Study of Polybenzoxazole Precursors for Low Temperature Curing

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1. Introduction

Photodefinable polybenzoxazoles (PD-PBOs) are attracting positive-tone materials in silicon technology process integration such as insulating and buffer coatings, because of their excellent electrical, thermal, and mechanical properties comparable to those of polyimides (PIs) [1]. For these applications, PBOs are formed through cyclization of PBO precursors, for example, poly(*o*-hydroxyamide)s (PHAs), by thermal treatment at over 300 °C. This high-temperature process is hardly applicable to novel organic devices such as gate dielectric layers [2] and insulation layers [3], because these devices require curing temperatures below 300 °C to obtain satisfactory results. In PI application, there are several approaches to reduce the imidization temperature including the introduction of flexible structures [4].

In this paper, we focused on PHAs containing flexible structures. We synthesized the PHAs and then evaluated the cyclization degree and the photolithographic properties for positive-tone low temperature curing materials.

2. Method

PHAs were prepared from several dicarboxylic acids and bis(*o*-aminophenol)s (BAPs) by an acid chlorination method. The photoactive compound diazonaphthoquinone (DNQ) and the solvent *N*-methyl-2-pyrrolidone (NMP) were used as

purchased.

A solution of a PHA was spin-coated on a silicon wafer, which was then soft-baked on a hot plate at 120 °C for 3 min to give a thin film whose thickness was adjusted to 15 μm. The resulting film was cured at 200 °C for 1 h under a nitrogen atmosphere. The cyclization percentage was estimated by infrared (IR) spectroscopy (Shimadzu FTIR-8300).

Each photopolymer solution was prepared by dissolving PHA, DNQ, and other additives such as adhesion promoter in NMP. The solution was spin-coated on a silicon wafer, soft-baked on a hot plate, and exposed to the radiation of a contact aligner and an *i*-line stepper (Canon FPA-3000iw). The puddle method with 2.38% aqueous TMAH as the developer was applied for the development.

Figure 1. Structures of monomers used.

3. Results and Discussion

3.1. Thermal cyclization of PBO precursors

To investigate the relationship between the cyclization ability of PHAs and their chemical structures, we synthesized several PHAs that were derived from BAPs and aromatic or alicyclic dicarboxylic acids (Figure 1). Molecular weights (M_w) of these PHAs were 5,700 ~ 21,600. We will introduce percentage of rigid chain length (PRCL) that expresses the rigidity parameter of polymer chains [5], because chemical structures of PHAs could be converted into numerical values. The PRCL of PHAs is defined by the following equation:

$$\text{PRCL} = L_{\text{rigid}}/L_{\text{total}} \times 100 \quad (1)$$

where L_{rigid} is the length of the rigid part in a monomer unit and L_{total} is the length of the whole unit. In this study, the amide part as a common structural unit is omitted in calculating PRCL for simplification. The extent of cyclization of PHAs was estimated with IR spectra of the PHA films cured at 200 °C for 1 h on silicon wafers.

Figure 2 shows the relationship between the cyclization percentages and the PRCLs of PHAs. It is found that the cyclization percentage of cured films increases with decreasing the PRCL. Among the structures of monomers examined, PHAs derived from CHAP, ADAP22, AdAP13, CHDA, and ADA (PRCL $\leq 63\%$) showed higher cyclization percentages of 50%. These results suggest that the PHAs having alicyclic structures show higher cyclization ability.

Figure 2. PRCLs of PBO precursors versus cyclization percentages of films cured at 200 °C.

3.2. Photolithography

On the basis of the above survey, the PHAs derived from hopeful monomers were subjected to the photolithographic study. The photosensitivity

of resists with the 12- μm -thick prebaked film consisting of PHAs and DNQ was evaluated. Its sensitivity curve is shown in Figure 3. The sensitivity (D_0 : dose to clear) was 200 mJ/cm^2 along with 80% film retention after 2.38% aqueous TMAH development; moreover, 3- μm hole could be resolved. The aliphatic backbone structure is known to have good transparency. We therefore concluded that this high performance is resulted from the good transparency of PHA afforded by the alicyclic structure adopted.

Figure 3. Sensitivity curve of the photodefinable PBO for 12- μm -thick prebaked film at 365 nm.

4. Conclusion

The relationship between the cyclization percentages and the PRCLs of PHAs was examined. We found that the PHAs containing alicyclic structures in BAP part or dicarboxylic acid part showed high cyclization percentages at the cured temperature of 200 °C. In addition, high sensitivity and fine resolution of patterns were obtained from the PHAs and DNQ resists. The incorporation of alicyclic structure was advantageous to PD-PBOs, because of lowering curing temperature and giving high photolithographic performance.

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