

Comparison of Positive-tone Photosensitive Polyimides

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Introduction

Polyimides are widely used as buffer coatings and interlayer dielectrics of semiconductor devices¹. For those applications, polyimides are required to obtain fine pattern formation by photo-lithographic technique. To meet the requirement, solvent developable negative-tone photosensitive polyimides were commercialized^{2,3}. Recently, in order to take account of environment and finer pattern capability, water base alkaline developable positive-tone photosensitive polyimides were required. Concept of positive-tone photosensitive polyimide was known long time ago⁴. But no one could develop positive-tone photosensitive polyimide as a commercial base due to its difficulties of controlling alkaline developer solubility. On the other hand, Rubner invented positive-tone photosensitive polybenzoxazole successfully⁵. The positive-tone photosensitive polybenzoxazole technologies were transferred to many companies and commercialized successfully⁶. However, we still kept on developing polyimide based positive-tone photosensitive materials. In this article, we developed novel simple positive-tone photosensitive polyimide by using partial esterification reaction. Including this type of the photosensitive polyimide, we investigated various types of positive-tone photosensitive polyimides. In this article, we will review performance comparison of various types of positive-tone photosensitive polyimides.

Results and Discussion

We examined the 3 types of positive tone photosensitive polyimides, namely, a photosensitive polyimide from partial esterified poly(amic acid), a photosensitive polyimide from preimidized polymer, and positive-tone patterning from ionic bonded photosensitive polyimide. Those 3 methods are easy to prepare the photosensitive polyimide solutions. It is quite important from the point of commercialization.

1. Photosensitive polyimide from partial esterified poly(amic acid)

Poly(amic acid) from 4,4'-Diamino-diphenylether (ODA) and 3,3',4,4'-diphenylether-tetracarboxylic acid dianhydride (ODPA) was partial esterified by N,N-dimethylformamide-diethylacetal(DFA). The partial esterification was carried out after polymerization continuously. Selectivity of the esterification to imidization is quite high. The partial esterification reaction is effective to control the dissolution rate of poly(amic acid) The esterification reaction is shown in Scheme1. The method for partial esterification is able to apply for various types of poly(amic acids). The method made us to control the dissolution rate of the partial esterified poly(amic acids) precisely (Figure 1). Positive-tone polyimide precursor solution was obtained by mixing the partial esterified poly(amic acid) and diazonaphthoquinone sulfonate (DNQ)⁷.

The positive-tone photosensitive polyimide preparation technology enable us to develop many products easily. For example, high refractive index positive-tone photosensitive polyimide was obtained by mixing with partial esterified poly(amic acid) from 2,2-Bis(3-amino-4-hydroxyphenyl)hexafluoropropane (6FAP) and ODPA, high refractive index titania nano sol and DNQ⁸. The chemical composition of positive-tone photosensitive polyimide is summarized in Table 1 and cross sectional view is shown in Figure 2.

2. Photosensitive polyimide from pre-imidized polymer

It is easy to obtain the positive-tone photosensitive polyimide by mixing preimidized phenol containing polymer and DNQ. In addition, the positive-tone photosensitive polyimide shows quite low shrinkage during curing process. Dissolution rate of pre-imidized polymer to alkaline developer is determined by polymer's phenolic OH or carboxylic acid concentration. So freedom of polymer structure selectivity is limited. The pre-imidized polymer shows large optical absorbance at i-line(365nm) region. The polymers absorbance made the positive-tone photosensitive low sensitivity especially at i-line exposure.

In order to minimize i-line absorption of the base resin, polyimide from 6FAP and ODPA were chosen for pre-imidized polymer due to solubility. Polymerization was carried out at 180C for 4hrs under nitrogen flow. Positive-tone photosensitive polyimide was obtained by mixing pre-imidized polymer and DNQ⁹.

This method is quite useful to develop low shrinkage and low temperature curable photosensitive polyimide. To enhance chemical resistance after cured photosensitive polyimide film cross-linkers were investigated. Some cross-linker gave good chemical resistance.

3. Positive-tone patterning from ionic bonded photosensitive polyimide

Toray found that ionic bonded photosensitive polyimide which shows negative-tone patterning³. The photosensitive polyimide was commercialized first in the world. The photosensitive polyimide was composed of poly(amic acid) and photosensitive amine. Preparation of photosensitive polyimide solution is simple. We found that positive-tone pattern was obtained by baking treatment after exposure of the negative-tone photosensitive polyimide¹⁰. The patterning mechanism is due to glass transition temperature (Tg) difference between exposure area and unexposure area¹¹. Tg of exposure area is higher than that of unexposure area. Molecular motion in the

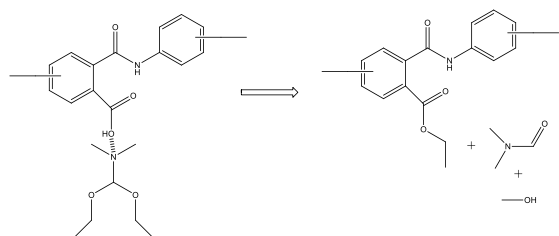
exposed area is thought to be higher than that in the unexposed area. Imidization rate of exposed area is slower than that of unexposed area. Accordingly dissolution rate of exposed area is higher than that of unexposed area due to imidization ratio difference by determining the optimum baking condition. This method is unique from the point of none DNQ system. However this process required very strict temperature control in polyimide patterning process, it is very difficult to apply the photosensitive polyimide process in semiconductor industries. In addition, it is not easy to obtain fine resolution pattern. Because patterning formation mechanism is difference of imidization ratio between exposed area and unexposed area, thickness at exposed area is thicker than that at unexposed area after baking treatment. This thickness difference between exposed area and unexposed area made difficult to make fine pattern.

Conclusions

We compared the 3 different types of positive-tone photosensitive polyimides. The partial esterification reaction of poly(amic acid) by using N,N-dimethylformamide dialkylacetal is quite useful for development of practical positive-tone photosensitive polyimide. The photosensitive polyimide from pre-imidized polymer is attractive from the points of low temperature cure and low shrinkage during cure. Positive-tone pattern formation by using ionic bonded photosensitive polyimide is interesting not to use DNQ.

Reference

1. Tomikawa, M.; Suwa, M.; Yoshida, S.; Fujita, Y.; Okuda, R.; Ohbayashi, G. *J. Photopolym. Sci. & Technol.*, **13**, 357 (2000).
2. Rubner, R.; Ahne, H.; Kuhn, E.; Koloddieg, G. *Photogr. Sci. Eng.*, **23**, 303 (1979)
3. Yoda, N.; Hiramoto, H.; Eguchi, E. *Macromol. Review*, **34**, 550 (1984)
4. Loprest, R.J.; McInerney, E.F., U.S. Patent 4093461 (1978).
5. Rubner, R.; Hammerschmidt, A.; Leuschner, R.; Ahne, H. in "Polymer Microelectronics: Proceeding of the International Symposium," ed. by Y. Tabata, Kodansha, Tokyo (1990), p 789
6. Yamamoto, K.; Hirano, T. *J. Photopolym. Sci. & Technol.*, **15**, 173 (2002)
7. Tomikawa, M.; Yoshida, S.; Okamoto, N. *Polym. J.*, **41**, 604 (2009)
8. Tomikawa, M.; Suwa, M.; Niwa, H.; Minamihashi, K. *High Perform. Polym.*, **23**, 66 (2011)
9. Toikawa, M.; Yuba, T.; Ohbayashi, G.; Kim, J.H.; Kim, T. *High Perform. Polym.*, **18**, 603 (2007)
10. Tamura, K.; Eguchi, M.; Asano, M. *JP1994-273942*
11. Yoshida, S.; Eguchi, M.; Tamura, K.; Tomikawa, M. *J. Photopolym. Sci. & Technol.*, **20**, 145 (2007)



Scheme 1. Partial Esterification of Poly(amic acid) by N,N-Dimethylformamide diethylacetal

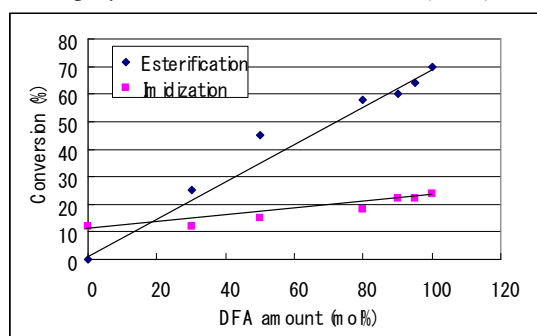


Figure 1. DFA amount dependency on esterification and imidization of poly(amic acid)

Table 1. Chemical composition of positive-tone photosensitive polyimide from partial esterified poly(amic acid)

Composition	Weight Parts
<p>Base Polymer</p> <p>ODPA/ODA/APl=100/90/20 Mw:9000 DFA 93mol%</p>	10
<p>Photo Active Compound</p> <p>5 : 1</p>	2

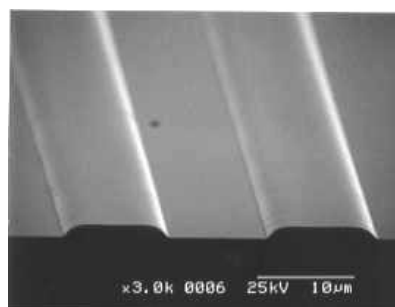


Figure 2. Cross sectional view the photosensitive polyimide