

A new class of positive electron beam resists: methyl methacrylate–styrene and butyl methacrylate–styrene comb copolymers

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Electron beam sensitivity and plasma etch resistance measurements are presented on a series of comb copolymers synthesized from methyl methacrylate and butyl methacrylate with a methyl methacrylate-terminated styrene macromer. It is observed that, with a suitable selection of the ratio of the concentrations of the monomers in the copolymers and also of the molecular weight of the pendant groups, a resist material can be obtained with characteristics similar to those of the positive homopolymer, but with significantly different plasma etch resistance properties. The comb copolymers based on a butyl methacrylate backbone are significantly faster than the equivalent materials with methyl methacrylate backbone. The plasma etch resistances of the combs are significantly better than that for poly(methyl methacrylate) and are comparable to that for polystyrene. These resists have the potential of enhanced plasma etch resistance whilst still retaining the advantageous qualities of a positive acting material.

(Keywords: positive resists; electron beam resists; methyl methacrylate–styrene copolymers; butyl methacrylate–styrene copolymers; plasma etch resistance; comb copolymers; chain scission; chain crosslinking)

INTRODUCTION

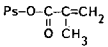
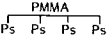
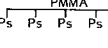
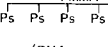
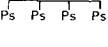
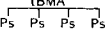
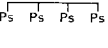
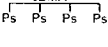
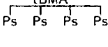
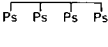
Most of the successful molecular architectures for positive electron beam resists are based on methyl methacrylate copolymer structure^{1,2}. The intrinsic sensitivity of the basic methyl methacrylate structure can be enhanced by the incorporation of methacrylic acid and/or methacryloyl chloride into the polymer backbone, which after prebaking generates anhydride linkages³. A wide variety of copolymers have been studied¹, including copolymers containing a wide variety of chemical functions, and from these certain systems have been selected for further study because of either their sensitivity or their ability to generate high-resolution lithography. In general, the most successful resists are the simplest and are based on the methyl methacrylate–methacrylic acid–methanhydride copolymer structure. The ideal positive electron beam resist should to some extent satisfy the following criteria:

- (i) the polymer should, on irradiation with an electron beam, undergo chain scission to produce exposed areas of low-molecular-weight, readily soluble resist;
- (ii) the polymer should be capable of being spun to give a pinhole-free film of between 0.5 and 1 μm ;
- (iii) the resist should be able to withstand degradation by various types of chemical and gaseous plasma etching reagents; and
- (iv) the solvent development process must lead to pattern generation without lift-off at the profile edges, swelling or solvent resist thinning.

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Current positive resist materials suffer from limitations in terms of adhesion of the polymer to the substrate, and/or poor plasma etch resistance. In contrast, negative resists are more susceptible to resist thinning–swelling, but usually have good plasma etch resistance. It has been shown recently⁴, by examination of a wide range of polymers, that plasma etch resistance can be achieved by incorporation of aromatic or silicon groups into a resist. Previously, we have investigated the effects of copolymerizing styrene with methyl methacrylate and observed that increasing the aromatic content leads to a reduction in the sensitivity and contrast, the resist eventually becoming negative and attaining the properties of polystyrene. A similar study of these copolymers has indicated that the resistance to plasma etching is increased⁵ by the incorporation of styrene. It is found that, once a minimum composition of 20% has been achieved, there is little or no increase in the plasma etch resistance. An alternating copolymer of styrene and methyl methacrylate was found to have approximately the same sensitivity as the random copolymer, but has about twice the contrast⁶, indicating that the stereochemistry around the radical site formed on scission can have a major effect on the radiation chemistry occurring in this type of resist. Consideration of this and related data has led us to propose that the criteria indicated above for the generation of an ‘ideal’ positive resist might be achieved by use of a ‘comb’ copolymer structure, and our observations on two selected systems are presented in this paper.

Table 1 Structure, molecular weight and electron beam characteristics of the resist materials

Code	Polymer structure	Number of arms	Molecular weight of macromer, M_n	Ratio of methyl methacrylate to macromer	Molecular weight of copolymer	Composition of development solvent mixture ^a	Sensitivity ($\mu\text{C cm}^{-3}$)	Contrast
R1		—	10^4	—	10 000		7000	2.1
R2	PMMA	—	—	—	80 000	25% MIBK/IPA	440	3.5
R3	Ps-PMMA-Ps	—	—	—	33 000	20% Tol/IPA	1000	0.77
R4		3-4	10^4	100:1	44 000	20% Tol/Ch	460	2.9
R5		5	10^4	50:1	52 000	20% Tol/Ch	960	0.8
R6		6	10^4	25:1	60 000	20% Tol/Ch	880	1.18
R7		4	10^4	100:1	77 000	20% Tol/Ch	31	2.0
R8		4	10^4	25:1	66 000	20% Tol/Ch	Negative image	—
R9		4	4×10^2	50:1	60 000	20% Tol/Ch	63	1.5
R10		4	4×10^2	25:1	27 000	20% Tol/Ch	Negative image	—
R11		4	4×10^4	100:1	55 000	20% Tol/Ch	No image	—
R12		4	4×10^2	100:1	37 000	20% Tol/Ch	50	1.4

^a MIBK, methyl isobutyl ketone; IPA, isopropyl alcohol; Tol, toluene; Ch, cyclohexane

EXPERIMENTAL

Synthesis of copolymers

The method of synthesis depends on the nature of the structure to be prepared.

Di- and triblock copolymers. An anionic mechanism was used and involved the addition of 2 g of styrene to approximately 20 ml of tetrahydrofuran; the mixture was then thoroughly degassed—by the application of a freeze-thaw method to the mixture under partial vacuum. The reaction mixture was cooled with a Drikold and acetone mixture; to the resultant solution was added *t*-butyllithium and the reaction was allowed to proceed for 1 h. At this point 1,1-diphenylethene was added to change the reactivity of the living site to produce a less reactive one.

A more reactive anion would react with the ester group of the methyl methacrylate as well as the double bond and hence lead to the production of a crosslinked product. Methyl methacrylate was then added to the reaction mixture and the vessel left overnight for completion of the reaction. When a triblock was required, additional styrene was added approximately 1 h after the addition of the methyl methacrylate, leading to the formation of a third block in the polymer structure. The reaction was terminated in both cases by the addition of methanol, which is both a terminating agent and a non-solvent, and led to precipitation of the block copolymer.

Comb copolymer structure with more than two pendant groups. The method used was different from the above and involved radical copolymerization of methacrylate-terminated polystyrene (5 g) ($M_n = 10\,000$) with methyl methacrylate (1.7–5 ml) dissolved in 30 ml of toluene using 0.04–0.08 g of azobisisobutyronitrile (AIBN) in a sealed dilatometer, which was placed in a thermostat bath

for approximately 2–3 h. In the early stages of this study, the macromer was produced by generation of the ester from methacryloyl chloride and hydroxy-terminated polystyrene. Fortunately, a commercial source of the macromer subsequently became available and the polymers described in this paper were obtained using macromers obtained from Polyscience Co. and marketed under the tradename Sartomer. The polymer was then precipitated by pouring the reaction mixture into cooled methanol.

The unreacted macromer was removed by solvent extraction using warm cyclohexane (35–40°C), this process being repeated seven or eight times. Details of the conditions used in the synthesis and the resultant characteristics of the polymers are summarized in *Table 1*. The molecular weights were checked by gel permeation chromatography using tetrahydrofuran as the solvent and narrow-molecular-weight-distribution linear polystyrene and poly(methyl methacrylate) reference samples. The branched chain nature of the polymer led to differences between the calculated and observed molecular-weight data consistent with expected changes in the hydrodynamic volume on generation of the comb structure. The composition and level of branching in the polymer structure were determined using a combination of ^1H and ^{13}C n.m.r. and elemental analysis. The values obtained are summarized in *Table 1*.

Electron beam characterization

A solution of approximately 5% w/v of the polymer was produced by dissolving the copolymer in toluene and a thin film was produced by spinning the solution onto chromium-coated glass slides to give a 2000 Å thick resist film. The films were baked in an oven at 130°C for 1 h. The exposure was carried out using a modified electron

microscope, the dose being varied between 10 and $1000 \mu\text{C cm}^{-2}$ in equal steps. The apparatus and detailed procedure have been described elsewhere⁶. The sensitivity in this study is defined as the D_{100} value, the dose to clear down to the substrate for the positive resist, and D_0 , the dose to produce crosslinking for the negative resist. The contrast (γ) is defined as the ratio $\log_{10}(D_0/D_{100})^{-1}$. A wide range of solvents were used for the development of the pattern and included isopropyl alcohol, petroleum ether, diethyl ether and decane as non-solvents, and acetone, methyl ethyl ketone, methyl isobutyl ketone and toluene as solvents.

Many combinations of the above solvents and non-solvents were investigated. A mixture of 20% toluene in cyclohexane proved to be the best solvent mixture for pattern development with these copolymers. This solvent system is attractive as it does *not* contain components that are identified as potentially hazardous, a topic for concern with many of the current positive development systems. The solvent had no significant effect on unexposed areas, the development time was 2 min by dip development and the process was stopped by placing the wafer in cyclohexane. The films were then baked in an oven for several hours at 100°C . The effects of increase in the development time was studied and periods of 5, 10, 20, 30 and 60 min were used with no appreciable differences in the sensitivity being observed. The thickness-dose profile was obtained by use of a Decktac IIA surface profilometer.

Plasma etch resistance

The plasma etch resistance of the resists were determined using a Plasma Technology parallel-plate reactive-ion etcher. The films, deposited and baked as indicated above, were arranged in a mosaic of eight-by-eight slides. An area of approximately 50% of each slide was protected by covering part of the resist with a glass coverslip. The plasma mixtures and the conditions used in the exposure were those typically used in semiconductor processing. Part of the unexposed resist was removed by scraping with a blunt object to give a reference for measurement of the thickness in the exposed and unexposed areas. The etch rates were determined by measurement of the variation of the thickness as a function of time; typically five observations were made in attaining each data point.

RESULTS AND DISCUSSION

The underlying philosophy behind the development of these new resists was the desire to be able to increase the plasma etch resistance of a positive acting electron beam resist. The comb copolymer presents the following potential advantages over a conventional resist:

(i) The pendant chains can be chosen to be insensitive at the electron beam doses used to expose the main backbone and hence allow the design of a resist with either plasma etch resistance or enhanced adhesion to the substrate without the added functions participating in the initial radiation chemistry.

(ii) The ratio of the length of the chain forming the backbone relative to that of the pendant group can be altered so as to influence the sensitivity of the resist material to electron beam exposure and plasma etching.

(iii) Degradation of the backbone will lead to

fragments of narrower molecular-weight distribution than in the normal scission process, because in these comb copolymers the molecular weight of the scission product is dominated by that of the pendant group.

(iv) We would also anticipate that both topological and thermodynamic factors influenced by the compositional differences between the comb and the linear product of exposure would allow marked differences to be found between the response to solvents used for the film deposition and development. This is a more advantageous situation than that usually observed with positive resists, where the solvent used to spin the resist is very similar to that used in the development of the pattern.

Using the above philosophy, synthesis and electron beam characterization were undertaken of a range of comb copolymers with varying ratios of styrene to methyl methacrylate and also with different molecular weights of the styrene pendant chains. From these studies we were able to select the optimum structure for the 'comb' resist materials; however, as we will show, its sensitivity is rather poor. In order to increase the sensitivity, we have changed the backbone monomer, and these data form the second part of this study. The final section considers the relative plasma etch resistance of these comb resists.

Resists based on styrene-methyl methacrylate comb copolymer structures

Small additions of styrene into a methyl methacrylate polymer⁵ lead to a decrease in sensitivity and contrast; however, large additions lead to a reversal of the nature of the resist from being positive to having negative characteristics⁵. In order to design the comb resists, it was appropriate first to determine the characteristics of the macromer (R1) and of a free radically polymerized poly(methyl methacrylate) (PMMA) sample (R2). The macromer acted, as would be expected, as a negative resist and required a relatively high dose of $7000 \mu\text{C cm}^{-2}$ to achieve complete development (Figure 1). In contrast, the PMMA degrades with a dose to clearance of $440 \mu\text{C cm}^{-2}$ (Figure 1). The window of operation for the comb resists would therefore be expected to lie between these two limits.

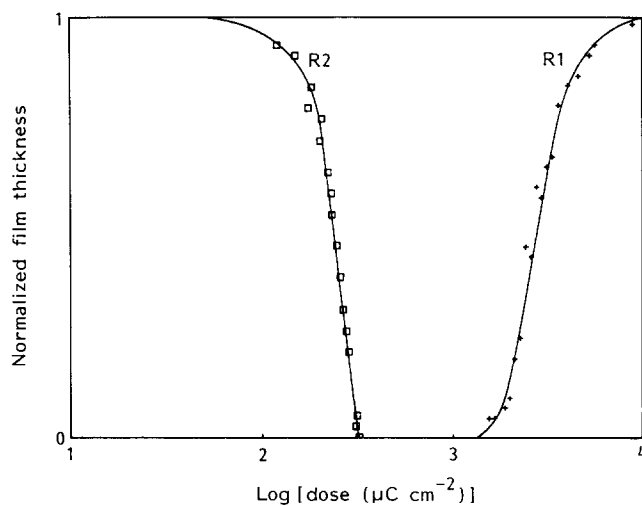


Figure 1 Electron beam exposure curves for the reference homopolymers

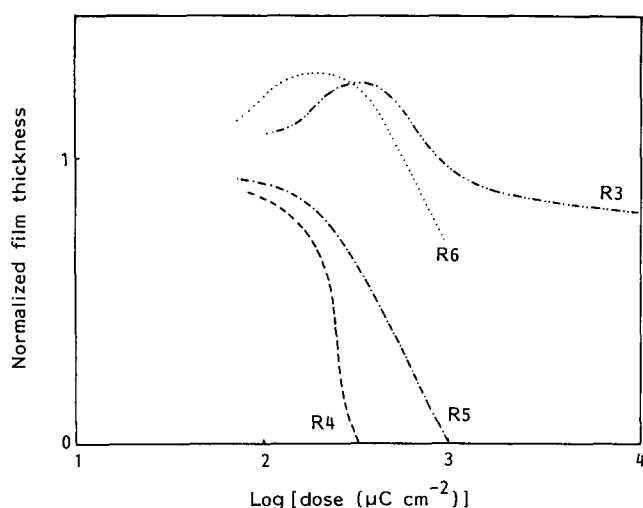


Figure 2 Electron beam exposure curves for comb copolymers

Exposure studies have been carried out on the copolymers and the data obtained are summarized in Table 1. The triblock copolymer (R3) exhibits behaviour that is characteristic of crosslinking as well as degradation. The initial increase in thickness is probably a consequence of crosslinking and despite the use of high doses the film thickness did not reduce below 70% of its initial value (Figure 2). The three- or four-arm comb copolymer (R4), in contrast, behaves as though it were a normal positive resist with a sensitivity of $460 \mu\text{C cm}^{-2}$ (Figure 2), which is little different from that of pure PMMA. The five-arm comb copolymer (R5) was slower than R4, and exhibited a loss in both sensitivity and contrast (Figure 2). The six-arm comb copolymer (R6), like the triblock copolymer, showed a tendency to crosslink before undergoing degradation (Figure 2). Once again the material was never completely developed as a positive resist and showed marked signs of negative resist behaviour. It therefore appears that the optimum behaviour in terms of a positive resist behaviour is achieved with the three- or four-arm comb copolymer. This study raises two points: first can one increase the basic sensitivity of the backbone to degradation, and secondly can we change the behaviour of the resist by changing the properties of the monomers present. In a parallel study, we have investigated the sensitivity of the poly(alkyl methacrylate) polymers to electron beam degradation and observed that an increase in sensitivity is achieved by converting the pendant group from methyl to *t*-butyl⁶. The second part of the study explores a group of comb resists based on the *t*-butyl methacrylate backbone structure.

Resists based on *t*-butyl methacrylate–styrene copolymers

In view of the results obtained on the methyl methacrylate–styrene comb copolymers, we chose to concentrate on resists with approximately four pendant groups. The equivalent of R4, a four-arm *t*-butyl methacrylate (tBMA) comb (R7) gave, as expected, a positive image and had a sensitivity of $31 \mu\text{C cm}^{-2}$. The ratio of the tBMA to styrene macromer in this comb is 50:1. A comb (R8) was prepared containing four arms but with a reduced ratio of tBMA to styrene macromer of 25:1. This comb exhibited negative resist behaviour, indicating the greater efficiency of the crosslinking in

comparison to the scission process. Another variation that was considered was to change the molecular weight of the macromer; the study detailed above had used a macromer with $M_n = 10\,000$, and in order to explore these effects comb copolymers were prepared with a macromer having $M_n = 4000$. The equivalent four-arm material with a monomer ratio of 50:1 (R9) gave a sensitivity of $63 \mu\text{C cm}^{-2}$, which is a significant reduction on the previous value of $31 \mu\text{C cm}^{-2}$. Once more, change of the monomer ratio to a value of 25:1 (R10) leads to a negative image being obtained. Adjustment of the monomer ratio in the opposite direction, to a value of 100:1, gave for the 10000 M_n comb (R11) no effective image and for the 4000 M_n (R12) a positive image with sensitivity $50 \mu\text{C cm}^{-2}$. It appears from these data that, as initially anticipated, there exists a narrow window of composition in which useful positive resist behaviour can be observed and that the optimum resists exhibit sensitivities close to those of the parent backbone copolymer.

A wide range of solvent mixtures were investigated for these systems and included cyclohexane/isopropyl alcohol, in varying proportions. It was observed that the development characteristics and also sensitivities were markedly influenced by the composition of the mixture. Change of the composition could lead to non-development of an image; R9 with 20% cyclohexane/isopropyl alcohol gave a film with positive character and sensitivity of $60 \mu\text{C cm}^{-2}$, whereas with 30% cyclohexane/isopropyl alcohol the sensitivity was reduced to $75 \mu\text{C cm}^{-2}$ and the resist never really cleared down to the substrate. Similar characteristics were observed with the rest of these materials. Once more, as indicated initially, the comb resists are extremely sensitive to the development procedure used and preliminary results appear to indicate that resists behave differently in hand and spray development systems.

Plasma etch resistance

The main objective behind the development of these resist materials was to improve the plasma etch resistance of positively acting resists. Selected examples of these and related polymers were subjected to examination using a variety of different types of plasma (Table 2). In order to provide comparisons, we have included in the list of polymers examined polystyrene, poly(methyl methacrylate) and certain poly(ethyl methacrylates). The plasmas used are those conventionally used for semiconductor processing. Etching SiO_2 is achieved at a rate of 250 \AA min^{-1} by a mixture of CHF_3 and argon. Gallium arsenide is etched by SiCl_4 . Silicon and silicon nitride are etched by nitrogen trifluoride (NF_3), whereas NF_3/HCl is used as an etch for aluminium, and chromium is etched by oxygen/chlorine mixtures. The resist films studied were between 1500 and 2000 \AA thick.

Comparison of the poly(alkyl methacrylates) with poly(phenyl methacrylate) indicates that the introduction of a phenyl group into the side chain increases the plasma etch resistance and produces a value that approaches that observed with polystyrene. As anticipated initially, it was observed that the comb copolymers all exhibit plasma etch resistance rates comparable to those of polystyrene, indicating that their resistance to plasma treatment is comparable to that of a negative resist rather than that typically obtained for a positive resist.

Table 2 Plasma etch resistance of comb and related resists

Code	Polymer	Plasma etch resist rate ($\text{\AA} \text{ min}^{-1}$)				
		CHF_3/Ar	NF_3	SiCl_3	O_2/Cl_2	NF_3/HCl
R1	Poly(methyl methacrylate)	1450	1990	100	195	275
	Poly(ethyl methacrylate)	1200	—	200	—	—
	Poly(phenyl methacrylate)	800	—	60	—	—
	Poly(<i>t</i> -butyl methacrylate)	1000	1400	—	200	250
R2	Polystyrene (low M_n)	500	—	60	60	—
R4	4-arm PMMA, comb	400	900	60	50	220
R7	4-arm tBMA, comb	650	1150	65	95	230
R3	3-arm PMMA, comb	—	1350	80	130	250

CONCLUSIONS

This paper describes the electron beam characteristics of a new range of electron beam resists based on a comb copolymer structure. By optimizing the ratio of the monomers present and also the molecular weight of the pendant group, it is possible to design a copolymer with sensitivity close to that of the parent positive resist structure. Choice of an insensitive but plasma-etch-resistant side chain such as polystyrene allows the development of a material that has a high plasma etch resistance. The data presented in this paper indicate the potential of these polymers as effective and attractive electron beam resists, and it is hoped that further studies on these materials may lead to their commercial exploitation as plasma-etch-resistant positive resists.

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