

# Relationship between Electron Sensitivity and Chemical Structure of Polymers as EB Resists.

## I. Electron Sensitivity of Various Polyamides

NAOYA OGATA, KOHEI SANUI, CHIAKI AZUMA, HOZUMI TANAKA,  
and KIYOSHI OGUCHI, *Faculty of Science and Technology, Sophia  
University, 7-1 Kioi-cho, Chiyoda-ku, Tokyo 102, Japan*, and TOMIHIRO  
NAKADA and YOICHI TAKAHASHI, *Dai Nippon Printing Co., Ltd., 1500  
Fukuoka, Kamifukuoka-shi, Saitama 356, Japan*

### Synopsis

Polyamides containing double bonds or epoxy groups were synthesized and evaluated as electron beam (EB) resists, in order to find the relationship between electron beam sensitivity and chemical structure of the polyamides. It was found that polyamides containing double bonds, which have good solubility, are easily crosslinked by the electron beam exposure. The sensitivity of a polyamide with 70 mol % of the repeat units containing double bonds was equivalent to that of a 100% unsaturated polyamide which contained double bonds of 100% molar ratios, and thus it is not necessary that the polyamide be a homopolymer of unsaturated repeating units. The polyamides have good physical properties, and are adaptable to dry etching processes.

### INTRODUCTION

Until now, the fabrication of IC or LSI requires photoresists which are sensitive to light in order to print very fine patterns on wafers. Recently, very fine patterns with submicron resolution on LSI or VLSI have been increasingly needed, but organic based photoresists cannot print patterns with submicron resolution owing to limitations caused by the wavelength of light. Therefore, EB resists are being examined in place of photoresists since electron beams have much better resolution than light in theory and practice, and it is possible to print fine patterns with submicron resolution on wafers using EB resists. Several EB resists containing epoxy groups or double bonds such as poly(glycidyl methacrylate) (PGMA)<sup>1,2</sup> or poly(butadiene) (PB)<sup>3</sup> have been found to be negative EB resists with high sensitivity to the electron beam.

Generally, resist materials require many characteristics. These include not only high sensitivity and high resolution, but also good adhesion on the wafer, thermal stability, easy coating capability, good resistance to etching, and so on. Especially, in the process of etching, dry etching is coming to be used in place of wet etching because in this case less undercutting is produced. Thus it is important for EB resists to be highly resistant to dry etching. Resist materials which have a benzene ring as part of their fundamental structure show high resistance to dry etching,<sup>4,5</sup> while there are few resist polymers containing chemical structure with high resistance to dry etching known. Polyamides have good physical properties such as thermal stability, strength, good adhesion for substrates, and so on, which correspond with some characteristics needed in resist

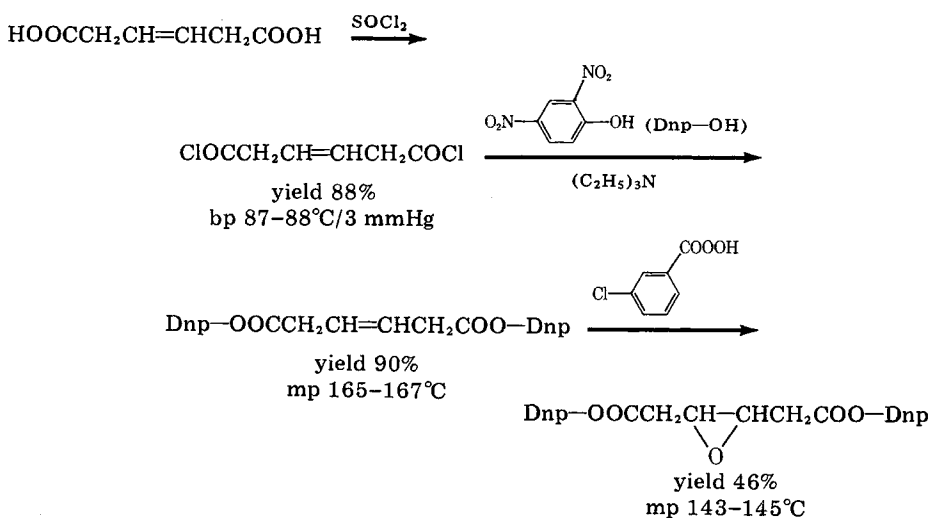
materials. Therefore, polyamides which are sensitive to electron beams and have good durability for dry etching may be useful as resists. For these reasons, polyamides containing double bonds or epoxy groups were synthesized, and their properties as negative-type EB resists investigated in terms of electron beam sensitivity and dry etch resistance.

## EXPERIMENTAL

### Syntheses of Monomers

#### *Di(2,4-Dinitro Phenyl)epoxy Adipate (DNPA)*

DNPA was synthesized from *trans*-3-hexendioic acid via the following route;



*Trans*-3-hexendioyl chloride (HC) was synthesized from *trans*-3-hexendioic acid and thionyl chloride and purified by vacuum distillation.

47.0 g of 2,4-dinitrophenol and 26.0 g of triethylamine were dissolved in 600 mL of acetone and 22.8 g of acid chloride (HC) was slowly added. After filtration, the precipitate was washed with water in order to remove hydrochloride from ester and purified by recrystallization from ethyl acetate.

15.0 g of di-2,4-dinitrophenyl ester was dissolved in 700 mL of benzene and 5.5 g of *m*-chloroperbenzoic acid was added with stirring. The mixed solution was refluxed and the end point of the epoxidation was determined by the disappearance of IR absorption at  $990 \text{ cm}^{-1}$  due to the double bond (*trans* C=C). After benzene was evaporated under reduced pressure, the epoxy ester was washed with cold methanol and purified by recrystallization from ethyl acetate.

#### *3-Amino-Perhydro-Azepine (APA)*

APA was synthesized by the reduction of commercial  $\alpha$ -amino- $\epsilon$ -caprolactam. The details have been previously reported.<sup>6</sup>

Other Monomers

Commercially available 4,4'-diaminodiphenyl ether was purified by recrystallization from 1,4-dioxane; *p,p'*-diaminodiphenyl methane was used as purchased.

Glycidyl methacrylate (GMA) was purified by vacuum distillation.

Adipoyl chloride (AC) and *trans*-3-hexendioyl chloride (HC) were synthesized by a conventional method from corresponding dicarboxylic acids and thionyl chloride. They were purified by vacuum distillation.

Syntheses of Polyamides

Polyamides as EB resist materials were synthesized according to solution, graft or interfacial methods. Synthetic routes to the polyamides are summarized in Figure 1.

Solution Polycondensation of DNEA with Diamine

Equimolar amounts of DNEA and diamine were dissolved in DMAc at a concentration of 0.2 mol/L and the solution was kept at 60°C for 20 h. The solution was poured into excess acetone or water and the polyamides were filtered, following by reprecipitation from DMAc into acetone.

Graft Polymerization of GMA onto Nylon 6

Graft polymerization of GMA onto nylon 6 was carried out by the radical polymerization method.<sup>7</sup> 26.0 g of calcium chloride was dissolved in methanol, and 5.0 g of nylon 6 was dissolved in this solution with heating. After passing nitrogen gas for 30 min, 0.1 g of 2,2'-azobisisobutyronitrile (AIBN) as a radical initiator was added in this solution and heated at 60°C for 1 h under nitrogen atmosphere. A mixture of 12.5 g of GMA containing 10 mol % of methacrylic acid was added in this solution, which was kept at 60°C for a given period. The solution was poured into excess water. The precipitate was filtered and dried under vacuum. Homopolymers formed by radical polymerization of GMA were extracted by refluxing with acetone in a Soxhlet extractor. The mole fraction of graft polymer was determined by elemental analysis.

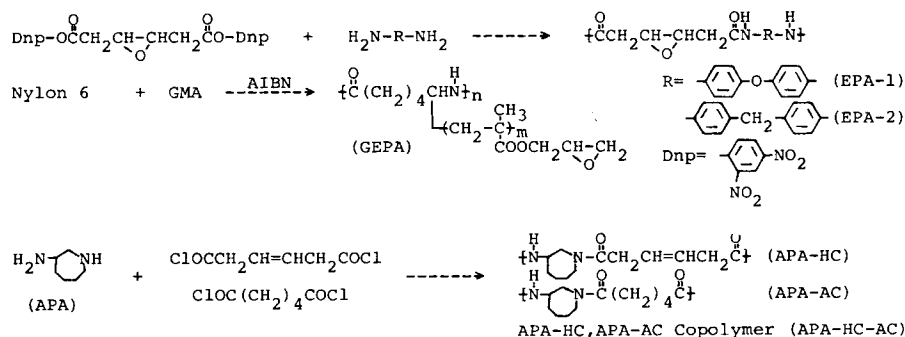


Fig. 1. Syntheses of polyamides.

*Interfacial Polycondensation of APA with Diacid Chloride*

1.36 g of APA was dissolved in 60 mL of water in the presence of 0.96 g of sodium hydroxide, and 2.27 g of HC which was dissolved in 60 mL of benzene was added to the aqueous solution with vigorous stirring in a homoblender. After stirring was continued for 5 min, the precipitated polymer was filtered, followed by reprecipitation from methanol into water, and dried under vacuum.

Polycondensation of APA with AC and copolycondensation of APA with HC and AC were synthesized as mentioned above. Physical properties of these prepared polyamides are summarized in Table I.

**Evaluation of Polyamides as EB Resist***Electron Beam Exposure*

The polyamides were spin-coated from solution on glass substrates coated with a chromium film and then prebaked in order to remove the remaining solvent and to promote adhesion. The film thickness was determined by a talystep instrument. The conditions of resist coating and prebake are summarized in Table II.

The resists were subsequently exposed using a computer-controlled scanning electron microscope with test patterns of two types. One type is to determine the sensitivity of resists, and the other is to determine the resolution. The accelerating voltage was 10 keV and the beam diameter was 0.25 or 0.50  $\mu\text{m}$ . Several different lines with widths between 0.5 and 5.0  $\mu\text{m}$  were exposed to determine the resolution.

*Development*

Exposed resists were developed by an immersion method. The conditions of development are summarized in Table II. The resists were then rinsed for 30 s or 60 s in an appropriate solvent such as isopropyl alcohol or MEK.

TABLE I  
Properties of Polyamide

Polyamide	$\eta_{sp}/C$	$T_d$ ( $^{\circ}\text{C}$ ) <sup>a</sup>	Solubility					
			DMAc	DMSO	MeOH	$\text{CHCl}_3$	Cellosolve	MEK/HCOOH
EPA-1	0.67 <sup>b</sup>	193	+	+	-	-	-	-
EPA-2	0.82 <sup>b</sup>	196	+	+	-	-	-	-
GEPA-2 <sup>c</sup>	0.81 <sup>d</sup>	320	-	-	-	-	-	+
GEPA-7 <sup>e</sup>	0.82 <sup>d</sup>	283	-	-	-	-	-	+
APA-HC	1.36 <sup>f</sup>	381	+	+	+	+	+	-
APA-AC	1.13 <sup>f</sup>	360	+	+	+	+	+	-
APA-HC-AC-4 <sup>g</sup>	1.03 <sup>f</sup>	377	+	+	+	+	+	-

<sup>a</sup> Measured by DTA.

<sup>b</sup> 0.1 g/10 cm<sup>3</sup> in DMAc at 30 $^{\circ}\text{C}$ .

<sup>c</sup> Mole fraction of GMA is 0.20.

<sup>d</sup> 0.1 g/10 cm<sup>3</sup> in  $\text{CHCl}_2\text{COOH}$  at 30 $^{\circ}\text{C}$ .

<sup>e</sup> Mole fraction of GMA is 0.69.

<sup>f</sup> 0.1 g/10 cm<sup>3</sup> in  $\text{H}_2\text{SO}_4$  at 30 $^{\circ}\text{C}$ .

<sup>g</sup> Mole fraction of HC is 0.40.

TABLE II  
Conditions of Evaluation as Electron Beam Resists

Polyamide	Resist coating		rpm	Film thickness (Å)	Prebake		Development	
	Solvent	Concn (%)			Temp (°C)	Time (min)	Solvent	Time (s)
EPA-1	DMAc	4.0	600	2400	170	20	DMAc	30
EPA-2	DMAc	4.0	1000	2800	170	20	DMAc	900
GEPA-2	MEK/HCOOH	2.8	1000	3000	110	30	MEK/HCOOH	60
GEPA-7	MEK/HCOOH	3.0	1000	5200	110	30	MEK/HCOOH	60
APA-HC	MeOH	10.0	4000	9500	80	30	MeOH	60
APA-AC	MeOH	10.0	4000	7500	80	30	MeOH	30
APA-HC-AC-4	MeOH	10.0	4000	5600	80	30	MeOH	60

After the development, the remaining film thickness was measured by the talystep instrument and normalized with respect to the initial film thickness. The resist sensitivity is defined as the irradiation dose required to get 50% of the initial film thickness. The  $\gamma$  value is defined as the slope angle of the straight line which passes through the points in the thickness vs. log dose plot corresponding to the minimum dose required for any detectable gel formation and the dose for 50% film thickness.

### Dry Etching

After development and postbaking, reactive ion etching was performed using a planar type reactor in order to determine the durability of polyamides for dry etching. The condition of dry etching was as follows: the etching gas was 20%  $\text{CCl}_4$  and 67% wet air. Gas pressure was 40 Pa. Impressed rf power was 300 W.

The etching rate of chromium under these conditions was about 100 Å/min. Some commercial resists were evaluated at the same condition in order to compare their dry etch resistance with that of the polyamides.

After development and dry etching, the resist patterns were examined under optical and scanning electron microscopes.

## RESULTS AND DISCUSSION

Exposure characteristics of EPA are shown in Figure 2. Coating by EPA-1 resulted in a smooth surface, while that by EPA-2 did not give a smooth surface, perhaps because the EPA-1 contains an ether bond in the diamine and is thus more flexible than the latter. Therefore, it was difficult to measure the sensitive curve of EPA-2. The sensitive curve of EPA-1 gave an EB sensitivity of  $1.7 \times 10^{-4} \text{ C/cm}^2$  and a  $\gamma$  value of 1.0.

GEPA required a mixed solvent of formic acid and MEK for coating because of poor solubility and a homogeneous surface could not be formed. Therefore,

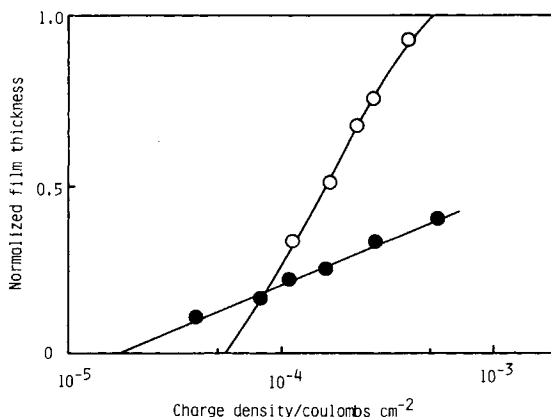


Fig. 2. Exposure characteristics of EPA: (O) EPA-1<sup>a</sup>; (●) EPA-2<sup>b</sup>. Film thickness: (a) 2400 Å; (b) 2800 Å. Prebake: 170°C, 20 min. Developer: DMAc. Development time: (a) 30 s; (b) 900 s.

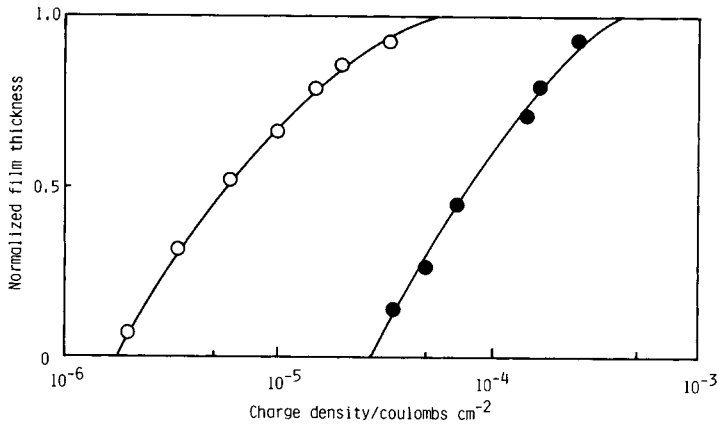


Fig. 3. Exposure characteristics of APA-HC and APA-AC: (O) APA-HC<sup>a</sup>; (●) APA-AC<sup>b</sup>. Film thickness: (a) 9500 Å; (b) 7500 Å. Prebake: 80°C, 30 min. Developer: Methanol. Development time: (a) 60 s; (b) 30 s.

the sensitive curve of GEPA could not be obtained. The sensitivity of GEPA might be on the order of  $10^{-4}$  C/cm<sup>2</sup> judging from the remaining pattern conditions after development.

In spite of having an epoxy group within the polyamide chain, both EPA and GEPA did not have a good sensitivity for EB. Perhaps, poor solubility of these polyamides may be one of the reasons for the poor sensitivity. Negative resist materials must develop a sharp difference in solubility between EB exposed parts

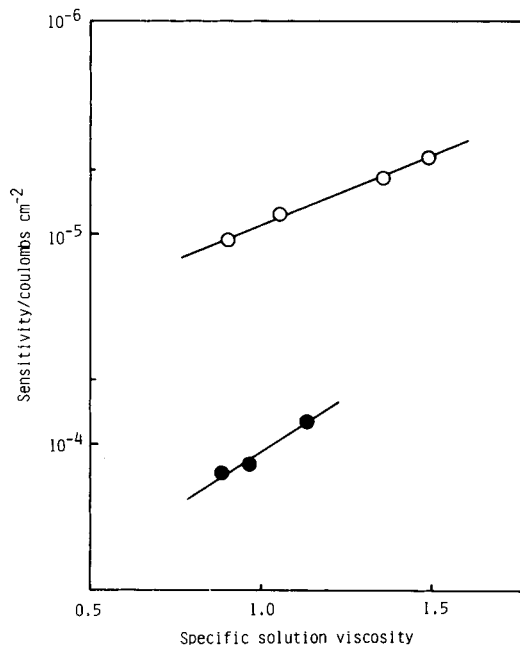


Fig. 4. Relationship between sensitivity and solution viscosity of polyamide: (O) APA-HC; (●) APA-AC. 0.1 g/10 cm<sup>3</sup> in H<sub>2</sub>SO<sub>4</sub> at 30°C.

TABLE III  
Properties of Copolymer (APA-HC-AC)

Polyamide	Mole fraction of HC	$\eta_{sp}/C^a$	Film thickness (Å)
APA-HC	1.00	1.06	4800
APA-HC-AC-8	0.78	1.08	4400
APA-HC-AC-7	0.72	1.06	4900
APA-HC-AC-6	0.65	1.04	6400
APA-HC-AC-5	0.57	0.98	6000
APA-HC-AC-4	0.40	1.05	5600
APA-HC-AC-3	0.33	1.03	5400
APA-HC-AC-2	0.25	1.02	5600
APA-AC	0.00	0.97	7800

<sup>a</sup> 0.1 g/10 cm<sup>3</sup> in H<sub>2</sub>SO<sub>4</sub> at 30°C.

of the resist and unexposed parts. EPA and GEPA did not have a good solubility, which might lead to a poor solubility differential and hence poor sensitivity.

Figure 3 shows the typical EB sensitivity curves of APA-HC ( $\eta_{sp}/C = 1.36$ ) and APA-AC ( $\eta_{sp}/C = 1.13$ ) having good solubility in methanol. Apparently, the sensitivity of these polymers was higher than EPA. The sensitivity curve of APA-HC gave an EB sensitivity of  $5.8 \times 10^{-6}$  C/cm<sup>2</sup> with a  $\gamma$  value of 1.0. The EB sensitivity of APA-AC was  $8.0 \times 10^{-5}$  C/cm<sup>2</sup> with a  $\gamma$  value of 1.0.

Generally speaking, it is known that the sensitivity of a polymer depends on its structure and is proportional to molecular weight. Figure 4 shows the effect of specific solution viscosity of APA-HC and APA-AC on their EB sensitivity. In each case, a linear relationship has been found, showing the sensitivity of APA-HC and APA-AC is proportional to molecular weight.

It is clear from Figure 4 that the sensitivity of APA-HC was higher than that of APA-AC and may be attributed to the existence of double bonds in the polymer main chains.

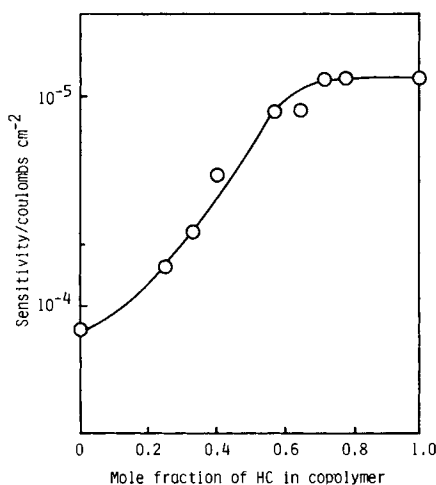


Fig. 5. Effect of double bond in copolymer (APA-HC-AC) on sensitivity.



TABLE IV  
Dry Etching Rates for Reactive Ion Etching

Resist	Etching rate (Å/min)
APA-HC	250
APA-HC-AC	240
APA-AC	217
EBR-1	390
PMMA	320
OEBR-100	540
CMS	170
AZ-1350	250

In order to examine the effect of double bonds on EB sensitivity, copolymers of APA-HC-AC of approximately equal molecular weight were synthesized. The EB sensitivity of these copolymers was evaluated under the same conditions. Table III shows some properties of APA-HC-AC copolymers. Figure 5 shows the effect of increasing mole fraction of HC in APA-HC-AC copolymers on the EB sensitivity. The EB sensitivity of APA-HC-AC copolymers increased gradually with the increasing amount of double bond in these copolymers and was saturated with the double bond ratio of about 70%. Thus, it is not necessary that the double bond content be 100% of the unsaturated repeating units in the copolymers for maximum electron sensitivity. It was possible to design different molecular structures derived from copolymers without changing the EB sensitivity.

Dry etching rates of polyamides and commercial resists are summarized in Table IV. Dry etching durability of resists is usually estimated by their etching rates, so that low etching rate shows high durability. It is clear from Table IV that polyamides have good dry etching durability in spite of the absence of aromatic structure. This good resistance to dry etching may be attributed to the strong hydrogen bonding between amide linkages in the polyamides.

Figure 6 shows the SEM micrographs of APA-HC resist patterns on a Chro-

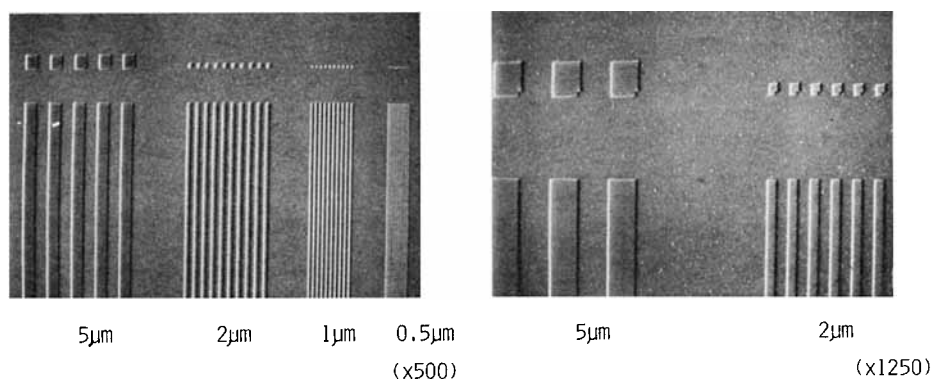


Fig. 6. SEM micrographs of APA-HC resist patterns after development: Film thickness: 3400 Å. Prebake: 80°C, 30 min. Beam diameter: 0.5 µm. Dose:  $8.5 \times 10^{-6}$  C/cm<sup>2</sup>. Developer: Methanol. Development time: 60 s. Rinse: Isopropyl alcohol.

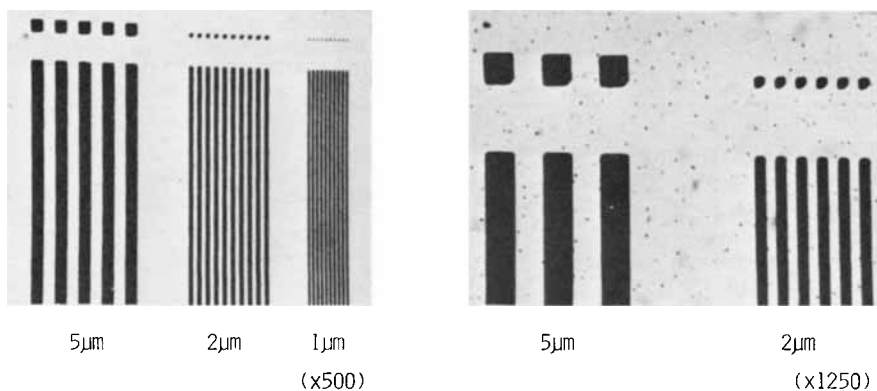


Fig. 7. Photomicrographs of etched patterns of Chromium by using APA-HC resist.

mium wafer after development. Resolution of  $1\ \mu\text{m}$  line and space could be obtained with APA-HC resist.

Figure 7 shows the photomicrographs of etched patterns of Chromium by using APA-HC resist. It was found in this experiment that APA-HC was satisfactorily useful in a dry etching process.

### References

1. T. Hirai, Y. Hatano, and S. Nonogaki, *J. Electrochem. Soc.*, **118**, 669 (1971).
2. Y. Taniguchi, Y. Hatano, H. Shiraishi, S. Horiguchi, and S. Nonogaki, *Jpn. J. Appl. Phys.*, **18**, 1143 (1979).
3. L. F. Thompson, F. D. Feit, and R. D. Heidenreich, *Polym. Eng. Sci.*, **14**, 529 (1974).
4. M. J. Bowden and L. F. Thompson, *J. Electrochem. Soc.*, **121**, 1620 (1974).
5. S. Imamura, *J. Electrochem. Soc.*, **126**, 1628 (1979).
6. H. Nakamura, T. Nakamura, K. Sanui, and N. Ogata, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 3035 (1978).
7. K. Kosai, T. Higashino and S. Ohue, *Nippon Kagakkukaishi*, **3**, 523 (1975).

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