Development of Negative-type Photosensitive Semi-alicyclic Polyimide using a Photobase Generator

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A negative-type photosensitive polyimide (PSPI) based on a semi-alicyclic poly(amic acid) (PAA) and a photobase generator (PBG), {[(4,5-dimethoxy-2-nitrobenzyl)oxy]carbonyl} 2,6-dimethyl piperidine (DNCDP) has been developed. PAA was readily prepared from cyclobutane-1,2,3,4-tetracarboxylic dianhydride (CBDA) and 4,4'-oxydianiline (ODA) in *N,N*-dimethylacetamide (DMAc) at room temperature, and used directly by the addition of the PBG for photolithography. The PSPI consisting of PAA (85 wt%) and PBG (15 wt%) showed the high sensitivity of 53 mJ/cm² and contrast of 39.5, respectively, after exposed to 365 nm UV light (i-line) and developed with 0.238 wt% tetramethylammonium hydroxide aqueous solution (TMAHaq) as a base-developer. A fine negative pattern with 6 μm features on a silicon wafer was obtained by a contact-printing mode and converted into a PI pattern by heating at 200 °C.

Keywords: polyimides / photoresist / photosensitive polymer / photobase generator

1. Introduction

PSPIs have been utilized in a variety of electronic devices such as insulators, buffer coatings and passivation layers because of their excellent thermal, electrical and mechanical properties. In addition, they are also attractive because they simplify the pattern-formation processes and avoid the use of additional photoresists in the microelectric industry.^{1–5}

A widely used negative-type PSPI is a poly(amic ester) (PAE) having a methacrylate unit, which is prepared in two step reaction. The reaction of a tetracarboxylic dianhydride with 2-hydroethylmethacrylate produces a corresponding diester-dicarboxylic acid, which is then reacted with a diamine in the presence of a condensing agent to produce the PAE. Thus, this synthesis requires a tedious and expensive process, and it is important to develop a direct PSPI formulation method. To remedy this problem, in a preceding paper,⁶ we reported a direct formulation of PSPI based on an aromatic PAA and DNCDP as a PBG. This photoresist showed a relatively high photosensitivity of 220 mJ/cm² and a contrast of 11.7, respectively.

Scheme 1. Patterning process of negative-type PSPI.

To expand the utility of this method, we applied it to the development of photosensitive semi-alicyclic polyimide (PSSAPI).

This report describes the successful development of an alkaline-developable, chemically amplified negative-type PSPI based on a semi-alicyclic PAA and a PBG.

The formulation of PSSAPI is simple, involving the addition of DNCDP to the polymerization solution of CBDA and ODA. The PSSAPI solution is spin-coated and baked in the usual way. Then, the film is exposed to UV light to produce 2,6-dimethylpiperidine from DNCDP. Upon post-exposure baking (PEB) treatment of the PSSAPI film, 2,6-dimethylpiperidine catalyzed the imidization of the semi-alicyclic PAA. The dissolution rate of the exposed area to TMAHaq decreases, and a negative image is provided. As a consequence, the direct formulation of chemically amplified PSSAPI simplifies the photolithographic process (Scheme 1).

2. Experimental

2.1. Materials

ODA was recrystallized with tetrahydrofuran (THF) under nitrogen. CBDA was kindly donated by JSR corporation. The CBDA dried for 12 h at 150 °C in *vacuo* was used. DNCDP was prepared according to the reported procedure in a 75 % yield after recrystallization from cyclohexane / hexane.⁷ Melting point: 139.2 °C (literature:122-124 °C). Anal. Calcd. for C₁₇H₂₄N₂O₆:C, 57.94 %; H, 6.86 %; N, 7.95 %; O, 27.24 %; Found: C, 58.09 %; H, 6.92 %; N, 7.87 %; O, 27.12 %. The 0.238 wt% TMAHaq was used as a base developer. *N,N*-dimethylacetamide (DMAc) was distilled under reduced pressure over calcium hydride and stored over 4-Å molecular sieves. Other reagents and solvents were obtained commercially and used as received.

2.2. Synthesis of PAA (CBDA/ODA type)

CBDA was added at one time to a ODA solution in DMAc with stirring at 3~5 °C in an ice water bath for 10 min as shown in Table 1.

Then, the mixture was stirred at room temperature for 17 h to give a viscous clear solution. The yields were quantitative. Inherent viscosities of those polymers were 2.47, 1.67 and 0.92 dl/g at a concentration of 0.5 g/dl in DMAc at 30 °C.

Table 1. Synthetic conditions of PAA.

CBDA : ODA (molar ratio)	CBDA (mmol ; g)	ODA (mmol ; g)	DMAc (ml)
(1) 1.00 : 1.00	3.00 ; 0.588	3.00 ; 0.601	7.19
(2) 1.02 : 1.00	3.06 ; 0.600	3.00 ; 0.601	7.27
(3) 1.05 : 1.00	3.15 ; 0.618	3.00 ; 0.601	7.38

2.3. Degree of imidization exposed and unexposed area

The polymer solution was diluted with DMAc to a concentration of 8.5 wt%, followed by the addition of 1.5 wt% DNCDP. The solid content was 10 wt% in DMAc. This solution was spin-coated on a silicon wafer, baked at 120 °C for 3 min in air. A half area of these films were exposed to 365 nm light (i-line) of 300 mJ/cm², and then, baked on a hotplate at 190 °C from 5 min to 1 h. A reference PI film was prepared by heating at 120 °C for 3 min, at 200, 250 °C for 0.5 h and at 350 °C for 1 h in air, respectively. Absorption intensities on a FT-IR spectrum at 1381, 1385 cm⁻¹ (A₁₃₈₁, A₁₃₈₅) assignable as the C-N stretching of the imide group and at 1223, 1234, 1250 cm⁻¹ (A₁₂₂₃, A₁₂₃₄, A₁₂₅₀) assignable as the C-O stretching of phenyl ether were measured, and the degrees of imidization were determined using the following equation (1)

Imidization (%) =

$$\frac{(A_{1381} / A_{1234(\text{samp})} - A_{1381} / A_{1223(\text{init})})}{(A_{1385} / A_{1250(\text{imid})} - A_{1381} / A_{1223(\text{init})})} \times 100 \quad (1)$$

Subscripts between parentheses following A₁₃₈₁/A₁₂₃₄ in the equation indicate states of the polymer films; e.g. (samp) is the polymer sampled at 190 °C for each PEB time (5~60 min) ; (init) is initially prebaked PAA at 120 °C for 3 min in air; (imid) is the fully cured at 350 °C for 1 h in air.

2.4. Photosensitivity

A 1.0 μm thick photosensitive polymer film was prepared by a 10 wt% solid content DMAc solution consisting of 85 wt% PAA, 15 wt% DNCDP, followed by spin-coating on a silicon wafer and then prebaked at 120 °C for 3 min. This

film was exposed to i-line using a filtered super-high-pressure mercury lamp, post-exposure baked (PEB) at 190 °C for 8.5 min. A development of the exposed film was performed with 0.238 wt% TMAHaq at 25 °C for 35 sec, rinsed in distilled water and dried with drier. The characteristic sensitivity curve was obtained by plotting a normalized film thickness against the exposure dose (unit: mJ/cm²). Image-wise exposure was carried out in a contact-printing mode.

2.5. Measurements

The Fourier-transformed (FT-IR) and UV-visible spectra were recorded on Horiba FL-720, JASCO V-560 spectrometer, respectively. Viscosity measurements were carried out by using an Ostwald viscometer at 30 °C in DMAc. Thermogravimetric analysis (TGA) was performed on Seiko TG/DTA 6300 at a heating rate of 10 °C/min under a nitrogen stream. The film thickness on silicon wafer was measured by a Veeco Instrument Dektak³ surface profiler. Field emission scanning electron microscopy (SEM) was taken with a Technex Lab Tiny-SEM 1540 with 15kV accelerating voltage for imaging. Pt/Pd was sputtered on film in advance of the SEM measurement.

3. Results and Discussion

3.1 Synthesis of semi-alicyclic PAA

Scheme 2. Synthesis of the semi-alicyclic PAA.

As an alicyclic tetracarboxylic dianhydride and a diamine, CBDA and ODA were selected, respectively. The polymerization was carried out in DMAc at room temperature, giving PAAs with high inherent viscosities (Scheme 2, Figure 1).

Figure 1. Inherent viscosities of PAAs.

The molecular weights of PAA influence the dissolution rate in TMAHaq. Thus, the molecular weight of PAA was controlled by changing the molar ratio of CBDA to ODA. The results are shown in Figure 1. The PAA having an inherent viscosity of 0.92 g/dL was used for the lithographic evaluation and pattern formation because of an appropriate dissolution to 0.238 wt% TMAHaq.

3.2 Properties of semi-alicyclic PI

The semi-alicyclic PAA was converted to the corresponding PI by thermal treatment at 300 °C for 2 h in air. The thermal stability of semi-alicyclic PI was examined by TGA (Figure 2). A 10 % weight loss temperature in nitrogen is at 469 °C. This decomposition temperature is lower than that of wholly aromatic PIs. It is, however, enough for microelectronics applications.

Figure 2. TG curve of PI (thermal treatment of PI; 300 °C; 2 h).

Figure 3. UV spectra of PI [film thickness on quartz plate : $1.4 \mu\text{m}$].

Further characterization of UV-vis spectrometry (Figure 3) was performed for the semi-alicyclic PAA to measure its transparency, which is an important parameter to conduct i-line photolithography. The film with $1.4 \mu\text{m}$ thickness shows high transparency in the i-line region ($>90\%$ T).

3.2. Lithographic Evaluation

Figure 4. Effect of PBG temperature on the dissolution rate of the exposed and unexposed $1.0 \mu\text{m}$ PAA film containing 15 wt% DNCDP.

A PBG plays a key role in this patterning process. DNCDP, which has a strong absorption centered at 350 nm and allows using a 365 nm exposure, was chosen as a PBG. Moreover, the

DNCDP is a thermal stable PBG, and the thermal decomposition temperature is at around 200°C (1 and 5 wt% weight loss temperatures T_{d1} : 197°C and T_{d5} : 222°C , respectively).

To clarify the difference of dissolution behavior between the exposed and unexposed areas, the effect of the PEB temperature and the PEB time was studied by measuring the film thickness after development.

The films were spin-cast on silicon wafers from the diluted polymerization solution of 8.5 wt% PAA containing 1.5 wt% DNCDP (15 wt% DNCDP to a total solid content) on silicon wafer, and then prebaked at 120°C for 3 min in air. These photosensitive polymer films were exposed to a filtered super-high-pressure mercury lamp (365 nm, $300 \text{ mJ}/\text{cm}^2$), and then post-exposure baked at various temperatures for 10 min. Finally, the films were developed with 0.238 wt% TMAH aq at room temperature. The dissolution rates were estimated by the change in film thickness before and after development.

Figure 4 exhibits the effect of PEB temperature on the dissolution rate of the exposed and unexposed films. The dissolution rate of the exposed area remarkably decreases with increasing the PEB temperature compared to that of the unexposed area. The difference of the dissolution rates between both areas reaches to 300 times at 190°C .

Figure 5. Effect of PEB time at 190°C on the dissolution rate of the exposed and unexposed $1.0 \mu\text{m}$ PAA film containing 15 wt% DNCDP.

Next, the effect of the PEB time on the dissolution rate was investigated at 190 °C in a similar manner (Figure 5). The high dissolution contrast is obtained with the PEB time ranging from 7.5 to 30 min. The largest dissolution contrast is attained for the PEB time of 8 min.

To make clear the relationship between the dissolution rate and the degree of imidization of PAA, the reaction was monitored by FT-IR spectroscopy. The degree of imidization of PAA in the solid phase was estimated by using two characteristic absorptions corresponding to the C-N stretching of the imide group (1381, 1385 cm^{-1}) and the C-O stretching of a phenyl ether comparing with those of thermally imidized PI cured at 350 °C for 1 h in air.

Imidization results are represented as normalized conversion values from PAA pre-baked at 120 °C into PI fully cured at 350 °C. The results are shown in Figure 6, where the PEB temperature is 190 °C. The high dissolution contrast is obtained when the degree of imidization is over 60 % in the exposed area and the difference of the degree of imidization between the exposed and unexposed areas is around 20 %.

Figure 6. Effect of PEB time at 190 °C on the degree of imidization of 1.0 μm PAA film containing 15 wt% DNCDP in both exposed and unexposed areas.

Figure 7. Characteristic photosensitivity curve of PSPI consisting of 85 wt% PAA and 15 wt% DNCDP in 1.0 μm film thickness.

Based on these preliminary optimization studies, a photosensitive polymer PSSAPI consisting of PAA (85 wt%) and DNCDP (15 wt%) was formulated. The photosensitivity curve of a film 1.0 μm thick is shown in Figure 7 (PEB treatment was conducted at 190 °C for 8.5 min and developed with 0.238 wt% TMAH aq). This resist system reveals the photosensitivity ($D_{0.5}$) of 53 mJ/cm^2 and the contrast ($\gamma_{0.5}$) of 39.5 with i-line exposure. This PSSAPI is more sensitive and has a higher contrast compared to those of the previously evaluated PSPI (BPDA/ODA-type; $D_{0.5} = 220 \text{ mJ}/\text{cm}^2$; $\gamma_{0.5} = 11.7$) because of its high transparency at i-line region.⁶

Figure 8 represents the SEM image of 1.05 μm resist film exposed with i-line of 300 mJ/cm^2 , post exposure baked at 190 °C for 8 min, developed with 0.238 wt% TMAH aq at room temperature, and rinsed with water. A clear negative-tone image with a 6 μm featured line and space resolution was obtained.

Figure 8. SEM image of PSSAPI pattern based on 75 wt% PAA and 25 wt% DNCDP. The lithographic conditions were as followed; 13 wt% solid content solution in DMAc spin-coated; prebaked at 120 °C, for 3 min; exposed 300 mJ/cm² in i-line; PEB at 190 °C for 8 min (film thickness = 1.2 μm) ; development with 0.238 wt% TMAH aq. for 2.5 min at room temperature (film thickness = 1.05 μm).

Figure 9. SEM image of PI pattern cured at 200 °C for 30 min (film thickness = 1.0 μm).

Figure 9 shows the SEM image of 1.0 μm resist film cured at 200 °C for 30 min after above treatment. The loss of the film after curing is small (ca. 5 % loss of film thickness).

3. Conclusions

A negative-type, alkaline-developable, and high sensitive PSPI (PSSAPI) was developed. The semi-alicyclic PAA was prepared from CBDA and ODA. The semi-alicyclic PAA was a high transparency in the 365 nm region. The PSSAPI film consisting of 85 wt% PAA and 15 wt% DNCDP exhibited the high photosensitivity and contrast 53 mJ/cm², 39.5, respectively, to 365 nm light exposure. The semi-alicyclic PAA containing 25 wt% DNCDP produced a clear negative-tone image with 6 μm features. Subsequently, this pattern was converted into the corresponding PI upon thermal treatment at 200 °C for 30 min. This methodology to develop a high sensitive PSPI that has a high contrast will provide a more effective and well-rounded patterning formation compared to another methods that require the multi-steps syntheses of PSPI.

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