High-Contrast Chemically Amplified Photodefinable Poly(benzoxazole) Using Dissolution Reversers

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A novel thermal-stable positive-tone photodefinable material has been proposed which applies chemical amplification system to a poly(benzoxazole). To fabricate thick film and also to obtain high dissolution contrast, we paid attention to a three-component system consisting of a poly(benzoxazole) precursor, photoacid generator, and dissolution reverser. In this paper, we describe the design concept of dissolution reversers affording a significant difference in dissolution rate between the exposed and the unexposed area. Moreover, we discuss the photolithographic and film properties of the proposed material. On the basis of the dissolution behavior study, we have designed some promising dicarboxylic acid derivatives for dissolution reversers. We found that the chemically amplified poly(benzoxazole) using the dissolution reversers will afford excellent photolithographic properties such as high sensitivity, fine resolution, and good critical dimension control, along with excellent film properties comparable to those of the conventional non-photodefinable polyimide.

Keywords: poly(benzoxazole), chemical amplification, positive-tone, photodefinable, buffer coating

1. Introduction

Polyimides (PI) are widely used in silicon technology process integration such as insulating, buffer coating, interlayer dielectrics, and so on, because of their excellent electrical, thermal, and mechanical properties [1]. To simplify opening connection via or bonding windows, self-definable PI have become popular. Solvent developable negative-tone photodefinable polyimides (PDPI) [2, 3] are mostly used in this field to fabricate electronic devices. Recently, the development of aqueous developable photodefinable materials has been requested to reduce cost and address environmental issues. Several types of such aqueous developable PDPI as well as photodefinable poly(benzoxazole)s (PBOs) having thermal and mechanical properties equivalent to those of PI have been reported to date [4–6]. For these aqueous developable materials, the

photodecomposition of naphthoquinonediazide into indene carboxylic acid is widely employed as a photochemical system based on the original design of novolac-based photoresist materials. Furthermore, the application of another well-known photochemical system, chemical amplification, has also been reported, in which OH-protected soluble PI [7, 8], COOH-protected PI precursors [9], and OH-protected PBO precursors [10, 11] were used. Some of these chemically amplified PI and PBOs showed high sensitivity and high contrast. However, their ability to make a film thicker than 5 μm and also to make precise patterns has not been confirmed so far. Such ability is highly requested for application to electronic devices. Instead of these two-component systems consisting of a polymer and a photoacid generator (PAG), we have focused on new three-component system including the

incorporation of small acid-labile dissolution-inhibiting compounds. This approach is expected to be able to afford a significant difference in dissolution rate between the exposed and the unexposed area. In addition, by optimizing the dissolution-inhibiting compound, it should become possible to obtain desirable photoimages without protecting polymer itself. This will be a more attractive approach in view of the flexibility in the selection of backbone polymers and the capability of easier and less costly resin synthesis than the two-component systems reported. Such three-component approaches have already been employed in chemically amplified photoresist materials using some phenol- or carboxylic acid-derivative containing polymers as dissolution-inhibiting compounds [12-15].

In this paper, we call the dissolution-inhibiting compound "dissolution reverser". We present the development of newly designed chemically amplified PBO using a three-component system consisting of a PBO precursor, PAG, and dissolution reverser.

2. Experimental

2.1. Materials

A poly(hydroxyamide) (PHA) was prepared from an aromatic dicarboxylic acid, aromatic hydroxydiamine, and endcap reagent by acid chlorination method. The carboxylic acids, photoacid generators, and solvents were used as purchased. Each dissolution reverser was derived from the corresponding carboxylic acid by esterification or acid-catalyzed addition of the corresponding vinyl ether.

2.2. Evaluation of model composition

Each polymer solution was prepared by dissolving 83.4 wt% of the PHA, 8.3 wt% of a carboxylic acid and 8.3 wt% of a PAG in 1-methy-2-pyrrolidone (NMP), and then filtered through a filter of 3 μm pore-size. For a less soluble carboxylic acid, it was used in its saturated amount. The polymer solution was spin-coated on a silicon wafer, which was then prebaked on a hot plate at 90°C for 3 min followed by 120°C for 3 min. A 2.38 wt% aqueous tetramethylammonium hydroxide (TMAH) was used as a developer. Dissolution rate (DR) was calculated based on the change of film thickness before and after development measured by Dektak³ST surface profiler (Veeco Instruments Inc.).

2.3. Preparation of photopolymer solution

Each photopolymer solution was prepared by dissolving the PHA, the dissolution reverser, a photoacid generator and other additives such as an adhesion promoter in a solvent, and then filtered through a filter of 3 μm pore-size.

2.4. Evaluation of photolithographic properties

The photopolymer solution was spin-coated on a silicon wafer, prebaked on a hot plate, and exposed to the radiation of an i-line stepper followed by post-exposure baking (PEB) conducted at 120°C for 3 min. The puddle method with 2.38 wt% aqueous TMAH as the developer was applied for the development.

2.5. Evaluation of film properties

Cyclization of the spin-coated PHA to the corresponding PBO was accomplished through curing at 320°C for 1 h under nitrogen atmosphere. Thermomechanical analysis (TMA) and thermogravimetric analysis (TGA) were conducted by using TMA/SS6000 and TG/DTA6300 (both Seiko Instruments Inc.), respectively. Tensile properties were measured by using Autograph AGS-100NH (Shimadzu).

3. Results and Discussion

3.1. Dissolution reversers

Since the DR of the exposed area is one of the important factors for such thick film application, we focused on the dissolution-promoting ability and tried to select carboxylic acids as backbones for dissolution reversers. The dissolution-promoting ability of several carboxylic acids (**1-11**) was evaluated on the model composition containing 83.4 wt% of the PHA, 8.3 wt% of a carboxylic acid, and 8.3 wt% of a PAG as an NMP solution. As summarized in Table 1, all of the carboxylic acids tested clearly worked as dissolution promoters, affording far higher dissolution rate than the formulation containing no carboxylic acid in nearly 10- μm -thick film. Relatively high promoting ability was observed for the carboxylic acids having three functional groups such as trimellitic acid (**11**) as well as for those having rigid structures such as benzophenone unit (**5**), xanthene units (**7, 8**), or adamantane unit (**10**).

Table 1. Dissolution-promoting ability of various carboxylic acids

Carboxylic acid	Relative DR
none	1
1	4.8
2	5.2
3	6.3
4 ^a	6.3
5 ^a	10.7
6	6.5
7	8.8
8	7.3
9	5.7
10	8.2
11	9.8

^a Owing to poorer solubility in NMP, 4 and 5 were loaded at their saturated amounts.

On the basis of the above material survey, some of the dissolution reversers derived from promising carboxylic acids while protecting their functional groups were subjected to the following study. The dissolution reversers prepared were shown in Figure 1.

Figure 1. Dissolution reversers prepared.

This system is required to have high sensitivity, fine resolution and reasonable short-time development as a thick film of 10 μm or above. Therefore, both the high DR of the exposed area and the high dissolution contrast defined by the following equation are being expected.

$$\text{Dissolution contrast} = \text{DR}_{\text{exp}} / \text{DR}_{\text{unexp}} \quad (1)$$

where DR_{exp} and DR_{unexp} are the dissolution rate of the exposed and the unexposed area, respectively. From this viewpoint, we focused on the dissolution behavior of each trial photopolymer composition including the PHA, each dissolution reverser, and a PAG. The DR_{exp} was evaluated on a 200-mJ/cm² exposed area. Measured DR_{exp} and dissolution contrast values were plotted in Figure 2.

Figure 2. Dissolution rate of exposed area versus dissolution contrast for photopolymer composition using various dissolution reversers.

Among the dissolution reversers examined, ethoxymethyl esters showed the most outstanding performance in both parameters. Considering the decomposition temperature (T_d) of these reversers shown in Table 2, it is inferred that hemiacetal esters except ethoxymethyl esters would be partially decomposed during the PEB process despite the absence of acid catalysts that might cause a low contrast. On the other hand, while the T_d of *tert*-butyl esters was as high as that of ethoxymethyl esters, the former exhibited smaller DR_{exp} and contrast than latter. It was previously reported that *tert*-butyl esters have higher activation energy than acetals [16]. Therefore, it is reasonable to say that the efficiency of acid catalyzed deprotection for *tert*-butyl esters is lower

than that for hemiacetal esters. On the basis of the above study, we were able to design the best three-component system as a prototype and then examined its photolithographic properties as well as cured film properties.

Table 2. Decomposition temperature of various dissolution reversers

Dissolution reverser	$T_d / ^\circ\text{C}^a$
3a	240
5a	n.a.
7a	250
10a	205
11a	245
3b	160
3c	145
3d	240 ^b
10d	175

^a Analyzed by TGA, ^b reference 17.

3.2. Photolithography

Photolithographic properties of the three-component system were evaluated on an 11- μm -thick prebaked film. Typical process conditions and film thickness change through the process are summarized in Table 3. Its sensitivity curve and the scanning electron micrographs of the obtained photoimage are shown in Figures 3 and 4, respectively, clearly demonstrating its quite high properties. The sensitivity (E_{th} : dose to clear) is 200 mJ/cm^2 along with over 90% film retention after development; moreover, 3- μm trench can be resolved. It will be concluded that this high performance is resulted from the high dissolution contrast afforded by the dissolution reverser adapted.

Table 3. Typical process conditions and the change in film thickness during the processes

Process	Conditions	Film thickness
Coating	1000 rpm, 10 s	10.8 μm
	3500 rpm, 30 s	
Prebaking	130 $^\circ\text{C}$, 3 min	n.a.
Exposure	i-line stepper	
PEB	120 $^\circ\text{C}$, 3 min	9.8 μm
Development ^a	50 s $\times$ 2	
Curing	320 $^\circ\text{C}$, 1 h, N_2	7.4 μm

^a 2.38 wt% TMAH was used as a developer.

Figure 3. Sensitivity curve of the photodefinable chemically amplified PBO for 11- μm -thick prebaked film.

Figure 4. SEM photographs after development (top: cross-sectional 3- μm trench, bottom: 5- μm -square hole).

Figure 5. Mask linearity of the photodefinable chemically amplified PBO.

Figure 6. Dependence of fabricated hole size on exposure dose.

Further study was conducted to ascertain the ability to make precise pattern. Figure 5 shows a good linear correlation between the mask size and the obtained hole size. Table 4 shows an excellent critical dimension (CD) uniformity of 5- μm -square holes fabricated on 150-mm-diameter silicon wafers. Both of the properties are comparable to those of our current products confirmed in the semiconductor manufacture. Figure 6 shows the dependence of fabricated hole size on exposure dose. This material showed insignificant dependence on exposure dose over a wide range, that is, from 250 to 500 mJ/cm^2 , along with slight deviation from the mask size.

Table 4. Pattern CD uniformity of 5- μm -square hole for the photodefinable chemically amplified PBO ^a

Items	After development / μm	After post bake / μm
Film thickness	9.6	7.2
Average of hole size	4.93	5.05
Max	5.26	5.36
Min	4.73	4.80
Range	0.53	0.56
Standard deviation	0.16	0.15

^a These data were collected from the patterns fabricated on 150-mm-diameter silicon wafers ($n=17$).

3.3. Film properties

In obtaining highly reliable semiconductor devices, film properties of the proposed PBO are also important. The cured film for the chemically amplified PBO was evaluated for thermal stability and mechanical properties as summarized in Table 5. The typical non-photodefinable polyimide PIX-3400, which is widely used in semiconductor manufacture, was chosen as a reference.

Table 5. Cured film property for the proposed photodefinable chemically amplified PBO

Items	Units	Proposed	PIX-3400 ^b
T_g ^a	$^{\circ}\text{C}$	302	298
CTE	$10^{-6}\cdot\text{K}^{-1}$	67	43
Tensile strength	MPa	119	112
Elongation	%	19	60
Elastic modulus	GPa	2.6	2.6
T_d (5%)	$^{\circ}\text{C}$	450	515

^a Determined by TMA, ^b trade name of HD MicroSystems, these data were collected from 350 $^{\circ}\text{C}$ -cured film.

As a result, it was shown that this proposed material has a sufficient thermal stability and mechanical properties, both of which are equivalent to those of PIX-3400.

4. Conclusion

A novel thermal-stable positive-tone photodefinable material has been proposed which applies chemical amplification system to PBO. To fabricate thick film and also to obtain high dissolution contrast, we paid attention to the three-component system consisting of a PHA, PAG and dissolution reverser. On the basis of dissolution behavior study, we newly designed some promising dicarboxylic acid derivatives for dissolution reversers, which afforded the

enhancement of dissolution contrast in this system. We also found that the chemically amplified PBO using the dissolution reverser will afford excellent photolithographic properties such as high sensitivity, fine resolution, and good critical dimension control. The chemically amplified PBO showed sufficiently fine film properties as well, which are comparable to those of the conventional non-photodefinable polyimide.

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