

# Positive-Working Aqueous Base Developable Photosensitive Polybenzoxazole Precursor/Organoclay Nanocomposites

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**ABSTRACT:** Positive-working aqueous base developable photosensitive polybenzoxazole (PBO) precursor/organoclay nanocomposites have been prepared through the addition of an organoclay to a PBO precursor. The organoclay was formed by a cation exchange reaction between a  $\text{Na}^+$ -montmorillonite clay and an ammonium salt of dodecylamine. The PBO precursor used in this study was a polyhydroxyamide that was prepared from a low-temperature polymerization of 2'2'-bis(3-amino-4-hydroxyphenyl) hexafluoropropane and 4,4'-oxydibenzoyl chloride with an inherent viscosity of 0.3 dL/g. The photosensitive resin/clay formulations were prepared from the precursor with 2,3,4-tris(1-oxo-2-diazonaphthoquinone-5-sulfonyloxy)-benzophenone photosensitive compound and 3–5 wt % organoclay. The PBO precursor/clay was subsequently thermally cured to PBO/clay at 350°C. Both X-ray

diffraction and transmission electron microscope analyses showed that the organoclay was dispersed in the PBO matrix in a nanometer scale. The thermal expansion coefficient of PBO/clay film, which contained 5 wt % organoclay, was decreased 33% compared to the pure PBO film. The PBO/clay nanocomposite films also displayed higher thermal stability, glass transition temperature, and water resistance than the pure PBO film. The photosensitive PBO precursor/clay nanocomposite showed a line/space pattern with a resolution of 5  $\mu\text{m}$  and its sensitivity and contrast were not affected by the organoclay. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 2350–2356, 2005

**Key words:** nanocomposite; photosensitive; polybenzoxazole; synthesis; photoresist

## INTRODUCTION

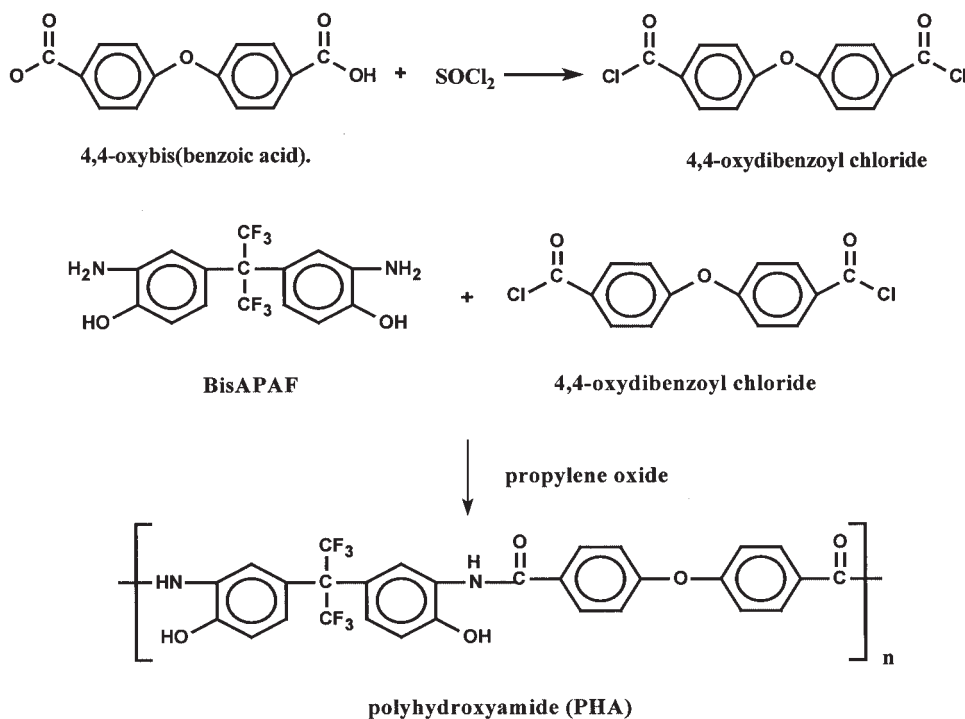
Several high-temperature polymers have been used in microelectronic applications, such as buffer coating, passivation layers, alpha particle barrier, interlayer dielectrics, and wafer scale packages, etc. Among them, polyimides (PIs) are the most popular materials used in the semiconductor industry.<sup>1,2</sup> However, polyimides contain polar carbonyl groups in the polymer backbone. Inherently, their water absorption and dielectric constants are higher than other less polar polymers. The polybenzoxazoles (PBOs) are another group of high-temperature polymers, which have no polar groups in the polymer backbone with a lower water absorption and dielectric constant. They are well suited for microelectronic applications and have received increasing interest in recent years for use in the semiconductor industry.<sup>3–8</sup> Aside from those charac-

teristics, the precursor of PBO, polyhydroxyamide, bears phenolic hydroxyl groups in the polymer backbone, which render the polymer soluble in the aqueous base. Similar to the novolak resin used in the commercial g-line (436 nm) or i-line (365 nm) photoresists, the aqueous base solubility of the precursor can be inhibited by the addition of diazonaphthoquinone (DNQ) photoactive compound and can be restored after exposure to UV light.<sup>9</sup> 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.<sup>10,11</sup>

When photosensitive PBOs are employed in microelectronics, differences in coefficients of thermal expansion (CTEs) between PBO and inorganic or metallic materials result in thermal stress in electronic devices. The differences are due to the multiple heating and cooling steps required in the fabrication of electronic devices. The buildup of stress could cause device failure through peeling and cracking of the PBO film and substrates.<sup>12–14</sup> Recently, Zhu et al. reported low CTE photosensitive PI/silica hybrids through a sol-gel process.<sup>15</sup> We also reported a new method to

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Scheme 1 BisAPAF-ODC PBO precursor synthesis.

reduce the CTEs of photosensitive PIs by the addition of a small amount of nanodispersed organoclay to the photosensitive PI system.<sup>16</sup> Due to the high surface-to-volume ratio of the nanodispersed clay, the thermal expansion and contraction of polymer molecules are highly restricted, which can effectively reduce its CTE. In this paper, we report our study on another new positive-working, aqueous base developable photosensitive polymer/clay system based on polybenzoxazole.

## EXPERIMENTAL

### Materials

2,2-bis(3-Amino-4-hydroxyphenyl)hexafluoropropane (BisAPAF) was purchased from Chriskev Co.. 4,4'-oxybis(Benzoic acid), thionyl chloride, propylene oxide, and anhydrous *N*-methyl-2-pyrrolidone (NMP) were obtained from Aldrich and used without further purification. Tetramethylammonium hydroxide (TMAH) in 25 wt % solution was obtained from Lancaster. 2,3,4-tris(1-oxo-2-Diazonaphthoquinone-5-sulfonyloxy)-benzophenone (PIC-3) photosensitive compound was obtained from Koyo Chemicals (Japan). The organoclay was prepared by a cation exchange reaction between a Na<sup>+</sup>-montmorillonite (Na<sup>+</sup>-Mont) clay and an ammonium salt of dodecylamine (DOA) as described in our previous paper.<sup>17</sup> The interlayer spacing of the original Na<sup>+</sup>-Mont clay is 12.7 Å. After modification,

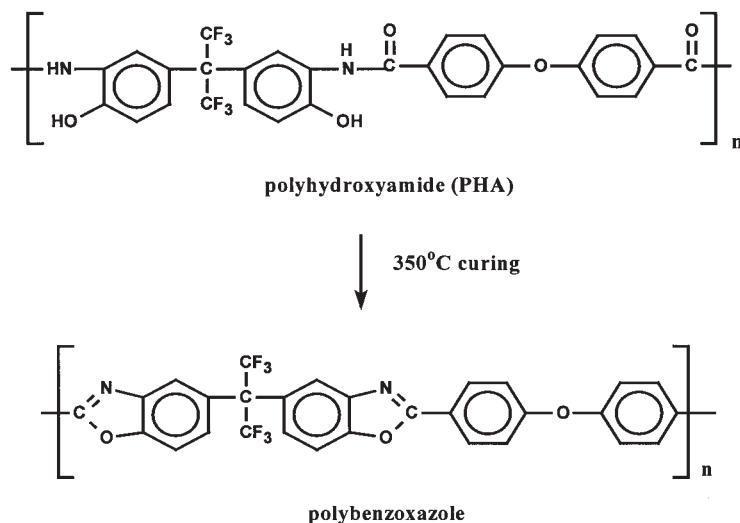
the interlayer spacing of organoclay was expanded to 18 Å.

### Synthesis of PBOprecursor

To a 250-mL three-neck round-bottom flask equipped with a mechanical stirrer and a condenser, 2.58 g (10 mmol) of 4,4'-oxybis(benzoic acid) and 50 g of anhydrous NMP were added. The solution was stirred until it became homogeneous and then cooled to 0°C. To the solution, 2.38 g (20 mmol) thionyl chloride was added dropwise and reacted for 1 h to form the 4,4'-oxydibenzoyl chloride (ODC). To the ODC solution, 3.66 g (10 mmol) of BisAPAF was added. After the BisAPAF was completely dissolved, the solution was cooled to 5°C, and 2.33 g (40 mmol) of propylene oxide was added. The solution was stirred at room temperature for 16 h. The resulting viscous solution was added dropwise to 1 L of stirring deionized water. The precipitated polymer was collected by filtration and washed with deionized water five times. The polymer was dried under vacuum at 60°C for 24 h. The yield was almost quantitative and the inherent viscosity of the polymer was 0.3 dL/g measured in NMP at the concentration of 0.5 g/dL at 30°C. The synthesis steps are illustrated in Scheme 1.

IR (KBr): 1650 cm<sup>-1</sup>(C = O, amide), 3400–3100 cm<sup>-1</sup>(NH, and OH)

<sup>1</sup>H-NMR (*d*-DMSO): 6–8.5 ppm (m, 14 H, aromatic ring), 9.6 ppm (s, 2H, NH), 10.3 ppm (s, 2H, OH)



Scheme 2 Thermal cyclization of PBO precursor to PBO.

#### Preparation of PBO precursor film and thermal conversion to PBO

A film was cast from the viscous PBO precursor solution on a glass plate by a doctor's knife. The film was dried in a vacuum oven at 80°C for 16 h to obtain the PBO precursor film. The film was further heated at 100°C for 1 h, 200°C for 1 h, and 350°C for 1 h in a heating oven to convert the PBO precursor to PBO as shown in Scheme 2.

IR (film): 1600  $\text{cm}^{-1}$  (C = O, benzoxazole). anal. calcd for  $\text{C}_{29}\text{N}_2\text{O}_3\text{F}_6\text{H}_{14}$ : C, 63.95; H, 2.55; N, 5.07. found: C, 62.86; H, 2.70; N, 4.69

#### Preparation of the PBO precursor/clay nanocomposite film and thermal conversion to a PBO/clay nanocomposite

A representative 5 wt % clay loading PBO/clay nanocomposite was prepared as follows: 0.2 g of organo-clay was dispersed in 6 g of NMP by vigorous mechanical stirring (600 rpm) for 1 h and then added to 10 g of PBO precursor solution (solids content is 40 wt % in NMP). After vigorous stirring for 6 h, the clear solution was coated on a glass plate with a doctor's knife and dried in a vacuum oven at 80°C for 16 h to obtain the PBO precursor/clay nanocomposite film. The film was further heated at 100°C for 1 h, 200°C for 1 h, and 350°C for 1 h in a heating oven to convert the PBO precursor/clay nanocomposite to a PBO/clay nanocomposite.

#### Characterization

The IR spectra were recorded on a Jasco 460 FTIR spectrometer. Inherent viscosity 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) 2050 at a heating rate of 10°C/min under nitrogen. The in-plane CTE of cured PBO film was determined using a TA Instruments Thermal Mechanical Analyzer (TMA) 2940 with an extension probe under 0.05N tension force on the film in the temperature range of 50–250°C at a heating rate of 5°C/min under nitrogen. The glass transition temperature ( $T_g$ ) of cured PBO film was obtained from the intersection point between the tangent lines of thermal expansion near the transition point in the TMA curve. The UV-visible spectrum was obtained on a Varian Cary 100 UV-vis spectrophotometer. The X-ray diffraction (XRD) experiment was conducted on a Rigaku D/MAX-IIIIV X-ray diffractometer using  $\text{CuK}\alpha$  radiation. The samples for transmission electron micrograph (TEM) study were prepared by placing the PBO/clay films in an epoxy resin, cured at 70°C overnight. The cured epoxies containing PBO/clay were microtomed with a diamond knife into 70-nm-thick slices. Next, they were placed on a 200-mesh copper grid and examined with a JOEL JEM-1200EX TEM using an acceleration voltage of 200 KV. The water absorption of PBO films was determined from the weight loss of the films immersed in deionized water for 24 h in a TGA, which was heated to 150°C at a heating rate of 5°C/min and held at 150°C for 1 h under nitrogen.

#### Preparation of photosensitive PBO precursor/clay formulations

A representative photosensitive PBO precursor/5 wt % clay formulation prepared from PBO precursor is as

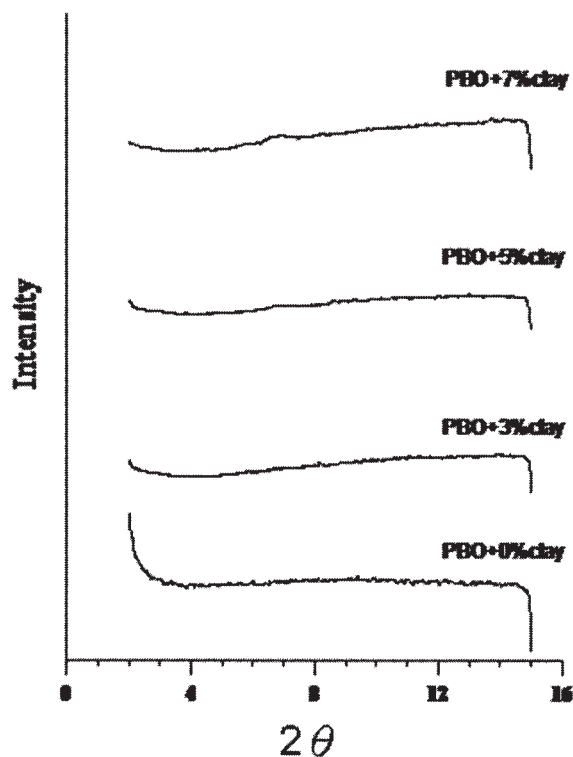


Figure 1 XRD patterns of PBO/clay nanocomposites.

follows: 1.4 g of the photoactive compound (PIC-3) was added to 10 g of PBO precursor solution (solids content is 40 wt % in NMP) to prepare the photoresist solution. In a separate flask, 0.2 g of organoclay was dispersed in 6 g of NMP by vigorous mechanical stirring for 1 h and then added to the photoresist solution. After vigorous stirring for 6 h, the photoresist/clay solution was filtered through a 5- $\mu\text{m}$  Teflon filter.

### Lithographic evaluation of photoresist/clay formulation

The photoresist/clay solution was spin-coated onto a silicon wafer and softbaked on a hotplate at 110°C for 5 min to obtain a film of about 3  $\mu\text{m}$  thick. The film was exposed to a broadband Single-Side Mask Aligner (OAI/J500-IR/VIS). The wafer was developed in a 1.2 wt % TMAH developer, followed by a deionized water rinse. The film thickness was measured with a Tenco instrument  $\alpha$ -Step 200. The characteristic curve was obtained by plotting the normalized film thickness against the exposure energy.

## RESULTS AND DISCUSSION

### Synthesis of PBO precursor and related PBO

The soluble PBO precursor was synthesized from the reaction of ODC and BisAPAF at 5°C in anhydrous NMP. To obtain a flexible polymer film, ODC was chosen as the diacid chloride monomer. The ODC was prepared *in situ* from the reaction of 4,4'-oxydibenzoyl acid and thionyl chloride without isolation. The inherent viscosity of the precursor was 0.3 dL/g measured at 30°C in NMP at a concentration of 0.5 g/dL. The formation of PBO precursor was confirmed by IR and  $^1\text{H-NMR}$  spectra. The polymer exhibited a broad absorption band at 3400–3100  $\text{cm}^{-1}$  due to amino (N-H) and hydroxyl (OH) groups and strong amide carbonyl absorption at 1650  $\text{cm}^{-1}$  in the IR spectrum.<sup>16</sup> The  $^1\text{H-NMR}$  spectrum of the polymer also showed the hydroxyl (10.3 ppm) and amino (9.6 ppm) groups.<sup>19</sup>

After being cured at 350°C for 1 h, the film prepared from the PBO precursor was transparent and tough, which indicated that the polymer had enough molecular weight. Due to the introduction of ether linkage

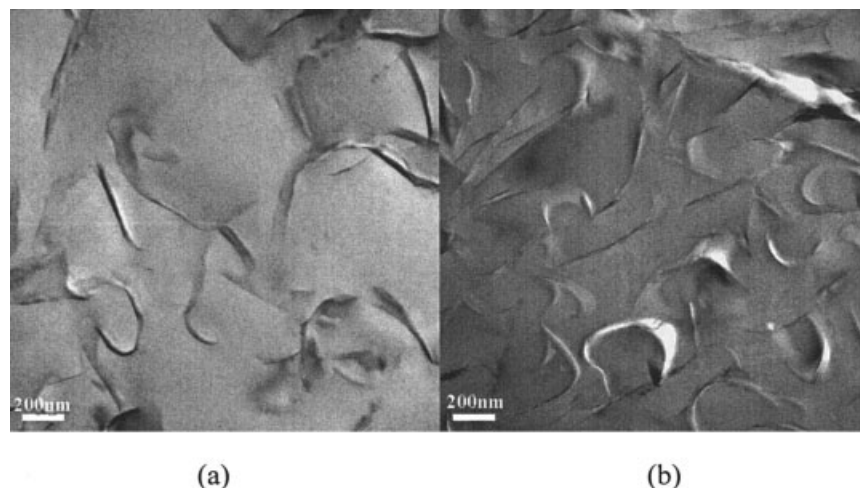


Figure 2 TEM micrographs of PBO/3 wt % clay nanocomposite (a) and PBO/5 wt % clay nanocomposite (b).

**TABLE I**  
Thermal Properties of PBO/Clay Nanocomposites

	CTE ( $\mu\text{m}/\text{m } ^\circ\text{C}$ ) <sup>a</sup>	$T_g^b$ ( $^\circ\text{C}$ )	Decomposition temperature ( $^\circ\text{C}$ ) <sup>c</sup>
PBO	85	328	539
PBO/3 wt% clay	68	333	543
PBO/5 wt% clay	57	339	546

<sup>a</sup> In-plane CTE measured by TMA at a heating rate of  $5^\circ\text{C}/\text{min}$  in nitrogen under a force of  $0.05\text{N}$  in the temperature range of  $50\text{--}250^\circ\text{C}$ .

<sup>b</sup> Determined by TMA at a heating rate of  $5^\circ\text{C}/\text{min}$  in nitrogen.

<sup>c</sup> A 5% weight loss temperature in nitrogen.

in the polymer backbone, the PBO film was flexible and creasable. Therefore, it can be used as a protection or insulation layer in microelectronic devices. In the IR spectrum of the cured PBO film a new characteristic absorption of benzoxazole ring appeared at  $1600\text{ cm}^{-1}$  and the broad absorption of OH groups at  $3400\text{--}3100\text{ cm}^{-1}$  and amide carbonyl absorption at  $1650\text{ cm}^{-1}$  disappeared.<sup>19</sup> The elemental analysis values of PBO are in good agreement with the calculated values of the polymer.

#### Polymer and polymer/organoclay nanocomposites characterization

To improve the dispersion of clay in the polymer matrix, the hydrophilic  $\text{Na}^+$ -montmorillonite clay was treated with the ammonium salt of DOA to form an organoclay as described in our previous paper.<sup>17</sup> Figure 1 shows the XRD patterns of PBO/3–7 wt % clay nanocomposites. The 3 and 5 wt % clay loaded nanocomposites do not have any diffraction peak in  $2\theta = 2\text{--}10^\circ$ . This indicates the possibility of having exfoliated silicate layers of organoclay dispersed in the PBO matrix. The 7 wt % clay loaded nanocomposite does show a small peak at  $6.90^\circ$  ( $d$  spacing =  $1.29\text{ nm}$ ) suggesting that a small amount of clay is not dispersed in the molecular level. The TEM micrographs of 3 and 5 wt % clay/PBO films (Fig. 2) further prove that the organoclay is dispersed randomly in the PBO matrix in a nanometer scale. The estimated size of the silicate sheets is  $\sim 1\text{ nm}$  in thickness and  $\sim 50\text{--}300\text{ nm}$  in length.

Table I shows the thermal properties of PBO and PBO/3–5 wt % clay nanocomposites. The organoclay exhibits significant effect on reducing the CTE of PBO. With only the addition of 5 wt % clay, the CTE of PBO film was decreased by 33%. The addition of organoclay slightly increased the thermal stability of PBO. Its 5% weight loss temperature increased  $7^\circ\text{C}$  and the glass transition temperature ( $T_g$ ) increased  $11^\circ\text{C}$  after the addition of 5 wt % clay. Even though 5 wt % clay

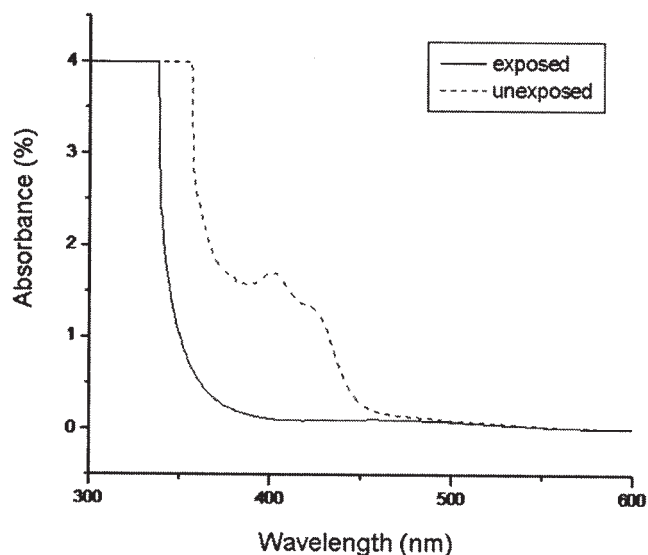
**TABLE II**  
Water Absorption of PBO and PBO/Clay Nanocomposite Films

Clay (%)	0	3	5
Water absorption (%)	0.29	0.14	0.11

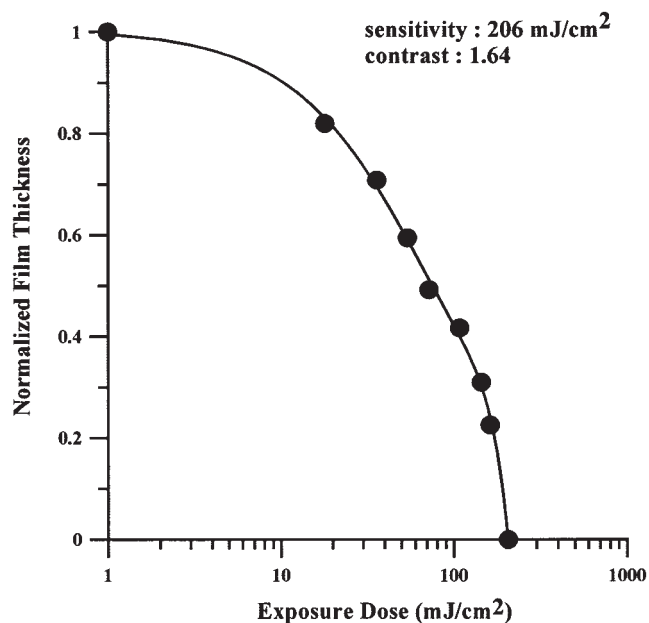
was added, the PBO film is still flexible and transparent. Table II shows the water absorption of PBO and PBO/clay nanocomposite films. As mentioned before, the PBO has low water absorption due to its less polar structure. The addition of clay further reduces its water absorption. The water absorption of PBO was decreased 62% after the addition of 5 wt % clay. That could be due to the exfoliated layer structure of clay, which produces an excellent barrier effect toward water molecules. The decrease in water absorption is desired when PBO is applied in microelectronic devices.

#### Lithographic evaluation

Because PBO precursors possess phenolic hydroxyl groups, they can be dissolved in an aqueous base solution. Similar to traditional novolac photoresists, their aqueous base solubility can be inhibited by the addition of DNQ photoactive compound through a molecular interaction, probably by hydrogen bonding. After exposure to UV light, DNQ is converted to indenecarboxylic acid that promotes dissolution in aqueous base.<sup>9,20</sup> The DNQ compound used in this study was PIC-3, which has a strong absorption in the 320- to 450-nm range. Figure 3 shows the UV-vis



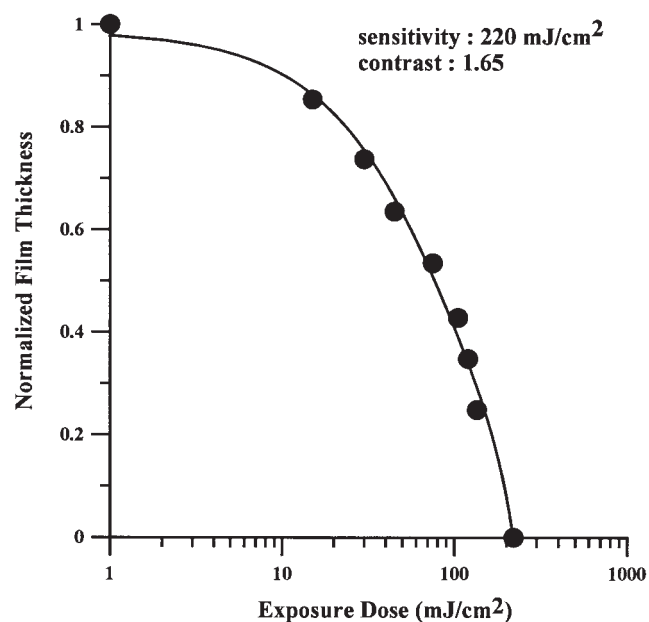
**Figure 3** UV-visible spectra of PBO precursor/PIC-3/5 wt % clay photoresist before and after exposure.



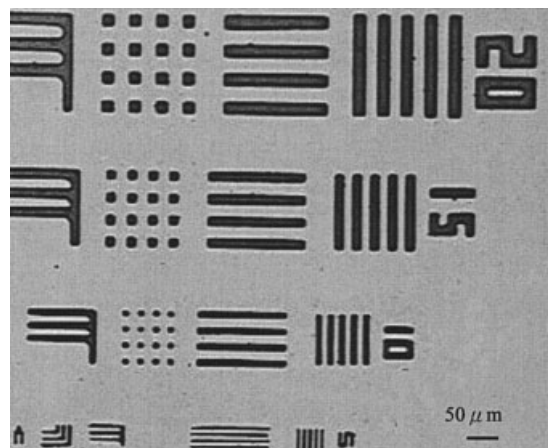
**Figure 4** Characteristic exposure curve of PBO precursor/PIC-3/photoresist.

spectra of PBO precursor/PIC-3/5 wt % clay photoresist before and after exposure. It is clear that the absorption at 365 nm is bleached after exposure, which ensures that the bottom of the resist layer can also be exposed.

Because the clay was dispersed in the PBO precursor matrix in a nanometer scale, it did not interfere with the photolithographic process. Figures 4 and 5



**Figure 5** Characteristic exposure curve of PBO precursor/PIC-3/5 wt % clay photoresist.



**Figure 6** Optical micrograph pattern of PBO precursor/PIC-3/5 wt % clay photoresist after development with 1.2 wt % TMAH solution and curing at 350°C for 1 h.

show the characteristic exposure curves of the PBO photoresists with and without the addition of clay. The photoresist without clay shows a sensitivity of 206 mJ/cm<sup>2</sup> and a contrast of 1.64. The photoresist with 5 wt % clay shows a slightly increased sensitivity of 220 mJ/cm<sup>2</sup> and a similar contrast of 1.65 with a 1.2 wt % TMAH developer. A resolution of 5 μm line/space pattern was obtained from the PBO precursor/PIC-3/5 wt % clay photoresist in a 3-μm film, as shown in Figure 6.

## CONCLUSIONS

Through the addition of an organoclay into the PBO/DNQ solution, new low CTE, positive-working aqueous base developable photosensitive PBO precursor/clay nanocomposites have been prepared. The glass transition temperature of 5 wt % organoclay added PBO film increased 11°C and its CTE decreased 33%. The sensitivity, contrast, and photolithographic performance of the photoresist were not affected due to the good dispersion of the organoclay. The photosensitive PBO precursor/5 wt % clay nanocomposite showed a sensitivity of 220 mJ/cm<sup>2</sup> and a contrast of 1.65 with a 1.2 wt % TMAH developer. A line/space pattern with a resolution of 5 μm was obtained from this formulation.

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