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Photosensitive poly(amic acid)/organoclay nanocomposites

Steve Lien-Chung Hsu[a,*], Ulin Wang[a], Jinn-Shing King[b], Jyh-Long Jeng[b]

[a]*Department of Material Science and Engineering, National Cheng-Kung University, Tainan 701-01, Taiwan, ROC*
[b]*Industrial Materials Research Laboratories, Industrial Technology Research Institute, Hsinchu, Taiwan, ROC*

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Abstract

A project was carried out aimed at reducing the coefficient of thermal expansion (CTE) of photosensitive polyimide formulations (photoresists) through the incorporation of small amounts of an organoclay. The organoclay was formed by a cation exchange reaction between a NA^+-montmorillonite clay and an ammonium salt of dodecylamine. Two polyimide precursors, a poly(amic ester) (PAE) and a poly(amic acid) (PAA), were used in this study. The PAE was prepared by direct polymerization of 2,2′-bis-(3-amino-4-hydroxyphenyl)hexafluoropropane and bis(*n*-butyl)ester of pyromellitic acid in the presence of phenylphosphonic dichloride as an activator. The polymer had an inherent viscosity of 0.23 dL/g. The PAA copolymer was prepared by polymerization of pyromellitic dianhydride, oxydiphthalic anhydride and oxydianiline. The polymer had an inherent viscosity of 1.00 dL/g. Two photosensitive resin/clay formulations were prepared from these two PI precursors using 2,3,4-tris(1-oxo-2-diazonaphthoquinone-5-sulfonyloxy)-benzophenone as the photosensitizer and 3 wt% organoclay. The films obtained from the PAA formulation were transparent and tough, while the films prepared from the PAE formulation were opaque and brittle. Both X-ray diffraction and transmission electron microscope analyses showed that, although the organoclay was not dispersed well in the PAE matrix, it was dispersed in the PAA matrix on a nanometer scale. The clay particles remained well dispersed after the PAA film was thermally imidized. The CTE of the polyimide film obtained was 23% lower than that of a similar film that did not contain the organoclay. The temperature at which the polyimide underwent a 5% weight loss when subjected to TGA in nitrogen was also increased by 13%. The photosensitive PAA/clay nanocomposite showed a sensitivity of 301 mJ/cm^2 and a contrast of 1.66 when a 0.2 wt% tetramethylammonium hydroxide developer was used. A line/space pattern with a resolution of 10 μm was obtained from this formulation.

Keywords: Nanocomposite; Photosensitive; Polyimide

1. Introduction

Polyimides (PI) are widely used in microelectronics industry as buffer coatings, passivation layers, alpha particle barriers, interlayer dielectrics, wafer scale packages, etc., because of their excellent mechanical and electrical properties, and outstanding thermal stability and chemical resistance [1]. Conventional PIs are commonly fabricated for microelectronic devices with the aid of photoresists and etchants [2]. Recently, photosensitive polyimides (PSPIs) have been developed that simplify processing by eliminating the need for these materials [3]. However, when PSPIs are employed in the fabrication of microelectronic devices, differences in the coefficients of thermal expansion (CTEs) between the PI and the inorganic or metallic substrates result in residual thermal stresses. The differences are due to the multiple heating and cooling steps required in their fabrication. The buildup of stress can cause device failure through peeling and cracking of the PI film and substrate [4–6]. The most frequently used approach to reduce the CTEs of PSPIs involves the design and synthesis of new polyimides that have linear, rigid-rod molecular structures that result in lower CTEs [7,8]. However, it is necessary to synthesize new monomers to achieve this goal, which is very expensive and tedious.

Recently, Zhu et al. prepared low CTE, photosensitive PI/silica hybrids using a sol–gel process [9]. In this article, we report a new method to reduce the CTEs of PSPIs that involves the incorporation of a small amount of nano-dispersed organoclay. Due to the high surface to volume ratio of the nano-dispersed clay, the thermal expansion and

* Corresponding author. Tel.: +886-6-2757575x62904; fax: +886-6-2346290.
E-mail address: lchsu@mail.ncku.edu.tw (S.L.C. Hsu).

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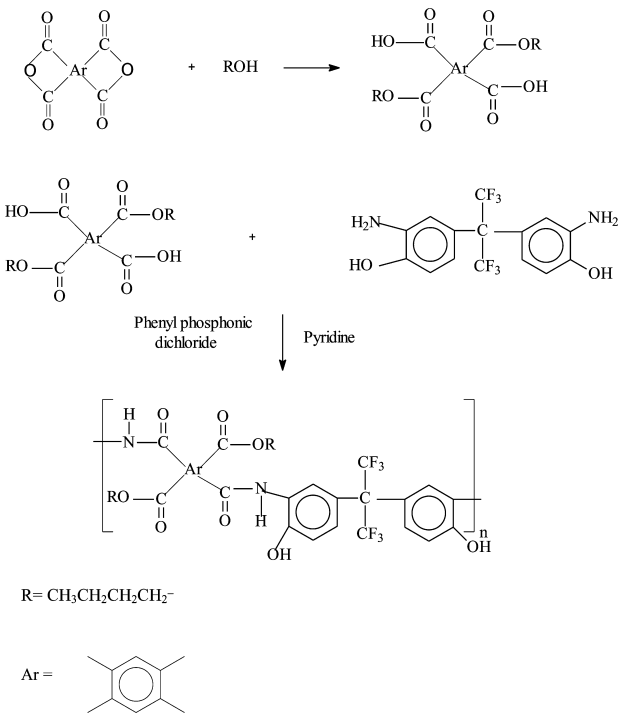


Scheme 1. BisAPAF-PMDA poly(amic acid)-*n*-butyl ester synthesis.

contraction of the polymer molecules are highly restricted, which effectively reduces its CTE [10,11]. Because the organoclay was to be nano-dispersed in the PSPI matrix and the particle size was to be smaller than the wavelength of the exposure light, we postulated that it would not interfere with the photolithographic process. We purposely chose a positive working PSPI system, because they have lower sensitivity to dust particles, which can result in small via holes on substrates, than negative working systems.

2. Experimental

2.1. Materials

Pyromellitic dianhydride (PMDA), 2,2-bis(3-amino-4-hydroxyphenol)hexafluoropropane (BisAPAF), 3,3′4,4′-benzophenone tetracarboxylic dianhydride (BTDA), oxydiphthalic anhydride (ODPA), 2,2′-bis(4-(4-amino-phenoxy)phenyl) propane (BAPP), and oxydianiline (ODA) were purchased from Chriskev. Anhydrous *N*-methyl-2-pyrrolidone (NMP) and pyridine 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). Other chemicals were used as received. The organoclay was prepared by a cation exchange reaction between a Na^+-montorillonite (Na^+-Mont) clay and an ammonium salt of dodecylamine (DOA) as described in our previous paper [12]. The interlayer spacing of the original Na^+-Mont clay was 12.7 Å. After modification, the interlayer spacing of organoclay was expanded to 18 Å. The clay particles were approximately 1 nm thick and had lateral dimensions of 50–300 nm.

2.2. Synthesis of poly(amic ester)

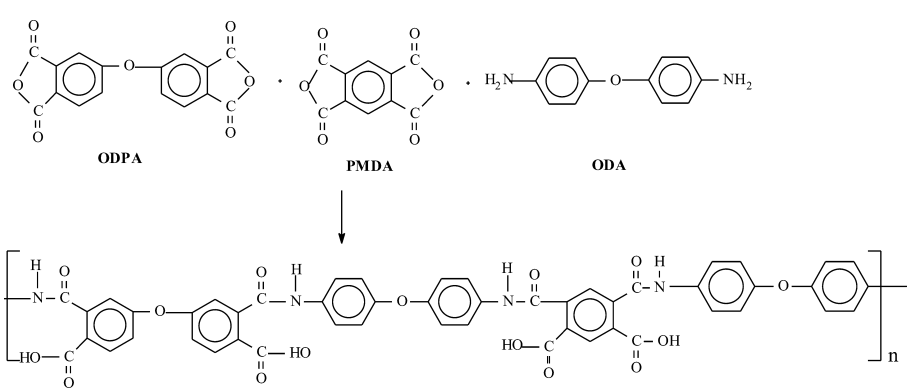
The synthesis of BisAPAF-PMDA poly(amic acid)-*n*-butyl ester is described in the previous paper [13]. The synthesis steps are illustrated in Scheme 1.

2.3. Synthesis of poly(amic acid)s

A representative example of ODPA/PMDA/ODA poly(amic acid) copolymer synthesis (Scheme 2) is as follows: to a 250 mL three-necked round bottom flask equipped with a mechanical stirrer and a condenser, 9.80 g (49 mmol) of ODA and 94 mL of NMP were added. The solution was stirred at ambient temperature until the ODA was totally dissolved, and then 8.72 g (40 mmol) of PMDA and 3.10 g (10 mmol) of ODPA were added. After being stirred for 6 h, a viscous poly(amic acid) solution was obtained.

2.4. Preparation of poly(amic acid) or poly(amic ester) films and thermal conversion to polyimides

A film was cast from the viscous poly(amic acid) or poly(amic ester) solution on a glass plate by a doctor's



Scheme 2. ODPA-PMDA-ODA polyamic acid synthesis.

Fig. 1. TEM of BisAPAF-PMDA polyimide/3 wt% clay nanocomposite prepared from BisAPAF-PMDA polyamic acid *n*-butyl ester.

knife. The film was dried in a vacuum oven at 80 °C for 16 h to obtain the poly(amic acid) or poly(amic ester) film. The film was further heated at 100 °C for 1 h, 200 °C for 1 h, and 300 °C for 1 h in a heating oven to convert the poly(amic acid) to a polyimide.

2.5. Preparation of poly(amic acid) or poly(amic ester)/clay nanocomposite films and thermal conversion to polyimide/clay nanocomposites

A representative 3 wt% clay loading polyimide/clay nanocomposite was prepared as follows: 0.06 g of organoclay was dispersed in 3 g of NMP by a vigorous mechanical stirring (600 rpm), and then added to 12.5 g of ODPA/PMDA/ODA poly(amic acid) copolymer solution (solids content is 16 wt% in NMP). After vigorous stirring for 6 h, the clear solution was coated on a glass plate with a doctor knife, and dried in a vacuum oven at 80 °C for 16 h to obtain the poly(amic acid)/clay nanocomposite film. The film was further heated at 100 °C for 1 h, 200 °C for 1 h, and 300 °C for 1 h in a heating oven to convert the poly(amic acid)/clay nanocomposite to a polyimide/clay nanocomposite.

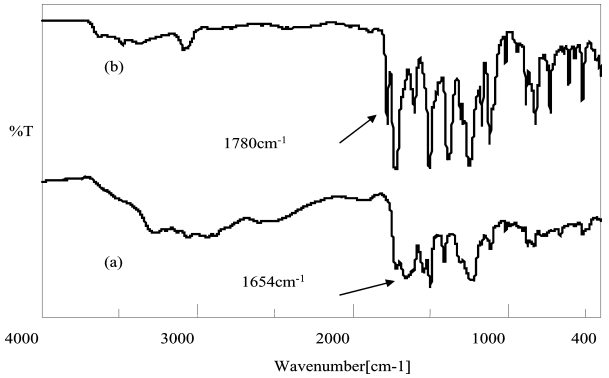


Fig. 2. FTIR spectra of ODPA-PMDA-ODA polyamic acid (a) and polyimide (b).

2.6. 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) Q500 at a heating rate of 10 °C/min under nitrogen. The in-plane CTE of cured polyimide film was determined using a TA Instruments Thermal Mechanical Analyzer (TMA) 2940 with a extension probe under 0.05N 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 100 UV–VIS spectrophotometer. X-ray diffraction (XRD) experiment was conducted on a Rigaku D/MAX-IIIV X-ray Diffractometer using Cu K_α radiation. Tensile properties of the cured films were measured at room temperature using an universal testing machine (Instron model 4501) according to ASTM D882. The samples for transmission electron micrograph (TEM) study were prepared by placing the PI/clay films in an epoxy resin, cured at 70 °C overnight. The cured epoxies containing PI/clay were microtomed with a diamond knife into

Table 1
Synthesis of polyamic acids and their solubilities in TMAH solution

Polyamic acid batch	Monomer composition (mol ratio)	Inherent viscosity[a] (dL/g)	Solubility in TMAH[b]
1	BTDA/BAPP (BTDA/BAPP = 1/1)	0.23	Insoluble
2	ODPA/BAPP (ODPA/BAPP = 1/0.98)	1.22	Insoluble
3	PMDA/BAPP/ODA (PMDA/BAPP/ODA = 1/0.5/0.5)	0.79	Insoluble
4	ODPA/PMDA/ODA (ODPA/PMDA/ODA = 0.5/0.5/0.98)	1.06	Dissolved fast
5	ODPA/PMDA/ODA (ODPA/PMDA/ODA = 0.2/0.8/0.98)	1.00	Dissolved moderately

[a] Inherent viscosity was measured at 30 °C in NMP at a concentration of 0.5 g/dL.
[b] The concentration of TMAH aqueous solution was 0.2 wt%.

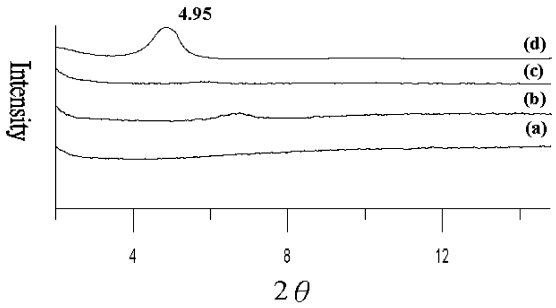


Fig. 3. XRD patterns of ODPA-PMDA-ODA polyamic acid (a), ODPA-PMDA-ODA polyamic acid/3 wt% clay nanocomposite (b), ODPA-PMDA-ODA polyamic acid/3 wt% clay/40% PIC-3 nanocomposite (c) and organoclay (d).

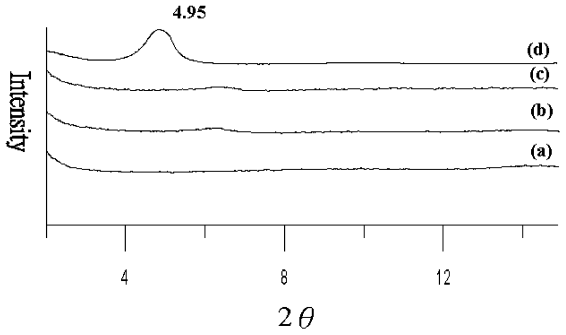


Fig. 4. XRD patterns of ODPA-PMDA-ODA polyimide (a), ODPA-PMDA-ODA polyimide/3 wt% clay nanocomposite (b), ODPA-PMDA-ODA polyimide/3 wt% clay/40% PIC-3 nanocomposite (c) and organoclay (d).

70 nm thick slices. Next, they were placed on a 200 mesh copper grid, and examined with a Zeiss 10 C TEM using an acceleration voltage of 200 KV.

2.7. Preparation of photoresist/clay formulations

A representative photoresist/clay formulation prepared from poly(amic acid) is as follows: 0.8 g of the photoactive compound (PIC-3) was added to 12.5 g of ODPA/PMDA/ODA poly(amic acid) copolymer solution (solids content is 16 wt% in NMP) to prepare the photoresist solution. In a separate flask, 0.06 g of organoclay was dispersed in 3 g of NMP by a vigorous mechanical stirring, and then added to the photoresist solution. After vigorous stirring for 6 h, the photoresist/clay solution was filtered through a 5 μm Teflon filter. Both the solution and the filtrate were clear indicating that no clay particles were removed during the filtration process.

2.8. Lithographic evaluation of photoresist/clay formulation

The photoresist/clay solution was spin-coated onto a silicon wafer and softbaked on a hotplate at 120 °C for 5 min to obtain a film of about 3 μm thick. The film was exposed to an unfiltered mercury arc lamp measured at 250–500 nm. The wafer was developed in a 0.2–06 wt% TMAH developer (the concentration of TMAH is 0.2 and 0.6 wt% for PAA and PAE respectively), followed by a de-ionized 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.

3. Results and discussion

3.1. Synthesis of BisAPAF-PMDA polyamic acid n-butyl ester and related poly(amic ester)/clay nanocomposite

As described in the previous paper [13], a poly(amic ester) (PAE) was prepared from direct polymerization of 2,2′-bis-(3-amino-4-hydroxyphenyl)hexafluoropropane and bis(*n*-butyl)ester of pyromellitic acid in the presence of phenylphosphonic dichloride as an activator. The PAE had an inherent viscosity of 0.23 dL/g. Since the PAE had been used to prepare a photosensitive polyimide [13], it was the first used to make a photosensitive polyimide precursor/clay nanocomposite. However, a PAE film containing only 3 wt% organoclay was quite opaque. Obviously, the clay did not disperse in the PAE film on a nanometer scale as seen in the TEM micrograph (Fig. 1). The poor dispersion could be due to the lack of strong polar interaction between the polyamic ester and the organoclay. Therefore, the preparation of a photosensitive polyimide precursor/clay nanocomposite was shifted from the PAE system to a poly(amic acid) (PAA) system.

Table 2
Thermal properties of ODPA-PMDA-ODA polyimide and ODPA-PMDA-ODA polyimide /3 wt% clay nanocomposite

	CTE (μm/m °C)[a]	T_g [b] (°C)	Decomposition temperature (°C)[c]
ODPA-PMDA-ODA polyimide	64.72	336	556
ODPA-PMDA-ODA polyimide /3 wt% clay nanocomposite	49.98	338	569

[a] In-plane CTE measured by TMA at a heating rate of 5 °C/min in nitrogen under a force of 0.05N in the temperature range of 75–250 °C.
[b] Determined by TMA at a heating rate of 5 °C/min in nitrogen.
[c] 5% weight loss temperature in nitrogen.

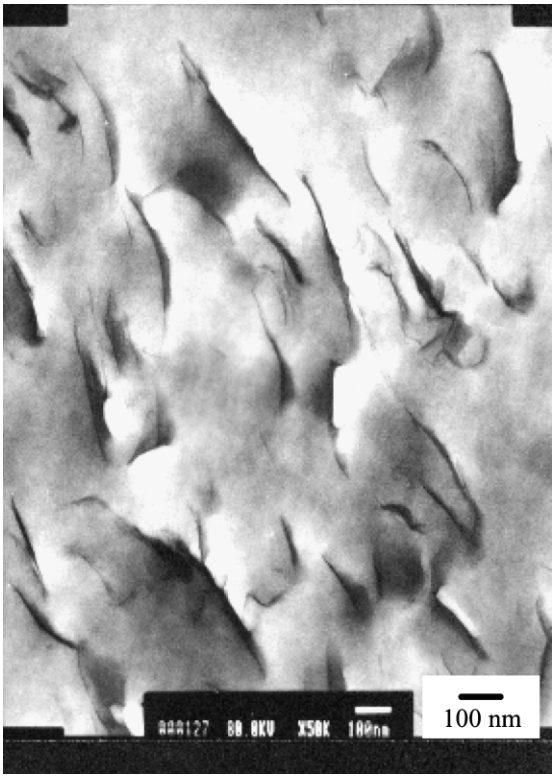


Fig. 5. TEM of ODPA-PMDA-ODA polyimide/3 wt% clay nanocomposite.

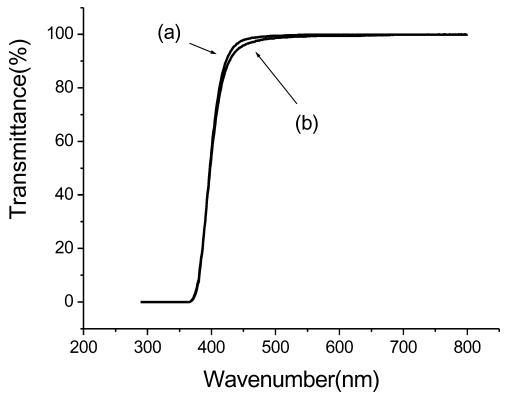


Fig. 6. UV–visible spectra of ODPA-PMDA-ODA polyimide film (a) and ODPA-PMDA-ODA polyimide/3 wt% clay film (b).

3.2. Synthesis of poly(amic acid)s and related polyimides

Several PAAs were prepared by the reaction of various dianhydrides with diamines at room temperature. Table 1 shows the inherent viscosities and solubility in 0.2 wt% TMAH of these PAAs. Because PAAs possess hydrophilic carboxyl groups, many can be dissolved in an alkaline solution such as TMAH. Unlike traditional novolac photoresists, their aqueous base solubility is hard to be inhibited by the diazonaphthoquinone (DNQ) photoactive compound. The initial molecular design of this PSPI precursor system was based on the use of BAPP monomer, which consists of more hydrophobic aromatic groups in the main chain. Unfortunately, the PAAs prepared from BAPP were not soluble in TMAH solution. The second choice was to prepare a PAA with moderate TMAH solubility through a copolymer approach. As seen in Table 1, a PAA prepared from 80% PMDA, 20% ODPA, with ODA had an optimum solubility in the TMAH solution, thus, this polymer was selected for further evaluation. In order to control the molecular weight of the polymer, we also used a stoichiometric imbalance in its preparation. The inherent viscosity of this PAA in NMP was 1.0 dL/g at a concentration of 0.5 g/dL at 30 °C. After being cured at 300 °C, the resulting polyimide (PS) was transparent and tough. The IR spectrum of the poly(amic acid) (Fig. 2) showed characteristic absorption bands at 1720 and 1654 cm^{-1} due to the carboxyl acid and amide groups, respectively. The appearance of a strong imide absorption at 1780 cm^{-1} and the disappearance of the amide carbonyl absorption at 1654 cm^{-1} in the IR spectrum (Fig. 2) of the film during the thermal imidization were used to follow the conversion from PAA to PI.

3.3. Polymer and polymer/clay nanocomposite characterization

In order to improve the dispersion of clay in the polymer matrix, the hydrophilic Na^{+}-montorillonite clay was treated with the ammonium salt of DOA to form an organoclay as described in our previous paper [12]. Fig. 3 shows the XRD patterns of polyamic acid/3 wt% clay and polyamic acid/3 wt% clay/40 wt% PIC-3 nanocomposites. Both of them do not have any diffraction peak in the $2\theta = 2–10°$ region. This indicates that exfoliated silicate layers of organoclay were dispersed in the PAA matrix. Even after thermal curing, the resulting PI/clay nanocomposites displayed the same patterns (Fig. 4). The TEM of the 3 wt% clay/PI film (Fig. 5) provides further evidence that the organoclay was dispersed randomly in the PI matrix in a nanometer scale. Table 2 shows the thermal properties of PI and PI/3 wt% clay nanocomposite. The

Table 3
Mechanical properties of ODPA-PMDA-ODA polyimide and ODPA-PMDA-ODA polyimide/3 wt% clay nanocomposite

	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
ODPA-PMDA-ODA polyimide	90.5	1.81	12.1
ODPA-PMDA-ODA polyimide /3 wt% clay nanocomposite	77.3	2.06	8.1

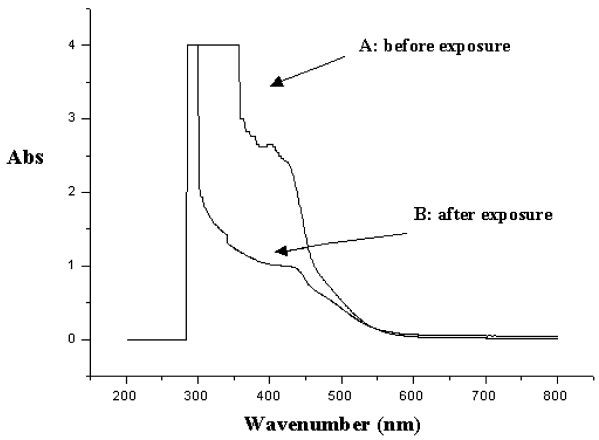


Fig. 7. UV–visible spectra of ODPA-PMDA-ODA polyamic acid/PIC-3/3 wt% clay photoresist before exposure (a) and after exposure (b).

organoclay exhibited a significant effect on reducing the CTE of the PI. With only the addition of 3 wt% clay, the CTE of the PI film was decreased by 23%. The addition of organoclay also increased the thermal stability of the PI. When subjected to TGA in nitrogen, its 5% weight loss temperature increased by 13 °C. The glass transition temperature (T_g) of the PI film increased only slightly from 336 to 338 °C. Even though 3 wt% clay was added, the polyimide film was still flexible and transparent. The UV–visible spectra of the PI films are shown in Fig. 6. The transparency of the film containing 3 wt% clay is close to that of the original film, which can be attributed to the clay being dispersed on a nanometer scale. Table 3 shows the mechanical properties of the PI films with and without 3 wt% clay. The increase of modulus in the clay containing film was expected because of the reinforcement effect of the rigid clay. Both the elongation and tensile strength of the clay containing film were lower, as reported for other PI/clay nanocomposites [14].

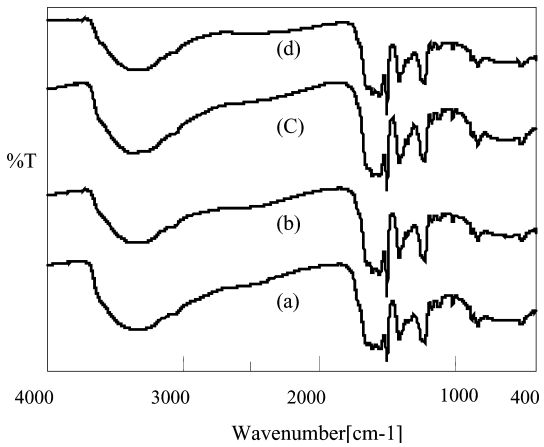


Fig. 8. FTIR spectra of ODPA-PMDA-ODA polyamic acid film at varies softbaking temperatures for 4 min: (a) 90 °C (b) 100 °C (c) 110 °C (d) 120 °C.

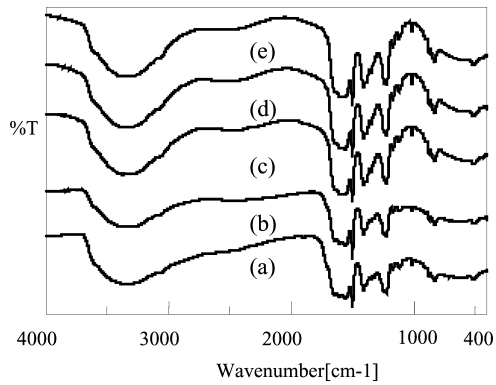


Fig. 9. FTIR spectra of ODPA-PMDA-ODA polyamic acid film softbaked at 120 °C for varies times: (a) 3 min (b) 4 min (c) 5 min (d) 6 min (e) 7 min.

3.4. Lithographic evaluation

As described in the previous section, we chose the ODPA/PMDA/ODA PAA copolymer as the base resin for the PSPI/clay formulation. Because PAAs contain carboxylic groups, they can dissolve in an aqueous base solution. Similar to traditional novolac photoresists, their aqueous base solubility can be inhibited by interaction with diazonaphthoquinone (DNQ) photoactive compounds presumably through hydrogen bonding. After exposure to UV light, DNQ is converted to indenecarboxylic acid that promotes dissolution in aqueous base [15,16]. Several PSPIs based on a PAA/DNQ system have been reported [17–21]. The DNQ compound used in this study was 2,3,4-tris(1-oxo-2-diazonaphthoquinone-5-sulfonyloxy)-benzophenone (PIC-3), which has a strong absorption in the 320–450 nm range. Fig. 7 shows the UV–vis spectra of PAA/PIC-3/3 wt% clay photoresist before and after exposure. It is clear that the absorption at 365 nm was bleached after exposure, which shows that the bottom of the resist layer was also exposed.

When using a PAA as the matrix in a PSPI, partial imidization may occur during softbaking, which will leave residue on the wafer after development. In order to avoid partial imidization, various softbaking temperatures were tried. Fig. 8 shows FTIR spectra of PAA/PIC-3 film after softbaking at varies temperatures. It is clear that in the temperature range from 90 to 120 °C, no partial imidization occurred, which is supported by the disappearance of imidization peak at 1780 cm^{-1}. Fig. 9 shows FTIR spectra of PAA/PIC-3 film softbaked at 120 °C at various times. One can also see that there was no partial imidization occurring in the time period from 3 to 7 min. Based on these data, we chose the softbaking condition of 120 °C for 5 min.

Because the clay was dispersed in the PAA matrix in a nanometer scale, it did not interfere with the photolithographic process. The characteristic exposure curves of the PAA photoresists with and without clay, are shown in Figs. 10 and 11. The photoresist without clay displayed a sensitivity of 292 mJ/cm^2 and a contrast of 1.83, and the

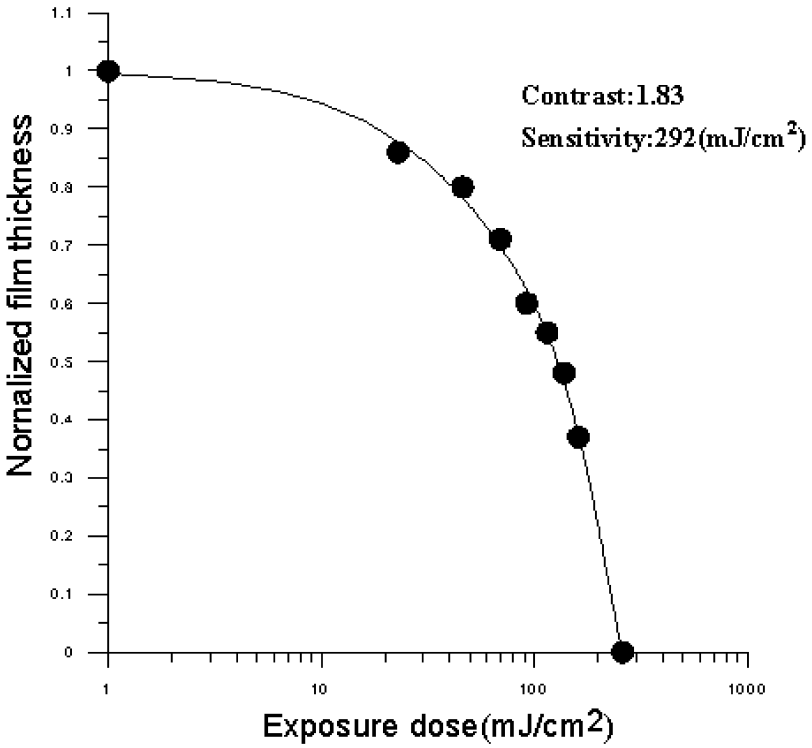


Fig. 10. Characteristic exposure cure of ODPA-PMDA-ODA polyamic acid/PIC-3 photoresist.

photoresist with 3 wt% clay shows a slightly increased sensitivity of 301 mJ/cm^2 and a slightly decreased contrast of 1.66. A resolution of 10 μm line/space pattern was obtained from the PAA/PIC-3/3 wt% clay photoresist in a 3 μm film, as shown in Fig. 12.

4. Conclusions

Organoclay particles can be well dispersed in photosensitive PAA films containing a DNQ compound so that the photosensitivity of the films are not significantly affected.

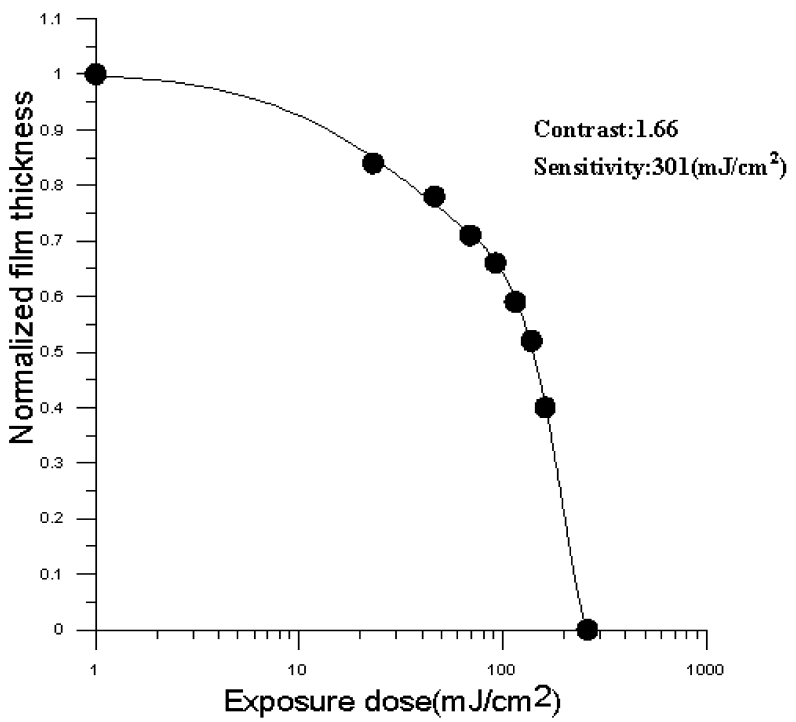


Fig. 11. Characteristic exposure cure of ODPA-PMDA-ODA polyamic acid/PIC-3/3 wt% clay photoresist.

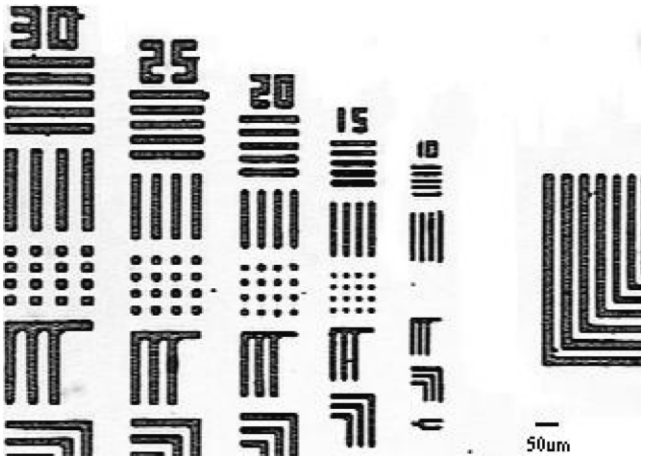


Fig. 12. Optical micrograph pattern of ODPA-PMDA-ODA polyamic acid/PIC-3/3 wt% clay photoresist after development with 0.2 wt% TMAH solution and cured at 300 °C for 1 h.

The thermal conversions of these films to their PI analogs can be carried out without affecting the dispersion of the clay. The PI/organoclay nanocomposite films display significantly lower CTEs and higher thermal stability than similar PI films that do not contain clay.

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