New thermally crosslinkable electron-beam resists: 1. Itaconic anhydride–methyl methacrylate copolymers

A. F. Miles and J. M. G. Cowie*
Department of Chemistry, Heriot-Watt University, Riccarton, Edinburgh, UK

R. H. Bennett and D. R. Brambley
Allen Clark Research Centre, Plessey Research (Caswell), Towcester, Northamptonshire, UK
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This paper describes the lithographic evaluation of copolymers of itaconic anhydride (IT.ANH) and methyl methacrylate (MMA) as thermally crosslinkable electron-beam resists. Their properties were investigated as a function of copolymer composition and primary number-average molecular weight in order to determine an optimum formulation for the preparation of high-resolution resist patterns. Line and space test patterns with features smaller than 0.5 μm have been prepared using a copolymer containing 46 mol% IT.ANH with $M_n = 5.30 \times 10^5$ g mol^{-1}, which was thermally crosslinked by pre-baking at 170°C for 1 h. The electron exposure dose required to solubilise the resist (α_D) has been shown to be very much less than the exposure dose required for the preparation of high-resolution resist patterns.

(Keywords: resist materials; electron-beam lithography; itaconic anhydride copolymers; gel degradation)

INTRODUCTION

Polymer resist materials are grouped under two general categories according to their response to exposure by a source of electromagnetic radiation. For the case of exposure to an electron beam, negative acting resists form an insoluble fraction in the regions of resist exposed to the radiation, normally as the result of crosslinking reactions, and can be patterned by the selective removal of the uncrosslinked material in a suitable solvent developer. Positive acting resists normally undergo mass loss and chain scission, leading to the degradation of the polymer in exposed regions, and therefore giving exposed regions of the resist a higher rate of dissolution in a developing solvent as compared to the unexposed regions of the resist. For both positive and negative acting resists the performance of the resist can depend strongly on the solvent developer and development conditions employed[1].

For positive acting resists, improvements in resist sensitivity (defined as the exposure dose D_0 required for the complete removal of resist from a large exposed area under given development conditions) can be achieved by the use of stronger developing solvents or through the use of longer development times[2]. In extreme cases, however, this can lead to significant thinning of the unexposed regions of resist and reductions in resist resolution[3].

Thermally crosslinkable electron-beam resists were first described by Roberts[4,5] and have significant advantages for certain manufacturing operations including the preparation of gate recesses and gate metallization patterns on gallium arsenide (GaAs) substrates[6]. The resist formulation typically consists of a linear polymer with reactive side groups, or a mixture of two or more reactive precursors that are baked above their glass transition temperature (T_g) in order to produce a lightly crosslinked film prior to the exposure of the film. Exposure of the resist leads to scission of the pre-crosslinked network, allowing development of the exposed areas of resist in a suitable solvent or solvent mixture.

At the present time, materials of the type first described by Roberts, consisting of a mixture of two copolymers, poly(methacrylic acid-*co*-methyl methacrylate) with poly(methacryloyl chloride-*co*-methyl methacrylate), are still used in industrial applications; and although this material has a number of useful properties, in particular its good adhesion to GaAs, it has the disadvantage of high moisture sensitivity. Hydrolysis of acid chloride units in the methacryloyl chloride copolymer is thought to reduce the number of reactive groups available for crosslinking and to lead to a variation in performance between batches. The exposure dose required for the development of the resist is also relatively high (~100 μC cm^{-2}). Characteristics that would give any new material an advantage over those presently in use are therefore greater electron sensitivity and/or reduced moisture sensitivity. Continued reductions in the minimum feature sizes of resist patterns also places increasing demands on resist–substrate adhesion.

The potential of polymers containing itaconic anhydride (IT.ANH) for use in electron-beam or X-ray resist technology was first considered by Bargon and Hiroaka[7]. These authors reported that poly(IT.ANH) exhibited good adhesion to silicon surfaces and behaved as a positive acting electron-beam resist, although few details were given.

As an alternative to existing formulations containing acid chloride units we have considered the use of IT.ANH

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* To whom all correspondence should be addressed

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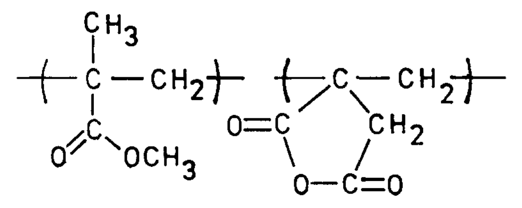

Figure 1 IT.ANH-*co*-MMA

in various copolymers, which might operate as thermally crosslinkable electron-beam resist materials, including its use in a two-part resist system containing an alcohol functional group such as that of 2-hydroxyethyl methacrylate (HEMA). The first part of this study, an investigation into the behaviour of itaconic anhydride–methyl methacrylate (IT.ANH–MMA) copolymers (*Figure 1*), is reported here.

EXPERIMENTAL

Copolymers used in this work were prepared by bulk or solution copolymerization techniques using α,α'-azobisisobutyronitrile (AIBN) as initiator. AIBN was recrystallized twice from methanol prior to use. Solution copolymerization was carried out using *p*-dioxane as the solvent at 60°C; total monomer concentration was 0.67 mol dm^{-3}. Bulk copolymerizations were carried out in sealed and evacuated flasks at 70°C. All copolymerizations were terminated at low percentage conversion ($<14\%$) to minimize composition drift. The composition of the copolymers was determined by quantitative infra-red spectroscopy using the method of Sharabash and Guile[8]. Further details concerning the preparation and characterization of these materials are given elsewhere[9]. Selected samples were separated by fractional precipitation using ethyl acetate as the solvent, and cyclohexane or a mixture of 4:1 cyclohexane:ethyl acetate as the precipitant. Solvents used for the purification and fractionation of copolymers were dried using the standard procedures[10] in order to minimize hydrolysis of IT.ANH units in the copolymers. Number-average molecular weights were measured using a Knauer membrane osmometer and detecting bridge at 35°C. Membranes (Sartorius, regenerated cellulose) were conditioned to 2-butanone. Details of all samples used in this work are given in *Table 1*.

Lithographic evaluation

Unoxidized silicon wafers, 76 mm diameter, were baked at 170°C for several hours to remove surface moisture. The wafers were allowed to cool and were blown with dry nitrogen to remove contaminating particles. Resist films were prepared by spin coating from 5–10% solutions of the polymer in either 2-methoxyethyl acetate or chlorobenzene mixtures, using a two-speed Headway Research photoresist spinner. Following resist coating, all samples were pre-baked at 170°C for 1 h in a glove box with a N_2 purge.

A standard test pattern was exposed using a Cambridge Instruments Electron Beam Microfabricator (EBMF-2) using an accelerating voltage of 20 kV with beam currents in the range 0.20–0.50 nA. Unless otherwise stated, exposed patterns were developed by gently agitating the resist-coated wafer in a solvent or solvent mixture at 20–22°C. Samples were rinsed in isopropanol (IPA) and were blown dry with filtered nitrogen before post-baking for 30 min at 100°C.

Lithographic sensitivity (D_0) and contrast (γ) were measured from plots of normalized remaining thickness *versus* exposure dose following resist development and post-baking (*Figure 2*) where:

$$\gamma = [\log_{10}(D_{1.0}/D_0)]^{-1} \qquad (1)$$

RESULTS AND DISCUSSION

Copolymers of IT.ANH–MMA were found to crosslink when heated above T_g, possibly as a first stage in the thermal degradation of these materials[9]. Measurements of the gel fraction following pre-baking (*Table 1*) show some irregularities, although it can be seen that a gel fraction of $\sim$0.30–1.0 is generally observed for samples containing >10 mol% IT.ANH. Preliminary experiments confirmed that IT.ANH–MMA copolymers would degrade with exposure to electron-beam irradiation with lithographic sensitivity (D_0) values in the range 10–200 μC cm^{-2}.

Choice of solvent developer

Plots of normalized remaining thickness *versus* exposure dose for a copolymer containing 33 mol% IT.ANH with $M_n = 1.55 \times 10^5$ g mol^{-1} and developed in various solvents are presented in *Figure 3*. The results

Table 1 Resist films prepared from IT.ANH copolymers

Copolymer composition (mol%)	$M_n \times 10^5$ (g mol^{-1})	Film thickness (μm)	Gel fraction after baking[a]
5	–	0.41	0
10	2.27	0.46	0
24	4.44	0.59	0.83
33	1.33	0.34	0.44
33	4.44	0.64	0.89
46	1.11	0.60	0.83[b]
46	1.17	0.28	–
46	1.66	0.17	0.82[b]
46	4.24	0.18	0.98[b]
46	5.30	0.48	0.90, 1.04[b]
50	–	0.55	0.30[b]
67	–	0.52	0

[a] Samples soaked 62 h in 2-methoxyethyl acetate
[b] Boiling THF, 168 h

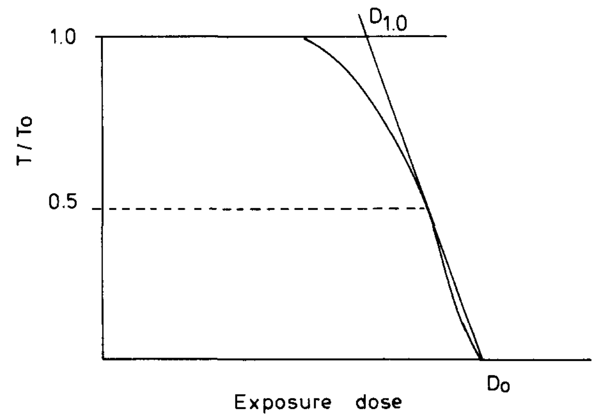

Figure 2 Measurement of lithographic sensitivity (D_0) and resist contrast (γ)

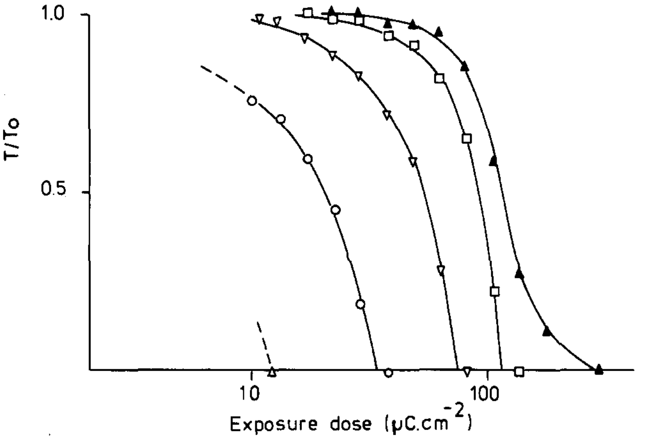

Figure 3 Normalized remaining thickness *versus* exposure dose for 33 mol% IT.ANH copolymer, $M_n = 1.55 \times 10^5$ g mol^{-1}. Developers: (△) ethyl acetate; (○) 4:1 mixture ethyl acetate:isopropanol; (▽) 2-ethoxyethyl acetate; (□) methyl isobutyl ketone; (▲) 1:1 mixture ethyl acetate:isopropanol

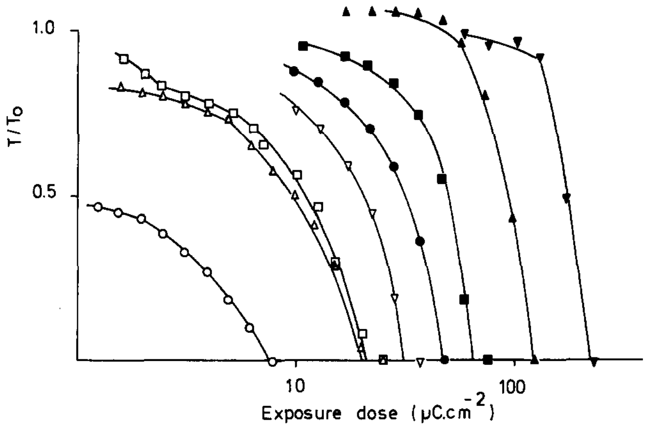

Figure 4 Normalized remaining thickness *versus* exposure dose for copolymers containing 5–67 mol% IT.ANH: (○) 5 mol%, (△) 10 mol%, (□) 24 mol%, $M_n = 4.44 \times 10^5$ g mol^{-1}; (▽) 33 mol%, $M_n = 1.55 \times 10^5$ g mol^{-1}; (●) 33 mol%, $M_n = 4.44 \times 10^5$ g mol^{-1}; (■) 46 mol%, $M_n = 4.42 \times 10^5$ g mol^{-1}; (▲) 50 mol%; (▼) 67 mol%

show that D_0 can be reduced from ~300 to ~12 μC cm^{-2} by increasing the proportion of ethyl acetate in a series of ethyl acetate:isopropanol mixtures (the developing time being maintained constant). However, quite severe thinning at the edges of the developed resist features was noted for samples developed in mixtures containing a high proportion of ethyl acetate. Comparison of the quality of the resist images obtained with each type of developing solvent showed that results obtained with a 4:1 mixture of ethyl acetate:isopropanol compared favourably with other solvent systems investigated. For copolymers containing 46 mol% IT.ANH, cyclohexanone was found to be more suitable for the preparation of high-resolution resist images.

Variation in resist performance with copolymer composition

Plots of normalized remaining thickness *versus* exposure dose for samples of 5–67 mol% IT.ANH are presented in *Figure 4*. All samples were developed for 90 s plus a further 30 s in a 4:1 mixture of ethyl acetate: isopropanol. The degree of thinning (measured as the loss in normalized remaining thickness in unexposed areas) was most pronounced for copolymers containing 5 and 10 mol% IT.ANH.

Values of D_0 and γ are presented as a function of copolymer composition in *Figure 5*. Examination of this plot suggested that an acceptable balance of D_0 and γ is obtained for copolymers containing 40–50 mol% IT.ANH. Further work was therefore concentrated on copolymers containing 46 mol% IT.ANH.

Variation in resist performance with primary molecular weight

Samples of 46 mol% IT.ANH copolymer with M_n in the range 1.11×10^5–5.30×10^5 g mol^{-1} were exposed and developed using (a) 4:1 mixture of ethyl acetate:isopropanol and (b) cyclohexanone. Measurements of D_0 as a function of primary molecular weight for the two developer systems are presented in *Figure 6*. In both cases there would appear to be a minimum in D_0 for particular values of M_n, being more pronounced for samples developed using cyclohexanone. The contrast γ was found to increase slightly from ~3.0 to ~4.3 with increase in

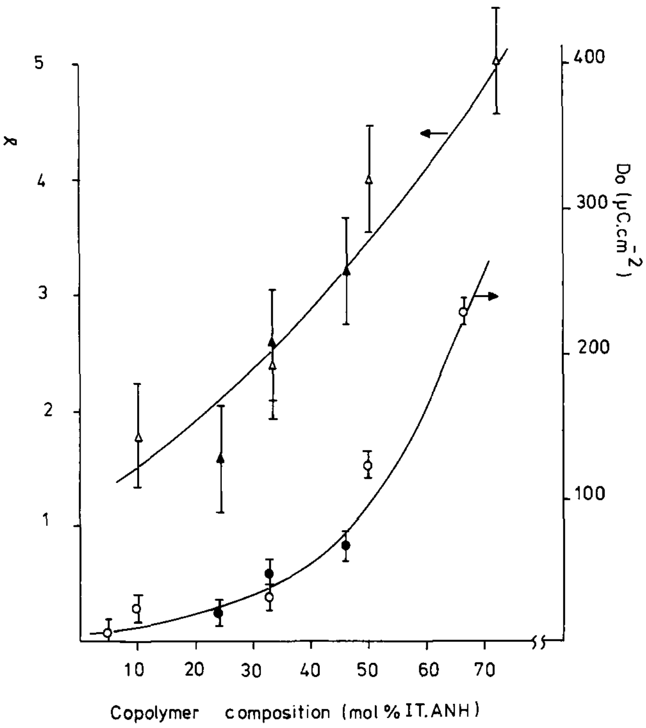

Figure 5 Lithographic sensitivity (D_0) and resist contrast (γ) as a function of copolymer composition for 5–67 mol% IT.ANH. Developed 90 s plus a further 30 s in 4:1 mixture ethyl acetate:isopropanol. Filled symbols (●, ▲) denote sample $M_n = 4.30 \times 10^5$ g mol^{-1}

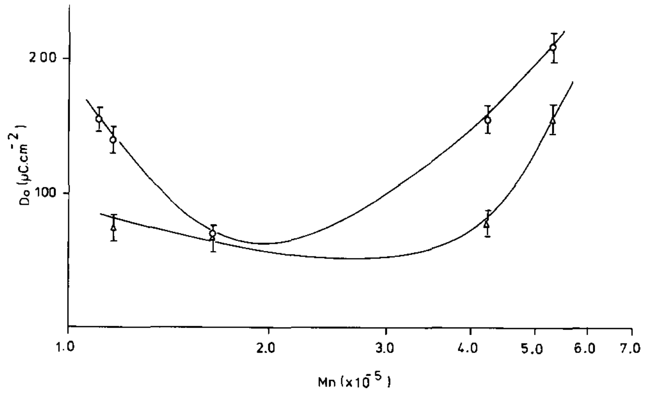

Figure 6 Lithographic sensitivity (D_0) as a function of primary molecular weight, 46 mol% IT.ANH. Developers: (○) cyclohexanone; (△) 4:1 mixture ethyl acetate:isopropanol

molecular weight from $M_n = 1.11 \times 10^5$ to $M_n = 5.30 \times 10^5$ for samples developed using cyclohexanone. No clear trend in resist contrast with M_n was found for samples developed using a mixture of 4:1 ethyl acetate: isopropanol for which $\gamma \sim 3$.

Although few firm conclusions can be drawn from these data, it is apparent that for this formulation of resist the primary molecular weight can have a significant influence upon resist performance. Not considered here is the possible variation in response with the primary molecular-weight distribution (*MWD*). This factor might have some bearing on the data presented in *Figure 6*, although its exact influence is uncertain. The lithographic sensitivity D_0 can in most cases be enhanced by using 4:1 ethyl acetate:isopropanol mixture as developer, although resist contrast is greatest for development in cyclohexanone.

Lithographic resolution

Resist patterns prepared with copolymers containing 24, 33 and 46 mol% IT.ANH were examined by scanning electron microscopy in order to determine the most suitable resist formulation for high-resolution lithography. Optimum resolution appeared to be obtained for a copolymer containing 46 mol% IT.ANH with $M_n = 5.30 \times 10^5$ g mol^{-1} using cyclohexanone as the developing solvent. Scanning electron micrographs of resist features prepared using this material are shown in *Figures 7* and *8*. Resist features prepared in a copolymer of lower primary number-average molecular weight ($M_n = 1.66 \times 10^5$ g mol^{-1}) showed a similar level of resolution to that found for $M_n = 5.30 \times 10^5$ g mol^{-1}, although resist features prepared using the former sample were more rounded with reduced edge acuity.

Degradation of the gel fraction

Following pre-baking, resist materials of the type described here can be expected to consist of two major components: (1) a soluble fraction, made up of linear and branched materials not connected to the crosslinked network; and (2) an insoluble or gel fraction, later to be destroyed during the irradiation of the resist. The gel fraction might typically constitute 0.6–1.0 of the total polymer system, although Flory[11] has pointed out that at such low levels of crosslinking the gel fraction will also contain a relatively high number of network imperfections including network loose ends, chain entanglements and closed loops.

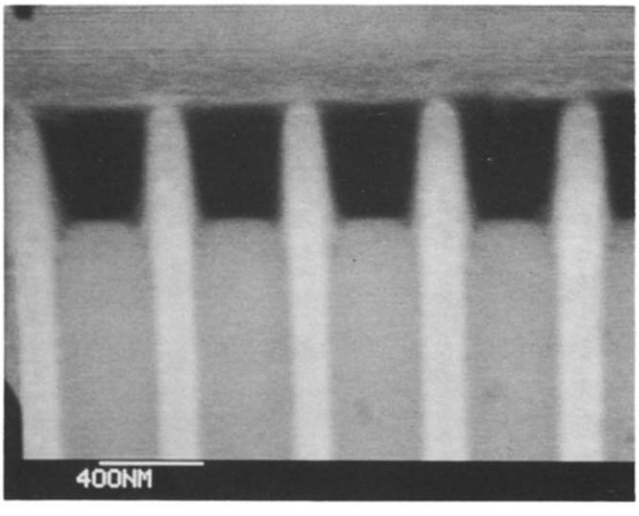

Figure 7 Line and space test patterns with 500 nm pitch prepared in copolymer containing 46 mol% IT.ANH with $M_n = 5.30 \times 10^5$ g mol^{-1}. Exposure dose = 200 μC cm^{-2}. Developer = cyclohexanone

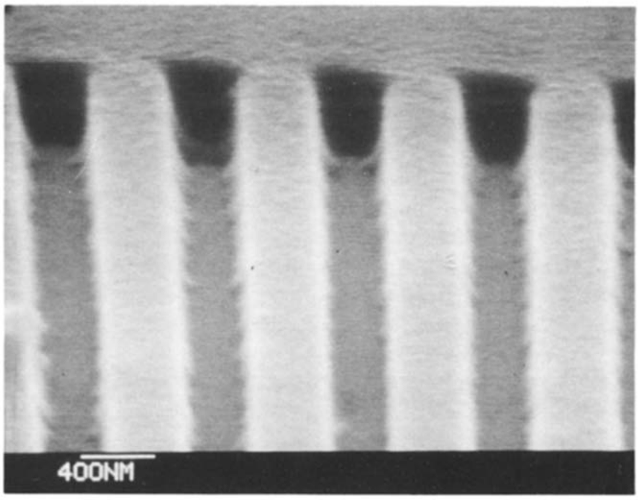

Figure 8 Line and space test patterns with 750 nm pitch prepared in copolymer containing 46 mol% IT.ANH with $M_n = 5.30 \times 10^5$ g mol^{-1}. Exposure dose = 200 μC cm^{-2}. Developer = cyclohexanone

During irradiation, molecules in the sol fraction will undergo chain scission leading to a direct reduction in the average molecular weight which, for linear molecules is given[12] by:

$$\frac{1}{M_n'} = \frac{1}{M_n} + \frac{G_s Q}{100 N_A} \tag{2}$$

where M_n' = number-average molecular weight following irradiation, M_n = primary number-average molecular weight, G_s = number of main-chain breaks per 100 eV absorbed energy, Q = absorbed energy (eV g^{-1}) and N_A = Avogadro's number. In addition to the decrease in average molecular weight, random main-chain scission is also likely to cause a change in the *MWD*[12] with M_w/M_n tending towards the most probable distribution with $M_w/M_n = 2$.

In the only theoretical approach published to date concerning the breakdown of the gel fraction during electron-beam exposure, Suzuki and Ohnishi[13] have proposed that the degradation of the pre-crosslinked network can be considered to depend upon the scission of the primary chains, and can be calculated using an expression analogous to equation (2). The highest attainable sensitivity (equivalent to the point at which the gel fraction is first destroyed) was given by:

$$D \geqslant \frac{200 \rho N_A (\delta - 1)}{[4 G_c P_c + G_s (1 - P_c)] A M_w} \tag{3}$$

Provided that P_c, the ratio of the energy absorbed by the crosslinkages only to the energy absorbed by the complete network, is given by $P_c \ll 1$, this can be approximated by:

$$D \geqslant \frac{200 \rho N_A (\delta - 1)}{G_s A M_w} \tag{4}$$

where D = exposure dose (C cm^{-2}), ρ = polymer density (g cm^{-3}), δ = crosslinking coefficient (equal to the number of crosslinked units per molecule of primary weight-

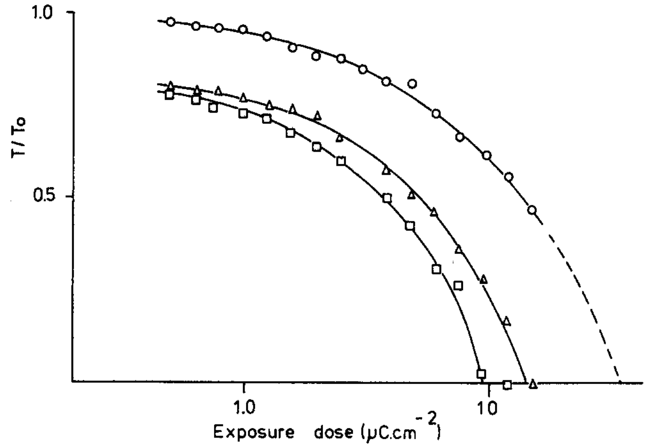

Figure 9 Normalized remaining thickness *versus* exposure dose for copolymers of 46 mol% IT.ANH: (□) $M_n = 1.11 \times 10^5$ g mol^{-1}; (Δ) $M_n = 1.66 \times 10^5$ g mol^{-1}; (○) $M_n = 4.24 \times 10^5$ g mol^{-1}. Samples immersed 96 h in 2-methoxyethyl acetate

average molecular weight), G_c = number of crosslink breakages per 100 eV absorbed energy, P_c = ratio of energy absorbed by the crosslinks to the entire polymer system and A = proportionality constant between absorbed energy per unit volume and the exposure dose D. It was concluded that resist materials with a high primary molecular weight, high G_s and a low value of $(\delta - 1)$ were required for maximum sensitivity.

To test the predicted dependence of the gel clearing dose (which we will call α_D) upon reciprocal molecular weight, samples of 46 mol% IT.ANH with $M_n = 1.11 \times 10^5$, 1.66×10^5 and 4.24×10^5 were exposed over the range 0.5–1.5 μC cm^{-2} and placed in covered Petri dishes filled with 2-methoxyethyl acetate for a total of 96 h. The samples were removed and rebaked for 1 h at 170°C. Normalized remaining thickness *versus* exposure dose is shown for each of these samples in *Figure 9*. It can be seen that in each case α_D is considerably lower than D_0 observed for development in cyclohexanone or ethyl acetate:isopropanol mixtures, and that for the range of primary molecular weights investigated here, the trend in α_D is opposite to that predicted by the existing theory. The fact that $D_0 \gg \alpha_D$ would suggest that continued degradation of the fragments once forming part of the gel fraction, or the molecules originally constituting the sol fraction, is an important requirement for the development of resist features at relatively short development times and for the production of high-resolution resist images. A corollary of this, however, must be that the observed lithographic sensitivity D_0 will in most cases be dependent upon resist development time and the particular solvent developer used in much the same way as for conventional positive acting resists.

CONCLUSIONS

It has been demonstrated that IT.ANH–MMA copolymers can operate as thermally crosslinkable electron-beam resists. A range of copolymer compositions have been investigated and a general variation in resist sensitivity D_0 and resist contrast γ have been noted with copolymer composition. An acceptable balance of resist sensitivity and contrast is obtained for copolymers containing ~46 mol% IT.ANH, and resist patterns with features smaller than 0.5 μm have been prepared using a copolymer containing 46 mol% IT.ANH with $M_n = 5.30 \times 10^5$ g mol^{-1}. Resist sensitivity for this formulation is relatively poor, however (~200 μC cm^{-2}).

The exposure dose required to solubilise the resist (α_D) has been found to be many times less than the exposure dose D_0 required for the preparation of lithographically useful resist patterns. A general dependence of lithographic sensitivity D_0 and the gel clearing dose upon the primary average molecular weight has been found. The variation in α_D with primary molecular weight for the materials investigated here has been opposite to that predicted in the theoretical expression due to Suzuki and Ohnishi[13]. It is hoped to address this latter observation in a future publication.

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