Development of Negative-type Photosensitive Polyimide, Based on Poly(amic acid)s, Photo Base Generator and Thermal Base Generator

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A negative-type photosensitive polyimide (PSPI) based on poly(amic acid) (PAA), a photo base generator (PBG), {[4,5-dimethoxy-2-nitrobenzyl]oxy}carbonyl-2,6-dimethyl piperidine (DNCDP) and a thermal base generator (TBG), *N*-(*p*-nitrophenyl)-2,6-dimethylpiperidine (NDP) has been developed. The PAA was prepared from 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and 3,3'-sulfonyldianiline (SDA) in *N,N*-dimethylacetamide (DMAc) and used directly for lithographic evaluations. The TBG was easily prepared by the reaction of *p*-nitrophenyl chloroformate with 2,6-dimethylpiperidine. The PAA film containing 10 wt % NDP was converted the polyimide (PI) at 200 °C. The PSPI consisting of PAA (83 wt %), PBG (8.5 wt %) and TBG (8.5 wt %) exhibited a high sensitivity ($D_{0.5}$) of 38 mJ/cm² and a contrast ($\gamma_{0.5}$) of 0.56 when it was exposed to a 365 nm line (*i*-line), post-baked at 170 °C for 2 min, and developed with 2.38 wt % TMAH. A clear negative image of 8 μm line and space pattern was printed in a film which was exposed to 500 mJ/cm² of *i*-line by contact printing mode, fully converted to the corresponding PI pattern upon heating at 200 °C, and confirmed by SEM and FTIR spectroscopy.

Keywords: polyimides / photosensitive polymer / photobase generator / thermal base generator

1. Introduction

Photosensitive polyimides (PSPIs) [1-5] are used as buffer coatings to protect bare chips from stresses induced by fillers or thermal mismatches between a passivation layer and molding materials. PSPIs possess high mechanical strength, thermal stability, and low dielectric constants. Most of the negative-type PSPIs are prepared from poly(amic acids) (PAAs), where cross-linking sites are introduced to PAAs through ester [1-2], acid amine ion interactions [3] or direct attachment to the aromatic rings in PAAs [4]. Moreover the chemically amplified PSPIs using cross-linkers were developed [5-6]. Finally, the patterns of PAAs are converted to those of the corresponding polyimides (PIs) by high temperature thermal treatment. Recently, the

thermally unstable components and the thinner silicone wafers for stacking silicone chips have been begun to use in microelectronic devices. Therefore, these materials are very difficult to use because of thermal decomposition and thermal stress. To remedy these problems, a low temperature imidization is required in industry. In a previous paper, we reported a direct formulation of PSPI based on an aromatic PAA and a photobase generator (PBG) [7]. This patterning process also provides a low-temperature imidization lower than 200 °C. However, a large amount of PBG is required to carry out the low-temperature imidization. On the other hand, we also reported several carbamate derivatives as a TBG that enhances both storage stability and processability of PAA

solutions because of non-reactivity at storage temperatures, while the cyclization of PAA is promoted within a specific range of elevated temperatures [8].

In this study, we report an alkaline-developable, chemically amplified negative-type PSPI based on a PAA, a PBG, $\{[(4,5\text{-dimethoxy-2-nitrobenzyl})\text{oxy}]\text{carbonyl}\}_n$, 2,6-dimethylpiperidine (DNCDP) and a TBG, *N*-(*p*-nitrophenyl)-2,6-dimethylpiperidine (NDP) that provides a high sensitive and low temperature curable PSPI. An amount of PBG is decreased by using a high transparent PAA at 365 nm. Decomposition of NDP will be promoted by the base generated from the PBG, and the generated base from NDP will act as a catalyst for the low temperature imidization. This patterning process and the subsequent low-temperature cyclization using PSPI are shown in Scheme 1.

Scheme 1. Patterning process of low temperature curable PSPI.

The formulation of PSPI is very simple, just the addition of DNCDP and NDP to a PAA solution which is prepared from BPDA and SDA in DMAc. The PSPI 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 PSPI film, 2,6-dimethylpiperidine catalyzes the imidization of the PAA. The dissolution rate of the exposed area to TMAHaq decreases and a negative image is formed. The subsequent low-temperature cyclization of a PAA into a PI pattern proceeds at 200 °C with 2,6-dimethylpiperidine generated from thermal decomposition of NDP. As a consequence, the direct formulation of chemically amplified PSPI simplifies the photolithographic process, and the following thermal treatment at 200 °C promotes

the imidization of the PAA

2. Experimental

2.1. Materials

DMAc was purified by vacuum distillation. SDA purchased from Tokyo Chemical Industry Co., Ltd. was recrystallized from tetrahydrofuran (THF) under nitrogen. BPDA purchased from Tokyo Chemical Industry Co., Ltd. was dried for 12 h at 180 °C *in vacuo* before use. DNCDP was prepared according to the reported procedure. Other reagents and solvents were obtained commercially and used as received.

2.2. Synthesis of the PAA (BPDA/SDA)

BPDA (0.294 g, 1.00 mmol) was added to a solution of SDA (0.248 g, 1.00 mmol) in DMAc (3.10 mL). The mixture was stirred at room temperature for 12 h to give a viscous clear solution. The yield was quantitative. An inherent viscosity of PAA was 0.43 dL/g at a concentration of 0.5 dL/g in DMAc at 30 °C.

2.3. Synthesis of NDP

A 100 mL round-bottomed flask equipped with a dropping funnel and a magnetic stirring bar was flushed with nitrogen, charged with dry THF (30.0 mL) and 2,6-dimethylpiperidine (2.83 g, 25.0 mmol), and cooled in an ice-bath. A solution of *p*-nitrophenyl chloroformate (2.01 g, 10.0 mmol) in dry THF (10.0 mL) was then added dropwise through the dropping funnel to the flask. After the addition was completed, the solution was stirred for 4 h at room temperature under nitrogen, and poured into water. The solution was extracted with ethyl acetate (30 mL $\times$ 3), and the organic layer was washed with sodium hydrogen carbonate solution (50 mL $\times$ 2), dried over with anhydrous magnesium sulfate, and concentrated under reduced pressure. The residue was recrystallized from hexane/toluene (5:1 v/v) to afford a white plate (1.96 g, 71%). IR (KBr, ν , cm^{-1}): 3112 (Ar-H), 3081 (Ar-H), 2969 (C-H), 2935 (C-H), 1712 (O-CO-N), 1523 (ArNO₂), 1347 (ArNO₂). ¹H NMR (300 MHz, CDCl₃, σ , ppm): 1.33 (d, *J* = 7.0 Hz, 6H), 1.51–1.87 (m, 6H), 4.45 (m, 2H), 7.30 (d, 2H), 8.25 (d, 2H). ¹³C NMR (300 MHz, CDCl₃, σ , ppm): 13.96, 21.36, 30.39, 47.50, 122.73, 125.44, 145.05, 153.16, 157.08. Elemental analysis: Calcd. for C₁₄H₁₈N₂O₄: C, 60.42; H, 6.52; N, 10.07; O, 23.00; Found C, 60.50; H, 6.47; N, 10.02; O, 23.01.

2.4. Degree of imidization

The polymer solution was diluted with DMAc to a concentration of 15 wt %, followed by addition of DNCDP or NDP. The solution was spin-coated on a silicon wafer, baked at 100 °C for 10 min in air. The film thickness was about 1.0~1.2 µm. Then, the films were baked on a hot-plate at each temperature (110~200 °C) for 10 min. A reference PI film was prepared by heating at 250 °C for 0.5 h and 350 °C for 1h. Absorption intensities on a FT-IR spectrum at 1376 cm⁻¹ (A₁₃₇₆) assignable to the C-N stretching of the imide group and at 1500 cm⁻¹ (A₁₅₀₀) assignable to the aromatic C=C stretching were measured, and the degrees of imidization were determined using the following equation (1)

$$\text{Imidization (\%)} = \frac{(A_{1376} / A_{1500(\text{samp})}) - (A_{1376} / A_{1500(\text{init})})}{(A_{1376} / A_{1500(\text{imid})}) - (A_{1376} / A_{1500(\text{init})})} \times 100 \quad (1)$$

Subscripts between parentheses following A₁₃₇₆/A₁₅₀₀ in the equation indicate states of the polymer films; e.g. (samp) is the polymer sampled at each heating temperature level (110~120 °C); (init) is initially prebaked PAA at 100 °C; (imid) is the fully cured at 350 °C for 1 h in air.

2.5. Photosensitivity

A 1.2 µm thick photosensitive polymer film was prepared by a 15 wt % solid content DMAc solution consisting of PAA (83 wt %), DNCDP (8.5 wt %) and NDP (8.5 wt %), followed by spin-coating on a silicon wafer and then prebaked at 100 °C for 5 min. This film was exposed to *i*-line using a filtered supper-high-pressure mercury lamp, PEB at 170 °C for 2 min. A development of the exposed film was carried out with the developer of 2.38 wt % TMAH aq. at 25 °C for 130 sec, rinsed with distilled water, and dried with a drier. The characteristic sensitivity curve was obtained by plotting a normalized film thickness to the exposure dose (unit: mJ/cm²). Image-wise exposure was carried out in a contact-printing mode.

2.6. Measurements

The Fourier-transferred (FT-IR) and UV-visible spectra were recorded on a Horiba FT-720, a 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 a 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 High Transparency PAA

In the aromatic PI and PAA, the absorption wavelength of polymers is determined by the energy band-gap between a dianhydrides and a diamine, which is involved a highest occupied molecular orbital (HOMO) and a lowest unoccupied molecular orbital (LUMO), respectively. Therefore, the PAA with high transparency is obtained from a dianhydride which has small electron affinity and a diamine which has a low ionization potential. Thus, we selected BPDA and SDA as a dianhydride and a diamine, respectively. These compounds have reasonable potential to increase the transparency of the resulting PAA and PI.

Figure 1. UV-vis spectra of [BPDA/SDA] type PAA (film thickness 2.8 µm) and [BPDA/ ODA] type PAA (film thickness 2.5 µm).

The PAA with an inherent viscosity of 0.43 dL/g was prepared from BPDA and SDA. The UV-vis spectra of the PAA film with thickness of 2.8 µm is shown in Figure 1 with that of the reference PAA film from BPDA and ODA with thickness of 2.5 µm. The transmittance of the PAA (BPDA/ODA) film measured at 365 nm is 89%, which is much higher than that (26%) of

the reference PAA. Thus, the PSPI using the PAA (BPDA/ODA) as a matrix polymer is expected to show a high sensitivity with a 365 nm light.

3.2 Synthesis of NDP.

Although several TBGs have been reported, their thermal stability is not so high. In this PSPI system, a PEB temperature may be high at about 160 °C because of imidization reaction. Therefore, a new TBG with thermal stability at around 200 °C should be developed. NDP was designed and synthesized from 2,6-dimethyl piperidine and *p*-nitrophenyl chloroformate. NDP would be decomposed into *p*-nitrophenol and 2,6-dimethylpiperidine by hydrolysis on a carbamate bond. NDP was obtained good yield and indicated high thermal stability ($T_{d5\%} = 210$ °C).

A degree of imidization (DI) of the PAA film containing 10 wt % NDP or no TBG up to 200 °C was monitored with FT-IR spectroscopy. The DI in the solid state was calculated from two characteristic absorptions corresponding to the aromatic C=C (1500 cm^{-1}) and imide C-N stretching (1375 cm^{-1}) as compared with thermally imidized PI (cured at 350 °C for 1 h). The effect of NDP loading in the PAA film and the influence of temperature on the DI was investigated (Fig. 2).

Figure 2. The DI of the PAA film with NDP (●) with 10 wt % additive for PAA and no additive-free (□).

The DI of PAA films containing NDP is accelerated at around 180 °C, which is corresponding to the decomposition temperature of NDP, and reached 100% at 200 °C. On the other hand, the DI of the TBG-free PAA film is

85% of imidization at 200 °C. These results clearly indicate that NDP acts as a TBG.

3.3 Lithographic Evaluation

To obtain contrasting pattern profiles from exposed and unexposed areas, the effect of PEB temperature, PEB time, and exposure dose were investigated. The Films were obtained by spin-casting the diluted polymerization solution of the PAA containing DNCDP (8.5 wt %) and NDP (8.5 wt %) on a silicon wafer, and then pre-baking at 100 °C for 5 min in air. This photosensitive polymer film was irradiated with UV light at 365nm (*i*-line) using a filtered super-high-pressure mercury lamp, PEB at a set temperature, and developed with TMAH at 25 °C.

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 dissolution rates were estimated by the change in film thickness before and after development.

First, the effect of the PEB temperature on the dissolution rate was investigated and the results are shown in Figure 3. Although the dissolution rate of both in the exposed and unexposed areas decreases with increasing the PEB temperature, the highest dissolution contrast is obtained at 170 °C, where the PEB time and exposure dose are for 2 min and 500 mJ/cm², respectively.

Figure 3. Effect of PEB temperature to PAA on the dissolution rate for the PAA/DNCDP/NDP (83/8.5/8.5 wt/wt/wt) resist system in exposed (◆) and unexposed area (□). The pre-bake, the *i*-line exposure and PEB time were fixed as 100 °C for 5 min, 500 mJ/cm² and for 5 min, respectively.

The effect of PEB time is summarized in Figure 4. The PEB times are changed from 1 to 5 min where the PEB temperature and exposure dose are fixed at 170 °C and 500 mJ/cm², respectively. The dissolution rate becomes almost zero at 170 °C for 2 min and the highest dissolution contrast is obtained. Thus, the PEB temperature and time are critical to lithographic evaluation in this PSPI.

Figure 4. Effect of PEB time to PAA on the dissolution rate for the PAA/DNCDP/NDP (83/8.5/8.5 wt/wt/wt) resist system in exposed (◆) and unexposed area (□). The pre-bake, the *i*-line exposure and PEB temperature were fixed as 100 °C for 5 min, 500 mJ/cm² and at 170 °C, respectively.

Figure 5. Characteristic photosensitive curve for the PAA/DNCDP/NDP (83/8.5/8.5 wt/wt/wt) resist system in 1.2 μm film thickness. The pre-bake and PEB were fixed as 100 °C for 5 min and at 170 °C for 2 min, respectively.

Based on these preliminary optimization studies, a photosensitive polymer consisting of PAA (83 wt %), DNCDP (15 wt %) and NDP (8.5 wt %) was formulated. The photosensitivity curve of a film 1.2 μm thick is shown in Figure 5 (PEB treatment was conducted at 170 °C for 2 min and developed with 2.38 wt % TMAH(aq.)). This resist system reveals the photosensitivity ($D_{0.5}$) of 38 mJ/cm² and the contrast ($\gamma_{0.5}$) of 0.56 with *i*-line exposure. This PSPI has high sensitivity but its contrast is low compared to that of the PSPI (BPDA/ODA). The high sensitivity is attributed to the high transparency of the PAA.

3.4 Low Temperature Imidization of PSPI

To investigate the imidization of PSPI using FT-IR spectroscopy, the PAA film containing DNCDP (8.5 wt %) and NDP (8.5 wt %) was baked on a hotplate at designated temperatures, such as a pre-bake at 100 °C for 10 min, PEB at each temperature (110~200 °C) for 10 min after exposure (500 mJ/cm² of *i*-line). A reference PI film was prepared by the following thermal treatment, such as at 250 °C for 0.5 hr and 350 °C for 1 h in air.

Figure 6. The DI of the PAA film containing DNCDP (8.5 wt %) and NDP (8.5 wt %) (■), only DNCDP (10 wt %) (◆), only NDP (10 wt %) (●), and no additive (□).

Figure 6 shows that the imidization starts from 130 °C, and completely finishes until 200 °C because of influence of the base from DNCDP. It is interesting that the DI of the PAA film containing DNCDP (10 wt %) which was also exposed at 500 mJ/cm² of *i*-line is lower than that of the PAA film containing DNCDP and NDP. Moreover, the DI of the PAA film containing only NDP (10 wt %) is 80% at around 180 °C. It indicates that hydrolysis of NDP is accelerated by the base from DNCDP.

These films were baked on the condition of lithographic evaluation. The DIs of the PAA films containing DNCDP (8.5 wt %) and NDP (8.5 wt %), only DNCDP (10 wt %), only NDP (10 wt %), and no additive are 100, 91, 80, and 71%, respectively at 180 °C. Thus, the effect of NDP on the DI is around 10%.

3.5 Image formation of PSPI

Figure 7 presents a scanning electron micrograph of a contact-printed image obtained with the aforementioned system: the resist was exposed to 500 mJ/cm², post baked at 170 °C for 2 min, and developed with 2.38 wt % TMAH aq.

Figure 7. SEM image of negative-pattern of 2.0 μm-thick film based on PAA/DNCDP/ NDP (83/8.5/8.5 wt/wt/wt). The pre-bake, the *i*-line exposure and PEB were fixed as 100 °C for 5 min, 500 mJ/cm² and at 170 °C for 2 min, respectively.

Figure 8. SEM image of PI pattern cured at 200 °C for 1 h.

A clear, negative PAA pattern with an 8 μm feature can be observed when a 2.0 μm thick

film was used. The printed pattern was converted to the PI pattern without deformation by heating at elevated temperature up to 200 °C for 1 h in air (Figure 8). The film thickness decreased to 1.8 μm due to the evaporation of water, amine, and phenol which were by-products and the solvent.

4. Conclusions

A negative-type PSPI based on the PAA solution, PBG, and TBG was developed. The photosensitivity and contrast of 1.2 μm thick resist film consisting of PAA (83 wt %), DNCDP (8.5 wt %), and NDP (8.5 wt %) were 38 mJ/cm² and 0.56, respectively and this PSPI produced a clear negative-tone image with 8-μm features. This pattern was converted subsequently into the corresponding PI upon heating at 200 °C. In addition, NDP indicated a weak effect of base amplification. This new patterning process using a hydrolysis type TBG potentially provide a more efficient and versatile patterning process for PSPIs compared to the standard route that requires the modification of PAAs and high imidization temperatures.

5. References

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