Sensitivity enhancement of α-methylstyrene copolymer electron beam resists by force development

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The sensitivity of poly(α-methylstyrene-*co*-methyl methacrylate) resist containing 37–39 mol% α-methylstyrene, the plasma-etching durability of which was as large as that of poly(α-methylstyrene), was enhanced up to 3.3–5.9 μC cm^{-2} by force development of linear copolymer or crosslinked terpolymer. The force development was effective for the linear copolymer with high molecular weight, $\bar{M}_w \approx 650\,000$, and the terpolymer loosely crosslinked with less than 1.0 mol% *N*-methylolated methacrylamide. Therefore, crosslinking density must be kept small enough not to increase the electron beam (EB) dose required for solubilizing the exposed area, and molecular weight before EB exposure must be large enough to restrain the thickness reduction in the unexposed area. The *in situ* crosslinking during prebake can be regarded as a method of increasing molecular weight before EB exposure.

(Keywords: positive-working; high molecular weight; loose crosslinking; *N*-methylolated methacrylamide; plasma-etching durability)

INTRODUCTION

The resists for VLSI and ULSI (very large and ultra-large scale integrated circuit) fabrication are required to have balanced performance including high contrast, large dry-etching durability and high sensitivity. In general, positive-working electron beam (EB) resists are of high contrast, but it is shown by theoretical consideration and experimental results that there is a trade-off relationship between dry-etching, durability and sensitivity[1]. This relationship was derived from the study of one-component resist systems composed of degradable linear homopolymer. It does not deny the possibility of realising excellent resist system with all three characteristics mentioned above, if the candidates to be investigated are extended toward multicomponent, crosslinked polymer and/or copolymer system. For example, the durability of highly sensitive, but undurable poly(olefin sulphone) was extensively improved by blending with an aromatic resin, at the expense of a decrease in sensitivity, as was observed with the poly(2-methyl-1-pentene sulphone)–novolac system[2]. Durable, but not so sensitive poly(phenyl methacrylate) was sensitized by copolymerizing with crosslinkable monomer and developing under stronger conditions, at a slight expense of its dry-etching durability[3]. Through poly(methyl methacrylate (PMMA) was desensitized by copolymerization with a stable aromatic monomer such as styrene[4], its sensitivity was enhanced by copolymerization with a fragile monomer, e.g. methyl chloroacrylate or ethyl cyanoacrylate, but there was no description of the effect on dry-etching durability[5].

We have already demonstrated that the durability of PMMA against O_2, CCl_4 and CF_4/O_2 plasmas was remarkably increased by copolymerizing with α-methylstyrene (MSt) or blending with poly(α-methylstyrene) (PMSt)[6,7,8]. The durability increase was much larger than that calculated by following the weight or mole percentage additivity based on the constituent monomer units. The MSt–MMA copolymers containing ≈40 mol% MSt units showed plasma-etching durability as large as PMSt homopolymer. In addition, the glass transition temperature of the polymers was observed at 157–170°C, and was 50–65°C higher than that of PMMA. On the other hand, sensitivity decreased linearly in proportion to MSt content in the MSt–MMA copolymer, when compared under the same developing conditions: when flood-exposed to 4 keV electron flux and developed with neat methyl isobutyl ketone (MIBK) at 25°C for 90 s, the sensitivity of the 39 mol% MSt–MMA copolymer was 65 μC cm^{-2}, which approximately coincided with the average of the values for PMSt and PMMA (140 and 25 μC cm^{-2}, respectively). The sensitivity was still of the same magnitude as that of PMMA developed by the standard developer composed of MIBK and isopropanol (IPA) (1:3, by volume) (59 and 78 μC cm^{-2} at Vaccel = 4 and 10 kV, respectively[9], and 80 μC cm^{-2} at

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Vaccel = 20 kV[10]), and, therefore, it remains to be greatly enhanced.

Since lithographic sensitivity and contrast of positive-working resists depend on the change of dissolution rate before and after EB exposure[11,12], dissolution kinetics concerning each combination of the resist polymer and the developer are more essential to the EB exposure characteristics of the resist film than the intrinsic radiation sensitivity (G-value for scission) of the polymer of interest. Of course the polymer backbone structure and tacticity have a significant effect on both sensitivity and contrast of EB resists, but high sensitivity of the order of several $\mu C\,cm^{-2}$ has not been attained just by copolymerization or tacticity control of PMSt[13,14,15]. It seems very difficult to increase sensitivity by several orders of magnitude by increasing the G-value through chemical modification of molecular structure, but some successful results have been reported on tenfold enhancement of the sensitivity by choosing the most suitable developing conditions[12]. In other words, finding new preferred developing conditions for a resist polymer is as significant as establishing a novel resist polymer of high performance to be processed with a conventional developer.

In this study we tried to enhance the sensitivity of 39 mol% MSt–MMA copolymer by changing the developing conditions. This method will provide a possibility of sensitization without decreasing the dry-etching durability. We prepared, besides the MSt–MMA copolymer, terpolymers containing MSt, MMA and small amounts of *N*-methylolated methacrylamide (MMAm), which was a very reactive group forming crosslinkage by the aid of mutual thermal condensation[16] and did not lower the plasma-etching durability at all[7]. EB exposure characteristics, such as sensitivity and contrast, were measured as a function of MAAm content in the terpolymer after development under stronger conditions (so-called force development). At first, it was expected that the sensitivity would be greatly enhanced by force development, if serious thickness reduction in the unexposed area was restrained by the formation of network structure due to crosslinking during the prebake.

EXPERIMENTAL

Preparation of resist polymers

Poly(α-methylstyrene-*co*-methyl methacrylate) (PMSt–MMA), C21 and C39, and poly(α-methylstyrene-*co*-methyl methacrylate-*co*-*N*-methylolated methacrylamide) (PMSt–MMA–MAAm), T24-1.2 and T38-0.1–T38-0.9, were prepared by emulsion polymerization at 80°C with $K_2S_2O_8$ as initiator. These polymers were fractionated from a tetrahydrofuran/hexane system. PMSt–MMA–MAAm, T37-1.2, T37-1.3 and T37-1.7, was prepared by emulsion polymerization of α-methylstyrene, methyl methacrylate and methacrylamide at 80°C with $K_2S_2O_8$ and *N*-methylolation in tetrahydrofuran with a formaldehyde solution in n-butanol in the presence of maleic anhydride, and fractionated from a tetrahydrofuran/hexane system.

The copolymerization ratio in moles was estimated by elementary analysis, $\bar{M}_n$ and $\bar{M}_w$ were estimated by gel permeation chromatography (g.p.c.) and T_g by differential scanning calorimetry (d.s.c). The polymer data are summarized in *Table 1*.

Table 1 Summary of polymer data

Polymer		MSt:MMA:MAAm (mol ratio)	$10^{-4}\times$ $\bar{M}_w$	MWD M_w/M_n	T_g (°C)
Copolymer	C21	21:79	31.9	2.14	152
	C39	39:61	64.5	1.90	157
Terpolymer	T24-1.2	24.3:74.6:1.2	34.8	2.59	156
	T38-0.1	37.7:62.2:0.1	51.9	1.72	
	T37-0.2	37.0:62.8:0.2	50.3	2.23	
	T39-0.4	38.7:60.9:0.4	63.2	1.82	
	T39-0.7	38.6:60.7:0.7	64.8	3.85	166
	T38-0.9	37.5:61.6:0.9	49.0	1.85	
	T37-1.2	37.0:61.9:1.2	40.8	2.11	158
	T37-1.3	37.0:61.7:1.3	53.1	2.56	
	T37-1.7	37.1:61.3:1.7	41.6	1.88	

Film preparation and thickness measurement

Resist films around 4000 Å thick were prepared by spin-coating at about 2800 rev min^{-1} from toluene solutions on copper-evaporated glass plates or silicon wafers. The films without MAAm were prebaked in an air-circulating oven at 180°C for 20 min, and those containing MAAm were prebaked at 200°C for 60 min. After the latter prebake, thickness reduction of the film was not observed on dipping in MIBK at 25°C for 90 s, due to network structure formation or a molecular weight increase caused by the thermal crosslinking of MAAm units incorporated in the polymer chain.

To study EB exposure characteristics, the specimen was exposed in the way described below, developed by dipping in a developer without agitation, rinsed with IPA and postbaked at 140°C for 20 min. The developed depth was measured with an interference microscope, Nikon Surface Finish Microscope, after evaporating aluminium onto the surface of the specimen. The initial thickness of the resist film and the thickness reduction in the unexposed area during development were measured in the same way after partial scratching.

Electron beam exposure characteristics

A wide area (2.0 mm diameter) of the resist film, which was prepared as described above, was exposed through a mesh mask uniformly to the electron flux emitted from a filament and accelerated at 4 kV (flood exposure). The mesh pattern was transferred to the resist, and the depth, which was the difference of the film thicknesses between the exposed and the unexposed areas after development, was plotted against the logarithm of varying dose to get the characteristic curve. A more detailed description of the apparatus was given in a previous paper[6].

The conventional method of expressing sensitivity and contrast is not suitable for the resist system accompanied by thickness reduction, and moreover, it cannot be free from the influence of the initial thickness of the resist. The sensitivity was obtained here as the critical dose required just to remove the last trace of resist film in the exposed area by development of the resist film of thickness 4000 Å, and is denoted by D^{4000}. The contrast, γ, was determined as usual from the slope of the normalized characteristic curve, in which the depth was normalized to the remaining thickness in the unexposed area[17]. When the film was thicker or thinner than 4000 Å, D^{4000} and γ were calculated by the method described previously[6].

In addition, γ' was calculated from the slope of a straight line directly connecting the toe (the dose which started to solubilize the resist film) with the shoulder (the saturated depth of 4000 Å, which was obtained by development after EB exposure to the critical dose, D^{4000}) of the characteristic curve. When the tail was negligible and the shoulder was angular, γ' was substantially equal to γ, but γ' was generally smaller than γ for the S-shaped characteristic curve accompanied with some tail and round shoulder.

RESULTS AND DISCUSSION

Sensitivity enhancement by force development

EB exposure characteristic curves were measured with the terpolymer and the copolymer resists under various developing conditions much stronger than the standard for PMMA. These conditions were, in strengthening order, with neat MIBK at 25°C for 90 s (MIBK 25°C 90 s) < MIBK 35°C 90 s < 3:1 (by volume) mixed solvent of MIBK and tetrahydrofuran (MIBK(3) + THF(1)) 25°C 450 s < MIBK(3) + THF(1) 35°C 600 s ≈ methyl ethyl ketone (MEK) 25°C 90 s. The results are summarized in *Table 2*.

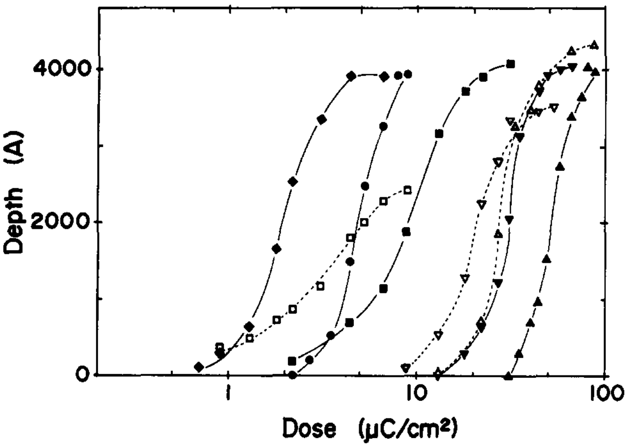

Figure 1 Effect of crosslinking and developing conditions on the characteristics of T24-1.2 (———) and C21 (– – –) developed with MIBK 25°C 90 s (▲, △), MIBK 35°C 90 s (▼, ▽), MIBK(3) + THF(1) 25°C 450 s (■, □), MIBK(3) + THF(1) 35°C 600 s (◆) and MEK 25°C 90 s (●)

Since the sensitivity of MSt–MMA copolymer resists depended on the MSt content[6], the terpolymer containing MSt, MMA and MAAm was compared with the copolymer of similar MSt content. The characteristic curves obtained for T24-1.2 and C21 are shown in *Figure 1*. The terpolymer, T24-1.2, containing 24 mol % MSt and 1.2 mol % MAAm, was loosely crosslinked by the aid of mutual thermal condensation between the methylol groups during the prebake. The copolymer, C21, was a linear polymer containing 21 mol % MSt. When they were compared under the same developing conditions, T24-1.2 showed a little lower sensitivity than C21. Virtually no thickness reduction was observed with T24-1.2 by development under these conditions. C21 decreased in thickness by 1300 Å after development with MIBK(3) + THF(1) 25°C 450 s and completely dissolved away after development with MIBK(3) + THF(1) 35°C 600 s, while T24-1.2 withstood these developing conditions and showed sensitivities of 22 and 4.5 μC cm^{-2}, respectively. That is, when serious thickness reduction in the unexposed area was restrained by crosslinking, it was possible to enhance the sensitivity by force development.

The curves for T39-0.7 and C39 are shown in *Figure 2*. Similarly T39-0.7 showed lower sensitivity than C39 under the same developing conditions. The sensitivity of T39-0.7 was enhanced up to 5.9 μC cm^{-2}, as the developing conditions became strong. Surprisingly, after development with MIBK(3) + THF(1) 35°C 600 s, C39 did not dissolve away but decreased in thickness by 280 Å, which was as small as the decrease with T39-0.7, and a very high sensitivity of 3.3 μC cm^{-2} was attained. This was ascribed to the high molecular weight (MW) and narrow molecular weight distribution (MWD) of C39, compared with those of C21. Accordingly, if MW is high and MWD is narrow enough to keep the dissolution rate in the unexposed are a very low, quite strong developing conditions can be applied to linear polymer to get high sensitivity.

In this way the sensitivity of the dry-etching durable MSt copolymer resist was enhanced about 20 times, up to the order of several μC cm^{-2}, by force development, even though the accelerating voltage employed here was low (4 kV).

Table 2 Sensitivity[a], contrast γ and γ', and thickness reduction[b]

	MIBK 25°C 90 s			MIBK 35°C 90 s			MIBK(3)+THF(1) 25°C 450 s			MIBK(3)+THF(1) 35°C 600 s				MEK 25°C 90 s		
Polymer	D^{4000}	γ	γ'	D^{4000}	γ	γ'	D^{4000}	γ	γ'	D^{4000}	γ	γ'	TR	D^{4000}	γ	γ'
C21	46	2.5	1.9	37	2.1	1.8	22	0.8	0.8[c]		–	–	–[d]	–	–	–[d]
T24-1.2	79	3.3	2.4	56	4.2	1.6	22	1.7	0.9	4.5	1.8	1.2	0	7.9	2.4	2.1
C39	64	2.5	2.0	49	3.3	1.7	7.1	1.5	1.1	3.3	1.4	1.0	280	4.1	1.2	0.6[e]
T38-0.1	78	3.3	2.6	55	3.0	2.2	15	1.5	1.2	7.6	1.1	1.0	240[e]	9.1	1.6	1.6
T37-0.2	93	3.8	2.0	64	3.1	1.8	37	1.5[e]	1.2	13	1.4	1.2	300	23	1.7	–[e]
T39-0.4	91	3.3	2.1	56	3.1	2.2	20	1.7	1.2	7.1	1.6	1.3	110	11	1.9	1.7
T39-0.7	74	3.2	2.2	53	2.5	1.7	21	1.7	1.0	5.9	1.0	0.8	300	11	1.8	1.3
T38-0.9	75	3.5	2.3	54	3.6	2.1	33	1.4	1.1	14	1.6	1.0	160	14	1.8	1.5
T37-1.2	110	5.0	2.3	66	2.9	2.1	53	2.4	1.1	42	1.7	1.0	160	22	2.5	1.9
T37-1.3	110	4.0	1.8	76	3.4	1.7	46	1.9	1.2	46	1.8	1.0	200	37	3.0	1.7
T37-1.7	110	3.8	1.8	75	3.2	1.8	67	2.5	1.0	46	1.4	1.0	0	46	2.2	1.2

[a] D^{4000} in μC cm^{-2}
[b] TR in Ångström
[c] TR = 1300 Å
[d] Dissolved
[e] Swelled

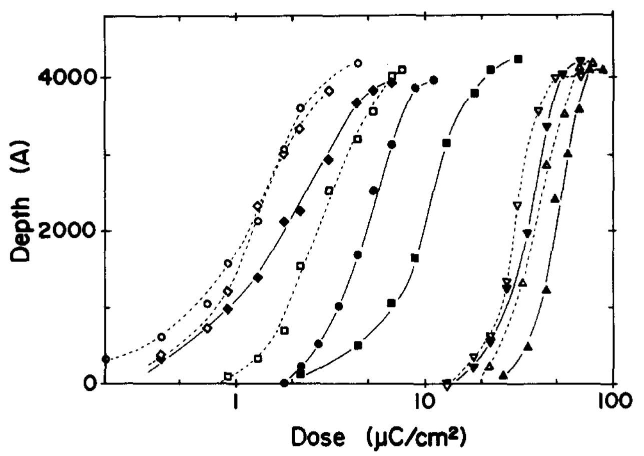

Figure 2 Effect of crosslinking and developing conditions on the characteristics of T39-0.7 (———) and C39 (- - -) developed with MIBK 25°C 90 s (▲, △), MIBK 35°C 90 s (▼, ▽), MIBK(3)+THF(1) 25°C 450 s (■, □), MIBK(3)+THF(1) 35°C 600 s (◆, ◇) and MEK 25°C 90 s (●, ○)

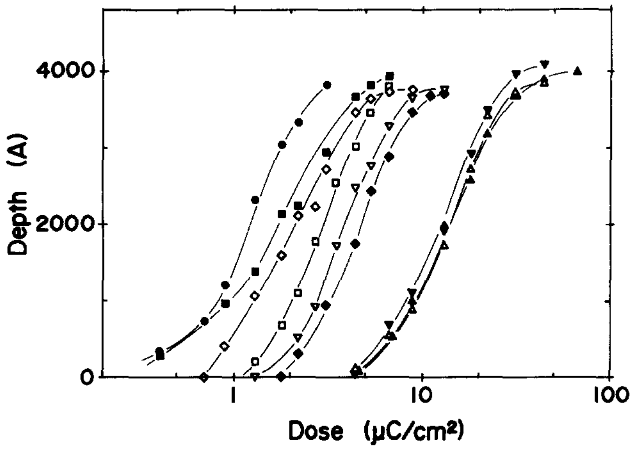

Figure 3 Effect of MAAm content on the characteristics of PMSt–MMA, C39 (●), and PMSt–MMA–MAAm, T38-0.1 (◇), T37-0.2 (◆), T39-0.4 (□), T39-0.7 (■), T38-0.9 (▽), T37-1.2 (▼), T37-1.3 (△) and T37-1.7 (▲), developed with MIBK(3)+THF(1) 35°C 600 s

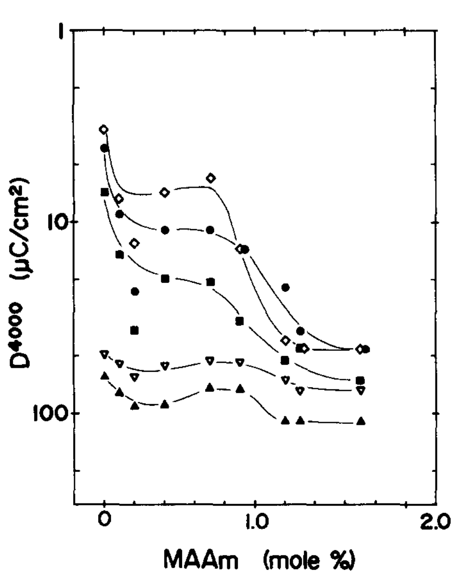

Figure 4 Effect of MAAm content on sensitivity enhancement by force development with MIBK 25°C 90 s (▲), MIBK 35°C 90 s (▽), MIBK(3)+THF(1) 25°C 450 s (■), MIBK(3)+THF(1) 35°C 600 s (◇) and MEK 25°C 90 s (●)

Effect of crosslinking density on EB exposure characteristics

The characteristic curves were obtained with terpolymers containing 37–39 mol% MSt and various amounts of MAAm under the developing conditions mentioned above. The curves developed with MIBK(3)+THF(1) 35°C 600 s are shown in *Figure 3* together with that of C39. The linear copolymer and the loosely crosslinked terpolymers which contained <1.0 mol% MAAm showed sensitivity $>15\,\mu\mathrm{C\,cm^{-2}}$, while the sensitivity of the terpolymers crosslinked with >1.0 mol% MAAm was found to be ≈ 40–$50\,\mu\mathrm{C\,cm^{-2}}$.

The sensitivity D^{4000} is plotted against MAAm content in *Figure 4*. This figure clearly indicates that: as the MAAm content increased, the sensitivity decreased gradually; force development, such as development with MIBK(3)+THF(1) 25°C 450 s, MIBK(3)+THF(1) 35°C 600 s and MEK 25°C 90 s, was effective in enhancing the sensitivity of the copolymer and the terpolymers which were loosely crosslinked with <1.0 mol% MAAm; the terpolymers crosslinked with >1.0 mol% MAAm were hardly enhanced in sensitivity by force development; the highest sensitivity was attained with C39 as long as the unexposed area withstood the developing conditions by virtue of high MW and narrow MWD.

The contrast γ observed after development with MIBK 25°C 90 s and with MIBK 35°C 90 s was >2.5, which was the value for PMMA developed by the standard developer. When stronger developing conditions were applied, γ of the terpolymers crosslinked with >1.0 mol% MAAm was kept high or moderate, while that of the copolymer and the loosely crosslinked terpolymers decreased in exchange for an increase in sensitivity. In particular, when sensitivity was enhanced higher than $10\,\mu\mathrm{C\,cm^{-2}}$ by force development, γ was observed to be between 1.0 and 1.6, and $\gamma' \approx 1.0$. Therefore, a problem which remains to be solved in the future is how contrast decrease by force development may be overcome.

Highest sensitivity of crosslinked positive-working resists attainable under the most suitable developing conditions

The calculation of critical sensitivity described below was based on the method presented by Charlesby[18]. It was also based on the assumption that the probability of chain scission was approximately equal to or smaller than that for linear PMMA, since the number of crosslinkable groups was much less than one fiftieth of linear monomer units and the MSt units were isolated in the polymer chain on account of the poor homopolymerizability by radical species and may or may not lower the scission yield of PMMA (G-value for PMSt is 0.23–0.25 [19]). Then the G-values for scission employed in this calculation were 2.2 and 1.3, which were the highest and the lowest values for PMMA in the literature, respectively[19,20].

First, averaged molecular weight between the points of crosslinking, $\bar{M}_c$, was calculated from the composition and $\bar{M}_w$ of the terpolymer, assuming that all crosslinkable groups had worked as crosslinking sites (see Appendix 1 and *Table 3*). Second, the lowest weight-averaged MW after scission, $\bar{M}'_w$, caused by various doses of EB exposure was calculated for the present experimental conditions with approximations of 100% energy absorption and chain scission probability equal to PMMA (see Appendix 2 and *Table 3*).

Table 3 MW between crosslinking points, $\bar{M}_c$, and MW after scission, $\bar{M}'_w$

			Dose[a]								
			1, 1.7	1.5, 2.5	2, 3.4	3, 5.1	4, 6.8	6, 10.2	8, 13.5	10, 17	15, 25
Polymer	$10^{-4} \times \bar{M}_w$	$\bar{M}_c$					$\bar{M}'_w$				
T38-0.1	51.9	106 800	87 000	61 400	47 500	32 700	24 900	16 900			
T37-0.2	50.3	53 500	86 600	61 200	47 400	32 600	24 800	16 800			
T39-0.4	63.2	26 800	89 700	62 800	48 300	33 000	25 100	17 000	12 800		
T39-0.7	64.8	15 300	90 000	62 900	48 400	33 100	25 100	17 000	12 800	10 300	
T38-0.9	49.0	11 900		61 000	47 200	32 500	24 800	16 800	12 700	10 200	6900
T37-1.2	40.8	8 900			46 300	32 100	24 600	16 700	12 700	10 200	6900
T37-1.3	53.1	8 200				32 700	24 900	16 900	12 800	10 300	6900
T37-1.7	41.6	6 300					24 600	16 700	12 700	10 200	6900

[a] Dose in μC cm^{-2}: for first values, $G_s = 2.2$, for second values, $G_s = 1.3$

Table 4 Highest sensitivity[a] attainable under the most suitable developing conditions

Polymer	$G_s = 2.2$	$G_s = 1.3$
T38-0.1	0.8	1.3
T37-0.2	1.7	3.0
T39-0.4	3.7	6.3
T39-0.7	6.7	11
T38-0.9	8.6	15
T37-1.2	12	19
T37-1.3	13	21
T37-1.7	16	28

[a] Dose in μC cm^{-2}

To solubilize the resist polymer in the exposed area, the necessary condition is more frequent occurrence of scission events than crosslinking density, i.e. $\bar{M}_c > \bar{M}'_w$. As the sensitivity of positive-working resists depends mainly on the change of dissolution rate before and after EB exposure, the condition $\bar{M}_c = \bar{M}'_w$ gives the highest sensitivity which is attainable under the most suitable developing conditions[21]. The results shown in *Table 4* indicate that a sensitivity $> 10\,\mu$C cm^{-2} is attained only by the loosely crosslinked resist containing < 1.0 or 0.6 mol % crosslinking sites in the case of $G_s = 2.2$ or 1.3. The necessary condition is the same as that employed by Suzuki and Ohnishi, but the results in *Table 4* are quite different from theirs[21]. This is probably because of some other differences in the experimental conditions and the assumptions, but their paper contained no detailed description of them.

So far, several or several tens of mol % of crosslinkable groups have been incorporated in the polymer chain of positive-working EB resists, e.g. poly(methyl methacrylate-co-methacrylic acid), poly(methyl methacrylate-*co*-methacryloyl chloride) and poly(methacrylonitrile-*co*-methacrylic acid) with or without crosslinking agent, and sensitivity has been reported to be as high as 3–20 μC cm^{-2} after force development[3,21–24]. When these results are compared with ours, we wonder if the crosslinkable groups such as methacrylic acid and methacryloyl chloride are not so reactive and do not work effectively as the crosslinking site.

Function of crosslinkable groups incorporated in the polymer chain

It is impossible to attain the highest sensitivity by actual development, so a dose higher than that calculated will be required to solubilize the polymer in the exposed area. Conversely, the crosslinkable groups will form crosslinkages in a definite yield $< 100\%$, and $\bar{M}_c$ will be larger than the calculated value, which will lower the critical dose for solubilization. Even though the actual development and the definite yield of crosslinking are considered together with the results of calculation, the effect of crosslinking density on the sensitivity which is indicated in *Figure 4* is outstanding.

Little contribution of force development to sensitivity enhancement seems to be due to the fact that crosslinking density in the terpolymer containing > 1.0 mol % MAAm was much larger than the occurrence of scission events caused by a small dose of EB exposure, e.g. $< 10\,\mu$C cm^{-2}. The density should then be kept small enough not to increase the EB dose required for solubilizing the polymer in the exposed area.

Successful results of sensitivity enhancement were obtained for linear copolymer with high MW and narrow MWD, and for loosely crosslinked terpolymers containing < 1.0 mol % MAAm. This was probably ascribed to the thickness reduction restriction in the unexposed area which was brought about by MW increase, rather than formation of network structure, as a result of thermal crosslinking of MAAm units. Therefore, it is worth noting that *in situ* crosslinking during prebake may be reviewed as a method of increasing MW of the resist polymer to be EB-exposed which restrains the thickness reduction in the unexposed area.

CONCLUSIONS

The sensitivity of MSt–MMA copolymer resist, the plasma-etching durability of which was as large as that of PMSt homopolymer, was enhanced about 20 times, up to 3.3–5.9 μC cm^{-2}, by force development. These values were observed at an accelerating voltage of 4 kV, but it is obvious that high sensitivity of the order of several μC cm^{-2} was attainable even if the voltage is raised up to 20 kV.

Force development was effective in enhancing the sensitivity, when thickness reduction in the unexposed area was restrained in the case of loosely crosslinked terpolymer or linear copolymer with high MW and narrow MWD. Terpolymers containing > 1.0 mol % crosslinkable groups were hardly sensitized by force development, because crosslinking increased the EB dose required for solubilizing the polymer in the exposed area.

EB exposure characteristics of positive-working resists depends on dissolution kinetics concerning each combination of the resist polymer and the developer, so correlation between sensitivity and contrast should be studied systematically under various developing conditions. As long as compared within the scope of this study, a new trade-off relationship was found between sensitivity and contrast obtained by force development.

The *in situ* crosslinking during prebake is regarded as a method of increasing the MW of the resist polymer to be EB-exposed.

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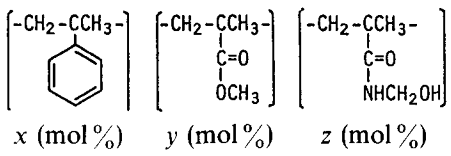
APPENDIX 1 MW BETWEEN CROSSLINKING POINTS

Terpolymer:



Monomer formula weight:

C_9H_{10}, 118; $C_5H_8O_2$, 100; $C_5H_9O_2N$, 115

Averaged formula weight:

$$FW = 118(x/100) + 100(y/100) + 115(z/100)$$

Assuming all crosslinkable groups work as crosslinking sites, the number of crosslinking points per $\bar{M}_w$ is:

$$\delta = (\bar{M}_w/FW) \times (z/100)$$

MW between crosslinking points:

$$\bar{M}_c = \bar{M}_w/\delta = FW \times 100/z$$

APPENDIX 2 WEIGHT-AVERAGED MW AFTER SCISSION

If accelerating voltage, $V_a = 4\,kV$, polymer density, $d = 1.2\ g\,cm^{-3}$, resist thickness, $t = 4000\ Å = 4 \times 10^{-5}\ cm$, D is dose in $\mu C\,cm^{-2}$, G_s is scission events per 100 eV absorbed energy, Q is electron charge ($= 1.6 \times 10^{-19}$ C), N is Avogadro's number ($= 6.0 \times 10^{23}$) and we approximate the energy absorption by the resist film 4000 Å thick as 1.00, since the Grün range of PMMA is calculated to be 4300 Å[12], then incident energy per unit area:

$$E_{in} = D \times 10^{-6} \times V_a/Q \qquad (eV/cm^2)$$

number of scissions per $\bar{M}_w$:

$$N_s = [(DV_a/Q) \times 10^{-6} \times G_s/100] / \{[dt/(\bar{M}_w/2)] \times N\}$$

$$= 4.34 \times 10^{-6} \times DG_s\bar{M}_w$$

and weight-averaged MW after scission:

$$\bar{M}'_w = \bar{M}_w/(1 + N_s)$$