A Novel Low Temperature Curable Photosensitive Polybenzoxazole

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ABSTRACT: A novel positive-tone photosensitive polybenzoxazole for low temperature cyclization has been developed. The matrix polymer (PHA-6F) was prepared from 4,4'-(hexafluoroisopropylidene)bis(*o*-aminophenol) (6FAP) and 4,4'-oxybis(benzoyl chloride) (OBBC) by low temperature solution polycondensation, and the photosensitive polymer was formulated with PHA-6F, a dissolution inhibitor 1-{1,1-bis[4-(2-diazo-1-(2*H*)naphthalenone-4-sulfonyloxy)phenyl]ethyl}-4-{1-[4-(2-diazo-1-(2*H*)naphthalenone-4-sulfonyloxy)phenyl]methylethyl}benzene (S-DNQ), and a photo- and thermoacid generator (5-propylsulfonylimino-5*H*-thiophen-2-ylidene)-2-(methylphenyl)acetonitrile (PTMA). The photosensitivity and contrast of the 2.4 μm thick film were 15 mJ/cm² and 2.5, respectively. A clear positive polybenzoxazole image featuring 8 μm line-and-space pattern was obtained, when a 2.1 μm -photosensitive film containing PHA-6F, S-DNQ, and PTMA (15:3:2 in weight ratio) was prebaked at 120 °C for 5 min, irradiated with 365 nm light (60 mJ/cm²), developed with an 2.38 wt % tetramethylammonium hydroxide (TMAH) solution for 90 s, washed with acetic acid, and cured at 250 °C for 10 min. [DOI 10.1295/polymj.37.517]

KEY WORDS Photosensitive Polybenzoxazole / Low Temperature Solid-phase Cyclization / *i*-Line Lithography / Poly(*o*-hydroxyamine) / Alkaline Developer / Thermoacid Generator /

Polybenzoxazoles (PBOs) have been used as protection and insulation layers for very large scale integration circuits (VLSI) and multi-chip modules for computers owing to their high thermal stability and excellent mechanical property.^{1–4} Photosensitive PBOs (PSPBOs)^{5–21} have been developed to simplify the processing steps because phenolic hydroxyl groups in precursors of PBOs provide adequate solubility toward an aqueous alkaline developer. Up to now PSPBO based on the poly(*o*-hydroxyamide) (PHA-6F) derived from 6FAP and 4,4'-oxybis(benzoic acid) derivatives^{22,23} with a photosensitive compound has been widely used, in which the image of PHA-6F is finally converted into that of PBO by thermal treatment at 350 °C. This high-temperature process is hardly applicable to the conventional electronic applications containing at least one or more thermally unstable organic components. Therefore, a novel method for the formation of PBO patterning at low temperature curing is desired.

Recently sulfonic acids were found to work as an effective catalyst for low temperature cyclization of PHA.²⁴ Especially, PTMA, which is known as an excellent photoacid generator with high quantum yield at 436 nm wavelength,²⁵ lowered the cyclization temperature at 250 °C,²⁶ significantly lower than non-catalytic cyclization at 350 °C. Thus, the development of low temperature cyclization system in a photosensitive PBO would be useful for expanding its applica-

Scheme 1.

tion to various fields. PTMA can also be used as a thermoacid generator,²⁶ and it will function as an acid catalyst for the cyclization by heating after development.

We describe here a novel photosensitive PBO consisting of PHA-6F, a dissolution inhibitor S-DNQ, and a photo- and thermoacid generator PTMA (Scheme 1), enabling low temperature solid-phase cyclization of PHA-6F after the patterning.

EXPERIMENTAL

Materials

6FAP was recrystallized from tetrahydrofuran (THF)/hexane. 4,4'-Oxybis(benzoyl chloride) (OBBC) was prepared from the corresponding acid with thionyl chloride. 1-Methyl-2-pyrrolidinone (NMP) was purified by vacuum distillation from calcium hydride and stored over 4 Å molecular sieves. PTMA and

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S-DNQ were kindly supplied from Ciba Specialty Chemicals and Sumitomo Bakelite Co. Ltd., respectively, and used as received. PHA-6F was prepared from 6FAP and OBBC in NMP by low temperature solution polycondensation in 93% yield ($M_n = 25000$, $M_w/M_n = 1.6$ determined by GPC (DMF, PSt standards)). Other reagents and solvents were used as received.

Dissolution Rate

All baking processes were performed on a hot plate with a digital thermo-controller. PTMA (10–30 wt % to PHA-6F) and S-DNQ (5–20 wt % to PHA-6F) were dissolved in PHA-6F solution in *N,N*-dimethylacetamide (DMAc) (20 wt % of PHA-6F) to construct a photosensitive polymer. The polymer film spin-cast on a silicon wafer was prebaked at 80–120 °C for 5 min, exposed to a filtered super-high-pressure mercury lamp at 365 nm wavelength, and developed with a 2.38 wt % TMAH solution at 25 °C.

Photosensitivity

A 2.4 μm -thick polymer film containing PHA-6F, S-DNQ, and PTMA (15:3:2 in weight ratio) on a silicon wafer was prebaked at 120 °C for 5 min, exposed to 365 nm light, and developed with a 2.38 wt % TMAH solution at 25 °C for 300 s. A characteristic curve was obtained by plotting a normalized film thickness against exposure energy.

Evaluation of Cyclization

The degree of cyclization was determined by Infrared (IR) spectroscopy, in which the absorption change at 1051 (C–O stretch of benzoxazole) and 1250 cm^{-1} (C–O stretch of phenyl ether) was monitored. No influence on these two absorptions by the catalyst and solvent was assumed.

Measurements

IR spectra were recorded on a Horiba FT-210 spectrophotometer. Thermal analyses were performed on a Seiko EXSTAR 6000 TG/DTA 6300 thermal analyzer at heating rate of 10 °C/min for thermogravimetry (TG). Number- and weight-average molecular weights (M_n and M_w) were determined by a gel permeation chromatography (GPC) with polystyrene calibration using Tosoh HLC-8120 system equipped with a consecutive polystyrene gel column (TSK GELs, GMH_{HR}-M and GMH_{HR}-L) at 40 °C in DMF containing 0.01 M of lithium bromide at a flow rate of 1.0 mL/min. Film thickness was measured by a Dektak³ surface profiler (Veeco Instrument Inc). Scanning electron micrograph (SEM) was taken by Technex Lab Co., Ltd. Tiny SEM 1540.

Figure 1. TG profiles of PHA-6F films without (solid line) and with 5 wt % additives of 4-hydroxybenzoic acid (4-HBA) (dashed-dotted line), imidazole (IZ) (short-dashed line), diazabicyclo[5.4.0]undec-7-ene (DBU) (broken line), *p*-toluenesulfonic acid (TSA) (long-dashed line), and methanesulfonic acid (MSA) (dotted line).

RESULTS AND DISCUSSION

Cyclization Catalyst

Several acid and base catalysts such as 4-hydroxybenzoic acid (4-HBA), imidazole (IZ), diazabicyclo[5.4.0]undec-7-ene (DBU), *p*-toluenesulfonic acid (TSA), and methanesulfonic acid (MSA) were employed to investigate the effect for cyclization of PHA-6F to PBO. Figure 1 illustrates the TG (10 °C/min under nitrogen) profiles in each sample. Without any additives, PHA-6F starts to decrease its weight from 250 °C, and the cyclization finishes at 350 °C. This weight loss of 6% agreed well with the calculated value of 5.8% if the water was completely removed during the cyclization. Sulfonic acids are more effective than the other catalysts such as benzoic acid and base catalysts, and the cyclization temperature can be lowered to 250 °C. Thus, as a thermoacid generator for the present photosensitive polymer system, sulfonic acid derivatives were chosen. PTMA was effective to lower the transformation temperature from PHA into PBO by protonation of carbonyl oxygen resulting in easy nucleophilic attack of phenol oxygen on amido carbonyl,²⁶ thus from the results mentioned above sulfonic acid generated from PTMA is a promoter, and we expected PTMA could play as a photoacid generator and promoter for fabrication of PBO image.

Lithographic Evaluation

PTMA is known as a dissolution inhibitor as well as a photoacid generator, thus a photosensitive polymer was constructed with PHA-6F and PTMA. The effect

Figure 2. Effect of PTMA loading on dissolution rate (nm/s). Conditions; PTMA (0–30 wt % to PHA-6F), DMAc solution (20 wt % of PHA-6F), prebaking at 120 °C for 5 min, development 2.38 wt % TMAH solution at 25 °C.

of PTMA loading on the dissolution rate of the film was investigated as shown in Figure 2. The dissolution rate was estimated by the measurement of the film thickness after development. Although increasing the amounts of PTMA up to 30 wt % to PHA-6F, the dissolution contrast between the PTMA un-loaded and loaded films is small probably because of its small size. Thus, the conventional dissolution inhibitor S-DNQ was decided to add in this system. The effect of S-DNQ loading on the dissolution rate of the polymer film was studied in similar conditions described in Figure 2. The PHA-6F film (containing 10 wt % PTMA to PHA-6F) spin-cast on a silicon wafer was irradiated with 365 nm light at 100 mJ/cm², and developed with a 2.38 wt % TMAH solution at 25 °C. The dissolution rate decreases with increasing the amounts of S-DNQ, and becomes zero with 15 wt % loading, where a large dissolution contrast between the exposed and unexposed areas is achieved as shown in Figure 3. This effective dissolution inhibition of S-DNQ attributes its bulky structure compared with PTMA. S-DNQ absorbs light, resulting in its transformation into indencarboxylic acid which accelerates solubility in alkaline developer. Prebaking conditions are important because they generally affect the dissolution rate of the film due to the residual solvent. Thus, the effect of prebaking temperature from 80–120 °C for 5 min was studied (Figure 4). Baking at 120 °C for 5 min effectively reduces the dissolution rate. Thus, the suitable prebaking temperature was determined to be 120 °C.

After these preliminary optimization studies involving S-DNQ loading and prebaking temperature, the photosensitive polymer was formulated using PHA-6F (20 wt % in DMAc), PTMA (10 wt % to PHA-6F),

Figure 3. Effect of S-DNQ loading on dissolution rate (nm/s). Conditions; PTMA (10 wt % to PHA-6F), S-DNQ (0–20 wt % to PHA-6F), DMAc solution (20 wt % of PHA-6F), prebaking at 120 °C for 5 min, development 2.38 wt % TMAH solution at 25 °C.

Figure 4. Effect of baking temperature on dissolution rate (nm/s). Conditions; PTMA (10 wt % to PHA-6F), S-DNQ (15 wt % to PHA-6F) DMAc solution (15 wt % of PHA-6F), prebaking at 80–120 °C for 5 min, development 2.38 wt % TMAH solution at 25 °C.

S-DNQ (15 wt % to PHA-6F). To evaluate the sensitivity and contrast of the photosensitive film, the film thickness after development is plotted as a function of irradiation dose as shown in Figure 5. The sensitivity and contrast was determined to be 15 mJ/cm² and 2.5, respectively, when 2.4 μm thick film containing PHA-6F, S-DNQ, and PTMA (15:3:2 in weight ratio) was irradiated with 365 nm light, and developed with a 2.38 wt % TMAH solution for 300 s.

To realize complete transformation of PHA-6F image into PBO at low curing temperature (Scheme 2), where the acid catalyst should work well, the 2.1 μm-photosensitive film containing PHA-6F, S-DNQ, and

Figure 5. A photosensitivity curve of PHA-6F based photo-sensitive polymer.

Scheme 2.

PTMA (15:3:2 in weight ratio) was prebaked at 120 °C for 5 min, irradiated with 365 nm light (60 mJ/cm²), developed with a 2.38 wt % TMAH solution for 90 s. The remaining alkaline developer was first removed by rinsing the PHA-6F image with an acetic acid aqueous solution for 90 s, and the image was postbaked. Figure 6 shows IR spectra of PSPBO films (A) after prebaking (B) after postbaking at 250 °C for 10 min (rinsing with acetic acid) and (C) of corresponding PBO film. The characteristic absorption at 1650 cm⁻¹ corresponding to amide stretching was disappeared and a new absorption at 1051 (oxazole C–O stretching) was observed when the film was postbaked at 250 °C for 10 min. Figure 7 depicts a scanning electron micrograph of a contact printed image of the film cured at 250 °C for 10 min after development. Although the image after 250 °C curing shows rounded edges compared with PHA-6F image, a clear PBO image featuring 8 μm line-and-space was observed without serious deformation.

CONCLUSIONS

A novel low curable PSPBO was formulated using PHA-6F (75 wt %), S-DNQ (15 wt %), and PTMA (10 wt %). The positive-tone image featuring 8 μm

Figure 6. IR spectra of PSPBO films (A) after prebaking (B) after postbaking at 250 °C for 10 min (rinsing with acetic acid) and (C) of corresponding PBO film.

Figure 7. SEM image of PSPBO.

line-and-space was obtained by 365 nm exposures followed by development with a 2.38 wt % TMAH solution. The PHA-6F image was successfully converted into PBO image at as low as 250 °C for 10 min. This photo-patterning system with low temperature curing for the formation of PBO image is a promising method and will be applied for practical use.

REFERENCES

1. T. Kubota and R. Nakanishi, *J. Polym. Sci. Part B: Polym. Lett.*, **2**, 655 (1964).
2. Y. Imai, I. Taoka, K. Uno, and Y. Iwakura, *Macromol. Chem.*, **83**, 167 (1965).
3. C. Arnold, Jr., *J. Polym. Sci., Macromol. Rev.*, **14**, 265 (1979).
4. G. Maiyer, *Prog. Polym. Sci.*, **26**, 3 (2001).
5. R. Rubner, A. Hammerschmidt, R. Leuschner, and H. Ahne, in "Polym. Microelectron, Proc. Int. Symp," Y. Tabata, Ed., Kodansha, Tokyo, 1990, p 789.
6. H. Ahne, A. Hammerschmidt, and E. Schmidt, *Proceedings of Polym. Mater. Sci. Eng. Am. Chem. Soc.*, **60**, 629 (1989).

7. H. Ahne, R. Rubner, and R. Sezi, *Appl. Surf. Sci.*, **106**, 311 (1996).
8. D. F. Huang, J. Y. Chiou, C. C. Hung, and B. R. Young, *Proc. SPIE*, **4277**, 375 (2001).
9. R. Sezi, A. Maltenberger, W. Radlik, G. Schmid, A. Weber, and K. Buschick, *Proc. SPIE*, **3582**, 236 (1998).
10. H. Makabe, T. Banba, and T. Hirano, *J. Photopolym. Sci. Technol.*, **10**, 307 (1997).
11. T. Yamaoka, N. Nakajima, K. Koseki, and Y. Maruyama, *J. Polym. Sci., Part A: Polym. Chem.*, **28**, 2517 (1990).
12. D. N. Khanna, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **1**, 348 (1990).
13. D. N. Khanna and W. H. Mueller, *Polym. Eng. Sci.*, **29**, 954 (1989).
14. R. Rubner, *Adv. Mater.*, **2**, 452 (1990).
15. K. Ebara, Y. Shibasaki, and M. Ueda, *J. Polym. Sci., Part A: Polym. Chem.*, **40**, 3399 (2002).
16. K. Ebara, Y. Shibasaki, and M. Ueda, *Polymer*, **44**, 333 (2003).
17. K. Ebara, Y. Shibasaki, and M. Ueda, *J. Photopolym. Sci. Technol.*, **16**, 287 (2003).
18. C. S. Hong, M. Jikei, and M. Kakimoto, *Polym. J.*, **35**, 586 (2003).
19. K. Fukukawa, Y. Shibasaki, and M. Ueda, *Polym. J.*, **36**, 489 (2004).
20. K. Fukukawa, Y. Shibasaki, and M. Ueda, *Macromolecules*, **37**, 8256 (2004).
21. K. Fukukawa, Y. Shibasaki, and M. Ueda, *Polym. J.*, **37**, 74 (2005).
22. M. D. Houtz, J. M. Lavoie, D. L. Pedrick, E. G. Jones, M. R. Unroe, and L. S. Tan, *Polym. Prepr.*, **35**, 437 (1994).
23. W. D. Joseph, J. C. Abed, T. H. Yoon, and J. E. McGrath, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **35**, 551 (1994).
24. T.-K. Kim, K.-Y. Choi, K.-S. Lee, D.-W. Park, and M.-Y. Jin, *Polym. Bull.*, **44**, 55 (2000).
25. T. Asakura, H. Yamato, and M. Ohwa, *J. Photopolym. Sci. Technol.*, **13**, 223 (2000).
26. F. Toyokawa, Y. Shibasaki, and M. Ueda, *Chem. Lett.*, 1342 (2004).