Ultra-low-modulus Photosensitive Poly(siloxane-benzoxazole) Systems

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Abstract: This work proposes ultra-low-modulus poly(siloxane-benzoxazole), which was derived from 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (6FAP), a siloxanediamine (Si-DA), isophthaloyl chloride (IPC), and pyromellitic dianhydride (PMDA). The thermally cured poly(siloxane-benzoxazole) films achieved an ultra-low modulus (<0.44GPa). The poly(siloxane-benzoxazole) precursor (polyhydroxyamide, PHA) films possessed a relatively high *i*-line transmittance ($T_{365} > 44\%$), good tetramethylammonium hydroxide (TMAH) solubility. The PHA films dispersed diazonaphthoquinone (DNQ) allowed the formation of fine positive-tone patterns. Thus, the present poly(siloxane-benzoxazole) systems can be promising candidates as novel buffer-coating materials in semiconductor applications.

Keywords: Photosensitive Poly(siloxane-benzoxazole)s, Ultra-low Modulus

1. INTRODUCTION

Aromatic polybenzoxazoles (PBOs) have been utilized in buffer-coating films in semiconductor devices for their combined excellent properties, i.e., high glass transition temperature (T_g), high resistance to chemicals, and excellent thermal stability. A remarkable merit of applying PBO systems is their high-resolution patterning ability; a diazonaphthoquinone(DNQ)-dispersed PBO precursor film (polyhydroxyamide, PHA) can give rise to fine patterns by development with a standard organic alkaline developer, 2.38% tetramethylammonium hydroxide (TMAH) aqueous solution [1,2]. This results from the fact that the phenolic OH groups in the PHA structures possess an adequate acidity (pK_a), whereas polyimide precursors as an opponent are too soluble in a TMAH solution owing to the presence of the carboxylic acid groups with a much higher acidity.

The progress of recent semiconductor technologies requires the use of thinner silicon wafers for LSI chip fabrications. Such trend causes a forthcoming serious problem, i.e., wafer deformation arising from mismatching of the linear coefficient of thermal expansion in the film plane direction (CTE) between silicon wafers (CTE ~ 3 ppm K^{-1}) and buffer coat films (50–80 ppm K^{-1}) as protection coatings. Two approaches to solve the serious problem are known: the use of low-CTE (< 10 ppm K^{-1}) or low-modulus materials.

There are some attempts addressing to the development of film-processable PBO systems with considerably linear/stiff main chain structures [3,4]. The most important structural factor for obtaining low-CTE of PBO films is the main chain linearity/stiffness in the PBO structure. For example, a PBO film prepared with great difficult, which was derived from terephthaloyl chloride (TPC) and bis(3-hydroxy-4-amino)biphenyl (*p*-HAB) derivative, showed an extremely low CTE (5.3 ppm K^{-1}) [3]. However, the TPC/*p*-HAB system possesses a serious disadvantage in the film preparation process; once the as-polymerized PHA solution was poured into the excess of water to remove some residual polymerization reagents and unnecessary by-products, the precipitate formed becomes quite insoluble in any solvents. The use of a *p*-HAB isomer, bis(4-hydroxy-3-amino)biphenyl (*m*-HAB) drastically improved the solubility at the stage of the PHA owing to its highly distorted chain structure [3]. This system also led to a high-quality of low-CTE PBO film on the conventional solution casting method and successive heating for cyclodehydration.

However, this PHA film was highly colored. The poor light transmittance of the PHA film itself is supposed to inhibit the photoreaction of DNQ dispersed in the film. Recently, GBL, which has lower dissolution ability than NMP, is mainly used as a solvent for buffer-coating materials. Therefore, PHAs need to be highly soluble in GBL rather than NMP. However, the molecular designs toward low-CTE PBOs drastically decrease the GBL solubility of the rigid PHAs. Thus, it is very difficult to overcome the obstacles for acquiring low-CTE photosensitive PBO systems with sufficient transparency at the stage of the precursors. This situation motivated us to challenge the development of novel photosensitive PBO systems possessing sufficiently low modulus.

We have previously studied ultra-low-modulus siloxane-containing polyimides (PIs) as screen-printable cover layer materials, although it possessed no photo-patterning functionality [5]. This PI was highly soluble even in less hygroscopic solvents such as triglyme (Tri-GL) and GBL so that it provided a rather stable solution with a very high solid content (> 60 wt% in GBL). However, this feature also caused a serious problem: the absence of solubility in a 2.38% TMAH solution due to its strong hydrophobicity originating from of the long siloxane chains as the flexible units.

In this work, we challenged to significantly improve the TMAH solubility of our poly(siloxane-benzoxazole) systems by a structural modification without sacrificing their inherent ultra-low modulus characteristics.

2. EXPERIMENTAL

2.1 Siloxane-containing PHAs: Siloxane-containing PHAs were polymerized by a trialkyl-silylation technique [6] according to the reaction scheme shown in Fig.1. A typical polymerization procedure using 2,2-bis(3-amino-4-hydroxyphenyl) hexafluoropropane (6FAP), siloxanediamine (Si-DA; average molecular weight = 1290 g mol^{-1}), and diacid chlorides is as follows: in a 100 mL flask sealed with a septum cap, 6FAP (3.0 mmol) was dissolved in 6 mL GBL containing pyridine (12 mmol) as an HCl acceptor. Trimethylsilyl chloride (12 mmol) as a silylation reagent was slowly added to the 6FAP solution by a syringe, then stirred for 1 h at room temperature. After Si-DA (2.0 mmol) and 1 mL GBL were added to this solution, isophthaloyl chloride (IPC; 4.0 mmol) dissolved in 2 mL GBL was gradually added and stirred at room temperature for 1 h. Finally, pyromellitic dianhydride (PMDA; 1.0 mmol) powder, pyridine (10 mmol), and 1 mL GBL were added, then stirred at room temperature for 24 h. A homogeneous/viscus solution of the silylated PHA was formed. It was poured into a large amount of an HCl aqueous solution (ca. pH4). The fibrous white precipitate obtained was collected by filtration, repeatedly washed with water and dried in vacuum at 70 °C for 12 h.

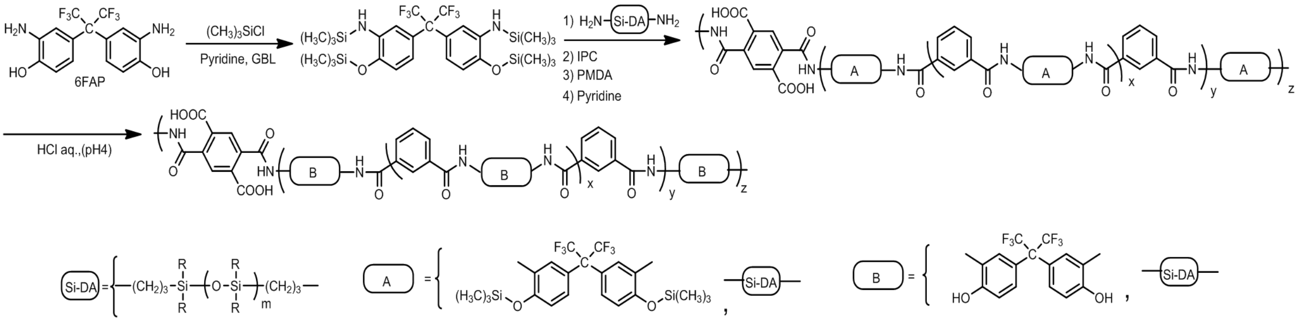

Fig.1 Polymarization scheme for siloxane-containing PHAs.

2.2 Preparation of poly(siloxane-benzoxazole) films for property evaluation: The PHA powder samples were completely dissolved in GBL by stirring at room temperature for 24 h, and the solution was coated on an electrodeposited copper foil and dried at 100 °C for 10 min. The PHA films on the copper foil were heated in a vacuum-oven at 300 °C for 1 h. The copper foil of the laminates was removed by etching it out with a $FeCl_3$ aqueous solution. The free-standing poly(siloxane-benzoxazole) films were washed with water and dried at 100 °C for 1 h.

2.3 Evaluation of photosensitivity:

Diazonaphthoquinone (DNQ) as a positive-type photosensitizer and an adhesion promoter were dissolved in a GBL solution of PHAs by stirring at room temperature for 24 h while shading to form a photosensitive film with a DNQ content of 30 wt%. The mixed solutions were spin-coated on a silicon wafer pre-treated with a silane coupling agent, and dried at 100 °C for 10 min. The 5–10 μm thick photosensitive PHA films were irradiated at 365 nm by a high-pressure mercury lump (Toshiba Lighting & Technology Corp., TOSCURE 251) with an exposure dose of 3000 mJ cm^{-2} through a photo-mask. The uv-irradiated films were developed in a 2.38% TMAH solution at room temperature, then rinsed with water at room temperature. The patterned PHA films were converted to poly(siloxane-benzoxazole) by heating at 300 °C for 1 h in vacuum. The positive-tone patterns of the poly(siloxane-benzoxazole) films were observed by a scanning electron microscope (SEM; ELIONIX, EXM-3500).

2.4 Other measurements

The reduced viscosities (η_{red}) of PHAs were determined at 30 °C in GBL at a concentration of 0.5 wt% using an Ostwald viscometer. The light transmittance at 365 nm (T_{365}) of PHA films was measured on an ultraviolet-visible spectrophotometer (JASCO, V-530). Mechanical properties [tensile modulus (E) and elongation at break (ε_b)] of poly(siloxane-benzoxazole) films (3 mm wide, 35 mm long, 15–20 μm thick) were measured using a mechanical testing machine (A & D, Tension UTM-II) at a cross head speed of 8 mm min^{-1} at room temperature. Thermal stability of poly(siloxane-benzoxazole) films were evaluated from the 5% weight loss temperatures ($T_d{}^5$) at heating rate of 10 °C min^{-1} in a nitrogen atmosphere by thermogravimetric analysis (TGA, NETZSCH, TG-DTA2000S).

3. RESULTS AND DISCUSSION

In DNQ-dispersed PHA films, high light transparency of the PHA films themselves at an exposure wavelength (often *i*-line of high-pressure mercury lamp, 365 nm) should be maintained from the viewpoints of obtaining higher sensitivity. The 8–10 μm–thick DNQ-free siloxane-containing PHA films (#1–#3) showed a relatively high transmittance transparence higher than 44% at 365 nm as listed in Table 1. The results are probably attributed to suppressed charge-transfer (CT) interactions by using an aliphatic diamine, Si-DA and an electron-withdrawing CF_3-containing diamine, 6FAP. A previous paper revealed that there exists CT interactions not only in aromatic polyimides but also aromatic polyamides [7]. The present PHAs are the case. Fig.2 displays a transmission spectrum of the PHA film (#3) and an absorption spectrum of a dilute GBL solution of DNQ. The spectral comparison indicates that the irradiated light at 365 nm can be effectively absorbed by the DNQ dispersed in PHA films without an overwhelming shield effect by the matrix polymers. It is known well that unexposed DNQ in a PHA film acts as a dissolution inhibitor against an alkaline solution because of its originally hydrophobic structure. On the other hand, the exposed portion of DNQ is converted to ketene via the Wolff rearrangement, then finally to alkali-soluble indencarboxylic acid in the presence of water.

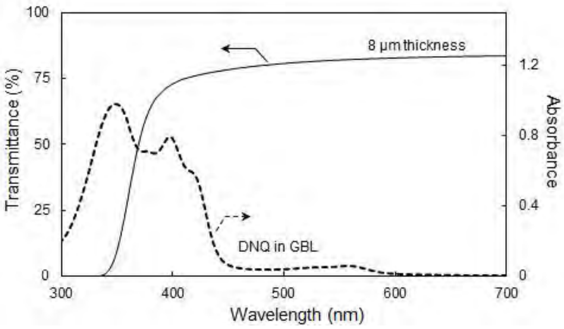

Fig.2 Transmission spectrum of PHA film (#3) and UV-visible absorption spectrum of DNQ in GBL.

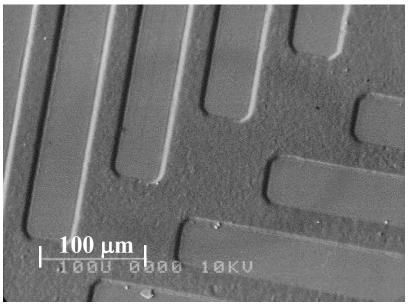

Fig.3 SEM photograph of positive-tone pattern cured film (6 µm thick) obtained from siloxane-containing PHA film (#3).

We first attempted to form a positive-tone pattern from DNQ-containing PHA films. However, insufficient adhesion strength with silicon wafers disturbed fine pattern formation owing to partial removal of the unexposed area during the development process. A combination of adequate silane coupling agents for modifying the PHA solutions and the silicon wafer surface significantly improved the adhesion strength, consequently allowed the formation of positive-tone patterns. Fig.3 displays a tentatively formed positive-tone pattern with a resolution (line and space) of 40 µm as obtained by development using a 2.38% TMAH solution at room temperature for 60 sec.

Table 1 Film properties of PHAs and poly(siloxane-benzoxazole) (6FAP 60 mol%; Si-DA 40 mol%) systems.

Entry	Monomer		PHA		Poly(siloxane-benzoxazole)		
	IPC (mol%)	PMDA (mol%)	η_{red} (dL g^{-1})	T_{365} (%)	E (GPa)	ε_b (%)	T_d^5 (in N$_2$) (°C)
1	90	10	0.36	46.0	0.15	11	399
2	85	15	0.11	44.0	0.26	9	364
3	80	20	0.11	44.8	0.44	9	394

4. Conclusions: In this work, we obtained novel poly(siloxane-benzoxazole) precursors with sufficient *i*-line transparency and an adequate TMAH solubility. The DNQ/PHA films allowed to form fine positive-tone patterns by development with 2.38% TMAH at room temperature. The corresponding thermally cured poly(siloxane-benzoxazole) films (DNQ-free) achieved a relatively low modulus of 0.44 GPa, sufficient thermal stability (T_d^5 = 394 °C). Thus, our ultra-low-modulus poly(siloxane-benzoxazole) systems can be promising candidates as novel buffer-coating materials.

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