

# Preparation of Positive Photoreactive Polyimides and Their Characterization

SHIGERU KUBOTA, TOSHIMOTO MORIWAKI, TORAHIKO ANDO, and AKIRA FUKAMI, *Polymer Engineering Department, Materials and Electronic Devices Laboratory, Mitsubishi Electric Corporation, Tsukaguchi-honmachi Amagasaki, 661, Japan*

## Synopsis

Polyimide precursors were synthesized from a diamine and a diacid chloride that was derived from the reactant with promellitic dianhydride and *o*-nitrobenzyl alcohol. Their thermal properties were studied in nitrogen using dynamic thermogravimetry, and the photoreaction mechanism was investigated by ultraviolet and infrared spectrophotometry. The polyimide precursors were spin-coated onto silicon wafers, prebaked, and then exposed to UV light from a high pressure Hg-Xe lamp. When the films were dipped into 2% aqueous KOH after irradiation, the exposed area dissolved forming high resolution patterns. Relative sensitivities of the polymers were determined.

## INTRODUCTION

Because of the excellent heat resistance and electrical properties, polyimides are used in microelectronic devices as insulators for multilevel interconnections and as surface passivation layers.<sup>1</sup> Although polyimides have many excellent characteristics, their use has been limited by their poor solubilities. Therefore, they are handled in the form of their precursor, polyamic acid, which is sensitive to hydrolysis by atmospheric moisture. In an effort to overcome these problems, we have evaluated the preparation and properties of quinazolone-imide copolymers as insulators in multilevel interconnections.<sup>2</sup>

On the other hand, for microelectronics applications, patterns, derived from a photoresist, need to be formed into a polyimide layer (forming wiring gates and vias for multilevel interconnections, etc.). However, there are a number of problems. For example, the steps for processing polyimide layer with photoresist, photoimaging the resist, etching the polyimide with the etchant and removing the resist, etc.). Also, the etchant, hydrazine hydrate, is a harmful material, etc.

Photoreactive polyimide precursors have been recently developed for producing polyimide patterns directly,<sup>3</sup> and photopatternable polyimides of the same sort have been reported.<sup>4</sup> They make it possible to shorten the steps for processing polyimides; however, as negative photoresists they swell in a developing solution resulting lower resolution.<sup>5</sup>

We are interested in synthesizing a positive photoreactive polyimide which will produce a high resolution pattern. This study deals with monomer synthesis, polymerization, and characterization of polyimides.

## EXPERIMENTAL

## Solvents and Reagents

Pyromellitic dianhydride (PMDA) was obtained from commercial sources and purified by recrystallization from acetic anhydride. 4,4'-Diaminodiphenylmethane (MDA) was purified by recrystallization from toluene. 4,4'-Diaminodicyclohexylmethane (MCH) was purified by distillation under reduced pressure. 1,2-Dichloroethane was distilled at atmospheric pressure. *o*-Nitrobenzyl alcohol (NB), toluene, thionyl chloride, *m*-cresol, *N*-methylpyrrolidone (NMP), and sodium carbonate were obtained from commercial sources and used without purification.

## Materials

Pyromellitic acid di(*o*-nitrobenzyl)ester (NBPA) was prepared from the reaction of PMDA with NB in toluene. The precipitate of NBPA separated out when the reaction solution was refluxed with stirring for 4–6 h: yield 83%; mp 186°C.

ANAL. Calcd for  $C_{24}H_{16}N_2O_{12}$ : C, 54.97%; H, 3.08%; N, 5.34%. Found: C, 55.03%; H, 3.01%; N, 5.36%.

Pyromellitic acid dichloride di(*o*-nitrobenzyl)ester (NBPC) was prepared from NBPA in thionyl chloride. After the reaction, a part of thionyl chloride was removed by a rotary evaporator. NBPC was recovered as a crystal from a concentrated solution at room temperature: yield 66.5%; mp 168°C.

ANAL. Calcd for  $C_{24}H_{14}N_2O_{10}Cl_2$ : C, 51.36%; H, 2.51%; N, 4.99%. Found: C, 51.52%; H, 2.50%; N, 5.08%.

## Polymerizations

Polyimide precursors were synthesized by an interfacial polycondensation technique. Sodium carbonates were used as acid acceptors. A typical polymerization was carried out in the following method.

In a 1-*L* flat-bottom flask, 1.05 g (5 mmol) of 4,4-diaminodicyclohexylmethane and 0.636 g (6 mmol) of sodium carbonate (anhydrous) were dissolved in a mixed solvent of 100 mL of acetone and 100 mL of distilled water. As the blender rotor was raised to a high speed, there was added in one portion a solution of 2.806 g (5 mmole) of NBPC in 500 mL of 1,2-dichloroethane. The mixture was stirred for 15 min at room temperature. After the

TABLE I  
Characteristics of Prepolymers

Polymer	Diamine	Yield (%)	$[\eta]^a$	Thermal analysis <sup>b</sup>	
				EPT <sup>c</sup> (°C)	IDT <sup>d</sup> (°C)
A	MDA	98	0.53	222	150
B	MCH	97	0.65	259	168

<sup>a</sup> Measured in *m*-cresol at 30°C.

<sup>b</sup> Determined in nitrogen at 10°C/min heating rate.

<sup>c</sup> Endothermic peak temperature by DTA.

<sup>d</sup> Initial decomposition temperature.

polymerization, the reaction suspension was poured into 500 mL of methanol, and the polymer was washed several times with water and finally with methanol. The polymer was collected by filtration and was dried in a vacuum oven for about 16 h at room temperature. The yield was 3.38 g (97%). The IR spectrum (film) showed absorptions 1730 (C=O ester), 1660 (C=O, amide), 1520, 1340, 860 (NO<sub>2</sub>) cm<sup>-1</sup>.

The intrinsic viscosities of the obtained polymers were measured at 30°C in *m*-cresol by using a Ubbelohde suspended level viscometer. The results of polymer synthesis are summarized in Table I

### Measurements

Thermogravimetric analysis (TGA) and differential temperature analysis (DTA) were performed in a stream of nitrogen at 50 mL/min. The heating rate was 10°C/min, and the sample size was about 5 mg of polymer powders.

IR spectra were recorded on thin films of polymer cast on germanium plate, while UV spectra were recorded on thin films cast on quartz plate.

### Lithographic Evaluation

**Polymer Coating.** The polymer solution (13% solid in NMP) were spin-coated onto silicon wafers which were treated with  $\gamma$ -aminopropyl-trimethoxy-silane (0.5% in isopropanol) to increase the adhesion. The polymer film was prebaked at 80°C for 30 min. Film thickness was measured with a stylus instrument (Alpha step-100).

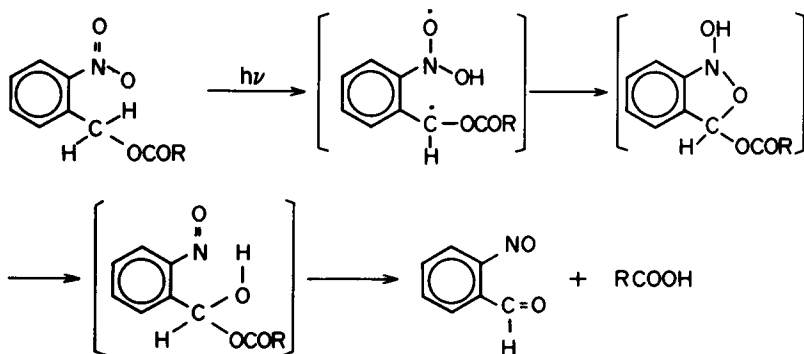
**Exposure.** The polymer film was exposed with 500 W Xe-Hg lamp (Ushio Electric Inc.) through a chromium mask on a quartz substrate in contact.

**Development.** The films irradiated were developed in 2% aqueous KOH at 23–25°C.

## RESULTS AND DISCUSSION

### Synthesis

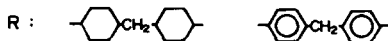
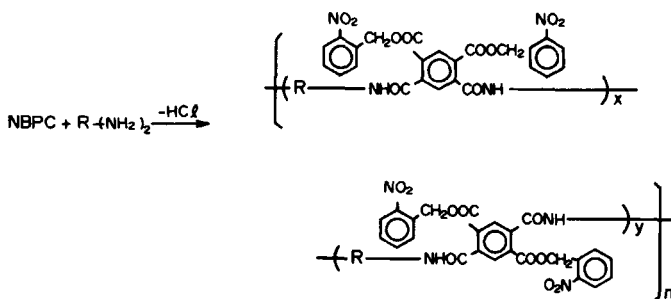
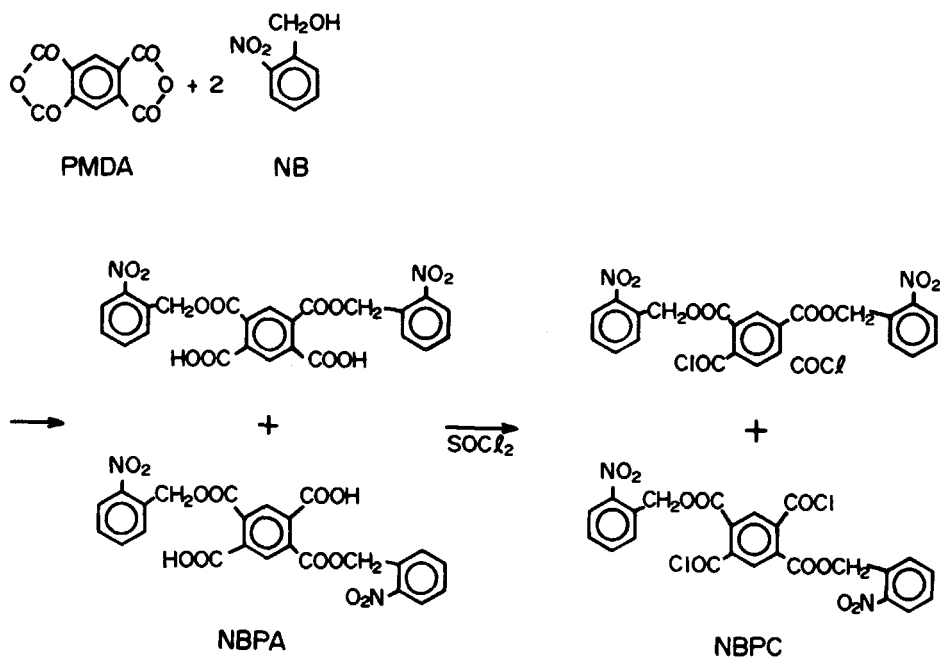
It is well known that an *o*-nitrobenzyl ester decomposes to a carboxylic acid and aldehyde by irradiation with ultraviolet light (Scheme 1) and have been used as photosensitive carboxyl-protecting groups:<sup>6</sup>



Scheme 1. *o*-Nitrobenzyl ester photorearrangement.

It was reported that this reaction mechanism was applied to the photoresist.<sup>7,8</sup> On the other hand, *N*-substituted *o*-nitroanilide is light-sensitive and also decomposes to a corresponding carboxylic acid and other photoproducts.<sup>9</sup> MacDonald et al. have developed a thermally stable resist which contains this photosensitive anilide in the backbone of polymer.<sup>10</sup>

We have considered that a positive photoreactive polyimide may be designed by the use of this reaction mechanism, and we carried out this study by using the former. That is to say, the *o*-nitrobenzyl group is introduced to the side chain (carboxylic acid) of polyamic acid which is a precursor to polyimide. The synthesis of the monomers and subsequent polymerization are described in Schemes 2 and 3:



Scheme 3. Synthesis of polymers.

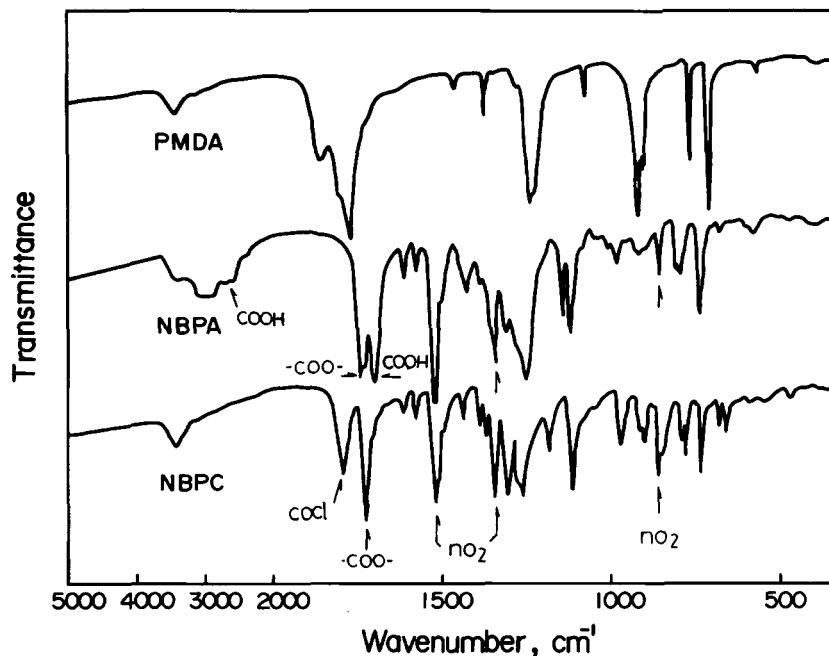


Fig. 1. The IR spectra of monomeric materials.

The monomers were synthesized by the method described in the experimental section. Figure 1 presents the IR spectra of the monomeric materials. PMDA reacted with NB to prepare NBPA. This NBPA exhibited new absorption of carboxylic acid at 2500 and 1700  $\text{cm}^{-1}$ , ester linkage at 1730  $\text{cm}^{-1}$ , and nitro group at 1520, 1340, and 860  $\text{cm}^{-1}$ . In IR spectra of NBPC obtained from the chlorination of NBPA, a carbonyl absorption at 1790  $\text{cm}^{-1}$  due to acid chloride appeared anew, while the acid absorption disappeared. The structure of monomers is confirmed by these measurements. However, these monomers are mixtures of two isomers as shown in Scheme 2, and they have been used without separating for further synthesis.

The polymerizations were carried out according to the pathway as shown in Scheme 3. These results are listed in Table I. Both polymers A and B were recovered in good yield and were prepared with intrinsic viscosities in the values of 0.53 and 0.63, respectively, in *m*-cresol at 30°C. This polymer solution in *m*-cresol or NMP was used to cast a film on plate glass by using spin coator.

### Thermal Analysis

TGA of the polymers were carried out in order to investigate their thermal characterization. Measurement was performed in a stream of nitrogen (50 mL/min); the heating rate was 10°C/min, and the sample weight was about 5 mg of polymer powder. TGA curves obtained are shown in Figure 2, and thermal behavior data are summarized in Table I.

Both polymers A and B exhibited the pronounced weight loss in two stages. The IR spectra of polymer A which has been heated at 300°C with a heating

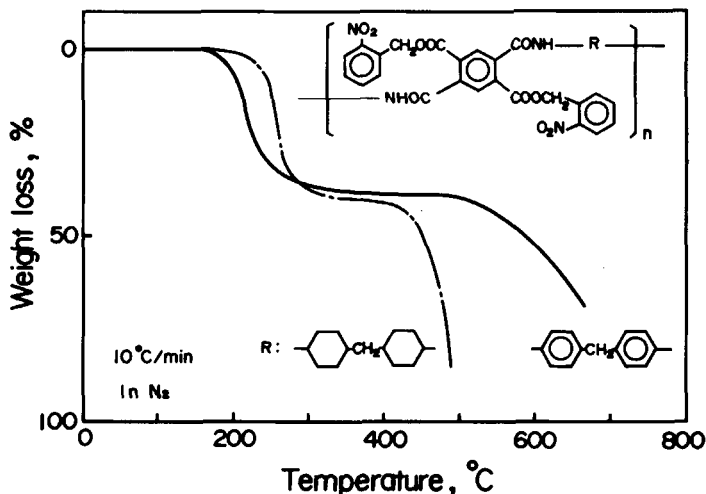


Fig. 2. TGA curves for polyimide precursors.

rate of  $10^{\circ}\text{C}/\text{min}$  in nitrogen, is shown in Figure 3. In Figure 3, the amide absorption at  $1650\text{ cm}^{-1}$  and the ester absorption at  $1730\text{ cm}^{-1}$  and the nitro absorption at  $1520$ ,  $1340$ , and  $860\text{ cm}^{-1}$  disappear by heating, while new bands at  $1780$ ,  $1720$ ,  $1380$ , and  $720\text{ cm}^{-1}$  appear in the place of them. These new bands are attributed to the imide absorption.

The first weight loss in Figure 2 is about 42%, and this value is in agreement with the values calculated for the elimination of *o*-nitrobenzyl groups (polymer A 44.6%, polymer B 43.8%). Therefore, it may be concluded from IR data and weight loss data that the first weight loss is due to the imidization. As shown in Table I, there is a difference in the initial weight loss temperature of the polymers. Their endothermic peak temperature by DTA also differs to a

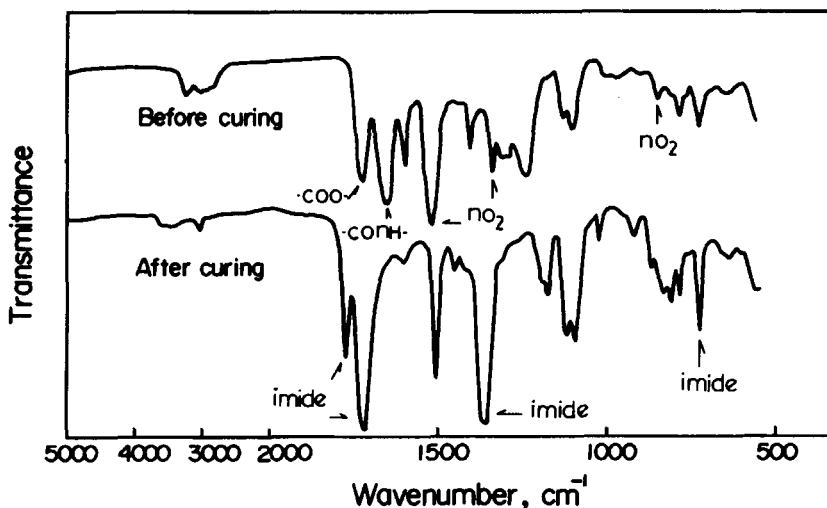


Fig. 3. The IR spectra of polymer A and their products cured at  $300^{\circ}\text{C}$  under nitrogen.

great extent. This result shows that polyimide esters obtained from aromatic diamines imidize more readily than aliphatic diamines.

The second weight loss in Figure 2 depends on the thermal degradation of polyimide. Noticeable weight loss is observed at about 400°C for polymer B and about 500°C for polymer A. Polymer A is wholly aromatic polyimide and has an excellent thermal stability.

### Photochemical Study

The polymers were spun onto a quartz plate to create thin films in order to measure their UV absorption spectra. The results are shown in Figures 4 and 5. Both polymers A and B exhibited an absorption peak due to nitrobenzyl group in the vicinity of 250 nm. There is a disappearance of a maximum at that wavelength after the irradiation with ultraviolet light, and this indicates that nitrobenzyl groups undergo the photoreaction to change. Further, the film colored into brown by the irradiation, and the absorbance over the wavenumber range 300 to 400 nm increased with irradiating. This coloration

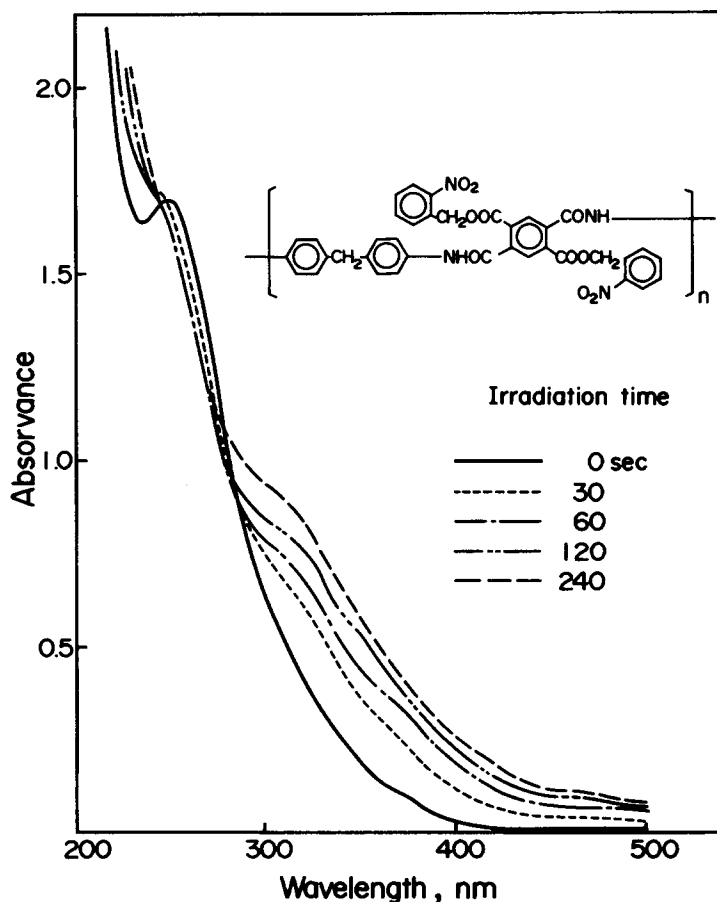


Fig. 4. Change in UV absorption upon irradiation of a 0.16  $\mu\text{m}$  film.

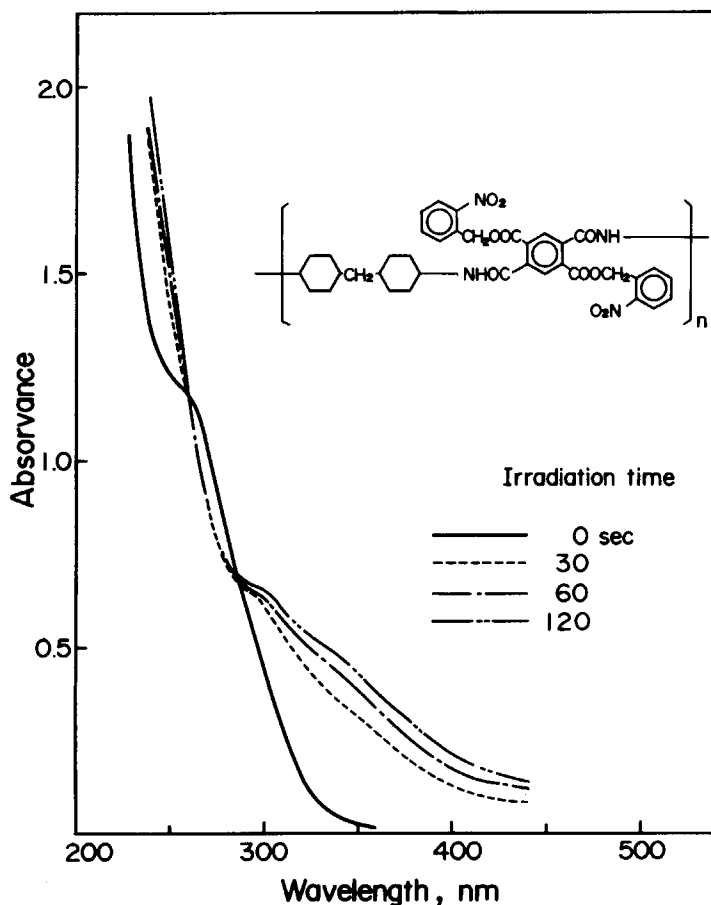


Fig. 5. Change in UV absorption upon irradiation of a 0.43  $\mu\text{m}$  film.

may be due to the products formed in the photoreaction (e.g., azobenzene-2,2'-dicarboxylic acid<sup>6</sup>).

On the other hand, Figure 6 presents the change in IR absorption spectra of a thin film of the polymer A upon irradiation. There is a marked decrease in the intensity of the nitro group peak at 1520, 1340, and 860  $\text{cm}^{-1}$ . Further, when the intensity of the ester linkage peak at 1730  $\text{cm}^{-1}$  is compared as the ratio for the aromatic peak at 160  $\text{cm}^{-1}$ , there is an observable decrease in the relative intensity of them with irradiation. Reichmanis et al. have compared the photochemistry of *o*- and *p*-nitrobenzyl ester and reported that there is no measurable decrease in nitro absorbance in the case of the para isomer.<sup>11</sup> Therefore, it is considered from the decrease in nitro group and ester linkage peaks on Figure 6 that characteristic rearrangement in the *o*-nitrobenzyl ester occurs in this system.

These spectrophotometry studies display that the *o*-nitrobenzyl ester group introduced into the side chain of a polyamic acid also undergoes the reaction described in Scheme 1.



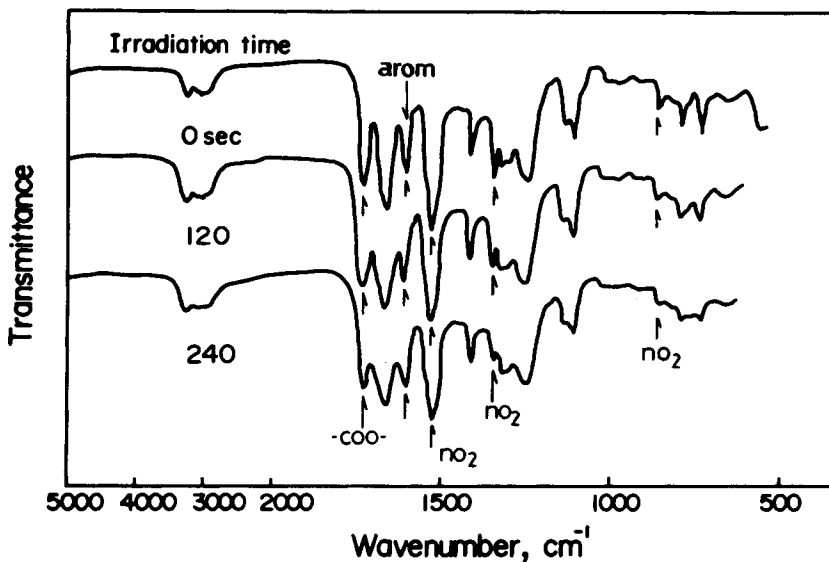


Fig. 6. Change in IR spectra upon irradiation of polymer A film.

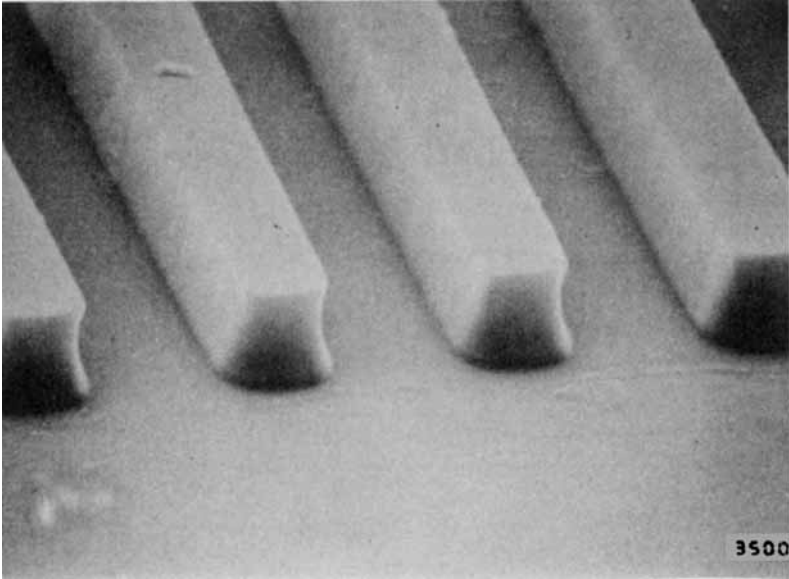
### Lithographic Performance

As described in the preceding chapters, ultraviolet irradiation of the esterified polyamic acid polymers led to the formation of carboxylic acid by the scission of an *o*-nitrobenzyl ester through intramolecular photorearrangement. Therefore, we may expect that the exposed areas of the film would be soluble in alkali solution.

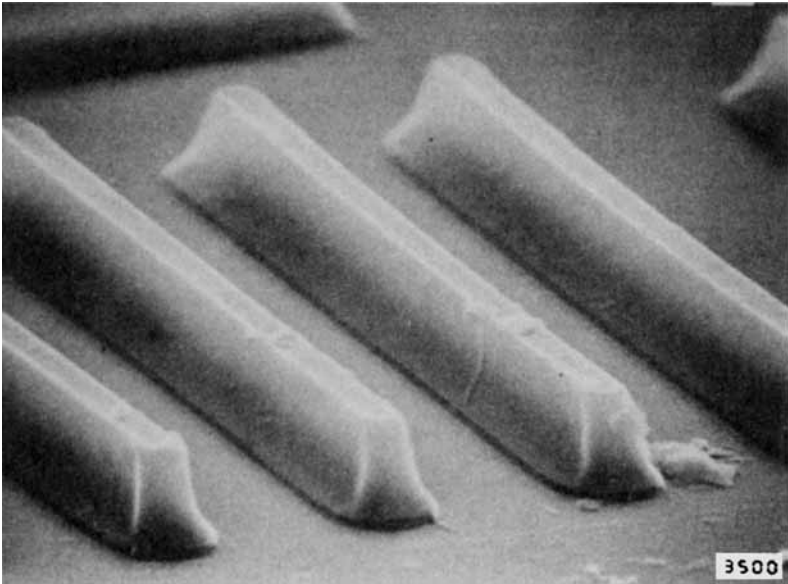
The polymer film was spin-coated onto silicon wafers from a 13% solution in NMP and prebaked at 80°C for 30 min. The thickness of film was about 4.0  $\mu\text{m}$ . Here, wafers were treated with  $\gamma$ -aminopropyl-trimethoxy-silane in isopropanol to increase the adhesion. The exposure was carried out using unfiltered ultraviolet light from a high pressure Hg-Xe lamp (500 W) for 20 min and 2% aqueous KOH was used as a developer.

Figures 7(A) and (B) shown a scanning electron micrograph (SEM) of the pattern obtained by using a photomask having 5  $\mu\text{m}$  lines and spaces. High-resolution patterns were obtained as shown in these photographs because they did not swell at all during developing process. The film pattern were aged at 350°C for 30 min under nitrogen in order to form the imide. Figures 7(C) and (D) show an SEM of the pattern after curing. A shrinkage in volume occurred as it was expected from the TGA results in Figure 2.

In order to evaluate the film thickness exposed and developed, we measured the exposure characteristics for the polymers A and B. This results are shown in Figure 8 where the developing depth is plotted against exposure time. The polymer obtained from aliphatic diamine displayed a higher sensitivity than that from aromatic diamine. When the exposure characteristics were evaluated using 500 W ultra high pressure Hg lamp, the developer dissolved only surface layer of the polymer film (1000–3000 Å depth). Figure 8 is the results obtained using 500 W Hg-Xe lamp which emits more rays of short wavelengths.

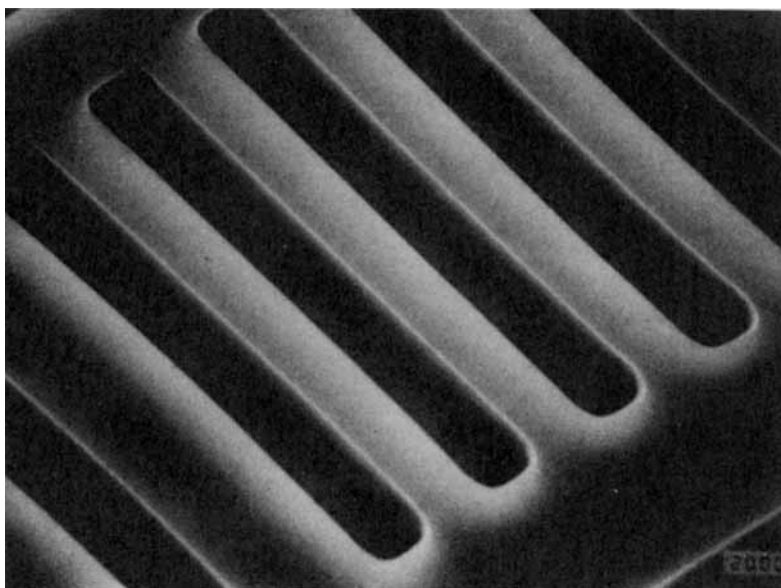


(a)

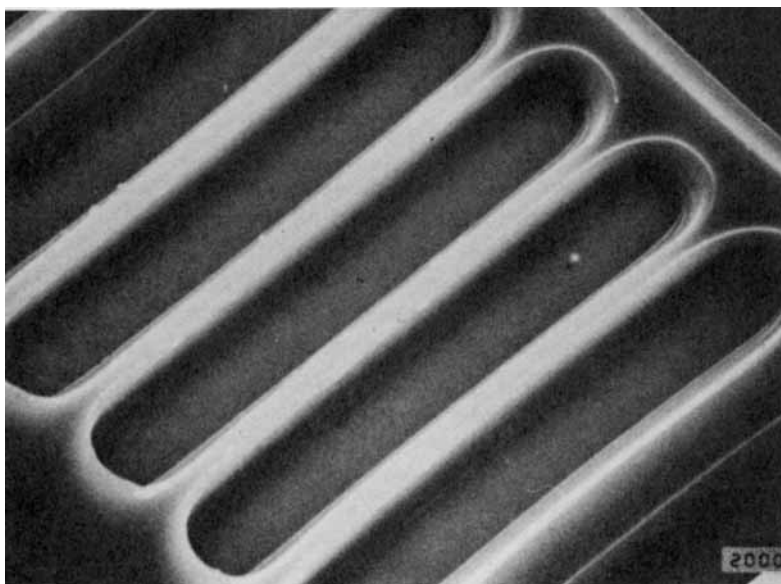


(c)

Fig. 7. SEM photographs of the patterns by using  $5\ \mu\text{m}$  lines and spaces mask: (A, B) after developing; (C, D) after curing at  $350^\circ\text{C}$  for 30 min.



(b)



(d)

Fig. 7. *Continued from previous page.*

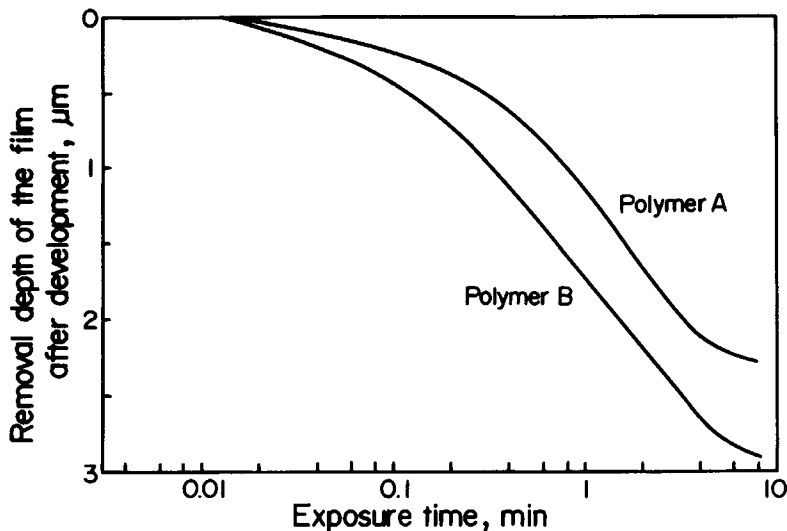


Fig. 8. Exposure characteristics of photoreactive polyimide precursors.

Therefore, nitrobenzyl-ester rearrangement occurs effectively at short wave lengths and the absorption due to polyimide segment may be little concerned in this reaction.

Polymer A exhibits stronger absorption in ultraviolet light than polymer B (Figs. 4 and 5). When these polymers are irradiated with an identical light source, ultraviolet-light intensities at the same depth of the film inside are different. This results in giving a difference of their sensitivity.

## CONCLUSIONS

In this study, we have tried to synthesize a positive photoreactive polyimide which is able to produce a high resolution pattern.

1. When *o*-nitrobenzyl group was introduced to the side chain of polyamic acid through ester linkage, the exposure area of the film were dissolved in aqueous alkali to exhibit positive photosensitive properties.

2. The spectrophotometry studies supported that *o*-nitrobenzyl ester group introduced to the side chain of the polyamic acid underwent the photoreaction by irradiation with UV light.

3. In a comparison of their sensitivity, the polymer obtained from an aliphatic diamine displayed a higher sensitivity than the polymer from an aromatic diamine.

4. The polymers obtained were able to be converted into usual polyimide by curing.

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