Relationship between Electron Sensitivity and Chemical Structures of Polymers as EB Resists. III. Electron Sensitivity of Various Polyamides Using 3-Amino Perhydroazepine

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Synopsis

Homopolyamides and copolyamides containing a variety of reactive and/or stabilizing groups, such as double bonds, epoxy groups, or naphthalene moieties, were synthesized using 3-amino perhydroazepine (APA) as a diamine monomer. These polymers were evaluated as electron beam (EB) resists, in order to investigate the relationship between EB sensitivity and chemical structure of the polyamides. It was found that polyamides containing double bonds were easily crosslinked by the EB exposure and that the sensitivity of a polyamide containing double bonds in the side chain was higher than that of a polyamide containing double bonds in the main chain. The sensitivity of a polyamide containing epoxy groups was lower than that of the above. Copolymer from APA, 77 mol % of *trans*-3-hexenedioyl chloride (HC) and 23 mol % of 2,6-naphthalenedioyl chloride (NC) had the same EB sensitivity as that of the homopolymer from APA and HC. The polyamides had excellent dry etching durability and were adaptable to EB lithography.
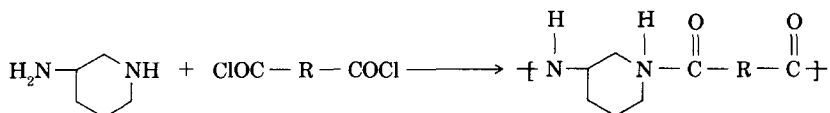
INTRODUCTION

Resist materials for making fine patterns on integrated circuits are used in the manufacture by lithographic process of a high density integrated circuits and photomask. Until now, photoresists which are sensitive to light are mainly used. The demand for making very fine patterns with submicron resolution is increasing and various electron beam (EB) resists designed to take advantage of the potentially higher resolution electron beam lithography have been investigated. Several kinds of EB resists have been reported, and some of them are commercially available. For example, poly(glycidyl methacrylate) (PGMA),[1,2] poly(glycidyl methacrylate-co-ethyl acrylate) (COP),[3] chloromethylated polystyrene (CMS),[4,5] and iodinated polystyrene (IPS)[6] are commercially available negative EB resists. EB lithography is primarily used to fabricate master-chromium photomask, although direct device fabrication with submicron patterns using EB resists is being considered.

Generally, resist materials require many characteristics. The most important characteristics of resists are high sensitivity and resolution. In addition, easy coating capability, thermal stability, good adhesion to sub-

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strates, excellent development characteristics, good resistance to etching, and so on, are necessary. In particular, durability of a resist in dry etching environments is required because of the increasing importance of dry etching process, where less undercutting is obtained as compared with wet etching process. It is known that polymers containing aromatic structures possess good resistance to dry etching environments.[4,7]

Polyamides have good physical properties such as thermal stability, strength, good adhesion to substrates, and so on, which are commensurate with many of the requirements of a resist. Therefore, polyamides containing radiation sensitive groups may be useful as EB resists.

It has previously been reported that polyamides having good solubility, which contain double bonds, are easily crosslinked by exposure to electrons and that such polyamides have good durability in dry etching environments in spite of the absence of aromatic structure.[8] From the results of a previous paper, we have now designed a polyamide based on 3-amino perhydro-azepine (APA) as a diamine monomer, in order to improve the sensitivity or the durability for dry etching. Since APA has antisymmetrical cyclic structure with both a primary and a secondary amino group, the resulting polyamide is amorphous and therefore soluble in common solvents such as chloroform:

$$H_2N-\!\!\!\bigcirc\!\!\!-NH \; + \; ClOC-R-COCl \longrightarrow \; \left[\!N-\!\!\!\bigcirc\!\!\!-N-\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}\!\right]$$

Therefore, it was expected that the polyamide should be able to be spin coated to give uniform thin films.

This paper describes the synthesis of polyamides based on APA and reports results of their evaluation as negative EB resists in terms of EB sensitivity and dry etching resistance.

EXPERIMENTAL

Syntheses of Monomers

3-Amino Perhydroazepine (APA). APA was synthesized by the reduction of commercial α-amino–ε-caprolactam. The reduction was carried out with LiAlH$_4$ in THF. The details have been previously reported.[9]

Diacid Chloride. The following diacid chlorides were synthesized by a conventional method from corresponding dicarboxylic acids and thionyl chloride. They were purified either by vacuum distillation or recrystallization from benzene after the residual thionyl chloride was removed: Adipoyl chloride (AC), bp 97–98°C/2 mm Hg; *trans*-3-hexenedioyl chloride (HC), bp 87–89°C/1.5 mm Hg; 2-methyleneglutaroyl chloride (MGC), bp 72–73°C/2 mm Hg; 2,6-naphthalenedioyl chloride (NC), mp 184–188°C.

Syntheses of Various Polyamides

Polyamides suitable as EB resist materials were synthesized by interfacial polycondensation. Those polyamides containing an olefinic hydrocarbon group were subsequently epoxidized.

Synthetic routes to the polyamides are summarized in Figure 1.

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 as an acid acceptor, and 2.20 g of AC which was dissolved in 60 mL of benzene was added to the aqueous solution with vigorous stirring in a homoblender. Stirring was continued for 5 min and the precipitated polymer was then filtered, followed by reprecipitation from methanol into water two times, and dried under vacuum.

Polycondensation of APA with HC, MGC, and NC was carried out according to the same method as mentioned above with various organic solvents.

Copolycondensation of APA with AC and HC, MGC and AC, or HC and NC was carried out using similar procedures.

Epoxidation of APA–HC. Equimolar amounts of APA–HC and m-chloroperbenzoic acid were dissolved in chloroform at a concentration of 0.20 or 0.05 mol/dm^3 and the solution was kept at 40–60°C for 3–40 h with stirring. The solution was poured into excess benzene, and the polymer was separated by filtration. It was further purified by reprecipitation from chloroform into methanol and dried under vacuum.
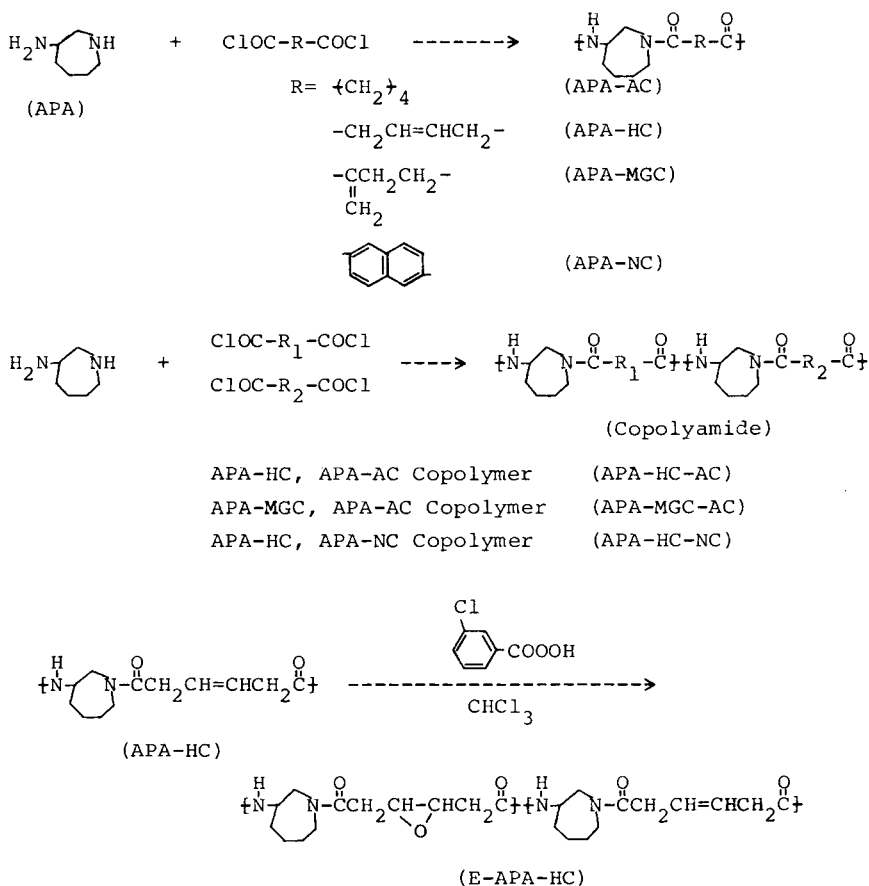

Fig. 1. Syntheses of polyamides.

Evaluation of Polyamides as EB Resists

The prepared polyamides were dissolved in appropriate organic solvents of low boiling point like methanol or cellosolve, and were spin-coated on glass substrates precoated with a chromium film and then prebaked at 80°C or 90°C for 30 min in order to remove the remaining solvent and to promote adhesion to the substrate. The film thickness was determined by a Talystep instrument.

The resists were exposed using an electron beam resist exposure apparatus, ERE-301(ELIONIX Co.) at an accelerating voltage of 10 kV. The exposure resists were developed by immersion in methanol for 30–60 s. The resist were then rinsed for 30 s in isopropyl alcohol (IPA). 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 leave 50% of the initial film thickness after development. The γ value is defined as the slope of the extrapolated linear portion of the sensitivity curve.[10]

After development and subsequent postbaking at 140°C for 30 min, 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% CCl_4 and 67% wet air. Gas pressure was 40 Pa and impressed rf power was 300 W. Some commercial resists were evaluated at the same conditions in order to compare their dry etch resistance with that of the polyamides.

After development and dry etching, the resist patterns were examined by optical and scanning electron microscopy.

RESULTS AND DISCUSSION

Syntheses and Characteristics of Polyamides

Interfacial polycondensation of APA with HC or MGC was carried out in several different organic solvents and at various concentrations in the

TABLE I
Interfacial Polycondensation[a] of APA with HC

Monomer concn (mol/dm³)	Organic solvent	Yield (%)	η_{sp}/C[b]
0.20	Benzene	53	1.50
0.25	Benzene	52	1.06
0.40	Benzene	55	0.85
0.20	m-Xylene	48	1.17
0.20	Toluene	45	1.24
0.20	Chlorobenzene	56	1.26
0.30	Chlorobenzene	48	1.61
0.20	1,2-dichloroethane	32	1.28
0.20	Cyclohexanone	4	0.51
0.20	n-Hexane	37	0.82
0.20	Butyl ether	43	0.97
0.20	Methyl ethyl ketone	0	—

[a] Time: 5 min. Acid acceptor: NaOH.
[b] 0.1 g/10 cm³ in H_2SO_4 at 30°C.

TABLE II
Interfacial Polycondensation[a] of APA with MGC.

Monomer concn (mol/dm^3)	Organic solvent	Yield (%)	η_{sp}/C[b]
0.20	Benzene	4	0.40
0.40	Benzene	13	0.41
0.60	Benzene	13	0.39
0.20	m-Xylene	19	0.31
0.30	m-Xylene	12	0.47
0.40	m-Xylene	29	0.44
0.60	m-Xylene	31	0.34
0.20	Toluene	10	0.43
0.20	Chlorobenzene	0	—
0.20	1,2-Dichloroethane	0	—
0.20	n-Hexane	0	—
0.20	Butyl ether	24	0.38

[a] Time: 5 min. Acid acceptor: NaOH.
[b] 0.1 g/10 cm^3 in H$_2$SO$_4$ at 30°C.

presence of sodium hydroxide as an acid acceptor in order to increase the molecular weight. Results are summarized in Tables I and II. Aromatic and halogen solvents yielded polymers of relatively high molecular weight as reflected in the solution viscosity for APA–HC. Halogenated solution were not effective in promoting formation of high molecular weight polymers from MGC. No satisfactory results were obtained in terms of yields of APA–HC and APA–MGC. These polyamides based on APA have good solubility and the molecular weight distribution may be rather wide, so that the poor yields may be ascribed to the dissolution of polyamides of low molecular weight in the reaction solvent.

Epoxidation of APA–HC was carried out using m-chloroperbenzoic acid. The reaction conditions and epoxidation ratio of APA–HC are shown in Table III and Figure 2, which shows the relationship between epoxidation and solution viscosity of E–APA–HC at various times. It is seen that the epoxidation of APA–HC is completed in a relatively short time, but that decomposition of amide group in the polymer occurs rapidly as well. Therefore, high molecular weights of E–APA–HC could not be obtained.

Physical properties of these prepared polyamides are summarized in Table IV. In contrast to conventional polyamides they are soluble in a variety

TABLE III
Epoxidation[a] of APA–HC with m-Chloroperbenzoic Acid

η_{sp}/C of APA–HC	Polymer and peroxy acid concn (mol/dm^3)	Time (h)	Temp (°C)	η_{sp}/C[b]	Epoxidation ratio (%)[c]
0.67	0.20	3	60	0.27	55
0.67	0.20	7	60	0.19	85
0.67	0.20	20	60	0.11	90
0.67	0.20	39	60	0.07	90
1.36	0.05	4	40	0.44	47
1.36	0.05	7	40	0.33	55

[a] Solvent: CHCl$_3$.
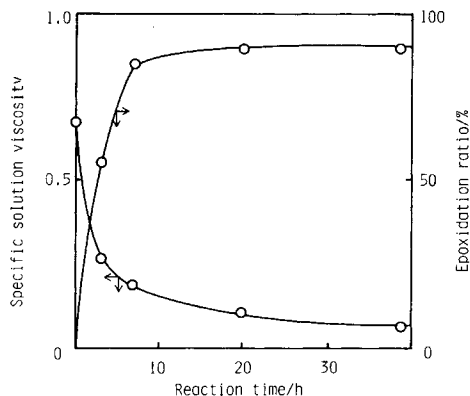[b] 0.1 g/10 cm^3 in H$_2$SO$_4$ at 30°C.
[c] Determined by IR.

Fig. 2. Relationship between epoxidation and solution viscosity of E–APA–HC on reaction time.

of solvents so that these polyamides could be spin-coated and developed by fractional dissolution in suitable solvents.

Properties of Polyamides as EB Resists

The polyamides were dissolved in cellosolve and spin-coated on chromium coated glass substrates to yield uniform pinhole-free films.

Exposure characteristics of various homopolyamides and copolyamides are shown in Figures 3 and 4, and their sensitivity and γ values listed in Table V. It is clear from Figure 3 and Table V that the sensitivity of polyamides having double bonds are higher than that of the others, reflecting the high reactivity of the double bond to EB exposure. Generally speaking, it is known that the sensitivity of a polymer greatly depends not only on its structure but also on its molecular weight with higher molecular weight resulting in higher sensitivity. The sensitivity dependence of the

TABLE IV
Properties of Polyamides

Polymer	η_{sp}/C^a	T_d (°C)[b]	Solubility					
			DMAc	DMSO	CH_3OH	$CHCl_3$	Cellosolve	H_2O
APA–AC	0.97	360	+	+	+	+	+	—
APA–HC	1.06	381	+	+	+	+	+	—
APA–MGC	0.39	380	+	+	+	+	+	—
APA–NC	0.91	390	+	+[c]	—[d]	±[e]	±	—
E–APA–HC	0.44	360	+	+	+	+	+	—
APA–HC–AC	1.05	377	+	+	+	+	+	—
APA–HC–NC	0.74	382	+	+	±	+	+	—
APA–MGC–AC	0.50	383	+	+	+	+	+	—

[a] 0.1 g/10 cm³ in H_2SO_4 at 30°C.
[b] Measured by DTA.
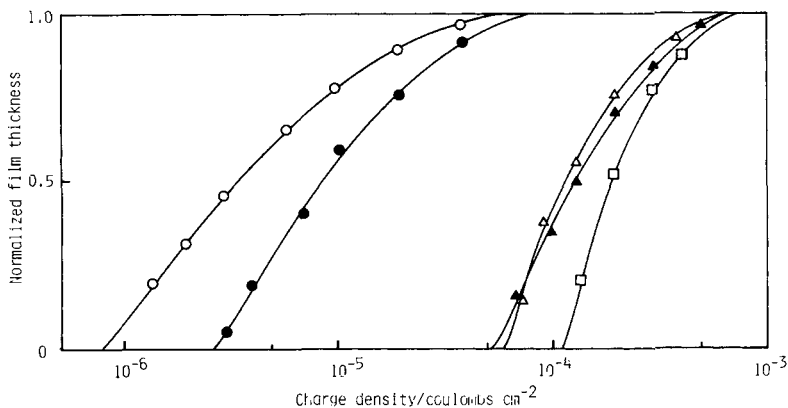[c] Easily soluble.
[d] Insoluble.
[e] Soluble.

Fig. 3.   Exposure characteristics of homopolyamides: (○) APA–MGC[a]; (●) APA–HC[b]; (△) E–APA–HC[c]; (▲) APA–AC[d]; (□) APA–NC[e]. Film thickness (μm): (a) 0.50; (b) 0.48; (c) 0.34; (d) 0.78; (e) 0.68. Prebake: 80°C, 30 min. Developer: (a,b,c) methanol; (c) 2-methoxyethanol; (e) CHCl$_3$/methanol (5/1). Development time: 60 s.

polyamides on molecular weight are shown in Figure 5. The sensitivity of APA–MGC is higher than that of APA–HC in spite of having a lower molecular weight, indicating that the double bonds are more effective in promoting electron sensitivity when present in the side chain rather than in the main chain. Perhaps, the mobility of double bond in the side chain is higher than that of double bond in the main chain and leads to more efficient crosslinking and consequent higher resist sensitivity.

It is clear from Figure 5 that E–APA–HC did not have good sensitivity in spite of having an epoxy group, and an extrapolation of the straight line of APA–HC to the direction of low molecular weight, may lead to lower sensitivity of E–APA–HC than that of APA–HC at the same molecular weight. Generally, polymers having epoxy groups have high sensitivity to EB. For example, the sensitivity of epoxidized polybutadiene is higher than that of polybutadiene[1] whereas in the present case the sensitivity of E–
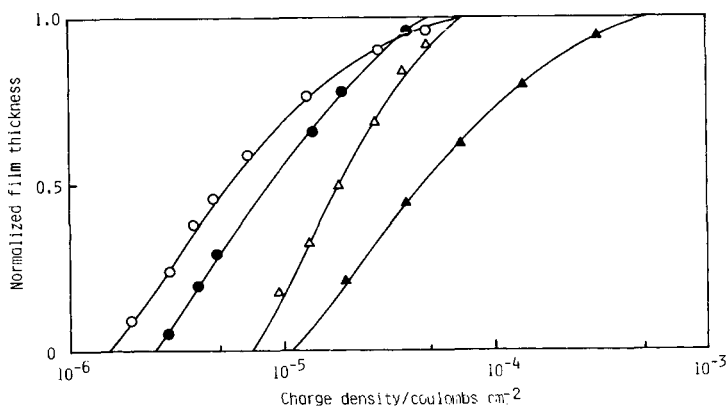

Fig. 4.   Exposure characteristics of copolyamides: (○) APA–MGC–AC[a]; (●) APA–HC–AC[b]; (△) APA–HC–NC[c]; (▲) APA–HC–AC[d]. Mole fraction of MGC or HC: (a) 0.57; (b) 0.72; (c) 0.77; (d) 0.33. Film thickness (μm): (a) 0.56; (b) 0.49; (c) 0.44; (d) 0.54. Prebake: (a) 90°C, 30 min; (b,c,d) 80°C, 30 min. Developer: methanol. Development time: (a) 45 s; (b,c,d) 60 s.

TABLE V
Properties of Polyamides as EB Resists

Polymer	η_{sp}/C	Mole fraction of HC or MGC	Sensitivity ($\mu C/cm^2$)	γ value
APA–AC	0.97	—	130	1.2
APA–HC	1.06	—	8.5	0.9
APA–MGC	0.39	—	3.3	0.7
APA–NC	0.91	—	190	1.7
E–APA–HC	0.33	—	120	1.3
APA–HC–AC	1.08	0.72	8.4	1.1
APA–HC–AC	1.03	0.33	45	0.7
APA–HC–NC	0.74	0.77	19	1.2
APA–MGC–AC	0.57	0.57	5.4	0.8

APA–HC is low in comparison with APA–HC. This low reactivity of epoxy groups in E–APA–HC may be due to a hydrogen bonding between the epoxy and amide groups which may retard the crosslinking reaction.

In a previous paper, the sensitivity of various copolymers of APA–HC–AC were examined in order to find the effect of double bonds on EB sensitivity, and it was found that the sensitivity was saturated with the double bond ratios of about 70%, i.e., it was not necessary that the double bond content of the repeating units should be 100% for maximum electron sensitivity.[8] This result led to the synthesis of the copolymer of APA–HC–NC, which contained naphthalene ring (NC) of 23% molar ratio, in order to
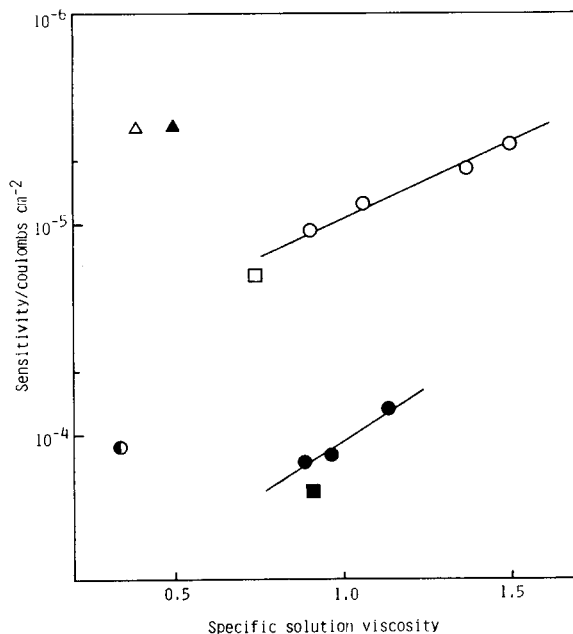

Fig. 5. Relationship between sensitivity and solution viscosity of various polyamides. (○) APA–HC; (●) APA–AC; (△) APA–MGC; (▲) APA–MGC–AC; (□) APA–HC–NC; (■) APA–NC; (◑) E–APA–HC.

TABLE VI
Dry Etching Rates for Reactive Ion Etching

Resist	Etching rate (Å/min)
APA–AC	217
APA–HC	250
APA–NC	140
APA–MGC	260
APA–HC–AC[a]	240
APA–HC–NC[b]	230
OEBR–100[c]	540
SEL–N[d]	450
CMS[e]	170
AZ-1350[f]	250

[a] Mole fraction of HC is 0.65.
[b] Mole fraction of HC is 0.77.
[c] Poly(glycidyl methacrylate).
[d] Polymer of methacrylate containing maleic ester.
[e] Chloromethylated polystyrene.
[f] Phenol resin containing naphthoquinone diazide.

improve the resistance to dry etching without changing the EB sensitivity. Figure 5 indicates that the sensitivity of APA–HC–NC was about equivalent to that of APA–HC as was expected.

Dry etching rates of polyamides and several commercial resists are summarized in Table VI. Low etching rate means a high durability to dry etching process. It is clear from Table VI that the polyamides have good dry etching durability. APA–NC which contains naphthalene ring in the chain is clearly superior. This good resistance to dry etching environments may be attributed to the aromatic structure and to the strong hydrogen bonding between amide linkages in the polyamide. The durability of APA–HC–NC to dry etching was a little higher than that of APA–HC, because the former contained a naphthalene ring.

Figure 6 shows the SEM micrographs of APA–MGC resist patterns on a chromium film after development. Resolution of 1 μm line and space could be obtained easily with APA–MGC resist. Resist patterns similar to APA–MGC could be obtained by using the other polyamides in the same way.

Figure 7 shows the photomicrographs of APA–MGC–AC resist patterns on a chromium film after development and etched chromium patterns by using the former resist. It is found from Figure 7 that the resist patterns were exactly copied on the chromium film by the dry etching process.

CONCLUSIONS

Polyamides were synthesized from APA with various acid chlorides by interfacial polycondensation and were evaluated as EB resists. The results are summarized as follows.

1. The polyamides from APA exhibit good solubility and function as negative electron resist.

2. The sensitivity of APA-MGC which had double bonds in the side chain
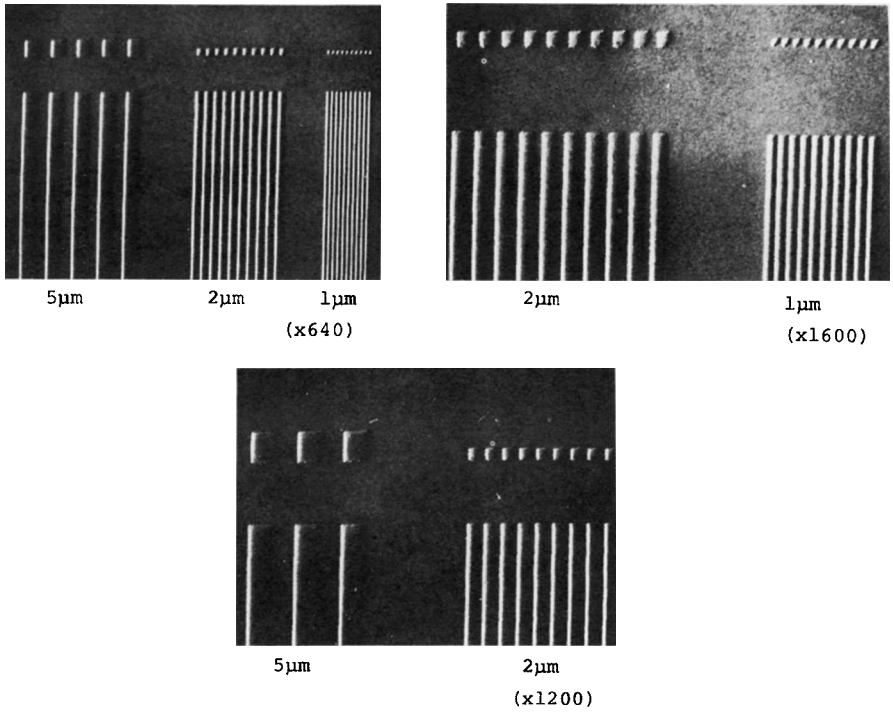
Fig. 6. SEM micrographs of APA–MGC resist patterns after development. Film thickness: 0.34 μm. Prebake: 80°C, 30 min. Beam diameter: 0.50 μm. Dose: 8.5×10^{-6} C/cm². Developer: methanol. Development time: 60 s. Rinse: isopropyl alcohol.

was higher than that of APA–HC which had double bonds in the main chain.

3. The sensitivity of epoxidized APA–HC was lower than that of APA–HC.

4. The sensitivity of APA–HC–NC was almost equal to that of APA–HC, so that various copolyamides from APA with acid chloride containing double bonds and other acid chloride can be obtained without changing EB sen-
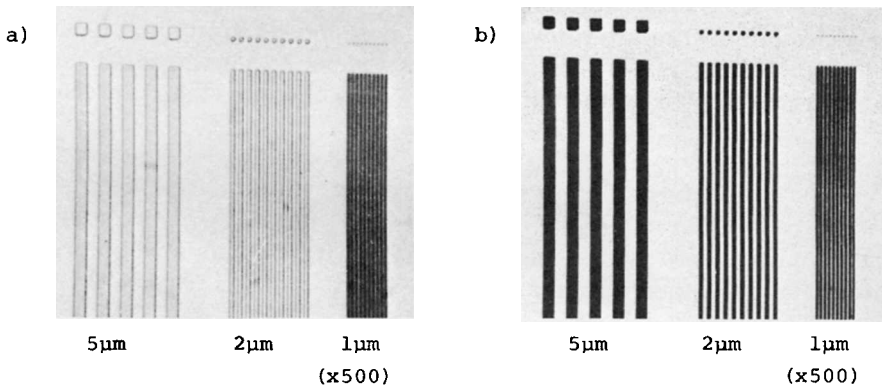

Fig. 7. Photomicrographs of after development and etched patterns using APA–MGC–AC: (a) after development; (b) after dry etching.

sitivity of a homopolyamide, which contains double bonds of 100% molar ratio.

5. The polyamides were durable to dry etching processes with APA–NC, which contains aromatic structure showing the highest dry etch resistance.

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