Benzophenone-Containing Methylthiomethyl Pendant Polyimides as Negative Acting Photoresists

WEN-YEN CHIANG* and WANG-PING MEI

Department of Chemical Engineering, Tatung Institute of Technology, 40 Chungshan North Rd., 3rd Sec., Taipei 10451, Taiwan, R.O.C.

SYNOPSIS

Four kinds of benzophenone-containing polyimides, each of which carries different amount or distribution of methylthiomethyl (MTM) pendant groups, are applied as negative photoresists. Lithographic evaluation of these polyimides shows that PI-42, the polyimide possessing the most, i.e., three MTM groups in a repeating unit on average, exhibits the highest sensitivity ($D_g^{0.5}$ = 129 mJ/cm^2), the highest contrast value (γ = 4.3), and the highest resolution capability (1.2-μm lines and spaces can be resolved in a 1.0 μm thick film). In the air, the photopatterned lines obtained from all these polyimides are thermally stable up to 280°C. Upon treating at 400°C for 30 min, a 8% reduction in the linewidth is observed for the 3.8-μm line of PI-42. The optimum developing conditions of each of these title polymers are determined. Contrast curve analysis indicates that this resist system exhibits higher sensitivity at near UV region than at deep UV region. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

In recent years many researchers in the field of polymeric photoresists for microelectronic application have directed their attention toward the photosensitive polyimides[1-5] because of their potential in reducing the number of processing steps in the manufacture of integrated circuits. One of the most important photoimageable polyimide systems developed is the benzophenone-containing alkyl-pendant polyimide system.[6] Since these polymers are fully imidized, they do not have the shelf life problem and will not shrink during the lithographic process. According to the photocrosslinking mechanism[7] of this type of polyimides, we have designed and prepared a series of benzophenone-containing methylthiomethy (MTM) pendant polyimides[8,9] to improve the photosensitivity of the original polyimide system. In this study, these novel polyimides, PI-42, PI-31, PI-2, and PI-1 (Fig. 1), are applied as photoresists to evaluate how lithographic characteristics such as sensitivity, resolution capability, and thermal stability of these polymers are affected by the polymer's nature. The optimum developing conditions for each of these polymers and the sensitive exposure region for this polyimide resist system are also investigated.

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 50, 2191-2195 (1993)
© 1993 John Wiley & Sons, Inc. CCC 0021-8995/93/122191-05

EXPERIMENTAL

Materials

Preparation of the title polyimides (PI-1, PI-2, PI-31 and PI-42) has been described earlier.[9]

Lithographic Evaluation

Spin coating is carrying out by spin casting the filtered (0.5 μm Millipore filter) resist solution [8% solid in N-methyl pyrrolidone (NMP)] on a silicon wafer, which is pretreated with adhesion promoter (0.5% γ-aminopropyl triethoxy silane in 95 : 5 MeOH/H_2O solution). The resist film is then baked at 100°C for 10 min. Film thickness is measured with a stylus instrument (Alpha step 200). Photopatterning with near-UV radiation is performed by using a Canon PLA-501F mask aligner in the contact

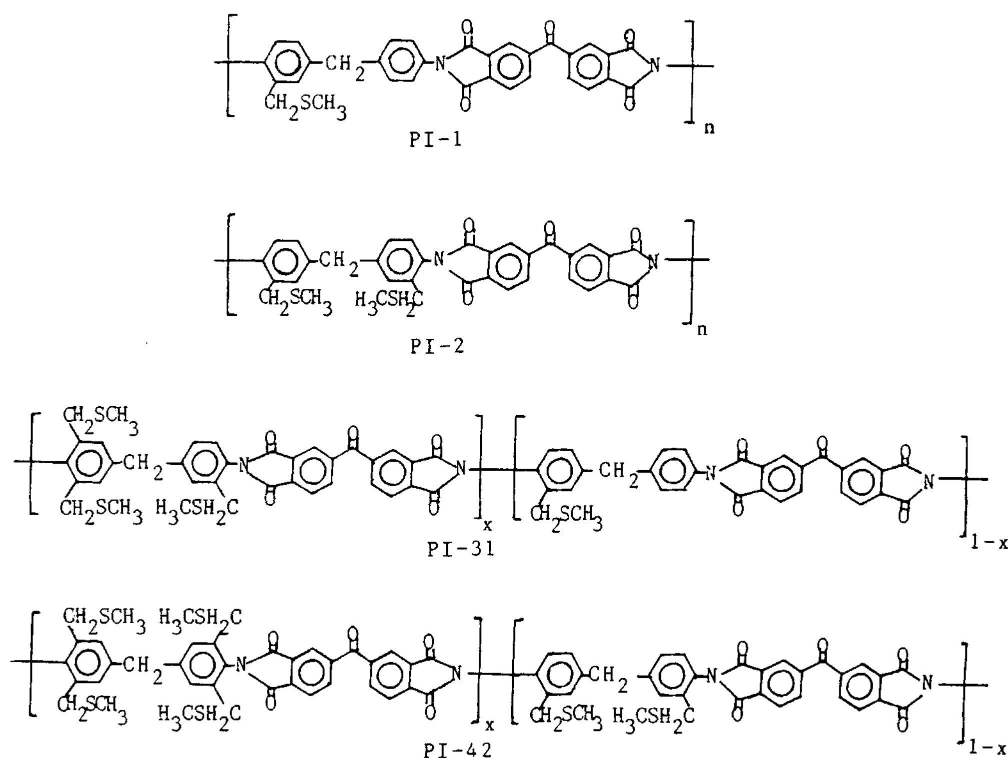


Figure 1 Structures of the polyimides.

mode while deep UV exposure is carried out by using a Hg-Xe lamp-filter combination (Oriel). The intensity of the light source is determined by the irradiance tester (Ushio, UIT-100). The exposed film is developed through a spray development process. The resist patterns are evaluated with a Akashi ABT-55 scanning electron microscope.

RESULTS AND DISCUSSION

Development

Since each of the title polyimides reveals different solubility due to their different structure, the optimum developer for each of the polymer is different. The most important criterion for selecting a proper developer is to minimize the pattern distortion due to swelling of the exposed areas. In this respect the solvent or solvent mixture that dissolves the 1-μm thick film of a specific polymer in 30 s of development time is chosen as its developer. The development conditions are shown in Table I. The function of the first rinse (rinse I) in the development sequence is to reduce the so-called blotch effect and the variation in pattern dimension.[10] Methanol, being a strong nonsolvent for these polyimides, is chosen as the second rinse (rinse II) to contract the polymer and thereby to fix the dimensions of the relief patterns.

Photosensitivity

There are three factors that affect the intrinsic photosensitivity of a polymer: chemical structure, mo-

Table I Development Conditions of the Polyimides

Polymer	Sequence	Component (DMAc : MeOH)[a]	Time (s)	Spin Speed (rpm)
PI-42	Developer	5 : 1	5	2000
	Rinse I	4 : 1	10	3000
	Rinse II	0 : 1	10	3000
PI-31	Developer	7 : 1	15	2000
	Rinse I	6 : 1	15	3000
	Rinse II	0 : 1	15	3000
PI-2	Developer	11 : 1	30	2000
	Rinse I	10 : 1	30	3000
	Rinse II	0 : 1	30	3000
PI-1	Developer	13 : 1	30	2000
	Rinse I	12 : 1	30	3000
	Rinse II	0 : 1	30	3000

[a] Volume ratio.

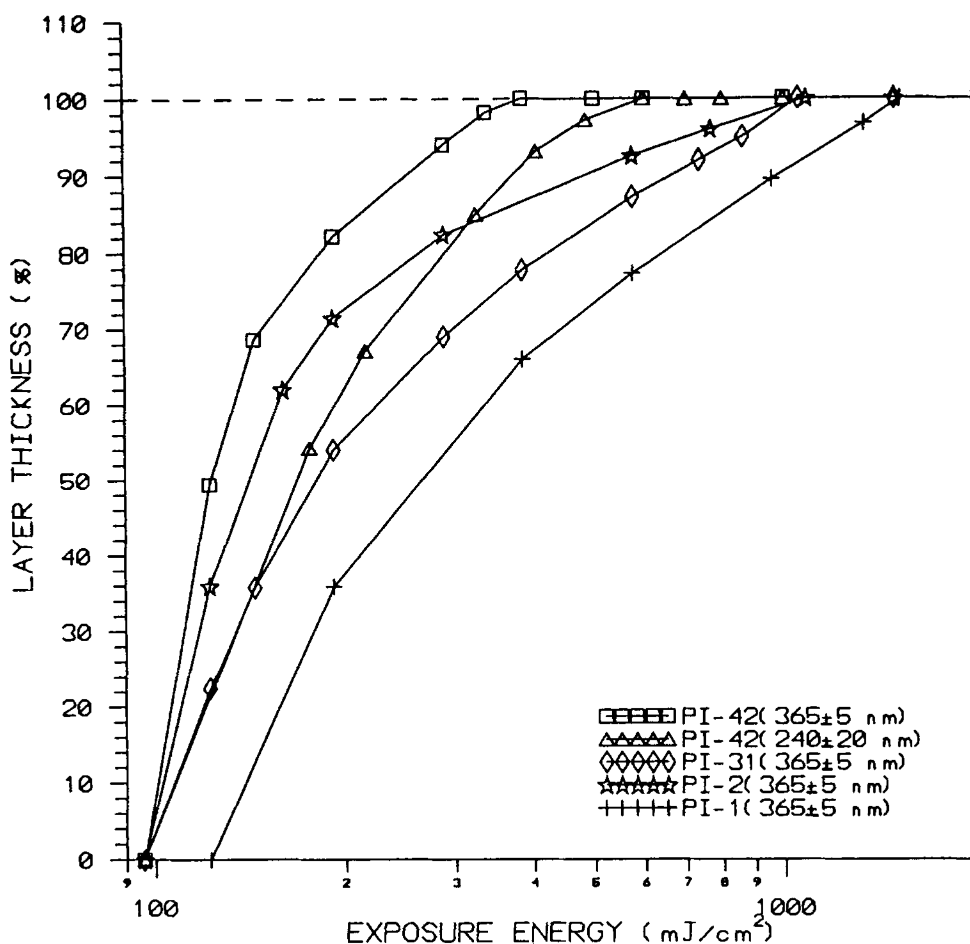


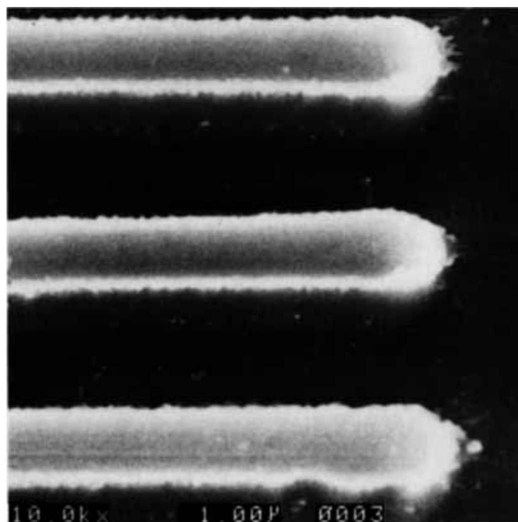
Figure 2 Contrast curves of the polyimides.

lecular weight, and molecular weight distribution. For the four polyimides studied, the later two factors are excluded according to the results of the viscosity and gel permeation chromatography (GPC) measurements obtained in the previous study.[9] Therefore, sensitivity discrimination in these polymers is resulted from their different chemical structures. According to the contrast curves of the four polyimides (Fig. 2), photosensitivities increase systematically with the increase of MTM content. PI-42, which possesses the highest MTM content, exhibits the highest photosensitivity ($D_g^{0.5}$ = 129 mJ/cm^2), while that for PI-31, PI-2, and PI-1 are 182, 148, and 273 mJ/cm^2, respectively. This result is in accordance with the finding of Pfeifer and Rohde,[6] that is, for the benzophenone-containing alkyl-pendant polyimide system, photosensitivity increases as the pendant group increases. Comparing PI-2 and PI-31, both of which carry two MTM groups in a repeating unit in average, we believe that the higher sensitivity observed for the former is due to the more average distribution of the pendant groups, which leads to a higher degree of photocrosslinking at the early stage of irradiation process. Another phenomena worthy of note is that PI-42 shows higher sensitivity when irradiated with the near-UV radiation (365 ± 5 nm), 129 mJ/cm^2, than with the deep-UV radiation (240 ± 20 nm), 174 mJ/cm^2, though the absorbance of benzophenone, photoreactive unit of

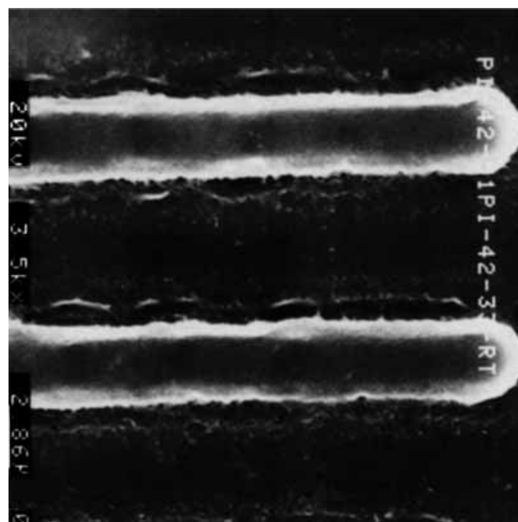
Table II Lithographic Characteristics of the Polyimides

Polymer	Contrast (γ)	Resolution[a] (μm)
PI-42	4.3	1.2
PI-31	2.1	2.6
PI-2	3.5	1.9
PI-1	1.9	3.8

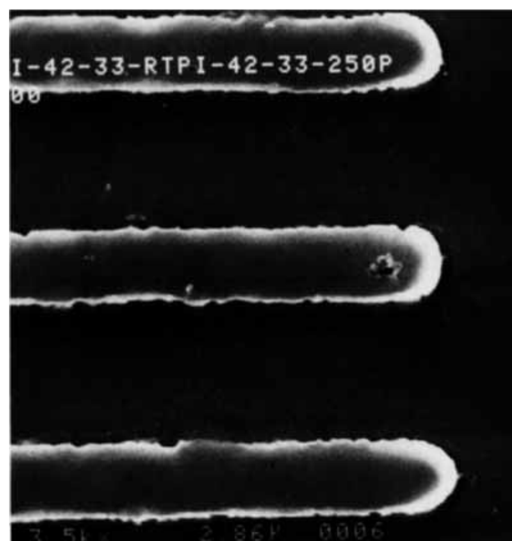
[a] Resolved lines and spaces in 1-μm film.



(a)



(b)



(c)

Figure 3 SEM micrographs of (a) 1.2-μm lines and spaces of PI-42, (b) 3.8-μm lines and spaces of PI-42, (c) 3.8-μm lines and spaces of PI-42 after baked at 400°C for 30 min.

this polymer, is much lower in the near-UV region (which is attributed to the $S_0 \rightarrow S_1$ transition of the benzophenone[11]) than in the deep-UV region (which is attributed to the $S_0 \rightarrow S_2$ transition). This conflict is explained as follows: Since S_2 state of benzophenone can deactivate by internal conversion to S_1 state followed by fast intersystem crossing to T_1 state, at which hydrogen abstraction takes place, both near- and deep-UV radiations are contributory to the photocrosslinking reaction in this type of resist system. However, it is probable that in the solid matrix the $S_2 \rightarrow S_1$ internal conversion is greatly depressed due to the limited nuclear motion, and the population of S_1 state resulted from exposing at the deep-UV light is less than that from the near-UV light. As a result, the total quantum yield of

photocrosslinking of the near-UV light irradiation is higher than that of the deep-UV light irradiation.

Resolution

The resolution capabilities of these resists are intimately related to their contrast (γ) values. As shown in Table II, PI-42 exhibits the highest contrast and the highest resolution capability. The lines and spaces resolved from 1-μm thick PI-42 film are shown in Figure 3(a). For PI-2 and PI-31, the more average MTM distribution for the former results in its higher contrast value and resolution capability than those of the latter. PI-1 carrying only one MTM group in a repeating unit is able to resolve 3.8-μm-wide lines and spaces in a 1-μm-thick film.

Thermal Stability

Although thermal resistance of these polyimides is lowered by the weak C–S bond of the pendant MTM group, still the dimension of the resist lines of the four polyimides remains unchanged after baked at 280°C for 30 min. When the baking temperature is raised to 400°C, a 8% of shrinkage of the 3.8-μm PI-42 line due to the decomposition of the MTM group is observed [Figs. 3(b), 3(c)]. Upon the same heat treatment, the degrees of shrinkage of the 3.8-μm line of PI-31 and PI-2 are both 5%, while that of PI-1 is negligible. Thus, more alkyl-pendant groups lead to higher photosensitivity and solubility but lower thermal stability.

CONCLUSION

We report here a detailed lithographic evaluation of the benzophenone-containing MTM pendant polyimide system. Increasing the content of the MTM group resulted in a systematic increase in sensitivity, contrast, and resolution but a systematic decrease in thermal stability. Contrast curve analysis leads to the conclusion that higher sensitivity of this system is obtained at the near-UV region rather than at the deep-UV region.

The authors wish to express their gratitude to Dr. T. S. Lin, the president of Tatung Institute of Technology, for his encouragement and support. Thanks are also due to the National Science Council of Republic of China for financial support under contract number NSC79-0405-E036-02 and NSC80-0405-E036-03.

REFERENCES

1. N. Yoda and H. Hiramota, *J. Macromol. Sci. Chem.*, **A21**, 1641 (1984).
2. L. Minnema and J. M. von der Zande, *Polym. Eng. Sci.*, **28**(12), 815 (1988).
3. K. K. Chakravorty, J. M. Tanielian, and P. L. Young, *J. Electrochem. Soc.*, **137**(3), 961 (1990).
4. J. V. Crivello, J. L. Lee, and D. A. Conlon, *J. Polym. Sci., Polym. Chem.*, **25**, 3293 (1987).
5. T. Omote, K. Koseki, and T. Yamaoka, *J. Polym. Sci., Polym. Lett.*, **28**, 59 (1990).
6. J. Pfeifer and O. Rohde, Proceedings of Second International Conference on Polyimides, 130 (1985).
7. A. A. Lin, V. R. Sastri, G. Tesoro, A. Reiser, and R. Eachus, *Macromolecules*, **21**, 1165 (1988).
8. W. Y. Chiang and W. P. Mei, *Tetrahedron Lett.*, **33**, 7869 (1992).
9. W. Y. Chiang and W. P. Mei, *J. Polym. Sci., Polym. Chem.*, **31**, 1195 (1993).
10. A. E. Novembre, L. M. Masakowski, and M. A. Hartney, *Polym. Eng. Sci.*, **26**(16), 1158 (1986).
11. N. J. Turro, *Modern Molecular Photochemistry*, Benjamin/Cummings, Menlo Park, CA, 1978, pp. 108, 179.

Received May 4, 1993
Accepted June 1, 1993