

Preparation of Quinazolone-Imide Copolymers and Their Thermal and Chemical Etching Properties

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Synopsis

Quinazolone-imide copolymers were prepared by polycondensation of 6,6'-methylenebis(2-methyl-3,1-benzoxazine-4-one) and 3,3',4,4'-benzophenonetetracarboxylic dianhydride and 4,4'-oxydianiline. Their thermal properties by TGA and their chemical etching properties by the use of the etchant composed of hydrazine hydrate and ethylenediamine were studied. The copolymers obtained had good solubility and excellent heat resistance and gave flexible and tough films. The chemical etching properties were more subject to influence of the polymer composition than the thermal properties were.

INTRODUCTION

In multilevel interconnections of large scale integrated circuits (LSI), the technology employing an organic polymer as an insulator has been developed instead of more commonly used chemical vapor deposited inorganic compounds.¹ The advantages of using a polymer are as follows: a polymer can be spun into a wafer to create a relatively planar surface² and can be applied in thicker coats without cracking (low residual stress)³; furthermore, a polymer can be synthesized in high purity.⁴ Polyimides have been widely investigated as an insulator in the above applications.⁵

Aromatic polyimides possess excellent heat resistance and mechanical and electrical performance. However, they are poorly soluble in organic solvents, so that they are treated in the form of their precursor, polyamic acid, which are soluble in the polar solvents such as *N*-methyl-2-pyrrolidone or dimethylformamide. The polyamic acid is sensitive to hydrolysis by water⁶ and their solutions change in viscosity during storage at room temperature. The lability of solution viscosity has a great influence on spin-coated film thickness. These problems may be solved by using the soluble polyimides or soluble heat resistant polymers.⁷ Quinazolone-imide block copolymers were reported to improve the solubility of polyimides.⁸

Our interest is whether the soluble polyimide can be employed as an insulator in multilevel interconnections. This article deals with the synthesis and characterization of a series of quinazolone-imide random copolymers. Further, we describe the chemical etching method using a photoresist mask.

EXPERIMENTAL

Materials

4,4'-Oxydianiline (ODA) was obtained from commercial sources and purified by recrystallization from ethanol.

3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA) was obtained from commercial sources and sublimed at 220–240°C at less than 1 torr.

6,6'-Methylenebis(2-methyl-3,1-benzoxazine-4-one) (MBO) was prepared by a previously reported procedure⁹ from the reaction of acetic anhydride with 5,5-methylenedianthranilic acid, and was purified by recrystallization from acetic anhydride (mp = 262°C).

ANAL. Calcd for C₁₉H₁₄N₂O₄: C, 68.26%; H, 4.22%; N, 8.38%.
Found: C, 68.06%; H, 4.18%; N, 8.46%.

Solvents and Reagents

m-Cresol was purified by distillation. Hydrazine hydrate, ethylenediamine, and other solvents were used without purification.

Polymerizations

All of the quinazolone-imide random copolymers were synthesized by solution polymerization at a concentration of 15–20% solids in *m*-cresol. The following procedure is a representative polycondensation.

The copolymer (P-55): In a three-neck 100 mL flask fitted with a stirrer, gas inlet tube, and a reflux condenser, ODA (4.0046 g, 0.02 mol) was completely dissolved in 42.3 g of *m*-cresol at room temperature and MBO (3.3448 g, 0.01 mol) and BTDA (3.2223 g, 0.01 mol) were added as a solid in one portion under a flow of dry nitrogen. The resulting solution was stirred for 30 min at room temperature and heated 2 h at 130°C, 4 h at 180°C, and 1 h at 190°C under nitrogen.

The viscous brown solution was cooled to room temperature and diluted with 50 mL of *m*-cresol. The polymer was precipitated as a yellow fibrous solid by pouring into acetone, washed with acetone, and filtered. The polymer was dried *in vacuo* at 120°C for 8 h.

Characterization of the Copolymers

The intrinsic viscosities of the polymers were measured at 30°C in *m*-cresol by using a Ubbelohde suspended level viscometer. Glass transition temperatures (T_g) were determined by differential scanning calorimetry (DSC) under nitrogen atmosphere at a heating rate of 10°C/min. Thermogravimetric analysis (TGA) was performed in a stream of air (50 mL/min); the heating rate was 10°C/min and the sample weight was about 5 mg of polymer film.

Chemical Etching of the Copolymers

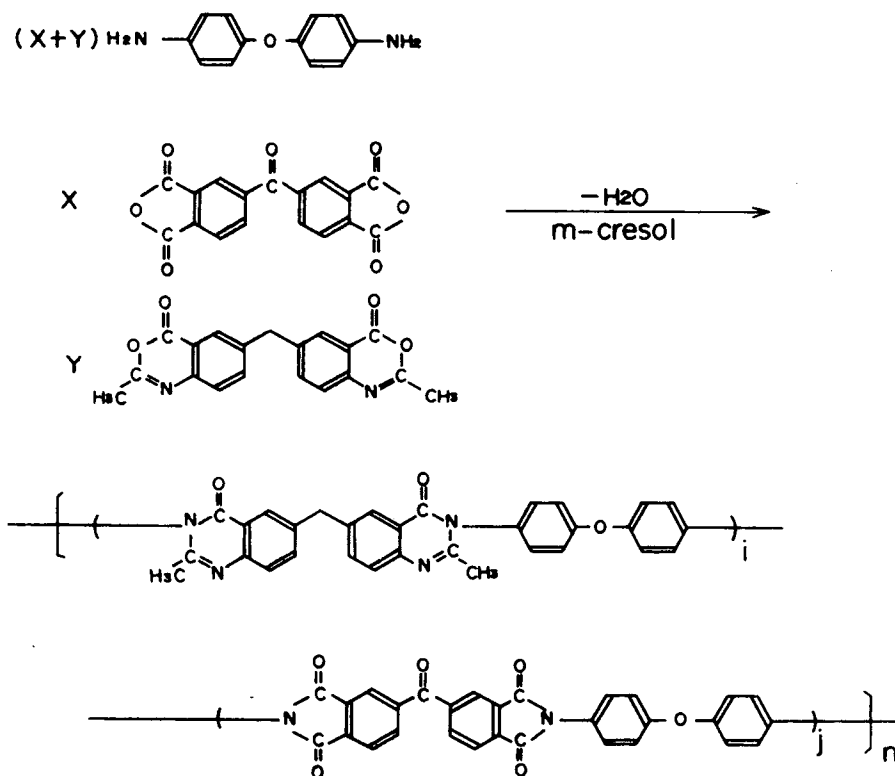
Polymer Coating. The polymer solutions were spin-coated onto silicon wafers which were treated with aminosilane (KBM-620, 1% solid in isopropanol) to increase the adhesion force with the coating films.¹⁰ These polymer films were baked at 200–300°C in an infrared image furnace under nitrogen.

Etchant. The etchant used was a mixture of ethylenediamine and hydrazine hydrate (3:2, weight ratio). The etching rate was calculated from the film thickness and the minimum etching time.

RESULTS AND DISCUSSION

Polymerization

The synthesis of quinazolone-imide copolymer is described in Scheme 1:



Scheme 1. The synthesis of quinazolone-imide copolymer

The polymerizations were carried out by adding BTDA and MBO to a solution of ODA in *m*-cresol. When the reaction temperature was raised to 130°C, water evolution was observed, and the reaction went to completion at 190°C. The results of polymer synthesis are summarized in Table I. All of the copolymers were soluble in *m*-cresol and were obtained in good yields. The copolymers prepared had high intrinsic viscosities, and it was found that increasing imide content in the polymer tended to increase the viscosity.

Figure 1 presents the IR spectra of typical copolymers, which show characteristic imide absorptions at 1780, 1720, 1380, and 730 cm^{-1} , indicating cyclization and quinazolone absorptions at 1680 and 1600 cm^{-1} . The relative intensities of imide and quinazolone absorptions vary with their individual content.

TABLE I
Preparation^a of Quinazolone-Imide Copolymers

Polymer	Reactants (mol)			Concentration (wt %)	[η] ^b
	MBO	BTDA	ODA		
p-100	1.0	—	1.0	20	0.71
p-82	0.8	0.2	1.0	20	0.59
p-73	0.7	0.3	1.0	20	0.64
p-64	0.6	0.4	1.0	20	0.76
p-55	0.5	0.5	1.0	20	0.85
p-46	0.4	0.6	1.0	18	0.78
p-37	0.3	0.7	1.0	15	1.18
p-28	0.2	0.8	1.0	15	0.86

^aThe polymerization was carried out in *m*-cresol under nitrogen at 130°C for 2 h at 180°C for 4 h and then at 190°C for 1 h.

^bMeasured in *m*-cresol at 30°C by using Ubbelohde suspended level viscometer.

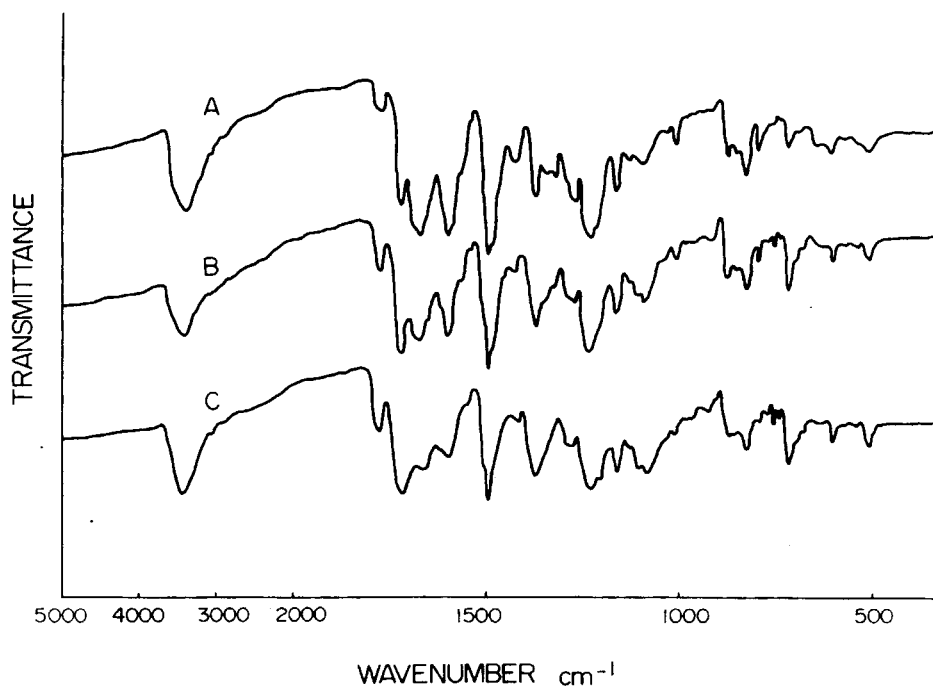


Fig. 1. Infrared spectra of quinazolone-imide copolymers. (A) p-82; (B) p-55; (C) p-28.

Thermal Analysis

TGA of the copolymer was carried out with films which were prepared from the *m*-cresol polymer solution and dried for 1 h each at 80 and 180°C in nitrogen. Typical TGA curves obtained in air are shown in Figure 2, and thermal behavior data are summarized in Table II. The TGA curves showed a

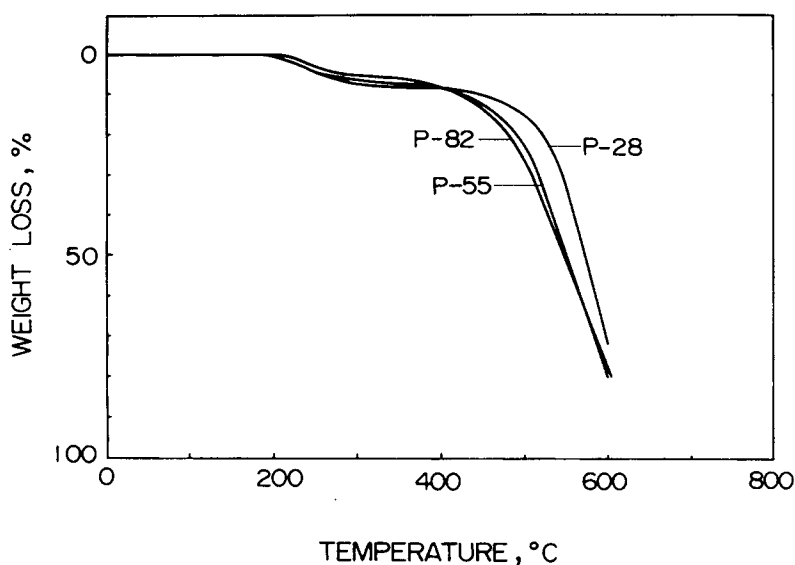


Fig. 2. TGA curves for quinazolone-imide copolymers in air.

first weight loss of 5–8% in the range 200–300°C and a second weight loss above 400°C.

The first weight loss may be caused by volatilization of the solvent, *m*-cresol, because the IR spectra of the polymers show imide and quinazolone absorptions (ring closure is almost complete). The second weight loss is distinctly caused by the decomposition of the polymer. The main degradation of the copolymers was initiated at a temperature near 380°C, but increased as MBO decreased. The temperatures of maximum degradation were recorded

TABLE II
Characterization of Quinazolone-Imide Copolymers

Polymer	Thermal analysis			
	T_g^a (°C)	TGA ^b (°C)		Solubility limit in NMP ^e (wt %)
		T_i^c	T_m^d	
p-100	220	380	480	> 20
p-82	218	380	480	> 20
p-73	218	390	480	< 20
p-64	222	384	490	< 15
p-55	244	384	485	< 10
p-46	256	386	490	< 5
p-37	248	394	500	< 5
p-28	236	396	505	< 5

^a Determined by DSC under nitrogen atmosphere at 10°C/min.

^b Performed in a stream of air. The heating rate was 10°C/min.

^c The temperature at which main degradation was initiated.

^d The temperature at which maximum degradation was observed.

^e NMP: *N*-methyl-2-pyrrolidone.

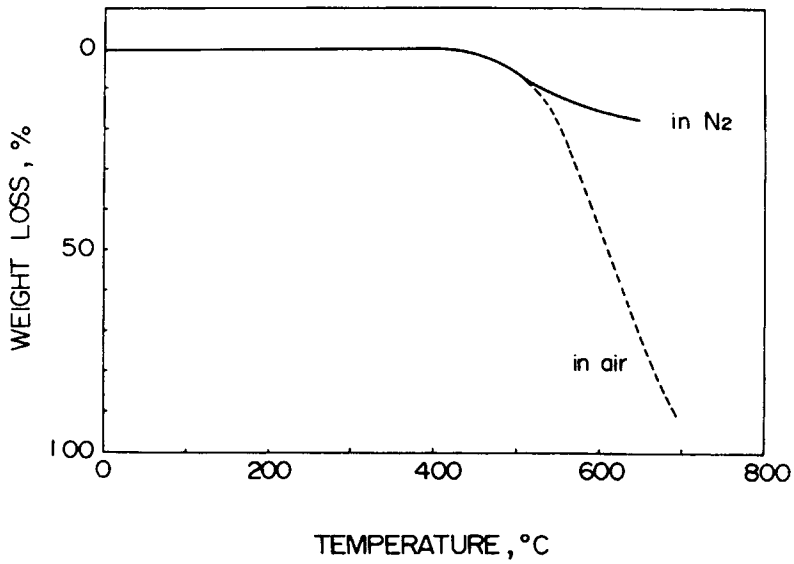


Fig. 3. TGA curves for polymer p-55 which were heated to 350°C for 1 h under nitrogen.

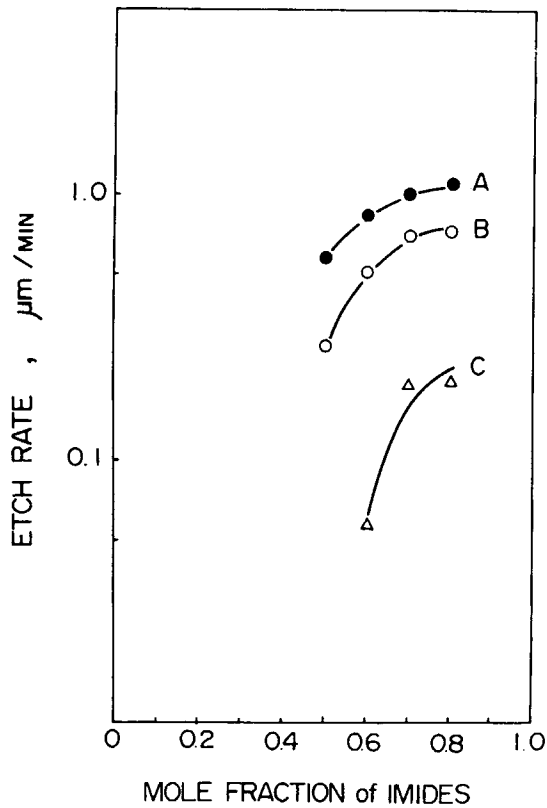


Fig. 4. Imide content dependence of the etch rate. The films were aged for 200 (A), 250 (B), and 300°C (C) under nitrogen.

in the vicinity of 480–500°C and also raised with increasing imide content in the copolymer.

When the polymer films were further aged at 350°C under nitrogen for 1 h in an infrared image furnace, the TGA curves showed very little loss of weight below 400°C. Typical TGA curves obtained in air and nitrogen are shown in Figure 3 (polymer p-55).

The determination of T_g was accomplished by DSC. The polymers obtained had a lower T_g than the polyimide prepared with ODA and BTDA (295°C).¹¹ There was no clear tendency for T_g value to depend on imide content in the polymer chain.

Solubility

The copolymers were synthesized in high concentration as shown in Table I, but a precipitate of the polymer did not separate out during the polymerization. The polymer solution obtained had high viscosity and flexible and tough films were prepared by spreading the solution (diluted with *m*-cresol) onto a silicon wafer.

The polymers recovered by the reprecipitation with acetone were soluble in *m*-cresol and NMP; however, their solubility decreased with an increase in imide content. Quantitative solubility data are presented in Table II where NMP is the solvent.

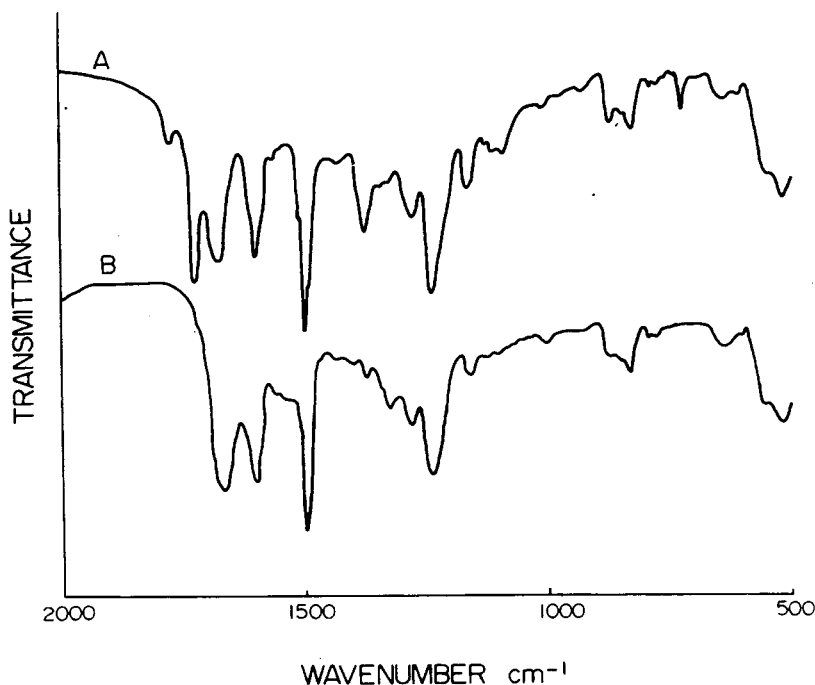
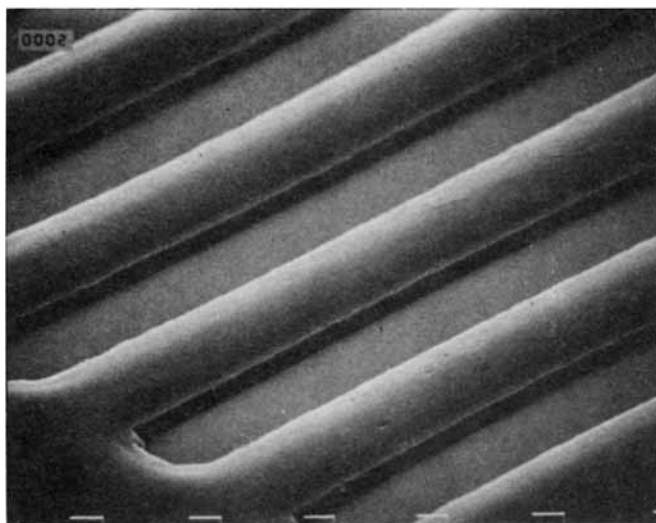


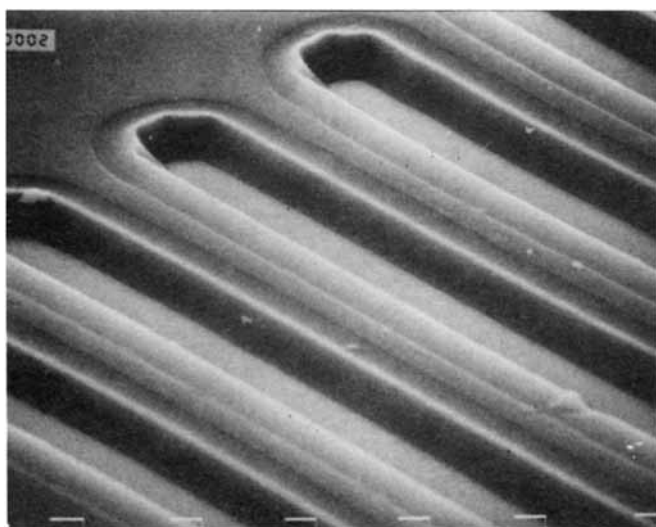
Fig. 5. Infrared spectra of polymer p-64 (A) and their products treated with hydrazine hydrate (B).

Chemical Etching

It is well known that *N*-substituted phthalimides react with hydrazine hydrate to form an intermediate, which is easily decomposed with the formation of phthalaz-1,4-dione and the primary amine.¹² The chemical etching of the polyimides are carried out through a photoresist mask by the use of this reaction¹³ (Ing-Manski reaction). In this paper, the chemical etching proper-



A

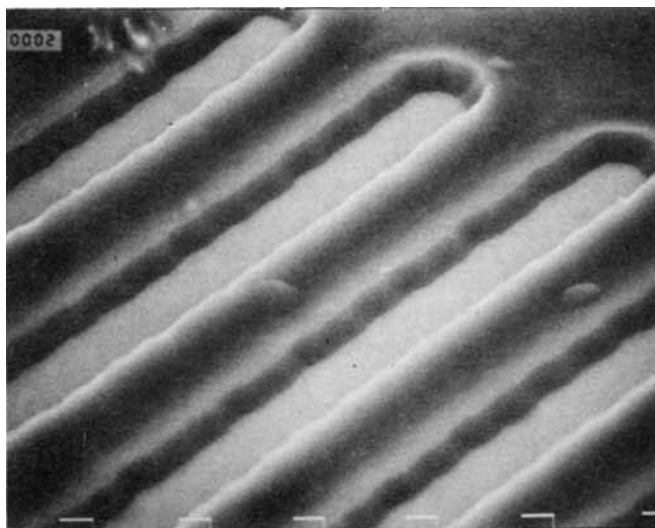


B

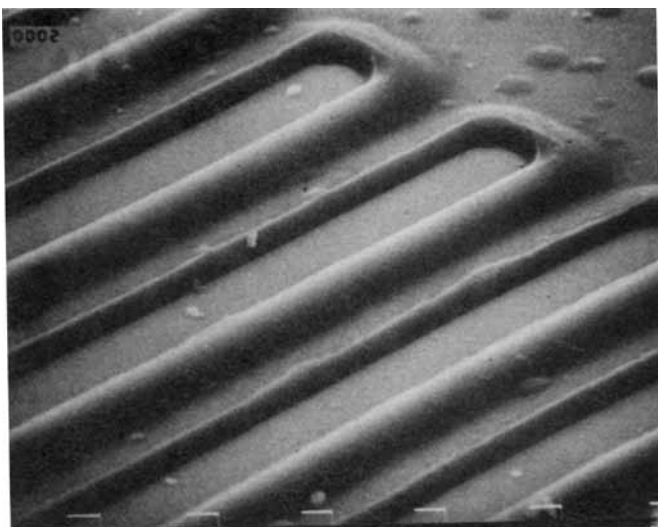
Fig. 6. The etched pattern obtained by the resist mask having 10 μm lines and spaces: (A) p-28; (B) p-37; (C) p-46; (D) p-55.

ties of the quinazolone-imide copolymers were investigated by using the same method.

The etch rate of the copolymers is shown in Figure 4. The polymer films were aged at 200, 250, and 300°C under nitrogen respectively, and treated at 20°C with the etchant which was a mixture of hydrazine hydrate and ethylenediamine (2:3, weight ratio). There was a marked tendency that the etch rate decreased with an increase in the quinazolone content and with a rise in the aged temperature.



C



D

Fig. 6. (Continued from the previous page.)

Figure 5 presents the IR spectra of the polymer film (p-64) and their products treated with hydrazine hydrate. The imide absorption at 1780, 1720, 1380, and 720 cm^{-1} disappears by the treatment, while the quinazolone absorption at 1680 and 1600 cm^{-1} remains unaltered and the new band at 1660 cm^{-1} appears.¹⁴ Hydrazine hydrate attacks only an imide structure, and the copolymer gave the dihydrazine derivative and the diamine derivative. This derivative has a higher molecular weight with an increase in the quinazolone content, and the dissolution rate in the etchant decreases with an increase in the molecular weight. Thus the effect lowers the etch rate of the polymer film which has a high quinazolone content.

Figure 6 shows a scanning electron micrograph (SEM) of the etched pattern obtained by using a resist mask having 10 μm lines and spaces. The top layer, resist, was removed (with a stripper) in the photographs; the polymer films were aged at 250°C.

The obtained pattern has a sharp edge in the polymer having a high imide content (p-28, p-38); however, the side etched part, which may have developed because of etchant permeation into the resist-polymer film interface, is broadened with decreasing imide content. Taper angle (θ) and normalized side etched length (N_L) were calculated by using the film thickness and the values determined from SEM photographs. These results are shown in Figure 7, and a definition of their terms and schematic presentation are described in Fig-

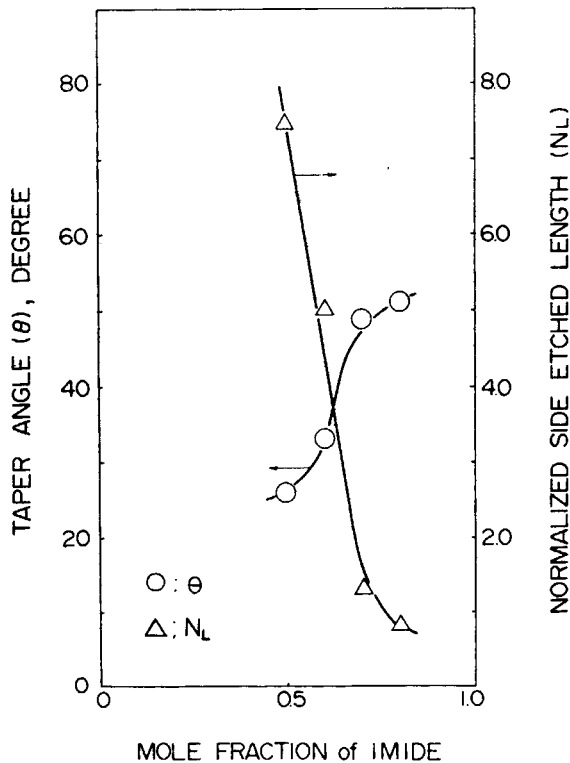
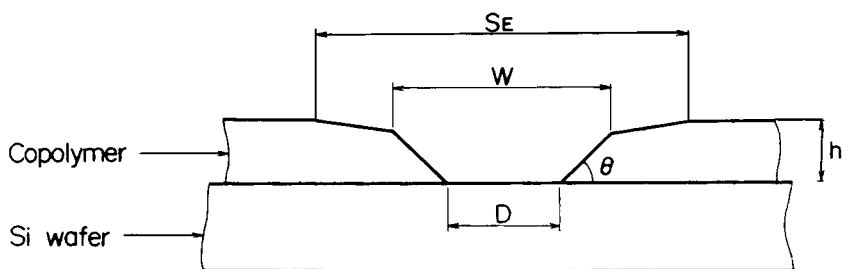


Fig. 7. Imide content dependence of taper angle (θ) and normalized side etched length (N_L) in the etched pattern.



TAPER ANGLE

$$\theta = \text{TAN}^{-1} \left(\frac{2 \cdot h}{W - D} \right)$$

NORMALIZED SIDE
ETCHED LENGTH

$$N_L = \frac{SE - W}{2h}$$

Fig. 8. Schematic presentation and a definition of taper angle (θ) and normalized side etched length (N_L).

ure 8. These phenomena may be caused by the different etch rates in each of the polymer films. That is to say, since the copolymer possessing a high quinazolone content (low etch rate) is treated with the etchant for long time, the degree of side etch increases with increasing a quinazoione content.

CONCLUSIONS

Quinazolone-imide random copolymers consisting of a different imide content were synthesized by solution polymerization in *m*-cresol. The copolymers prepared were soluble in *m*-cresol and NMP, but their solubility decreased with increasing imide content in the copolymer. Thermal stability of the copolymers increased with increasing imide content. In chemical etching studies, there was a marked tendency that the etch rate decreased with a decrease in imide content and with a rise in the aged temperature of films. Further, the side etch part was broadened with decreasing imide content.

Thermal and chemical etching properties are subject to influence of the polymer composition. However, it is possible to improve the solubility of polyimides by means of this studies, and polymer p-37 is a most suitable composition from a consideration of the results of solubility and etching properties. This polymer system can use as LSI dielectric by preparing in high purity.

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