Preparation of Negative Photoreactive Polyimide and Its Characterization

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SYNOPSIS

In this article, a polyimide precursor was synthesized from oxydianiline and a diacid chloride. This diacid chloride was prepared by the reaction of thionyl chloride with a diacid, which resulted from the reaction of pyromellitic dianhydride with cinnamyl alcohol in N-methylpyrrolidone (NMP). The photoresist, made from the above polyimide precursor, was spin-coated onto silicon wafers, prebaked, and then exposed to UV light with a high pressure Hg lamp. The pattern generation process was also investigated. The appropriate conditions of the photolithographic procedures, involving photoresist compounding, spin coating, prebaking, exposure, development, rinse, postbaking, etc., were determined. The experimental results show that the photoresist exhibited excellent thermal stability and adequate photosensitivity.

INTRODUCTION

In recent years, photoreactive polyimide precursors have been developed and used as important photoresist materials that have excellent thermal stability, high resolution, and low dielectric constant.[1]

The photolithographic use of nonphotoreactive polyimides is very complicated, and when a photoreactive polyimide is employed, the pattern generation process is simplified.[2,3]

Photoreactive polyimides have extensive applications in microelectronics[4] such as: (1) protection coating of integrated circuit; (2) multilayer circuit insulation of integrated circuit; (3) protective layer of diode and transistor; (4) ion-implantation mask, etc.

This article describes the synthesis of a photoreactive polyimide precursor, which contains a cinnamyl group. The study deals with monomer synthesis, polycondensation, characterization of polyimide precursor, and pattern generation process.

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Journal of Applied Polymer Science, Vol. 44, 1365–1370 (1992)
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EXPERIMENTAL

Solvents and Reagents

Pyromellitic dianhydride (PMDA) was obtained from commercial sources and was purified by sublimation. Oxydianiline (ODA) was purified by recrystallization from tetrahydrofuran (THF). Thionyl chloride was purified by distillation at atmospheric pressure.

Cinnamyl alcohol (CA), N-methylpyrrolidone (NMP), dimethylformamide (DMF), triethylamine (TEA), and photosensitizers, etc., were obtained from commercial sources and were used without purification.

Preparation of Polyimide Precursors (PIP)

In order to ensure an economic and reproducible method of preparation, we started and ended the reaction sequence using the same solvent system, and ensured that conversion was complete at every reaction step. Thus, the synthetic method of PIP is as follows: PMDA 10.90 g (0.05 mol) was dissolved in 50 mL NMP at 45°C with stirring, cinnamyl alcohol 13.42 g (0.1 mol) was added dropwise, and the solution was stirred at 45°C for 7–8 h, then the so-

lution was cooled to −2°C and was reacted dropwise with thionyl chloride 10.89 g (0.1 mol). The mixture was stirred for 2 h at −2−−5°C. A solution of ODA 10.40 g (0.05 mol) in NMP was added and stirring was continued at 0°C for 2-3 h, at the same time, TEA 0.1 mol was added in one portion. After the polycondensation, the PIP was precipitated by pouring the solution into water. The product was washed with water repeatedly until there was no chloride ion in product; the product was then dried at room temperature under vacuum. The yield was 92%.

The IR spectrum (KBr) showed absorption at 3250 cm^{-1} (N-H), 1720 cm^{-1} (C=0, ester), 1660 cm^{-1} (C=C).

Anal. caled. for $C_{40}H_{30}N_2O_6$:

C, 73.85%; H, 4.62%; N, 4.31%.

Found: C, 73.63%; H, 4.68%; N, 4.37%.

The molecular weight of PIP was determined by Toyo-Soda HLC-802A GPC. Mw=10,200, Mn=4786 (as polystyrene).

The intrinsic viscosity of the obtained PIP was measured at 30°C in DMF by using a Ubbelodhe viscometer: $[\eta] = 0.92$ dL/g.

Photolithographic Procedures

Photoresist Coating

The PIP solution (25% solids in NMP) containing a suitable amount of photosensitizers (Michler's ketone and bisazid) was spincoated onto silicon wafers for a period of 10 s at 2500 rpm. The polymer film was prebaked at 70°C for 70 min. Film thickness was measured with a stylus instrument (Alpha-Steper 200).

Exposure

The polymer film was exposed under a 400 W high-pressure Hg lamp at a distance of 18 cm through a mask for 100 s.

Development

The film irradiated was developed using an ED developer (Ethanol/DMF) at 25°C for 10 s.

Rinse

Rinse is in Ethanol/Triclene each at 25°C for 10 s.

Postbaking

The film pattern was aged at 150°C for 30 min, at 200°C for 30 min, at 250°C for 30 min, at 300°C for 30 min, respectively, to form the imide.

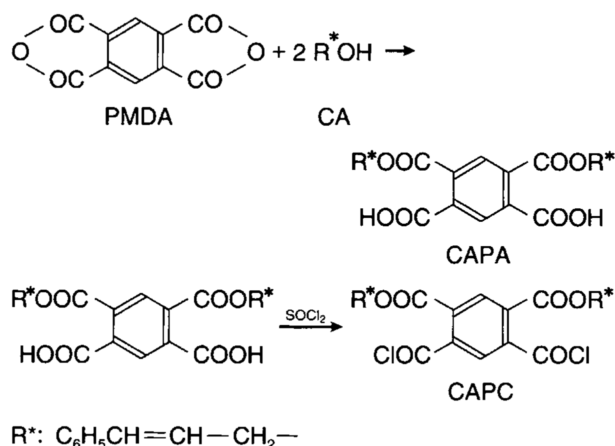
RESULTS AND DISCUSSION

Synthesis

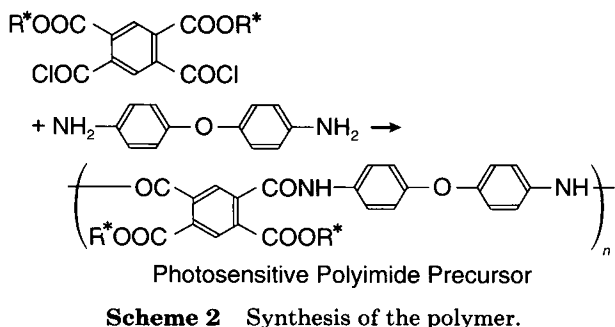
The synthesis of the monomers and subsequent polycondensation are described in Schemes 1 and 2.

The monomers were synthesized by the method described in the experimental section. The PMDA reacted with CA to prepare CAPA. Figure 1 gives the carboxylic group concentration changes with time in NMP medium at different temperatures. Experimental results showed that the carboxylic group concentration falls very sharply at the beginning of the reaction and then levels off. The higher the reaction temperature, the shorter the time for the carboxylic group concentration to become constant. Usually, the temperature is not higher than 100°C, otherwise, gel may appear.

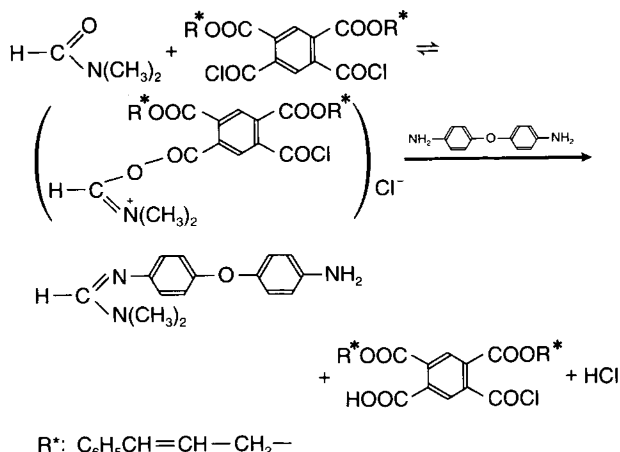
The reaction medium has an effect on $[\eta]$. When DMF is substituted for NMP under the same reaction conditions, we observed a decrease in $[\eta]$ from 0.92 dL/g (in NMP) to 0.65 dL/g (in DMF). Because DMF is a reactive solvent in the above reaction system, the side reactions, shown in Scheme 3, can be postulated. The results are that a monofunctional by-product will be produced,[5] resulting in decreasing molecular weight. Furthermore, the stoichiometric imbalance of the bifunctional monomers becomes too large, resulting in too low $[\eta]$.



Scheme 1 Synthesis of monomeric materials.



Scheme 2 Synthesis of the polymer.



Scheme 3 Monofunctional compounds postulated by the authors can be produced with DMF as solvent in the reaction of diacid chloride with diamine.

Photosensitivity Study

The PIP was spun onto a quartz plate to create a thin film in order to measure its UV absorption spectrum. The result is shown in Figure 2. The absorption peak, due to the cinnamyl group, is in the vicinity of 280 nm.

The emission lines of a high pressure Hg lamp are shown in Figure 3. The strongest emission strength is given as 365 nm and 435 nm.

PIP is photosensitive to the emission lines at 270–300 nm, but is not sensitive to the emission line at 365 nm, so that the use of photosensitizers is necessary. The effect of photosensitizers on sensitivity is shown in Table I.

Table I shows that the PIP resist, sensitized with a combination of MK and DA (1 : 1 by wt.), has a high sensitivity. The structure of DA is as follows:

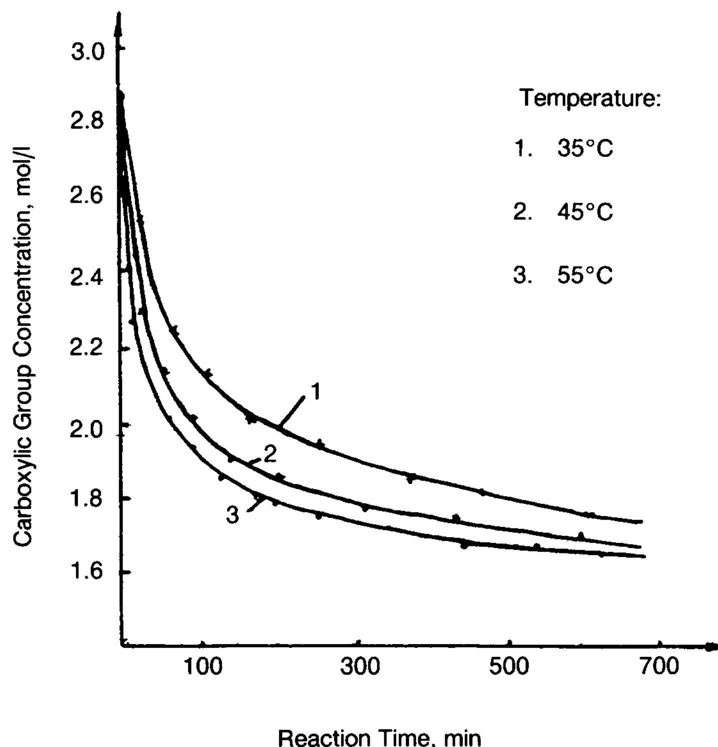


Figure 1 Dependence of carboxylic group concentration on reaction time at different temperatures in the NMP medium.

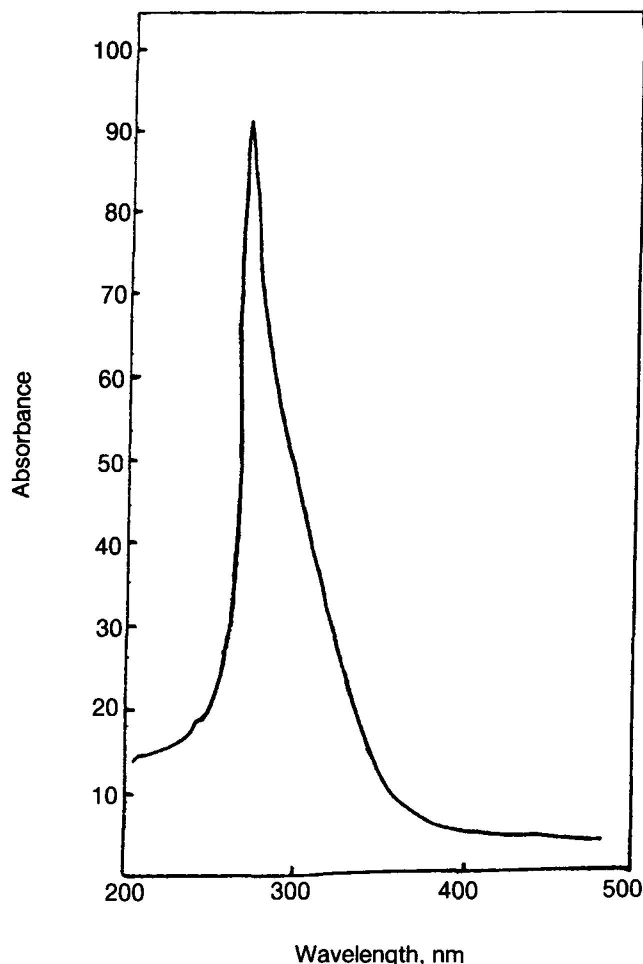
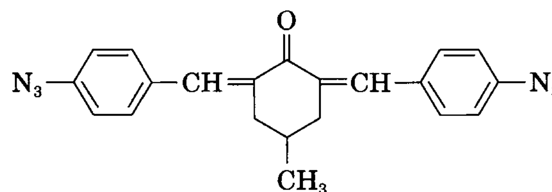


Figure 2 Change in UV absorption upon irradiation of a 0.17 μm film.



Solubility and Development

In the compounding of PIP resist, the selection of solvent is an important factor. Although NMP is a good solvent for PIP, when this solution was spun onto silicon wafers the flow leveling was poor. A few pin holes appeared on the surface of the film. The flow leveling can be modified by use of NMP and glycol monoethyl ether acetate (1 : 1 by volume) as a mixed solvent for PIP.

In the development process, the selection of developer is critical. A sharp contrast of polymer solubility in the crosslinked part and the noncrosslinked part is important. Otherwise, resolution is low. Solubility of the unexposed film and resistance of the exposed film to solvent have been examined in various solvents. The results are shown in Table II.

Experimental results showed that a mixed solvent consisting of a good solvent (DMF) and a poor solvent (ethanol) is a good developer that gives an excellent pattern. Resolution is 3–5 μm in the case of a final film thickness of 1–2 μm.

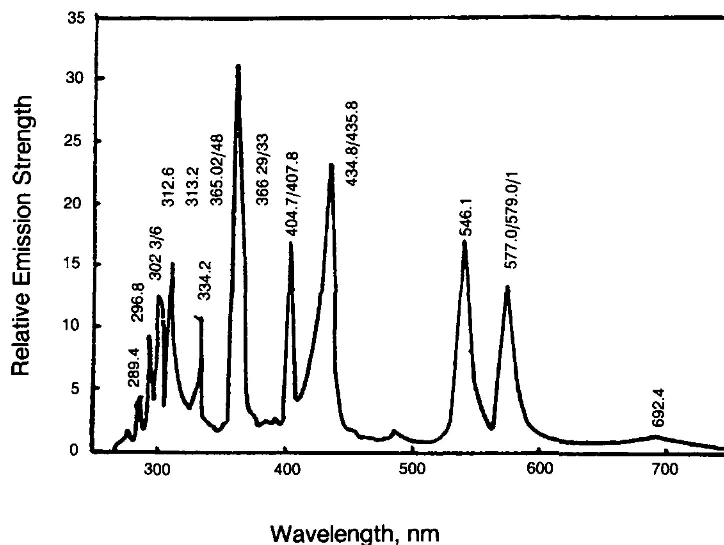


Figure 3 Emission lines of a high pressure Hg lamp.

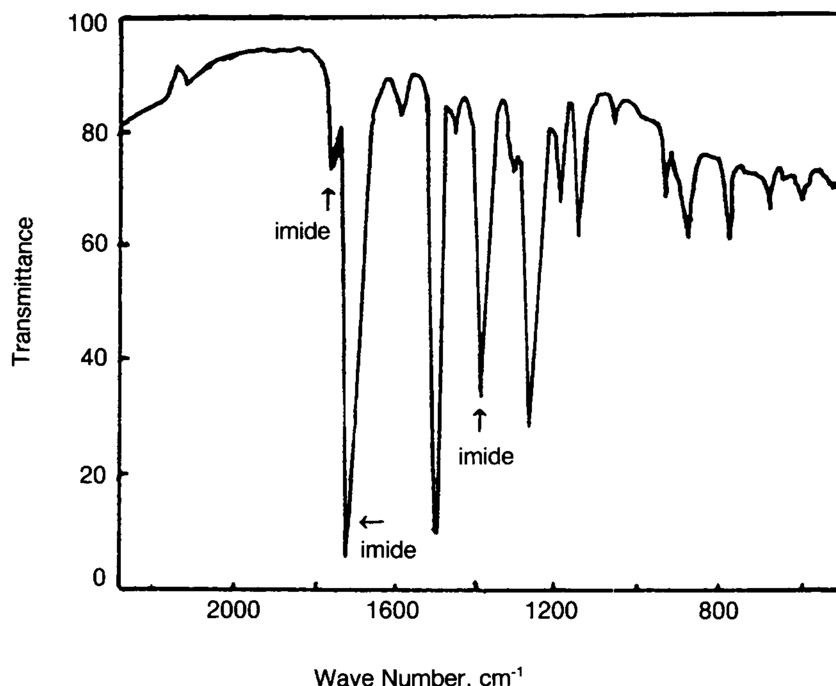


Figure 4 The IR spectrum of PIP after exposure and postbaking described in the experimental section.

Thermal Behavior

Because of the special structure of PIP, the cross-linked pattern can easily be converted into the polyimide pattern described in the experimental section by heating after exposure. The new IR bands at 1780, 1720, and 1380 cm^{-1}, shown in Figure 4, appear. These new bands are attributed to the imide absorption.

Thermogravimetric analysis (TGA) of postbaked product was performed in air at a heating rate of 2°C/min, 6°C/min, and 10°C/min, respectively. The TGA curves (Fig. 5) show stability to 400°C. Our group has studied the thermal decomposition

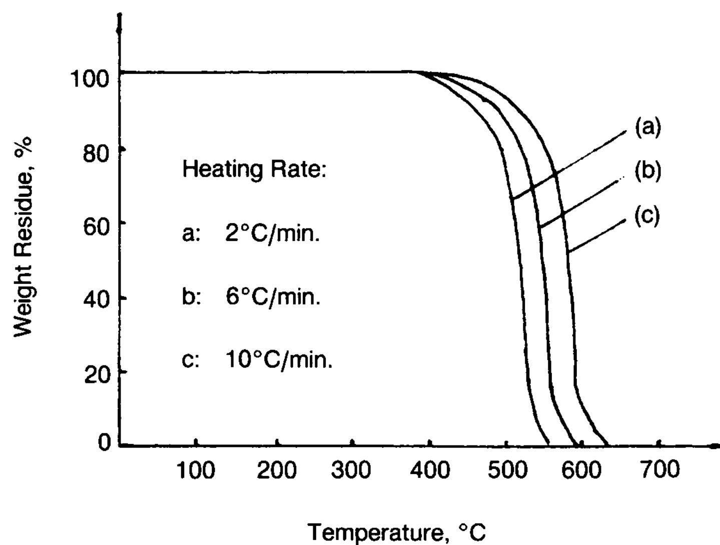


Figure 5 The TGA curves of the PIP.

Table I Effect of Photosensitizers on Sensitivity

Photosensitizers	MK + BN (1 : 1 by wt.)	MK + AIBN (1 : 1 by wt.)	MK + DP (1 : 1 by wt.)	MK + DA (1 : 1 by wt.)
Relative Sensitivity* (min)	10.2	9.6	8.5	1.3

MK = Michler's Ketone; BN = Benzoin; AIBN = Azobisisobutyronitrile; DP = Diphenylketone; DA = 2,6-bis-(4'-azidobenzylidene)-4-methyl cyclohexanone.
* The exposure time (min), when residual yield is at 50% on a silicon substrate, is defined as relative sensitivity.

kinetics of photoreactive polyimide, which contains acrylate groups.[6] As expected, the photosensitive polyimide, which contains cinnamyl groups, has high thermal stability as well.

CONCLUSIONS

1. In this study, we synthesized a photoreactive polyimide (PIP), which contains cinnamyl group under mild conditions. The unexposed area of the film was dissolved in a mixed solvent, consisting of DMF and ethanol, to exhibit negative photosensitive properties.
2. The reaction medium has an effect on intrinsic viscosity of the obtained polymer. When DMF is substituted for NMP under the same reaction conditions, a decrease in $[\eta]$ was observed.
3. The effect of photosensitizers on sensitivity showed that the PIP resist was sensitized strongly by combination of MK and DA (1 : 1 by wt.) with a 400 W high pressure Hg lamp, at a distance of 18 cm through a mask. The relative sensitivity is 1.3 min.
4. The exposed polymer was able to be converted into the usual polyimide by postbaking.

Table II Solubility of Unexposed Films and Solvent–Resistance of Exposed Films

Solvents	Unexposed Part	Exposed Part
DMF	S	SW
Butyrolactone	S	SW
Dimethylacetamide	S	SW
Dimethyl sulfoxide	S	SW
NMP	S	SW
Ethanol	I	I
Methanol	I	I
Dichloromethane	I	I
Trichloromethane	I	I

S = Soluble; I = Insoluble; SW = Swelling.

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Received April 29, 1991
Accepted May 14, 1991