Poly (α-methylstyrene) and α-methylstyrene–maleic anhydride copolymer: an electron beam lithographic study

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The electron beam sensitivity and contrast are reported for syndiotactic poly(α-methylstyrene), and random, and alternating copolymers of α-methylstyrene–maleic anhydride. Once again it has been observed that tacticity has a marked effect on the sensitivity of a homopolymer. Comparison of the properties of a random and alternating copolymer, indicate that the sensitivity and contrast are higher, for the alternating copolymer. Similar behaviour has been reported in another copolymer system, supporting this observation.

(Keywords: electron beam; lithography; poly(α-methylstyrene); α-methylstyrene–maleic anhydride copolymer; tacticity effects; alternating copolymer)

INTRODUCTION

In electron beam lithography, resist materials are required with both sensitivity and high contrast. It is usually found that high sensitivity is accompanied by low contrast and *vice versa*. In general, positive resists have moderate sensitivity and good contrast, whereas negative resists have high sensitivity and poor contrast[1]. The sensitivity of a positive resist is enhanced by copolymerization with highly radiation susceptible groups to promote chain scissions, while in negative resists the sensitivity is improved by incorporating radiation sensitive crosslinkable groups such as epoxy rings either into the backbone or on the side chain to promote crosslinking[2].

It has been shown that the contrast, which is achieved for a particular material is a function of the heterogeneity index[1-5]. Lai and Shepherd[5] examined polystyrene as a negative resist and indicated that a narrow molecular weight material yielded an improved contrast factor. Similar results have been reported by Itaya *et al.*[6] for negative resists with a very narrow molecular weight distribution ($M_w/M_n < 1.01$). These materials were reported to have comparable resolution to that obtained with positive resists. It has also been reported that copolymerization of methacrylic acid into methyl methacrylate and metallization of the resultant polymer, leads to a significant increase in resolution.

In a previous paper[7], we investigated the effects of tacticity of the behaviour of PMMA. It was observed that the molecular weight distribution of the product was functionally sensitive to the structure of the polymer. It was observed that syndiotactic PMMA was less susceptible to electron beam degradation, and was also observed to have low sensitivity in contrast to the isotactic

material. In another study[8] we examined the effect of change in the chemical composition on the sensitivity and contrast for copolymers of methyl methacrylate and styrene. It was observed that for a 1:1 copolymer the regular alternating material had higher contrast than the random material. In this paper we re-examine the effects of tacticity and alternation in structure, on the sensitivity of resist materials, and also report the electron beam behaviour of syndiotactic poly(α-methylstyrene), 1:1 alternating and random copolymers of α-methylstyrene with maleic anhydride. The sensitivity, contrast and development behaviour of these materials are reported.

EXPERIMENTAL

Preparation of polymers

The monomer alpha-methylstyrene (αMeSt) was distilled under vacuum and maleic anhydride (MAn) was recrystallized twice from ether before use. Syndiotactic poly(αMeSt) was prepared[9] using methylene chloride and concentrated sulphuric acid at −70°C (203 K). The reaction was carried out for one hour. The polymer was obtained by discharging the clear solution into methanol. The white granular solid obtained was dried at 100°C for 24 h. The tacticity was examined by ^{1}H n.m.r., and the bulk copolymerizations of α-methylstyrene with maleic anhydride were carried out in the presence of purified nitrogen using azobisisobutyronitrile (AIBN) as initiator. At 343K[10,11], 1:1 alternating copolymer was obtained while at 373K, 1:1 random copolymer of α-methylstyrene–maleic anhydride was obtained. Thus the copolymerization of these two monomers depends strongly upon the reaction temperature. The composition of the copolymers was determined by elemental analysis. The molecular weight and molecular weight distribution were determined using a Waters Analytical Gel

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Permeation Chromatograph equipped with both refractive index and ultraviolet detectors using tetrahydrofuran (THF) as solvent. Details of the polymer characteristics are presented in *Table 1*. The results for elemental analysis for the alternating copolymer were, carbon (exp. 72.48, theory 72.2), hydrogen (exp 5.88, theory 5.60), random copolymer carbon (exp 72.05, theory 72.2), hydrogen (exp 5.88, theory 5.60). These results indicate that the copolymer conforms to a 1:1 material.

Sample preparations

Resist films of thicknesses between 0.3 to 0.5 μm were prepared on the oxidized surface of a silicon wafer from the resist solution using a Dage-Precima Spinner. The resist films were prebaked in air at 433 K to remove solvent for one hour, and the copolymer films were found to have striations as seen under optical microscope. The milky colouration is presumably an indication of microphase separation. However, since the structures developed are significantly smaller than the areas exposed using the electron beam, it is assumed that this property does not have a significant effect on the data. The uniformity of thickness of the films was checked using a Rank Talystep.

Development curves

A Philips PSCM 500 scanning electron microscope (at Glasgow University) was used with an accelerating voltage of 25 KV to achieve electron beam exposure. The dosages were controlled by varying the exposure time and beam current. The system used involves monitoring the flux at the sample and adjusting the beam current to obtain the required dose. The information on the electron flux at the sample is fed to a computer which controls both the dosages and also generates the pattern. Exposed areas of approximately 150×200 μm were then developed at 293 K in suitable developer with gentle agitation to enhance the dissolution of soluble material. The thickness of resist left in the exposed areas after development was measured by using a Rank Talystep.

Properties of copolymers

The copolymers of α-methylstyrene and maleic anhydride were insoluble in most of the usual development solvents such as toluene, chlorobenzene, and methyl isobutyketone (MIBK). Since these copolymers undergo degradation, strong solvents such as MIBK, toluene can be used to develop the exposed areas without losing the thickness of the unexposed area. Copolymers were readily soluble in 1,4-dioxane and the mixed solvent solution with hexane in 2:3 ratio was used as developer. Toluene was also tried as developer and it was observed that almost the same sensitivity curves were obtained in both cases. The unexposed films of copolymers did not result in swelling of the pattern even after 3 min, which would imply good resolution.

Table 1 Polymer characteristics

Polymer	$M_W \times 10^4$	$M_n \times 10^4$	M_W/M_n
Syndiotactic poly(α-methylstyrene)	6.86	2.47	2.77
α-methylstyrene—maleic anhydride (alternating)	1.81	9.63	4.85
α-methylstyrene—maleic anhydride (random)	3.57	1.26	2.82

RESULTS AND DISCUSSION

Sensitivity and contrast of the samples were measured from a plot of the normalized thickness as a function of log dose (*Figure 1*). Since these materials act as positive resists, the sensitivity can be defined as the minimum electrical charge per unit area of resist film required for complete development of the exposed area and is measured in coulomb per square centimetre. The contrast was computed from $[\log(D_o/D_i)]^{-1}$ where D_o is the extrapolated dose for complete exposure and D_i is the extrapolated dose for full thickness of the film. D_o and D_i were obtained from the linear portion of the curve.

The sensitivity and contrast values of resist materials are given in *Table 2*. Poly(α-methylstyrene) is a vinyl polymer that undergoes electron beam degradation; and data on its characteristics have been reported earlier[12]. The sensitivity of the atactic polymer is of the order of 1×10^{-4} C/cm². The G_s value defined as the number of chain scission events per 100 eV of energy absorbed has been reported[13] to be 0.25, and G_s, the radical generation coefficient, is 0.03[14]. These observations were made on atactic poly(α-methylstyrene). Tacticity may be expected to have an effect on the mode of degradation, sensitivity and contrast of materials used as electron beam resists. As we have reported earlier[7], it is clear from the present
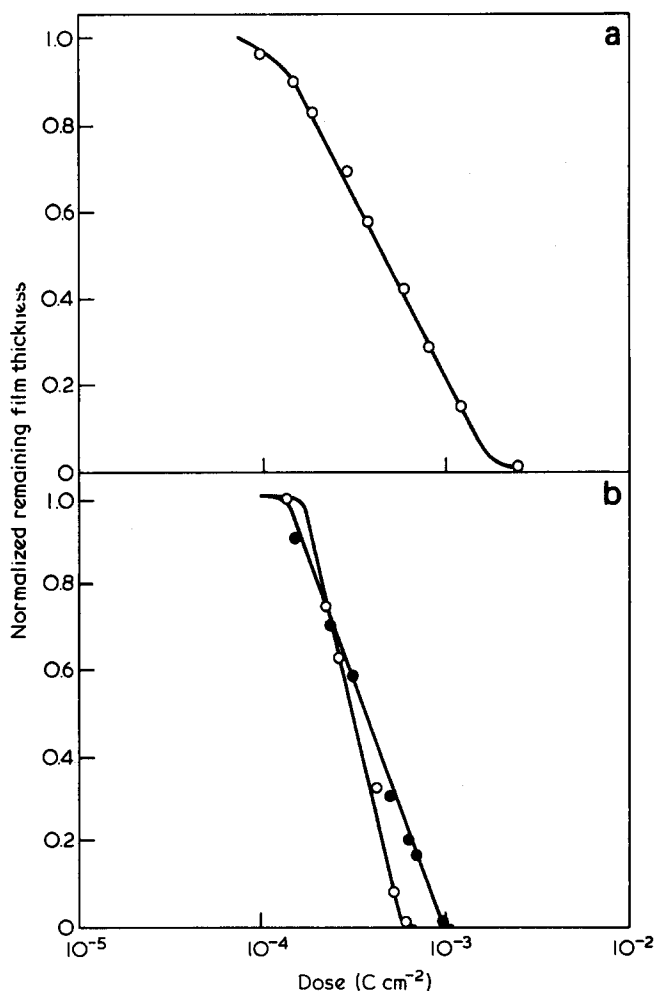

Figure 1 (a) Sensitivity curve of syndiotactic poly(α-methylstyrene). (b) Sensitivity curves of α-methylstyrene—maleic anhydride, 1:1 copolymers, O, alternating; ●, random

Table 2 Electron beam resist characteristics

Polymer	Casting solvent	Developer	Time(s)	Electron beam sensitivity at 25 keV (c cm^{-2})	Contrast γ
Syndiotactic poly(α-methylstyrene)	Toluene	Dioxane:IPA 2:3	120	2×10^{-3}	0.87
α-methylstyrene—maleic anhydride (alternating)	Dioxane	Dioxane/Hexane 2:3	90	6×10^{-4}	1.7
α-methylstyrene—maleic anhydride (random)	Dioxane	Dioxane/Hexane 2:3	90	1×10^{-3}	1.17

results that syndiotactic poly(α-methylstyrene) is less sensitive (by a factor of 10) in comparison with the atactic structure. The decrease in sensitivity is attributed to a lower scission efficiency and to the formation of some high molecular crosslinked materials during degradation.

A marked difference has been observed in contrast values between alternating and random copolymers[8]. Besides the higher value of contrast ($\gamma = 1.7$) in the alternating copolymer, there is also an increase in observed sensitivity. The contrast is dependent on the rate of degradation of the polymer materials. It appears that the interaction of the electron beam with the copolymer and subsequent generation of radicals, which leads to degradation is also influenced by the molecular structure of the copolymer. The contrast value of alternating copolymer is identical to that of PMMA. The glass transition temperature T_g of this copolymer (518 K[11]) is well above the T_g for PMMA (478 K) and has better thermal stability. The polymers used in this study were of rather broad molecular weight distribution and it is feasible that a more monodispersed material would exhibit higher values.

CONCLUSIONS

This study confirms our earlier observations that the polymer backbone structure and tacticity have a significant effect on both the sensitivity and contrast of electron beam resist materials and indicates the possibility of separate contrast of these factors in resist development.

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