Electron-beam-resist materials with enhanced dry etch resistance

Stanley Affrossman, Hassan Angadji, Masood Bakhshaee, Kathleen Coffey, Fong Lung Chow, David Hayward, Gordon G. McLeod, Richard A. Pethrick* and Paul Whittaker

Department of Pure and Applied Chemistry, University of Strathclyde, Cathedral Street, Glasgow G1 1XL, UK

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Electron-beam evaluation is reported for a series of polymer resists designed to enhance their dry etch resistance. Three systems are discussed: styrene and methyl methacrylate copolymers; poly(methacryloyl chloride); and a series of silicon-containing polymers. Poly(methyloyl chloride) as a resist has a very poor plasma etch resistance; however, significant improvement can be obtained either by pretreatment with phenol or aniline, in which case there is a substantial decrease in electron-beam sensitivity, or by post-treatment with aniline or silane modifiers. This paper reports measurements on these systems and identifies ladder polysilsesquioxane polymers as resists with good dry etch resistance. They have the potential for improvement of their sensitivity to an acceptable level for microlithography.

(Keywords: electron-beam resist; plasma etch resistance; poly(methacryloyl chloride); comb copolymers; styrene–methyl methacrylate; polysiloxanes, polysilsesquioxanes)

INTRODUCTION

Integrated-circuit manufacture employs at various stages a variety of reactive environments and in particular the plasma enhanced deposition and etching processes. Dry etching is increasingly used as part of two-layer microlithography and in this instance oxygen reactive-ion etching (r.i.e.) is used to transfer the image from a thin imaging layer into an underlying thick planarizing layer. Ideally the top layer should be highly resistant to oxygen plasma etching and a variety of silicon-containing materials have been used in this context[1]. Studies on the plasma etch resistance of a wide range of materials have indicated that incorporation of phenyl ring or silicone structures substantially reduces the susceptibility of the resist to plasma etching[2]. Electron-beam resists are usually designed to optimize sensitivity, adhesion, contrast and resolution, and it is only relatively recently that plasma etch resistance has become of interest.

In this paper we consider three systems:

(i) a copolymer of styrene and methyl methacrylate,
(ii) poly(methacryloyl chloride) and its derivatives, and
(iii) certain polymers based on a silicone structure.

In a previous study of random and alternating styrene and methyl methacrylate copolymers[3], it was found that control of stereoregularity of the polymer backbone led to enhanced values of the contrast with little or no loss in sensitivity of the resist. It has also been shown by Moss that incorporation of as little as 20% of styrene in the copolymer leads to a substantial increase in the etch resistance[2]. On this basis a new family of resists based on a comb copolymer structure were designed; their electron-beam characteristics have been reported in a recent paper[4]. These polymers exhibit electron-beam sensitivities comparable to those of the backbone polymer and plasma etch resistance similar to those of the pendant macromer. In this paper we report additional data on these systems.

Roberts[5] has reported the use of poly(methacryloyl chloride) (PMAC) as an electron-beam resist. This polymer is extremely sensitive and appears to be capable of high-resolution lithography. In this study we initially extend the evaluation of the PMAC electron-beam-resist system and also explore the possible derivatization of this polymer to provide a resist that has inherent plasma etch resistance and does not require post-development treatment to enhance its etch resistance.

Silicone polymers are inherently etch-resistant, exposure to oxygen generating an impervious silicon oxide layer which has a very low etch rate[6]. Many of the polymers so far proposed have low glass transition temperatures and also form films which are difficult to remove after plasma treatment. In this paper we discuss the electron-beam characteristics of some alternative types of silicon-containing structures.

EXPERIMENTAL

Materials

The polymers were synthesized as described in the Appendix. The resists were reprecipitated and carefully filtered using a 1 μm millipore filter before being spun onto chrome-coated glass substrates to form approximately 1 μm thick, uniform, pinhole-free films.

Electron-beam and plasma exposure

The films were exposed using the system described previously[4]. The electron-beam exposure was achieved

* To whom correspondence should be addressed

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using a modified electron microscope. The exposures were computer-controlled and generated using a 32-element matrix. The dose curves were obtained from an analysis of the dose–thickness profiles obtained using a Dektak surface profile apparatus. Plasma etch profiles were obtained using a Plasma Technology reactive etch apparatus with a variety of gas mixtures. Etch rates were obtained by comparison of the thicknesses of resist in an exposed area and in a region covered by a glass coverslip[4]. The studies aimed at obtaining comparative data, and no attempt was made to optimize the plasma etch conditions.

RESULTS AND DISCUSSION

The study is divided into three sections, as follows.

Poly(styrene–methyl methacrylate) comb copolymers

The comb structure allows electron-beam sensitivity to be imported to the resist whereas the pendant low-molecular-weight styrene side-chain introduces phenyl groups which import plasma etch resistance. Data complementing those presented in a previous publication[4] are presented in *Table 1*. These measurements confirm the enhancement of plasma etch resistance previously observed for these materials.

Poly(methacryloyl chloride) and related copolymers

The use of poly(methacryloyl chloride) (PMAC) as an electron-beam resist has been described by Roberts[5]. In this study we report additional data on the effects of molecular weight on the electron-beam characteristics of PMAC. The method used for the synthesis of these polymers and their characteristics are summarized in *Table 2* and the Appendix. Films of the resist were prepared by spinning of a 5% solution of the polymer in methyl ethyl ketone (MEK) or chlorobenzene onto chrome-coated glass substrates. The solutions were initially clear, but after several weeks turned straw yellow and then dark brown. The resists evolved hydrogen chloride by slow hydrolysis of the polymer. The baked films were exposed and developed using a solution of 50% methyl isobutyl ketone (MIBK)/50% toluene for 30 s and then rinsed for 30 s with MIBK. The developed pattern was then baked before being examined using the surface profile monitor. The development procedure used was varied with molecular weight and the values of the sensitivity to electron-beam irradiation were also found to vary with the solvent used in casting the films (*Table 1*). The higher-boiling-point chlorobenzene may not be completely removed from the films and residual solvent could be inhibiting the degradation reaction by promoting a crosslinking side-reaction. The measurements using MEK spun films exhibit a small decrease in sensitivity to electron-beam irradiation with increasing molecular weight. The sensitivity was also found to be dependent upon the solvent system used: an initial development with MIBK followed by a mixture of MIBK/IPA (isopropyl alcohol) gave a slight increase in sensitivity. No attempt has been made to optimize the resist behaviour. The electron-beam sensitivity was found to be more dependent on the solvent development system rather than on the molecular weight of the resist.

Roberts[5] has described the post-treatment of PMAC with aniline and silanes to reduce their plasma etch susceptibility; it would be desirable to eliminate this post-development processing. In an attempt to simplify the development procedure, a sample of PMAC was treated with phenol and aniline prior to being deposited as a thin film. The PMAC was dissolved in toluene and refluxed with varying amounts of phenol or aniline for 2 h and the resultant solid analysed in the normal way. The results of these measurements are presented in *Table 3*. The lack of consistency in the variation of the sensitivity with amount of reagent is a result of the apparent inactivity of the PMAC. It was observed, by infra-red spectroscopic examination, that the resists obtained were either unsubstituted or almost completely reacted. Considerable effort was put into attempting to obtain partially substituted phenol or aniline PMAC, however with little success. Results for some partially substituted polymers are presented in *Table 3*. If it were possible consistently to produce partially substituted

Table 1 Plasma etch studies of poly(styrene–methyl methacrylate) comb copolymers

Polymer	Plasma etch rate for CCl_4/O_2 (nm min^{-1})
PMMA	320
PS	110
Four-arm PMMA–PS comb	95
Three-arm PMMA–PS comb	100

Table 2 Characteristics of poly(methacryloyl chloride)

Code	M_n	M_w	M_w/M_n	D_0 (μC cm^{-2})	γ	Development system
Films deposited with methyl ethyl ketone						
PMAC1	4758	7705	1.62	14	1.17	100% MIBK 30 s
PMAC2	13177	36174	2.75	16	2.9	75% MIBK/25% Toluene 60 s
PMAC3	15251	33094	2.17	18	2.2	30% MIBK/50% Toluene 30 s
PMAC4	24940	62798	2.52	19	1.5	50% MIBK/50% Toluene 45 s
PMAC5	30810	59511	1.93	18	1.7	50% MIBK/50% Toluene 40 s
PMAC6	33099	51973	1.57	18	1.4	50% MIBK/50% Toluene 30 s
PMAC7	46069	75099	1.63	22	1.5	50% MIBK/50% Toluene 60 s
Films deposited with chlorobenzene						
PMAC1	4758	7705	1.62	15	1.32	100% MIBK 30 s
PMAC2	13177	36174	2.75	33	0.85	50% MIBK/50% Toluene 45 s
PMAC4	24940	62798	2.52	31	2.1	50% MIBK/50% Toluene 60 s
PMAC5	30810	59511	1.93	43	2.5	50% MIBK/50% Toluene 15 s
PMAC3	15251	33094	1.57	8	2.9	MIBK 20 s; MIBK/IPA 15 s
PMAC6	33099	51973	1.59	6	2.3	MIBK 15 s; MIBK/IPA 20 s

MIBK = methyl isobutyl ketone, IPA = isopropyl alcohol

Table 3 Electron-beam characteristics of modified poly(methacryloyl chloride)

Concentration of reactant	D_{50} (μC cm^{-2})	γ	Comment
0	6	2.1	Unsubstituted
1 g PMAC/0.2 g Phenol	6	2.2	Unsubstituted
1 g PMAC/0.4 g Phenol	6	2.3	Unsubstituted
1 g PMAC/0.6 g Phenol	6	2.2	Unsubstituted
1 g PMAC/1.0 g Phenol	18	2.4	Partially substituted
1 g PMAC/5.0 g Phenol	22	2.1	Partially substituted
1 g PMAC/10.0 g Phenol	27	2.0	Partially substituted
Poly(phenyl methacrylate)	3300	1.3	Completely substituted

polymers, this approach would be attractive as a method of obtaining an increase in the plasma etch resistance of the resist. However, inconsistency in the results of synthesis make this approach very unattractive. PMAC is relatively inert for an acid chloride and it appears that, once the backbone configuration is changed by an initial reaction, subsequent reaction occurs very rapidly. PMAC was studied for its stability in air and it was found that the initial polymer had an acid chloride content of 97% and after one year this had dropped to a value of 83%. It was also observed that this partial hydrolysis of PMAC promoted a crosslinking side-reaction, which led to the formation of a gel structure that inhibited the formation of a uniform layer of resist. Similar behaviour was observed where aniline was reacted with PMAC; however, in this case the situation was more dramatic and no partially substituted polymer could be obtained. It was therefore concluded that it is not practicable to generate plasma etch resistance by the generation of a partially substituted PMAC.

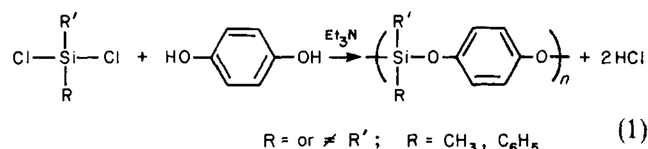
Poly(trimethyl silyl methacrylate) in theory should have a high plasma etch resistance and attempts were made to synthesize the polymer and also the copolymer with methacryloyl chloride. The synthesis of the polymer is described in the Appendix. Electron-beam characterization yielded a D_{50} value of 220 μC cm^{-2}. However, it was impossible to develop the resist completely as crosslinking appears to dominate at higher doses. Attempts to prepare a copolymer containing methacryloyl chloride failed due to hydrolytic side-reactions generating poly(methacrylic acid); the resultant polymer was an unstable and insensitive resist. These studies were not pursued further.

Plasma etch resistance of PMAC was investigated after treatment with certain selected silating agents and after treatment with aniline. Roberts[5] has previously indicated that this procedure reduces the susceptibility of the resist to oxygen plasma etching. Data were obtained using a Plasma Technology reactive-ion etcher and the results are presented in *Table 4*. The treatment with aniline reduces the rate of plasma erosion; however, the level of the effect varied between experiments and was difficult to reproduce. The silane treatments appear to be more effective than aniline in reducing the etch rate of PMAC to oxygen plasma. Poly(methacryloyl chloride) was also treated with aniline: the resultant resist was slow, typically 300 μC cm^{-2}, and the films were susceptible to microstress cracking and crazing on exposure to MIBK or other similar solvent systems.

Silicon-based resist materials

There has been considerable interest in resist materials containing silicon. Two types of base structure have been investigated in this study.

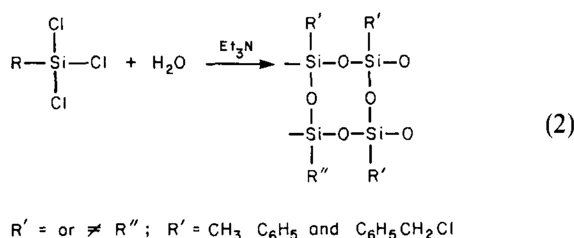
Linear silicon-containing resists. Linear polydimethylsiloxane polymers in principle could be used as a resist material. However, these polymers even at high molar mass are viscoelastic fluids. For a good resist it is important that it can be baked to form a uniform pinhole-free film and it is therefore desirable to explore structures which might have higher glass transition temperatures and possibly plasma etch resistance. The first structure explored was synthesized as follows:



(1)

The method of synthesis of the resists and their properties are summarized in the Appendix. The glass transitions of these materials were approximately 56°C for the diphenyl silyl oxyarylene, whereas the mixed methyl phenyl and dimethyl silyl polymers were only obtained as rather sticky viscoelastic liquids or pastes with glass transition temperatures around 1°C. No attempt was made to investigate the electron-beam characteristics of these materials. The diphenyl silyl oxyarylene resist was characterized and a D_{50} value of 300–500 μC cm^{-2} was obtained. These materials are therefore rather slow as electron-beam resists and so were not subjected to further study.

Polyphenylcyclosiloxane ladder polymers. A range of ladder polymers were prepared based on the following reaction:



(2)

$R' = \text{or} \neq R''$; $R' = CH_3$ C_6H_5 and $C_6H_5CH_2Cl$

The methyl-substituted material was a rather tacky solid and this was not studied further. The phenyl- and *p*-chloromethylphenyl-substituted and the mixed copolymers were prepared, and their properties are

Table 4 Results of oxygen plasma etching of treated poly(methacryloyl chloride)

Code	Polymer treatment[a]	Rate of etching (Å min^{-1})
1	Untreated polymer	2000
2	Hexamethyldisiloxane	~380
3	3-Aminopropyltriethoxysilane	~600
4	Trimethylsilyldimethylamine	~450
5	Aniline	~500

[a] Films were obtained by spinning a 5% solution of PMAC dissolved in dried toluene and heated for 1 h at 60°C. The etching was carried out using a mixture of carbon tetrachloride and oxygen with a power level of 40 W (0.2 W cm^{-2}) for 15 min

Table 5 Electron-beam characterization of polysilsesquioxane polymers

Polymer	M_n	M_w/M_n	D_{50} ($\mu C\ cm^{-2}$)
MPTS	1200	1.39	380
MPTS+5% CMPTS	4211	1.6	300
MPTS+5% CMPTS	5267	2.77	190
MPTS+5% CMPTS	5507	3.15	70
MPTS+8% CMPTS	3800	1.7	110
MPTS+12% CMPTS	2100	1.6	80

MPTS= , CMPTS=

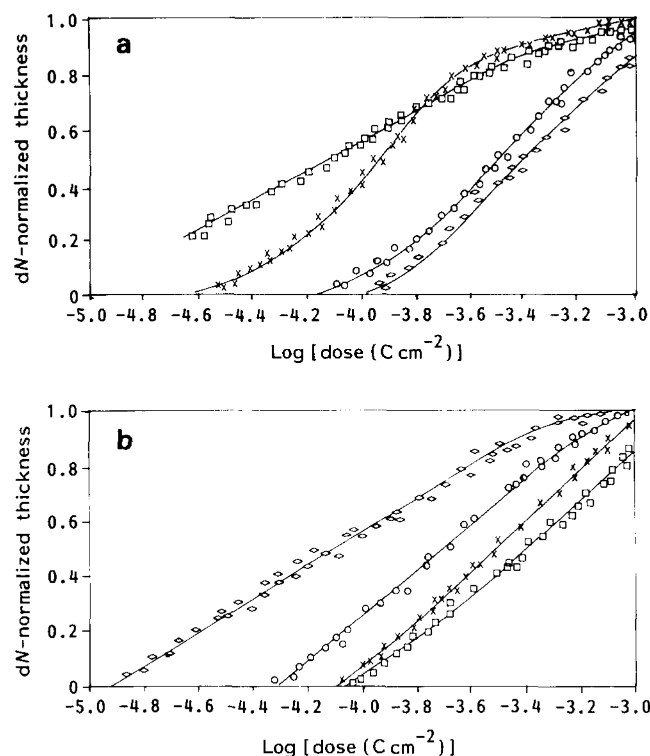


Figure 1 Electron-beam exposure curves for polysilsesquioxane resists. (a) Variation of CMPTS content: (◇) *p*-tolyl, (○) 5% CMPTS, (×) 8% CMPTS, (□) 12% CMPTS. (b) Variation of molar mass: (□) *p*-tolyl, (○) 5% CMPTS (M_n=4211), (×) 5% CMPTS (M_n=5267), (◇) 5% CMPTS (M_n=5507)

Table 6 Plasma etch resistance of some silicon-containing polymers[7]

Polymer	Silicon (wt%)	Etch rate in oxygen r.i.e. plasma (nm min^{-1})	Comment
1 Polydimethylsiloxane	38	1.9–1.8	Viscous liquid with low T_g
2 Polymethylsilsesquioxane	38	1.8–1.7	White soluble solid
3 Polyphenylsilsesquioxane	38	2.4–2.0	Etch rate shows initial high rate of degradation

summarized in *Table 5*. Electron-beam exposure curves for certain of these polymers are presented in *Figure 1*. The plasma etch resistance of these and related polymers have been reported recently[7] (*Table 6*). These preliminary measurements indicate that these polymers are of potential interest as negative electron-beam resists; however, their sensitivity requires enhancing. The copolymers of phenyl and 5% chloromethylphenyl (CMP) of varying molecular mass were investigated, and it was found that the sensitivity increases with increase in molecular weight. The sensitivity was also found to vary with CMP content, increasing with increasing chloromethyl content. This behaviour parallels similar behaviour observed in chloromethylstyrene–methylstyrene copolymers[8–10].

CONCLUSIONS

This paper describes various approaches that can be used to reduce the rate of plasma etching of electron-beam resists by reactive plasmas. Of the approaches explored, the one with the most potential appears to be that involving polysilsesquioxane resists. These polymers have the potential of being modified to give resists with a high level of plasma etch resistance, involve relatively easy, clean techniques when used as part of a bilayer system and with good electron-beam sensitivity and resolution. Further work on this type of resist is planned for the future.

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APPENDIX

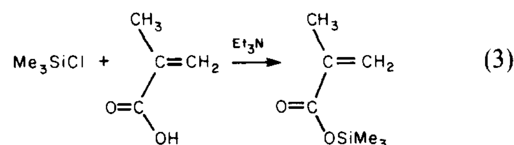
Synthesis of poly(methacryloyl chloride) (PMAC)

The PMAC was prepared by heating a mixture of 50 ml of methacryloyl chloride and 0.02 g of AIBN (azobisisobutyronitrile) in toluene, previously dried with sodium, for a period of 7 h. The polymer was precipitated by the addition of petroleum ether, filtered off and dried at 65°C under vacuum overnight. The molecular weights of the polymers were obtained by the hydrolysis of the polymer using methanol and the resultant material subject to g.p.c. analysis. The results of the analysis are presented in *Table 2*.

Synthesis of poly(trimethylsilyl methacrylate) and copolymer with methacryloyl chloride

In both cases it was essential first to prepare the monomer and then subsequently to synthesize the polymer.

Synthesis of trimethylsilyl methacrylate (TMSM). Trimethylchlorosilane and methacrylic acid were heated under vacuum (17 mmHg) for 4 h at between 36 and 40°C and subsequently distilled. The reaction was promoted by the addition of triethylamine and can be summarized as follows:



(3)

The product's structure was confirmed by i.r. and ^1H n.m.r. spectroscopy.

Synthesis of poly(trimethylsilyl methacrylate). Polymerization was produced by the addition of 0.2 mg of AIBN in tetrahydrofuran (THF) to 10 g of TMSM, the reaction being carried out under vacuum and initiated by heating to 70°C for 6 h. The polymer was separated by precipitation using petroleum ether. The molecular weight was found to be 20000 from g.p.c. analysis using THF as solvent.

Synthesis of poly(trimethylsilyl methacrylate-co-methacryloyl chloride). Varying amounts of the monomers were mixed and heated with AIBN under vacuum. Addition of petroleum ether precipitated a white solid. Spectroscopic examination of the polymer with ^1H n.m.r. and i.r. spectroscopy indicated that the Me_3Si–O bond had been hydrolysed during the reaction and the product was a copolymer of methacryloyl chloride and methacrylic acid. The product of this reaction was very unstable and quickly hydrolysed to poly(methacrylic acid).

Synthesis of silylene oxyarylene resists

The reaction described in scheme (1) was carried out using the method of Andrianov[11], in which triethylamine is used as a scavenger of the HCl generated. The materials generated produced very good thin films; however, these materials were found to turn cloudy after a few minutes. Spectroscopic examination of these films indicates that the clouding of the resists can be associated with the hydrolysis of the Si–Cl bond to give the SiOH bond. In an attempt to stop this complication, the resist was refluxed with phenol in toluene for 5 h, washed with water, dried and residual solvent removed by refluxing under reduced pressure. Elemental analysis of the polymer obtained on precipitation indicated a residual chlorine content of 2%; after treatment with phenol no trace of chlorine could be detected. The molar mass of the materials was found to be approximately 3500. The resist was purified by redissolving the polymer in toluene and reprecipitating with methanol. The glass transition temperature was found by d.s.c. to be 56°C.

Preparation of poly(alkyl and aryl silsesquioxane) resists

The synthesis[12] was carried out in two stages, hydrolysis followed by chain extension.

Hydrolysis. The monomer, an aryl or alkyl trichlorosilane, was slowly hydrolysed by the addition of water to a solution of the monomer in toluene according to scheme (2). The reaction mixture was cooled with ice. The reaction was facilitated by the addition of triethylamine as a scavenger of hydrogen chloride. The product was precipitated using petroleum ether. Molecular-weight analysis of the polymer indicated that this original material has a value of approximately 1500 with a distribution of 1.3.

Chain extension. Further increase in the molecular weight was achieved by refluxing the initial hydrolysate with potassium hydroxide for periods of up to 5 h. The product was precipitated with methanol and dried under vacuum overnight. Polymers containing methyl, methylphenyl and phenyl-*p*-chloromethylphenyl were prepared; their properties are summarized in *Table 6*.

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