Study of Low Temperature Curable Polybenzoxazole Precursors Containing Aliphatic Dicarboxylic Acid Structures

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As a demand for advanced packaging is growing, the photosensitive insulation material curable below 200 °C is required. We focused on photosensitive polybenzoxazoles derived from aliphatic dicarboxylic acids unit to reduce low cyclization temperature. We found that polybenzoxazole precursor having long methylene unit showed high cyclization percentage and elongation value at 200 °C of curing temperature.

Keywords: Polybenzoxazole, Low temperature curing, Aliphatic dicarboxylic acid, Photosensitive insulation material

1. Introduction

Recently, novel electronic devices, like mobile phones, tablets, and personal computers, have become dramatically small and more functionalized. Based on these market trends, the packages of semiconductor devices are also required to become smaller, thinner and more complicated. With the progress of miniaturization in size and advancement in functionality, further scaling down of Cu wiring and blind via is needed not only in LSI chips but also in packaging substrate [1]. The organic multi-chip package and fan-out wafer level packages (FO-WLPs) have received increasing attention in realizing the further advancements of electronic devices with high densities and large functions [2, 3].

Photosensitive organic materials, such as polyimides (PI) and polybenzoxazole (PBO), having great mechanical strength and heat resistance were mainly used as protection and insulation layers of very large scale integrated circuit [4], because they simplify blind via formation processing by photolithography. For these applications, photodefinable PBO (PD-PBO) are formed through cyclization of PBO precursors such as poly(o-hydroxyamide) (PHA), by thermal treatment over 300 °C. The high-temperature process is hardly applicable to organic interposer and FO-WLPs, because these devices contain low heat resistance material such as molding compounds. Actually, these devices require photosensitive insulation materials curable below 200 °C.

In the research of PI, there are several approaches to reduce the imidization temperature by introduction of flexible structures [5]. We have reported that PHA containing alicyclic structure as PBO precursors showed good film properties with low curing temperature [6, 7]. In this paper, we focused on PHA containing aliphatic structures. We synthesized several kinds of PHA from aliphatic dicarboxylic acids (DAs) and bis(o-aminophenol) (BAPs) and evaluated their cyclization degree, film properties and photolithographic properties for positive-tone low temperature curing materials.

2. Experimental

2.1. Synthesis of PHA
A typical procedure for synthesis of PHA as a PBO precursor containing aliphatic dicarboxylic acid structure is as follows: Into a 200 mL four-necked flask with a magnetic stirring bar, 10.44 g (28.5 mmol) of 2,2’-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (6FAP), 0.33 g (3 mmol) of m-aminophenol (m-AP) and 50 g of N-methylpyrrolidone (NMP) were added, and the mixture was stirred. After the solid was dissolved, the flask was cooled at 0 °C in ice water. Then, 8.02 g (30 mmol) of dodecandioyldichloride (C10DA) was added below 20 °C, and stirred at room temperature for 3 h. The reaction mixture was poured into water. The precipitate was washed with water of 60 °C collected by filtration and dried under vacuum overnight at 60 °C.

The molecular weight of PHA was measured by gel permeation chromatography (GPC).

The transparency of PHA was measured by an ultraviolet spectrophotometer (U-3310, Hitachi).

2.3. Measurement of elongation value of PBO

PHAs were dissolved in NMP. The solution was spin-coated on a silicon wafer which was soft-baked on a hot plate at 120 °C for 3 min and cured at 320 °C for 1 h under nitrogen atmosphere to give 10 μm cured film (PBO). Its elongation value was measured with a tensile testing machine (AGS-100NH, Shimazu).

2.4. Cyclization percentage

Differential scanning calorimetry (DSC) (DSC-6200, SII) was used to monitor the cyclization of PHA. The cyclization percentage of PBO film was measured with infrared (IR) spectroscopy (FTS-3000, DIGILAB) by measuring the intensity of the amide linkage signal appeared at 1539 cm⁻¹. The cyclization of film cured at 200 °C was calculated by the following equations (1).

\[
\text{Cyclization percentage (\%)} = \frac{A_{200} - A_{320}}{A_{0} - A_{320}} \times 100 \quad (1)
\]

where \(A_0\) is intensity value of prebaked film, \(A_{200}\) is that of film cured at 200 °C and \(A_{320}\) is that of film cured at 320 °C.

2.5. Dissolution Ratio

A test sample was prepared by blending 10 g of PHA, 1.1 g of diazonaphthoquinone (DNQ) as a photoactive compound and NMP. The test sample was spin-coated on a silicon wafer, and then the 12 μm thick thin film was obtained by soft-baking on a hot plate at 120 °C for 3 min. Then the film on a wafer was exposed at 200 mJ/cm² of exposure dose using a contact aligner.

Exposed and unexposed films were dipped in developer of 2.38 wt% tetramethylammonium hydroxide solution (TMAH) at 23 °C. Dissolution ratio (DR) and dissolution contrast were calculated by the following equations (2) and (3).

\[
\text{DR (nm/s)} = \frac{\text{resist thickness}}{\text{dissolution time}} \quad (2)
\]

\[
\text{Dissolution contrast} = \frac{\text{DR}_\text{exp}}{\text{DR}_\text{unexp}} \quad (3)
\]

where \(\text{DR}_\text{exp}\) is the dissolution ratio of exposed area and \(\text{DR}_\text{unexp}\) is the dissolution ratio of unexposed area.

2.6. Preparation of photosensitive composition

Photosensitive solution was prepared by adding 10 g of PHA, 1.1 g of DNQ, 7.5 g of...
methylol compound as a cross-linker, 3 g of silane coupling compound as an adhesion promoter, and additive to the mixture of γ-butyrolactone (GBL) and propyleneglycol monomethyl ether acetate (PGMEA).

2.7. Pattern formation

Photosensitive solution was spin-coated on a 6-inch silicon wafer and pre-baked at 120 °C for 3 min with a coater-developer (Mark-7, Tokyo Electron). The coated wafer with thickness of 11.7 μm was exposed through a patterning mask with i-line stepper (FPA-3000iw, Canon) from 200 to 1000 mJ/cm² of exposure dose. Puddle method with TMAH as a developer was applied for development. The developed patterns were cured at 180, 200, 225 or 320 °C to give PBO.

2.8. Thermal properties

Temperatures of 5% weight loss of PBO films were measured by thermogravimetric analysis (TG/DTA6300, SII). Glass transition temperature (Tg) of cured film was measured by thermomechanical analysis (TMA/SS6000, SII).

2.9. Dielectric constant

Aluminum was deposited on PBO film with silicon wafer through a patterning mask by vacuum evaporation. Dielectric constant was measured with an impedance analyzer (HP4192A and HP16451B, Yokogawa).

2.10. Chemical resistance

PBO film was dipped in chemical solution as shown in table 2 at 23 °C for 15 min. Appearance after dipping was observed by an optical microscope.

3. Results and discussion

3.1. Properties of PHA

To observe the effect of PHA structures on thermal cyclization, several kinds of PHA I were synthesized using various DA and BAP (Fig. 1). Table 1 shows the molecular weights (Mw) of PHA I. The Mw of PHA I were 12,100 to 36,900. Figure 2 shows the transparency of PHA 1a to 1l. The PHA derived from aliphatic dicarboxylic acid showed high transparency more than 95% (Table 1, PHA 1a to 1f and 1i to 1k). While those of PHA derived from aromatic dicarboxylic acid were low transparency less than 51% (Table 1, PHA 1g and 1l). We reported that the intra-molecular charge transfer interaction between acid and amine part influenced the transparency of PHA [8]. Therefore, we think that the PHA derived from aliphatic dicarboxylic acid showed high transparency because aliphatic dicarboxylic acid part does not have π conjugate.

We evaluated the elongation properties of PBO 2a to 2l obtained from PHA 1a to 1l films cured at 320 °C for 1 h (Fig. 3). We found that PBO having long methylene unit showed high elongation values. This result suggests that elongation value depends on the methylene chain length of PBO. In particular, the elongation values of PBO 2e and 2j derived from C10DA were higher than 100%.

Then, we investigated the thermal cyclization behavior of the PHA 1e and 1g in detail by DSC Fig. 4). Compared with aromatic PHA 1g, the top of the cyclization of PHA 1e derived from C10DA became remarkably low from 296 °C to 196 °C. These results suggest that PHA 1e derived from C10DA has flexible polymer chains, resulting in low cyclization temperature.

Table 1. Molecular Weight of PHA

| PHA | DA       | BAP | Mw  | PBO |
|-----|----------|-----|-----|-----|
| 1a  | C3DA     | 6FAP| 12,800 | 2a |
| 1b  | C4DA     |     | 29,300 | 2b |
| 1c  | C6DA     |     | 36,900 | 2c |
| 1d  | C8DA     |     | 33,100 | 2d |
| 1e  | C10DA    |     | 31,600 | 2e |
| 1f  | DMC1DA   |     | 22,200 | 2f |
| 1g  | DEDA     |     | 24,000 | 2g |
| 1h  | C3DA     | 6HAP| 16,400 | 2h |
| 1i  | C6DA     |     | 33,400 | 2i |
| 1j  | C10DA    |     | 24,300 | 2j |
| 1k  | DMC1DA   |     | 29,100 | 2k |
| 1l  | DEDA     |     | 12,100 | 2l |

1) Feed ratio of monomer (molar ratio): DA/BAP/m-AP = 20/19/2.

Fig. 2. Transparency of PHA. Thickness = 10 μm.
3.2. Photolithography

To obtain PD-PBO, the composition of PHA and DNQ need to show high solubility contrast with alkaline developer between exposed areas and unexposed area. We evaluated the dissolution contrast of simple composition consisting of 10 g of PHA \(1a\) to \(1l\) and 1.1 g of DNQ. As seen in Fig. 5, dissolution ratio and contrast were affected by structure of PHA. PHA having long methylene unit showed low dissolution ratio in unexposed area and high dissolution contrast. Especially, the dissolution contrast of PHA \(1e\) and \(1j\) derived from \(C_{10}DA\) showed highest value.

Based on the above results, PHA derived from \(C_{10}DA\) was subjected to photolithographic study. Photosensitive solution named as PD-PHA \(1e\) was prepared by mixing PHA \(1e\), DNQ, cross-linker, adhesion promoter, additive and solvent. The photosensitivity (\(D_o: \) dose to clear) of PD-PHA \(1e\) of 11.7 \(\mu\)m-thick film was 360 mJ/cm\(^2\) along with 78% film retention after development in 2.38% TMAH solution. After curing at 200 \(^\circ\)C for 1h, smooth tapered shape patterns with 30-\(\mu\)m via were obtained (Fig. 6).

3.3. Evaluation of cured film properties

Figure 7 shows the relationship between curing temperature and cyclization percentage measured by IR for PD-PHA \(1c\), \(1b\), \(1e\) and \(1g\). PD-PHA \(1c\), \(1b\), \(1e\) derived from aliphatic dicarboxylic acids were fully cyclized at 200 \(^\circ\)C. We compared PD-PHA \(1e\) derived from \(C_{10}DA\) with PD-PHA \(1g\)
consisting of aromatic structure to evaluate the influence of structure on cured film properties.

Figure 8 shows the thermal and mechanical properties of PD-PHA 1e and 1g. Compared with PD-PHA 1g, high elongation value and high thermal degradation temperature were obtained for PD-PHA 1e cured below 200 °C. On the other hand, $T_g$ of PD-PHA 1e was low compared with PD-PHA 1g. The electrical properties of PD-PHA 1e and 1g were shown in Fig. 9. PD-PHA1e derived from C10DA showed low dielectric constant cured at 200 °C due to full cyclization.

3.4. Chemical resistance

Table 2 shows the chemical resistance of PD-PHA 1e. As shown, the chemical resistance of PD-PHA 1e was excellent cured at 200 °C. These results suggest that PD-PHA 1e is applicable to re-distribution layer.

4. Conclusion

We focused on PHA containing aliphatic dicarboxylic acid unit for positive-tone low temperature curing material. We found that PHA having long methylene unit cured at 200 °C shows the high cyclization percentages and elongation value. In addition, the smooth tapered
The shape pattern was obtained with the photosensitive solution of PHA and DNQ. The incorporation of long methylene aliphatic structure was advantageous to PD-PBO, because of low curing temperature and giving excellent thermal, mechanical and electrical properties.

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**Table 2. Chemical resistance of PD-PHA 1e.**

| Chemicals                  | conditions     | Curing temperature |
|----------------------------|----------------|--------------------|
| GBL                        | 23 °C for 15 min | Good               |
| Acetone                    |                | Good               |
| TOK106<sup>1</sup>         |                | Good               |
| Hydrofluoric acid 0.27%    |                | Good               |
| Sulfuric acid 10%          |                | Good               |

<sup>1</sup> Photoresist stripper.