Copolymer electron resists: poly(styrene–methyl methacrylate) copolymers

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The factors influencing electron beam sensitivity are reviewed. The variation of electron beam sensitivity and constrast are reported for a series of random copolymers of styrene and methyl methacrylate. Data are also presented for an alternating copolymer of styrene and methyl methacrylate. This study indicates the effects which arise when a negative resist material, polystyrene, is incorporated into a positive resist material, poly(methyl methacrylate).

Keywords Poly(methyl methacrylate); polystyrene; copolymers; resists; alternating copolymer; electron beam

INTRODUCTION

Electron beam resist materials are broadly subdivided into two groups: those that degrade on exposure to electron beams (positive resists) and those which crosslink (negative resists)[1,2]. The choice of a resist for a particular application depends critically on the speed and resolution required[3]. The majority of positive resists are based on a $-CH_2-CXY$ type of structure, the steric constraints introduced by bulky X and Y groups assisting the chain scission process. The most important of the positive resist materials is poly(methyl methacrylate) (PMMA). In contrast, polystyrene (PS), with its ability to trap and stabilize the electron on the pendant phenyl ring, is one of the more useful negative resists. The sensitivity of negative resists is often an order of magnitude greater than that found in positive resists[1]. Interactions involving the aromatic ring can effectively use back-scattered low-energy electrons[4]. Unfortunately, the higher sensitivity of the latter group is also accompanied by lower resolution than is possible with positive resists. Recently, dry etch capability has become a further parameter to be included in the characterization of an electron resist material. Good dry etch characteristics require that the main chain depolymerization should be inhibited and this is contrary to the concept of a good positive resist.

Copolymer systems

During the last five years a number of copolymer materials have been considered as having applications as electron resist materials[5–16]. The emphasis in this area of research has been directed towards positive resists, but a number of negative resists have also been reported. One of the earliest and most widely used commercial electron resist materials is formed from copolymers of methyl methacrylate (MMA) with methacrylic acid and methyl methacrylate with methacryloyl chloride[5,6]. The important characteristic of this material is its ability to form anhydride crosslinks on heating, and hence stabilize the developed pattern. The resultant features have better high-temperature processing characteristics and hence the superior development characteristics of these materials when compared to PMMA.

Positive resist materials

Developments in the area of positive resists appear to have been directed towards attempting to improve either the speed or the adhesion characteristics of the resist. Early studies of PMMA indicated that the sensitivity and development characteristics are strongly influenced by molecular weight and molecular weight distribution[7]. Enhancement in the speed has been achieved with a copolymer of methyl methacrylate and methacrylic acid[8]. This type of material exhibits excellent adhesion characteristics consistent with the presence of the carboxylic acid grouping, high resolution and good sensitivity. The enhancement of the sensitivity is attributed to a high probability of chain scission and efficient formation of gaseous products. Increases in the sensitivity have also been reported[9] in copolymers formed using methyl methacrylate, methyl methacrylic acid and methyl acrylic anhydride. The sensitivity can also be increased by forming the metal salt of the copolymer of methyl methacrylate with methyl acrylic acid[10]. This result may in part be explained by the effects of increases in the atomic number on the electron scattering characteristics of the resist materials.

Negative resist materials

Much of the work on negative resists appears to have been directed towards changing the sensitivity and/or the dry etch resistance of the resist materials. Polystyrene[11], chloromethylated polystyrene[12] and copolymers of styrene with glycidyl methacrylate all form good negative resists[13–15]. The copolymer of glycidyl methacrylate and ethyl acrylate is one of the most widely used negative electron resist materials for chromium mask fabrication. As indicated earlier, the principal problem with negative resists is one of low resolution, which is a direct consequence of the efficiency of the phenyl ring to interact with the low-energy electrons produced by back-scattering. The resolution limitation is also associated with swelling during the development process and can be minimized by careful control of development conditions and polymer morphology. Polymer swelling can be minimized by designing a polymer which has a strong

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Table 1 Physical characteristics of the polymers

Polymer	Code	$M_w \times 10^4$	M_w/M_n
Poly(methyl methacrylate)	R1	12.3	2.12
MMA/styrene (3:1)	R2	9.63	2.64
MMA/styrene (2:1)	R3	13.4	2.1
MMA/styrene (1:1)	R4	13.0	1.94
Alternating copolymer			
MMA/styrene (1:1)	R5	13.0	2.06
Random copolymer			
MMA/styrene (1:2)	R6	8.8	2.5
MMA/styrene (1:3)	R7	14.2	2.48
Styrene	R8	22.5	4.3

backbone and is rheologically 'stiff' during the development cycle. Polymers possessing this rigidity generally are non-rubber and have high glass transition temperatures. Polymer flow during thermal cycles can also be a contributory factor to loss of resolution; inclusion of high glass transition elements assists in this direction. Polymers containing naphthalene and related groupings have also been investigated[16].

From the above review it is clear that it should be possible to design a polymer to optimize either radiation stability, for dry etch applications, or electron beam sensitivity. In this paper, a study of copolymers of styrene and methyl methacrylate is reported. These copolymers were chosen for study since they represent an interesting combination of elements which are traditionally considered to be classic positive and negative resists. A random copolymer will usually contain blocks of monomers of a particular type interspersed with elements of the other. It therefore appeared to be of interest to study the behaviour of a regular alternating material where the structure is completely A–B–A–B structures. This study would help to explore the possibilities of changing the backbone structure of a polymer either to increase its dry etch resistance or alternatively to improve its contrast resolution characteristics.

EXPERIMENTAL

Preparation of polymers

The monomers, styrene and methyl methacrylate, were obtained from BDH and were vacuum distilled before use. The polymerization was initiated using AIBN and was carried out at 353K under an atmosphere of nitrogen. The polymerization was stopped at approximately 30% conversion by cooling the reaction mixture in iced water. The polymer obtained was dissolved in toluene and reprecipitated using methanol. This process was repeated several times. The molecular weights and molecular weight distributions were determined using a Waters Analytical Gel Permeation Chromatograph equipped with both refractive index and ultra-violet detectors. The tacticity and sequence structure were investigated using ^{1}H n.m.r.[17] The polymer characteristics are summarized in *Table 1*. The copolymers possessed similar molecular weights and ^{1}H n.m.r. spectra to those described by Bovey[17] and exhibit sequences of iso-, syndio- and atactic structure[17].

An alternating copolymer was prepared using a Lewis acid catalyst (zinc chloride). The copolymer was precipitated with methanol and washed with acrylonitrile and cyclohexane to remove homopolymers. The ^{1}H n.m.r. spectrum was similar to that reported previously[18] and confirms the assignment of the sequence structure as being a regularly alternating 1:1 structure.

Sample preparation

A 5% solution of the copolymer in toluene was spun onto freshly cleaned silicon wafers. The films obtained were typically between 0.5 and 1 μm in thickness. The resist films were baked at 433K for 1 h prior to use.

Electron beam exposure and development

Electron beam exposure was achieved using a modified Philips PSCM 500 electron microscope at Glasgow University. Areas of approximately 150 μm × 200 μm were progressively exposed. The pattern was then solvent-developed. The composition of the solvent system was adjusted to give optimum development characteristics. The development system was usually checked several times, with and without agitation to enhance the dissolution of soluble material. The thickness of the developed films was monitored using a Rank Talystep.

RESULTS

Electron beam sensitivity measurements

Sensitivity and contrast were determined from plots of the normalized thickness against the logarithm of the electron beam dose required to retain 50% of the original film. For a positive resist it is the electron dose required to remove 100% of the original film. These polymer film. Sensitivity for a negative resist is the electron beam dose required to retain 50% of the original film. For a positive resist it is the electron dose required to remove 100% of the original film. These definitions have been used in this study. It can be seen from *Figure 1* that the copolymers fall neatly into being either positive or negative resist materials. The contrast as defined by Thompson and Kerwin[19] was computed from $(\log_{10}(D_i/D_j))^{-1}$, where D_i for a positive resist is the extrapolated dose for complete exposure and for a negative resist is the extrapolated dose for the full thickness, and D_j is the minimum dose for a negative resist and the extrapolated dose for full thickness for a positive resist. The contrast data were computed from the central linear portion of the curve. Data obtained from the analysis of the copolymers are presented in *Table 2*.

DISCUSSION

The copolymers of styrene and methyl methacrylate fall neatly into two groups: those with 60% or greater of methyl methacrylate which behave as positive resists and those with less than 60% which behave as negative resists. Although there are differences in the molecular weight of the polymers studied, they are sufficiently close both in M_w and M_w/M_n to suggest that the development characteristics are typical of these copolymers. It should also be noted that, in order to optimize the development characteristics, significant changes had to be made both in the nature of the ratio of the mixture of methyl isobutyl ketone (MIBK) with isopropyl alcohol (IPA) and also in the length of the exposure. These changes reflect both the

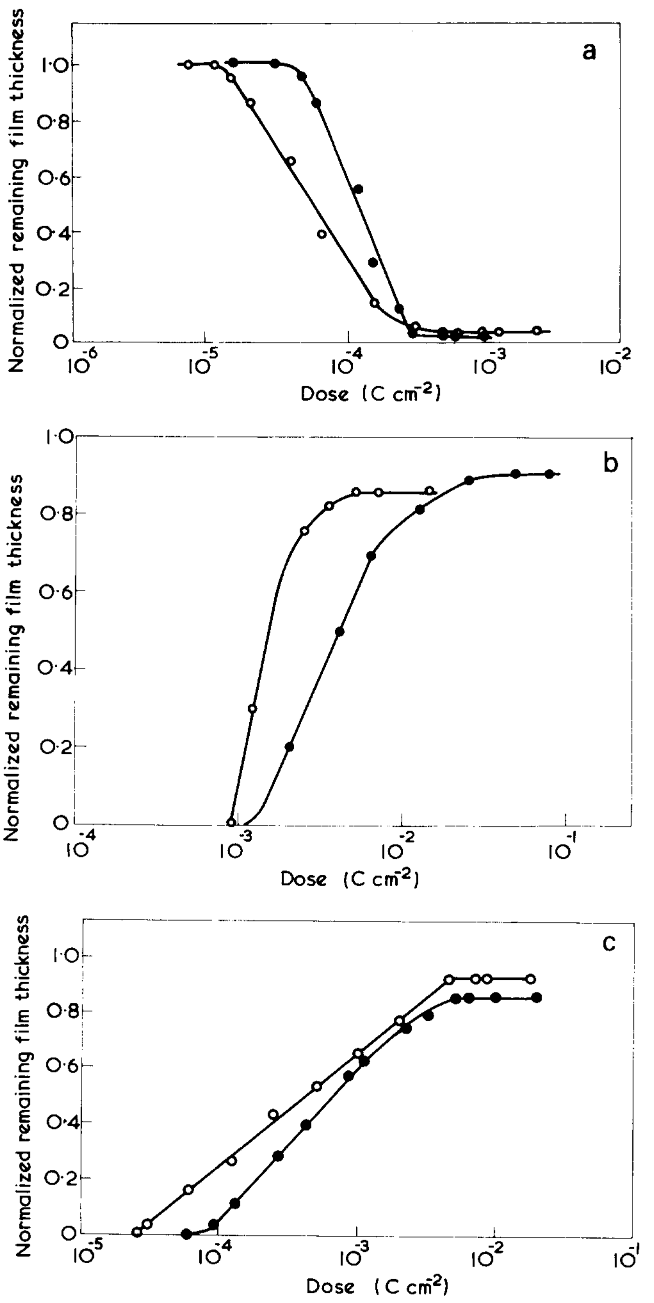

Figure 1 Development characteristics of the poly(styrene–methyl methacrylate) copolymers: (a) ○, methyl methacrylate/styrene, 3:1; ●, methyl methacrylate/styrene, 2:1; (b) ○, methyl methacrylate/styrene, 1:1 alternating; ●, methyl methacrylate/styrene, 1:1 random; (c) ○, methyl methacrylate/styrene, 1:3; ●, methyl methacrylate/styrene, 1:2

different nature of the process, viz. positive *versus* negative resists, and also the changes in the solubility characteristics of the polymers. It has been noted previously that changes in the tacticity of the poly(methyl methacrylate) polymer can produce significant effects on both its solution characteristics and its sensitivity to electron beam exposure. In the copolymers the sequence length is unlikely to be sufficient to influence the solubility behaviour significantly. However, it may have an effect on the nature of the electron interaction. The ^{1}H n.m.r. indicates that the copolymers have structures similar to those observed in 'normal' PMMA, which would imply that the principal effect of electron beam exposure would be to induce chain scission. The sensitivity of the phenyl ring to low-energy electrons is reflected in the loss of contrast when the resist is acting as a positive material and also in the fact that incorporation of over 30% of styrene produces a negative-type resist material.

One of the most interesting observations which arises from this study is the way in which the generation of a strictly alternating copolymer structure for the 1:1 copolymer dramatically increases the contrast. The reason for this effect is not obvious, but it must be a consequence of the gemoetrical constraints imposed by the sequence structure as well as changes in the chemistry associated with the electron interaction. The value of γ observed with this material is significantly higher than that traditionally reported for negative resists and implies that such polymers may be of interest in dry etch applications. One factor which makes this material less attractive than the usual negative developing polymers is their low electron sensitivity.

CONCLUSIONS

The introduction of styrene into PMMA initially decreases the value of γ and also the electron beam sensitivity. In contrast, the addition of methyl methacrylate to styrene leads to little loss in the sensitivity; however, there is a decrease in the contrast. It is interesting to note that the 1:1 random copolymer possesses similar characteristics to polystyrene from the point of view of contrast. The comparison with the behaviour in the case of the 1:1 alternating copolymer would suggest that the generation of a polymer with an intermediate structure might allow optimization of the contrast, however a significant improvement in sensitivity is desirable. It should be emphasized that in this study we have not been attempting to develop optimum characteristics but rather have been trying to determine the matrix of properties which are possible using copolymers of this type. A possible method of increasing the sensitivity of these copolymer systems would be to introduce methacrylic acid units and then connect these to the metal salt. Certain of these possibilities will be explored in the near future.

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Table 2 Electron development characteristics

Code	Nature of resist	Solvent	Time (s)	Electron beam sensitivity at 25 keV (C cm^{-2}) x 10^{-5}	Contrast, γ
R1	Positive	MIBK:IPA(2:3)	60	6	1.70
R2	Positive	MIBK:IPA(2:3)	60	48	0.80
R3	Positive	MIBK:IPA(2:3)	60	30	1.2
R4	Negative	MIBK:IPA(2:1)	30	140	2.5
R5	Negative	MIBK:IPA(3:1)	15	420	1.1
R6	Negative	MIBK	30	65	0.67
R7	Negative	MIBK	30	40	0.45
R8	Negative	MIBK	20	32	1.28

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