Positive photopolyimide based on vinyl ether

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ABSTRACT: A series of different acid value polyimides with carboxyl group in the ends of main chain were synthesized and used for the three-component photopolymers, consisting of the polyimide, a vinyl ether monomer and a photo-acid generator (PAG). This polyimide acts as a positive resist with the process of prebaking (PB), exposure to light and post-exposure baking (PEB). The effect of the acid value and the molecular weight on the characteristics of the photopolyimide, such as sensitivity and contrast, was investigated. A increase in the acid value and a decrease in the molecular weight enhance the increment of sensitivity based on solubilization rate by cleavage reaction. This positive working photopolyimide showed a sensitivity of 137 mJ / cm^2 and a gamma value of 2.9.

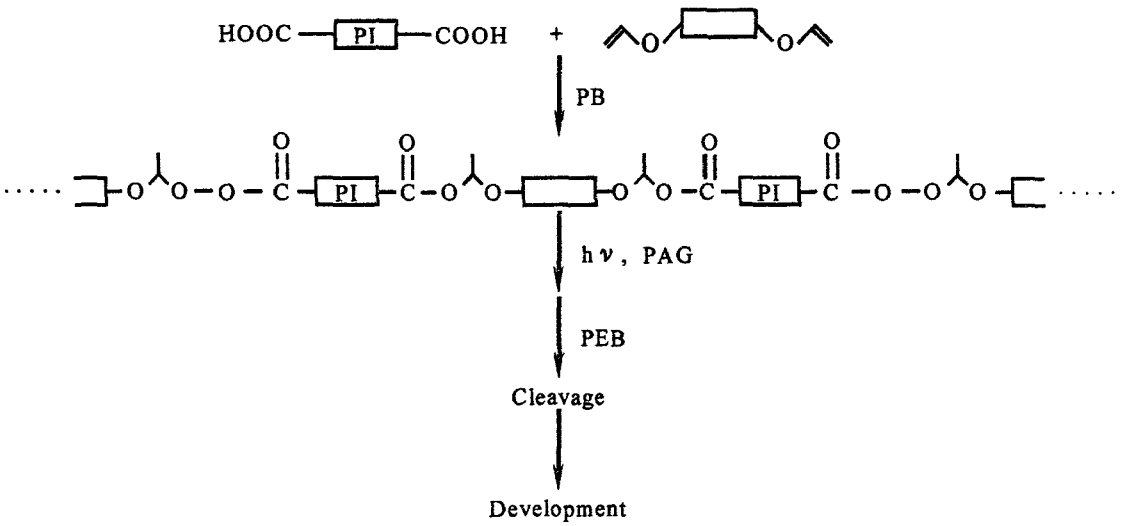
1. INTRODUCTION

Photosensitive polyimides are applied in the electronic industries, especially as a passivation coating for LSI. Most of them are negative type which shows resistivity to solvent due to the light-induced cross-linking structure.

On the other hand, positive type polyimides, which can be made soluble by UV irradiation, are used in the industries, too. Usually, they contain naphthoquinone diazide (NQD) showed imaginable properties. It is well-known that NQD becomes 3-indencarboxylic acid under UV irradiation. The mechanism of the type resist contains NQD in the difference of solubility in irradiated areas and unirradiated ones to alkaline aqueous solution. The mixture of polyimides with acid groups and NQD irradiated by UV light can be more soluble in alkaline aqueous solution that unirrdiated areas.

We propose a new positive photopolyimide system based on vinyl ether. Polyimide is connected linearly with vinyl ether to form film by prebaking (PB). The polyimide film becomes insoluble in alkaline aqueous solution. On exposure, the linear block polyimide are decoupled via acid-catalyzed hydrolysis of vinyl ether compound, and the polyimide film becomes soluble in the alkaline aqueous solution,

resulting in a positive-tone image. The concept of photopolyimide system is shown in scheme 1. We expected this linear blocked photopolyimide system would provide high dissolution rate contrast.



Scheme 1 The mechanism of Positive pattern Process in this three-component photopolyimide
PI: polyimide moiety

2. EXPERIMENTAL

2.1 Materials

The material composition and chemical structure of the photopolyimide system is shown Table 1. Polyimides were prepared by sequential addition of *p*-aminobenzoic acid. 2,2-Bis(4-(2-(vinyloxy)ethoxy)pheyl)hexafluoropropane (BIS-AF-DEVE) was synthesized from bis(4-hydroxyphenyl)hexafluoropropane and 2-chloroethylvinyl ether. [1,2] and diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate (DIAS) [3] were synthesized according to the literature. BIS-AF-DEVE and DIAS contents were fixed 50% and 3% for polyimide.

Table 1 Material composition and chemical structure of the photopolyimide system

Polyimide	Vinyl Ether	PAG
Z—X—(Y—X)$_n$—Z X: Y: H_2N—O—NH_2 Z: H_2N—COOH	RO—C(CF_3)$_2$—OR R: $-CH_2CH_2-O-CH=CH_2$ BIS-AF-DEVE	OCH_3, SO_3^-, OCH_3, I^+ DIAS

2.2 Lithographic Evaluation Method

Photopolyimide film were prepared by spin coating onto Si wafer to give a 0.5 or 1.0 μm film thickness and PB at 120℃ for 10 min. After exposure by 365 nm light with a filtered high pressure mercury lamp, post-exposure baking was carried at 120℃ for 10 min. Then the polyimide film were developed in a 3% aqueous solution of potassium hydroxide for 2 min and rinsed in water.

3.RESULT AND DISCUSSION

Differences in physical properties of polyimides are shown in Table 2. In order to investigate the bonding behavior of polyimide and vinyl ether in the polyimide film, the dissolution rate was measured. Figure 1 shows the dissolution rates of the polyimide film before and after exposure as a function of acid value and molecular weight. The higher acid value and the lower molecular weight polyimide (PI-1) is more dissolvable than the lower acid value and the higher molecular weight polymer (PI-2). Owing to hard solubility of the based polyimide in this system, development can be done stably in a strong alkaline aqueous solution. The rate of dissolution after PB is 0.1 ~ 0.2 nm/s. PI-1 is slightly dissolvable than PI-2 after PB. This phenomenon depends to the higher acid value. (see Figure 1) Figure 2 shows the characteristic curves of photopolyimide prepared by adding 50% BIS-AF-DEVE, irradiating at 365 nm and developing in 3% potassium hydroxide aqueous solution. PI-1 was dissolved completely by exposing by 137 mJ/cm^2.

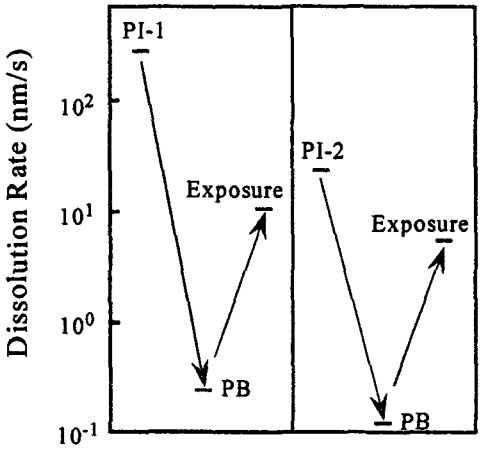


Figure 1 Dissolution contrast of the different AV polyimides

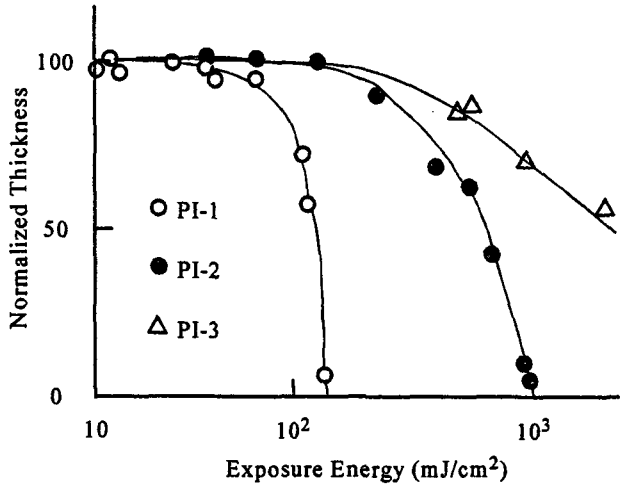


Figure 2 Characteristic curves of the polyimide films

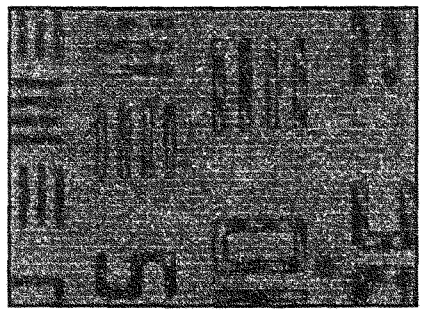


Figure 3 A photograph of 2.5–3.0 μm L/S patterns in 1 μm film thickness of PI-3

Table 2 Physical properties of polyimides

Polyimides	AV[a]	$\overline{Mn}$	$\overline{Mw}$	$\overline{Mn}/\overline{Mw}$
PI-1	191.1	3100	3600	1.15
PI-2	129.4	4500	5500	1.28
PI-3	112.1	5400	6900	1.21

[a] acid value (KOH mg / 1.0g resin)

4.CONCLUSION

Three component photopolyimide consisting alkaline developable polyimide with carboxyl group in the ends main chain, vinyl ether monomer and photo-acid generator (PAG) was examined. Low molecular weight polyimide are connected linearly by vinyl monomer to give high molecular weight polymers. Irradiation to the polymer, small molecular of polyimide with carboxyl group are reproduced and easily dissolution in alkaline aqueous solution. The photopolyimide showed a 137 mJ/cm^2 sensitivity and a 2.9 γ value.

Acknowledgment

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