synthesized by reacting BAPAF-



**Figure 4** The transmittance spectrum of 1  $\mu$ m-thick film of 6F-TMS.



**Figure 5** TGA and DSC curves for 6F-TMS at a heating rate of 10°C/min in nitrogen.

6FDA with trimethylchlorosilane in THF with a triethylamine catalyst at room temperature for 24 h. The structure characterizations of 6F-TMS were examined with IR and  $^1\text{H-NMR}$  spectra. Figure 2 depicts the IR spectra of 6F-TMS compared with BAPAF-6FDA. The disappearance of the  $-\text{OH}$  group at  $3000\text{--}3600\text{ cm}^{-1}$  and the appearances of a new  $-\text{Si}(\text{CH}_3)_2$  peak at ( $1265$  and  $815\text{ cm}^{-1}$ ) and a  $-\text{Si}-\text{O}$  peak at  $1065\text{ cm}^{-1}$  indicate that the silylation of BAPAF-6FDA was successful. The existence of a trimethylsilyl group in 6F-TMS was also confirmed by  $^1\text{H-NMR}$  (Fig. 3). The proton in the hydroxyl group ( $10.4\text{ ppm}$ ) disappears after the silylation reaction while new peaks which are due to the proton of the  $-\text{CH}_3$  of the trimethylsilyl group appear at  $0.15\text{ ppm}$ . From IR and  $^1\text{H-NMR}$  spectra, the trimethylsilyl group was proved to be 100% introduced into the hydroxyl group of BAPAF-6FDA.

Figure 4 displays the transmittance spectrum of  $1\text{ }\mu\text{m}$ -thick film of 6F-TMS. Strong absorptions with a cutoff located between  $300$  and  $400\text{ nm}$  are observed. The transmittance at  $365\text{ nm}$  is  $94\%$ , indicating that 6F-TMS exhibits a high transparency in this wavelength region. St Clair et al. demonstrated that polyimides containing the hexafluoroisopropylidene (6F) group exhibited a high transparency in the UV-visible region. Their approaches involved separating chromophoric groups and reducing the electronic interaction between color-causing centers in the polymer molec-

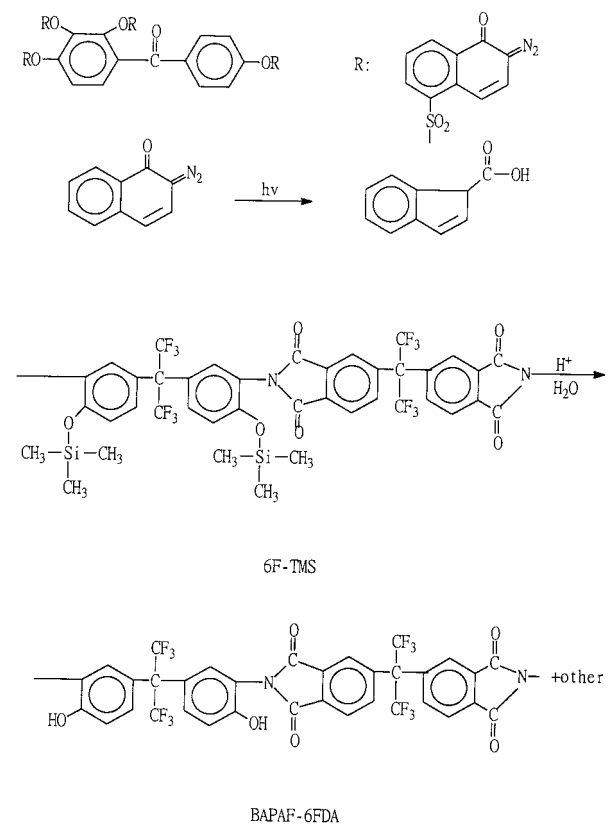
ular structure by employing the sterical hindrance effect of the 6F group.

### Thermal Behavior of 6F-TMS

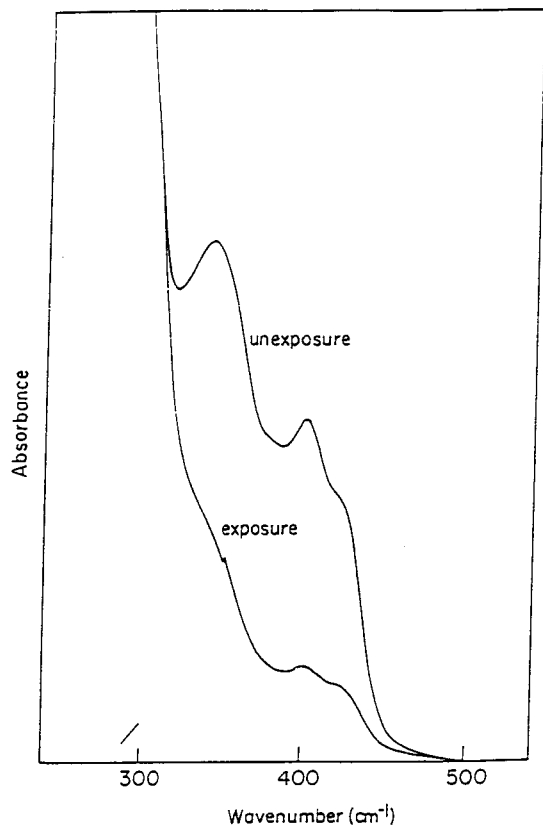
The thermal behavior of 6F-TMS was obtained with TGA and DSC measurements (Fig. 5). Two obvious weight loss regions, one representing an endothermic mass loss between  $157$  and  $285^\circ\text{C}$ , and the other, an exothermic mass loss starting at around  $400^\circ\text{C}$ , are observed. The  $15\%$  weight loss of the first region is closely related to the weight percent of the trimethylsilyl group in 6F-TMS.

### Acid Precursor

A variety of acid precursors used to generate an acid upon exposure to light include the well-studied onium salts, the conventional diazonaphthoquinone photosensitizer, a family of nitrobenzyl esters, and a variety of halogenated organic compounds including 1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethane and substituted *s*-triazine derivatives. In this study, a diazonaphthoquinone photo-



**Scheme 2**



**Figure 6** UV absorption spectrum of 6F-TMS 1  $\mu\text{m}$ -thick film with 20 wt % diazonaphthoquinone photosensitizer before and after exposure.

sensitizer is used and its structure is shown in Scheme 2. The diazonaphthoquinone photosensitizer is photochemically decomposed to give an acid which deblocks the trimethylsilyl group in 6F-TMS as shown in Scheme 2. Figure 6 displays the absorption spectrum of 1  $\mu\text{m}$ -thick film of 6F-TMS with the diazonaphthoquinone photosensitizer. On irradiating with UV light, the absorption peaks at 365 and 410 nm are bleached.

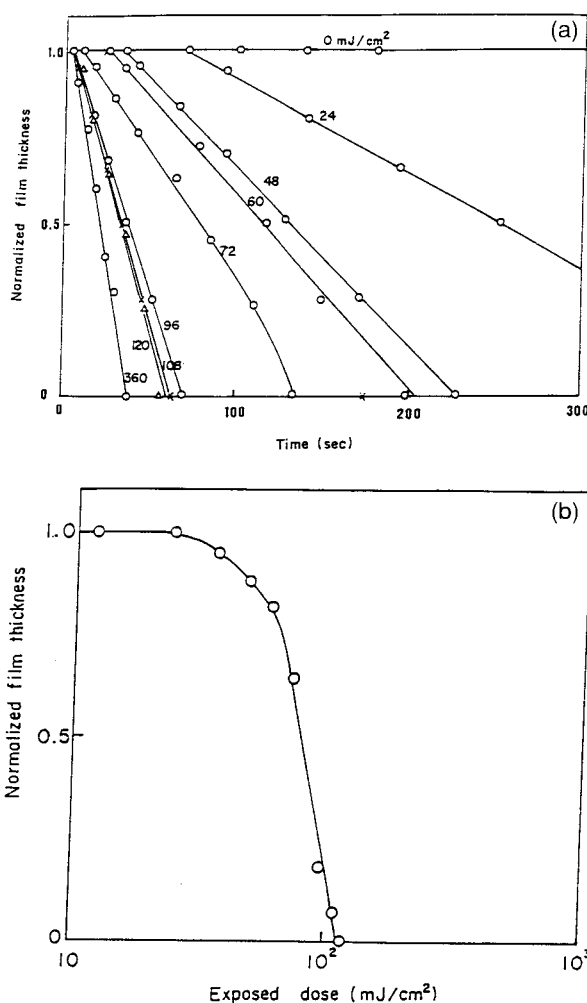
### Resist Characteristics

Unlike the conventional novolac positive photore-sist, where the insolubility in the unexposure areas is brought about by solubility inhibition of the diazonaphthoquinone photosensitizer, the advantage of this positive photoresist is that 6F-TMS is completely insoluble in aqueous bases unless it is exposed to UV light. The high solubility contrast between the exposed and the unexposed areas is expected to give a high resolution. The exposure characteristic for 6F-TMS with 20 wt % of the diazonaphthoquinone photosensitizer which

was developed in 0.05N NaOH was measured and is shown in Figure 7. This system's sensitivity is approximately 110  $\text{mJ}/\text{cm}^2$  and the contrast is 3.24, which were obtained at a development time of 60 s.

### CONCLUSION

A novel polyimide (6F-TMS) was synthesized by protecting BAPAF-6FDA with the trimethylsilyl group. This polyimide has adequate soluble characteristics and exhibits high transparency at 365 nm. It provides a positive-working resist when formulated with a diazonaphthoquinone sensi-



**Figure 7** (a) Normalized film thickness vs. time in developer curves for 6F-TMS with 20 wt % diazonaphthoquinone photosensitizer that received different exposure doses. (b) Normalized film thickness vs. exposure dose curve derived from (a).

tizer, showing a sensitivity about  $110 \text{ mJ/cm}^2$  and with a contrast around 3.24.

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