Radiation chemistry and the lithographic performance of chemical amplification resists formulated from poly(4-epoxystyrene-*stat*-styrene) and a photoacid generator

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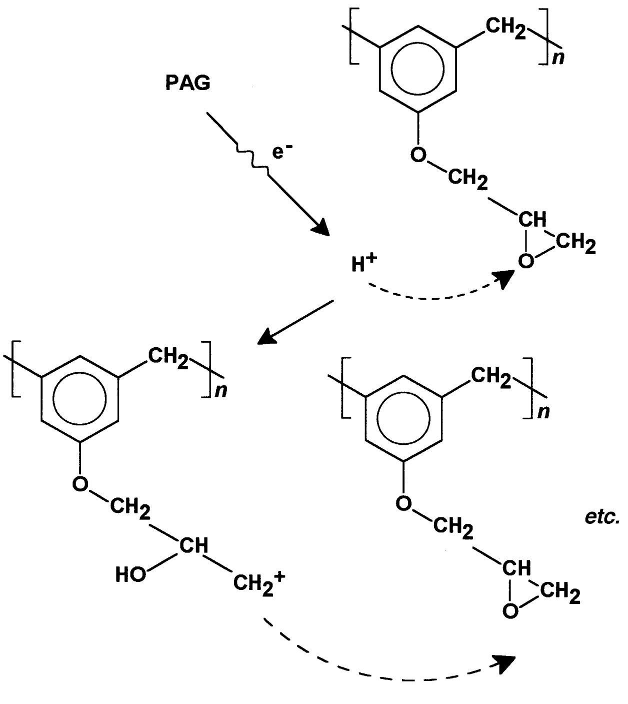
Copolymers of styrene and 4-epoxystyrene in formulations with triphenylsulfonium hexafluoroantimonate as a photoacid generator undergo a crosslinking reaction by a chain mechanism when irradiated with 20 keV electrons and hence act as negative-working electron-beam resists. The copolymers have been prepared by a free radical mechanism over the entire composition range and the lithographic performance of the materials has been evaluated. The sensitivities of the resist formulations are shown to correlate with the epoxystyrene content of the copolymers in accordance with a simple model of the radiation chemistry of the system. Contrast variations are explained in terms of the statistical structure of the copolymer and it is demonstrated that at low epoxystyrene contents the systems behave in accordance with an unsensitised single-stage crosslinking mechanism. The copolymers with epoxystyrene contents greater than *ca.* 8% have such high lithographic sensitivities and show such a good tolerance of processing variations as to commend the optimisation of their performance with a view to their subsequent application as electron-beam resists.

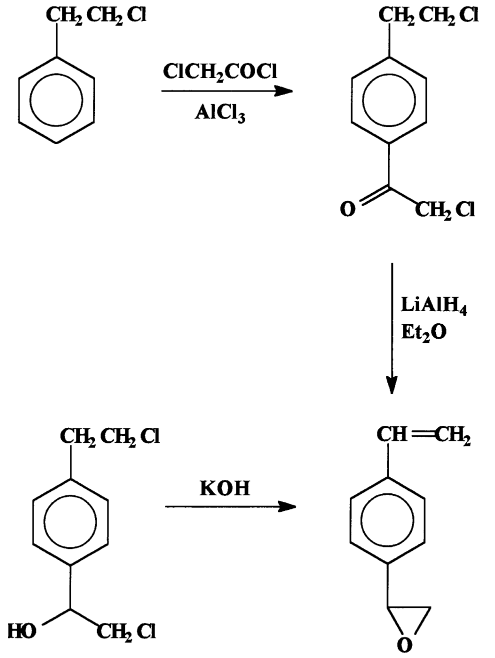
The use of so-called chemical amplification resists is becoming more commonplace in microlithography as their enhanced response, achieved through some radiation-induced chain mechanism, leads to the sensitivity necessary for the economic exploitation of many modern writing tools. However, many of those presently available are multicomponent systems which have little tolerance of process variations. Typically, even a very small change in the post exposure bake (PEB) temperature or time, required to realise the chemical amplification, might drastically alter the performance of the resist.[1] Some systems are also sensitive to environmental contaminants such as airborne amines.[2] Such problems make for great difficulty in achieving reproducibility. Positive-working systems commonly depend on the deprotection of a functional group by radiation-generated acid or base, which renders the exposed regions of the resist soluble in an aqueous-based development process. Negative-working systems usually rely on a chain crosslinking process which again is most commonly initiated by acid or base formed during exposure. Thus, two components, a polymer and a photoacid generator (PAG) such as an onium salt, are the minimum required in such formulations but it is by keeping to this minimum that processing difficulties can be contained.

Amongst the useful functional groups that might be employed in negative-working systems is the oxirane group. This group, which can undergo a radiation-induced chain crosslinking reaction, confers a high sensitivity upon polymeric resists that contain it. Oxirane functionalised polymers such as epoxidised poly(butadiene) or poly(isoprene)[3] and poly(glycidyl methacrylate)[4,5] were first investigated as electron-beam resists over twenty years ago. Unfortunately, the poor thermal stability of these aliphatic materials at the temperatures commonly encountered in lithographic processing has limited their exploitation. In terms of processibility, even the GMC series of resists (copolymers of glycidyl methacrylate and 3-chlorostyrene) with their considerable aromatic content fall far short of other copolymer resists based on poly(styrene) structures.[6–9] More recently, Hatzakis *et al.* have reported the lithographic performance of epoxy novalac resins in formulations with triphenylsulfonium hexafluoroantimonate as a PAG, as photo-, electron-beam and X-ray resists[10,11] as depicted in Scheme 1. Being aromatic materials, these display a number of the desirable properties associated with poly(styrene)-based resists such as excellent film forming ability, thermal stability allied with good resistance to oxygen plasma, and excellent tolerance to process variation. The measured contrasts for these systems tend to be low but this has little effect upon the resolution that can be attained, as features with dimensions as low as 0.1 μm have been demonstrated.[12]

One drawback of the Hatzakis systems is that it is not possible to prepare a range of polymers with structures sufficiently controlled as to allow a structure process optimisation. Novalac resins are not amenable to molecular mass control and the extent of their subsequent epoxidation cannot be controlled. Here we report the microlithographic performance of electron-beam resist formulations based on a series of poly(4-ethenylphenyloxirane-*stat*-styrene) copolymers. These can be viewed as epoxy novalac analogues, but their synthesis by radical polymerisation allows polymers of controlled molecular mass and epoxy content to be produced.



Scheme 1



Scheme 2

Experimental

Materials

Styrene (S) was supplied by Aldrich Chemical Co. Ltd. and distilled under reduced pressure at 40–50 °C prior to use. 4-Ethenylphenyloxirane (4-epoxystyrene, ES) was prepared in accordance with the method of Truxa and Suchopárek[13] shown in Scheme 2, and distilled under reduced pressure (65 °C at 0.1 mmHg) from sodium hydroxide prior to use.

Copolymerisations initiated by 2,2′-azoisobutyronitrile were carried out in toluene solution inside stoppered boiling tubes at 70 °C, under dry argon. The polymers were precipitated in a large excess of chilled methanol, reprecipitated from toluene solution, filtered and dried under vacuum. Precise experimental details of similar copolymer preparations have been reported elsewhere.[14]

Apparatus and procedures

Copolymer compositions were established from integration of 270 MHz ^1H NMR spectra obtained at room temperature, in $CDCl_3$ solution, using a JEOL JNM-GX270 spectrometer. Chemical shifts are relative to $SiMe_4$.

Molecular masses and polydispersities were determined as linear polystyrene equivalents using HPLC equipment supplied by Polymer Laboratories Ltd. and equipped with a mixed-bed 5 µm PLgel column. Glass transition temperatures were determined under a nitrogen atmosphere using a Perkin-Elmer DSC-7 differential scanning calorimeter operating at a scan rate of 10 °C min^{-1}.

Resist solutions were formulated by dissolving the polymers in propylene glycol methyl ether acetate to produce 15% solutions. Unless otherwise stated, the PAG, triphenylsulfonium hexafluoroantimonate, was also dissolved to 4%. The resist solutions were filtered through 0.5 µm Millipore filters and spun directly onto 3 inch† silicon wafers using a Headway EC-101 spinner to produce films of thickness in the range 0.5 µm. Lithographic assessment was accomplished using a Cambridge Instruments EBMF 10.5 electron-beam lithography tool operating at a 20 kV accelerating potential. After exposure the wafers were cut into segments which were then either developed immediately, or baked in an oven for 3 min at 90 °C prior to development. For process latitude studies, the post-exposure bake (PEB) times and temperatures were increased to up to 9 min and 150 °C respectively. Pattern development was accomplished by immersing the wafer segments in methyl isobutyl ketone (MIBK) for 60 s, rinsing in isopropyl alcohol‡ and drying in a stream of nitrogen. Film thickness measurements before and after exposure were measured using a Nanospec/AFT 210 Film Thickness System. All thicknesses were normalised to the original spun thickness. Sensitivities were estimated both as the gel dose (D^0) and as the dose corresponding to 50% thickness remaining after development ($D^{0.5}$). Lithographic contrasts, γ, were calculated from $D^{0.5}$ and D^0 using eqn. (1).

$$\gamma = 1/[2\log(D^{0.5}/D^0)] \qquad (1)$$

Conversion of the incident radiation dose in µC cm^{-2} to absorbed radiation dose in Mrad was carried out in accordance with the method developed by Novembre and Bowmer.[15] For a resist film having an approximate thickness of 0.5 µm and a density of 1 g cm^{-3}, it can be shown that a conversion factor of about 2 Mrad per (µC cm^{-2}) for 20 keV electrons applies. This is the value that has been used in this study.

Results

The effect of copolymer composition

All of the 4-epoxystyrene/styrene copolymers have glass transition temperatures that are sufficiently high to meet the demands of lithographic processing. These, together with the structural and lithographic parameters of a series of resists formulated from the copolymers and triphenylsulfonium hexaflouroantimonate, are recorded in Table 1. Representative contrast curves are depicted in Fig. 1. With the exception of P1, the number average molecular masses ($\bar{M}_n$) of the copolymers were controlled at about 15 000. The asymptotic departure of

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† 1 in = 2.54 cm.

‡ The solvent development system and development times have not been optimised and were chosen simply because they are regularly used with negative-working resists based on poly(styrene) derivatives.

Table 1 Structural parameters and lithographic properties of 4-ES/S copolymer resists in formulations containing 4% triphenylsulfonium hexafluoroantimonate

						baked resists				unbaked resists			
polymer	4-ES (%)	M_2	M_a	PD	T_g/°C	$D^{0.5}$	D^0	γ	*Gn*	$D^{0.5}$	D^0	γ	*Gn*
P1	100	15 500	9 700	1.56	140	0.190	0.045	0.80	160	0.263	0.051	0.70	110
P2	30	30 400	17 000	1.79	118	0.70	0.18	0.85	33	0.77	0.18	0.85	28
P3	18	28 000	15 100	1.85	113	1.14	0.35	0.97	24	1.45	0.41	0.91	19.3
P4	12	25 800	14 500	1.76	104	2.55	1.00	1.23	9.1	4.51	1.30	0.92	9.1
P5	10	28 400	16 300	1.75	104	3.84	1.27	1.0	7.3	7.93	2.67	1.1	5.7
P6	8	26 100	14 100	1.83	97	6.3	2.5	1.2	3.9	14.0	7.5	1.8	3.1
P7	4	25 100	14 500	1.72	93	56.5	33.5	2.2	1.0	65.5	41.0	2.5	1.0
P8	2	24 700	14 400	1.71	93	94.3	66.5	3.3	0.9	99.6	72.4	3.6	0.9

Table 2 The lithographic properties of 4-ES/S copolymer P6 in resist formulations over a range of triphenylsulphonium hexafluoroantimonate loadings

	baked resists			unbaked resists		
% PAG	$D^{0.5}$	D^{0}	γ	$D^{0.5}$	D^{0}	γ
0	—	—	—	37.9	23.1	2.30
0.25	17.1	3.3	0.70	23.5	10.5	1.43
0.5	14.8	3.6	0.81	22.4	10.6	1.54
1.0	10.1	2.6	0.85	21.6	11.0	1.71
2.0	7.6	2.0	0.86	21.5	10.6	1.63
4.0	6.3	2.5	1.25	14.0	7.5	1.84

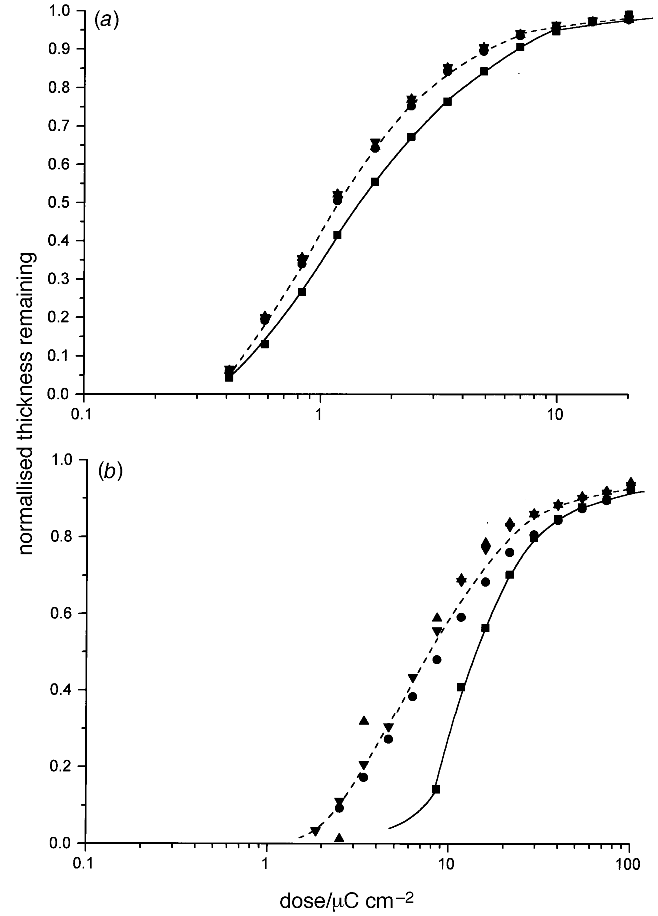

Fig. 1 Representative contrast curves of PAG sensitised resists: (*a*) polymer P3 baked at 120 °C for 0 (■), 180 (●), 360 (▲) and 540 s (▼); (*b*) polymer P6, unbaked (■) and baked at 90 (●), 120 (▲) and 150 °C (▼) for 180 s

the contrast curves from the dose axis at low doses, a characteristic of resist systems that undergo a chain crosslinking process, is discernible for all of the copolymers P1 to P5 and for the baked system of P6. The contrast curves for the remaining copolymers display a more acute departure from the dose axis, similar to that which is shown later in Fig. 5. The lithographic sensitivities of the resists increase sharply with the epoxide content but there is an accompanying loss of contrast. A plot of sensitivity against mole fraction of 4-epoxystyrene within the copolymers, shown in Fig. 2, levels off acutely at an epoxide content of *ca.* 10%; the sharpness of the knee in the curve is striking, being far more pronounced than those observed for the one component, single-stage crosslinking resists such as the chlorostyrene/methylstyrene copolymer systems.[14] Such a sensitivity variation might be expected for a resist system that crosslinks through a sensitised chain reaction. However, the contrast variation is also notably different from that observed for the single-stage crosslinking resists. The progressive inclusion of up to 30% epoxystyrene in this copolymer causes the contrast to drop to 0.85 from an initial value of 3.6 for the homopolymer, polystyrene. The contrast of the corresponding chlorostyrene/methylstyrene system of comparable molecular mass, over the same composition range, holds at *ca.* 2.5.

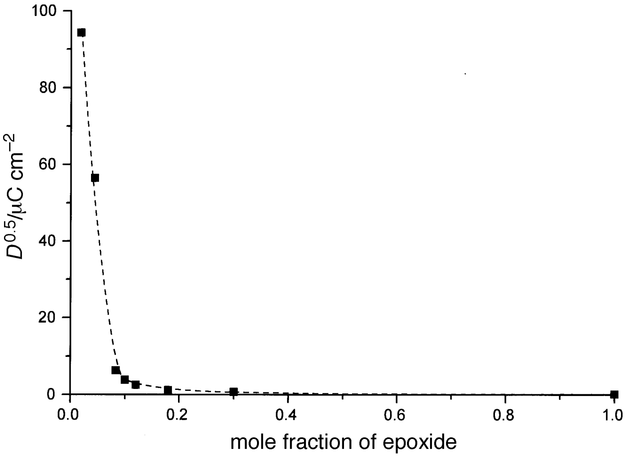

Fig. 2 Variation of lithographic sensitivity with copolymer composition

The effect of post exposure bake

From Fig. 1, it is evident that PEB temperatures greater than 90 °C and durations longer than 3 min are unnecessary. The effect of baking the exposed images is to decrease the sensitivity parameters, corresponding to an increased sensitivity, but not to an equivalent extent for both of D^0 and $D^{0.5}$. Thus, though the chemical amplification within these systems is evident it is not uniform at all compositions. For resists containing up to 10% epoxystyrene, baking results in a lesser contrast. At higher epoxystyrene contents the contrasts are marginally enhanced, baking having little or no effect on D^0 at the higher epoxystyrene contents. At an epoxystyrene content of 30% baking no longer has any noticeable effect, though one is again apparent for the formulation involving the poly(4-epoxystyrene) homopolymer. Only those resists containing less than 10% epoxystyrene show PEB effects that are comparable to the amplifications observed for the epoxy novolac systems.[16] Thus, for copolymer compositions that are lithographically useful, P2 to P6, the present resist system is notably more tolerant of processing variations than are the epoxy novolac formulations. Whilst not asserting a PEB to be unnecessary, it is nonetheless apparent that to all intents and purposes the maximum attainable level of crosslinking is achieved within the unbaked systems.

The effect of variations in PAG loading

Fig. 3 depicts the variation of the sensitivity of the copolymer P6 with PAG concentration. A sharp increase in sensitivity results from the inclusion of even the smallest amounts of the PAG, but for the unbaked systems the effect then seems to be more or less invariant up to a content of about 2%. In contrast, for the baked systems a steady increase in sensitivity is evident over the composition range investigated. Accordingly, the greatest chemical amplification is evident at a PAG content of 2%. The corresponding contrast variations are shown in Fig. 4. For both the unbaked and baked systems, a small but steady increase with PAG loading is evident following the initial sharp drop from the contrast of the unloaded system.

The relatively insensitive system in which no PAG is included has a contrast value of 2.3. This is characteristic of the optimum that can be obtained from a single-stage crosslinking resist

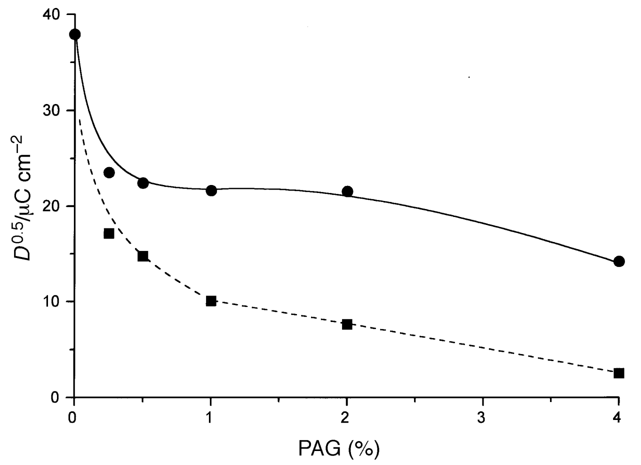

Fig. 3 Variation of lithographic sensitivity of polymer P6 with PAG loading, (●) unbaked and (■) baked for 180 s

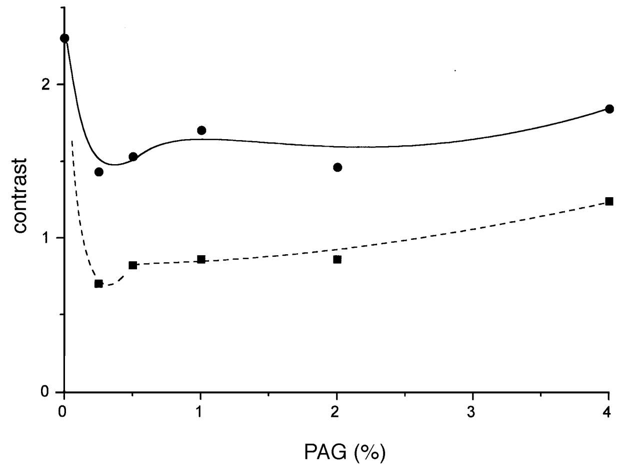

Fig. 4 Variation of lithographic contrast of polymer P6 with PAG loading, (●) unbaked and (■) baked for 180 s

with a normal (most probable) molecular mass distribution.[17,18] The contrast curve for this resist is shown in Fig. 5.

Discussion

We have previously adapted the Charlesby theory of polymer network formation by an uninhibited radiation-induced chain reaction[19] to derive a simple model, shown as eqn. (1), for the lithographic performance of negative-working resists based on the chemical amplification principle.[16]

$$s = e^{-\alpha r} \tag{1}$$

The sol fraction remaining in the irradiated polymer is s, and r is the absorbed dose in Mrad. The parameter α is given by eqn. (2) in which G is the radiation chemical yield for chain initiation (assumed to be the number of protons deriving from the photoacid generator that are effective in initiating the crosslinking process per 100 eV of energy absorbed), n is the number of polymer chains that are linked in the ensuing crosslinking, and $\bar{M}_n$ is the initial number-average molecular mass of the polymer.

$$\alpha = 1.04 \times 10^{-6} G n \bar{M}_n \tag{2}$$

Rearranging eqn. (1) gives eqn. (3).

$$\ln s = -\alpha r \tag{3}$$

This simple model predicts that plots of *ln s vs. r* would be linear with zero intercept, and knowledge of $\bar{M}_n$ allows the calculation of the product parameters, *Gn*, from their slopes. These values are listed in Table 1 and the chemical amplification effect is evident from a comparison of the values for the baked and unbaked resists. The effect is much more pronounced for the systems of lithographic interest in which the epoxystyrene content exceeds *ca.* 10%.

It is usual, when discussing the lithographic response of negative-working resists, to employ equations expressed in terms of the gel fraction, g, since this can be related directly to the thickness, t, of the resist layer that remains after development, normalised to its original spun thickness, t_0. Thus, since $s = 1 - g$ and $g = t/t_0$ it follows that $s = 1 - t/t_0$. Thus, the lithographic data can readily be plotted in accordance with eqn. (3). Fig. 6 shows representative plots derived from the primary data of the contrast curves shown in Fig. 1 for the

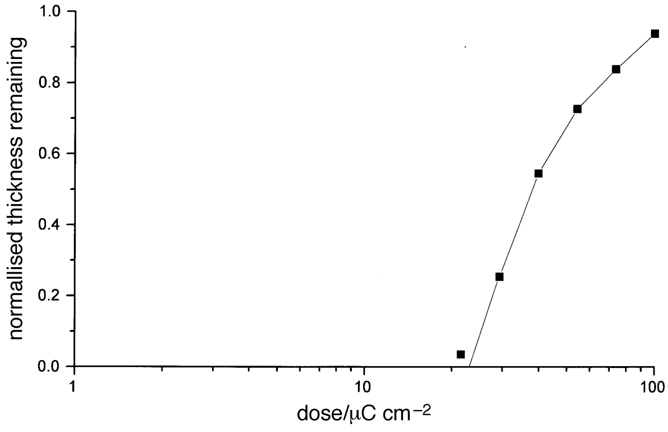

Fig. 5 Contrast curve for the unsensitised resist based on polymer P5

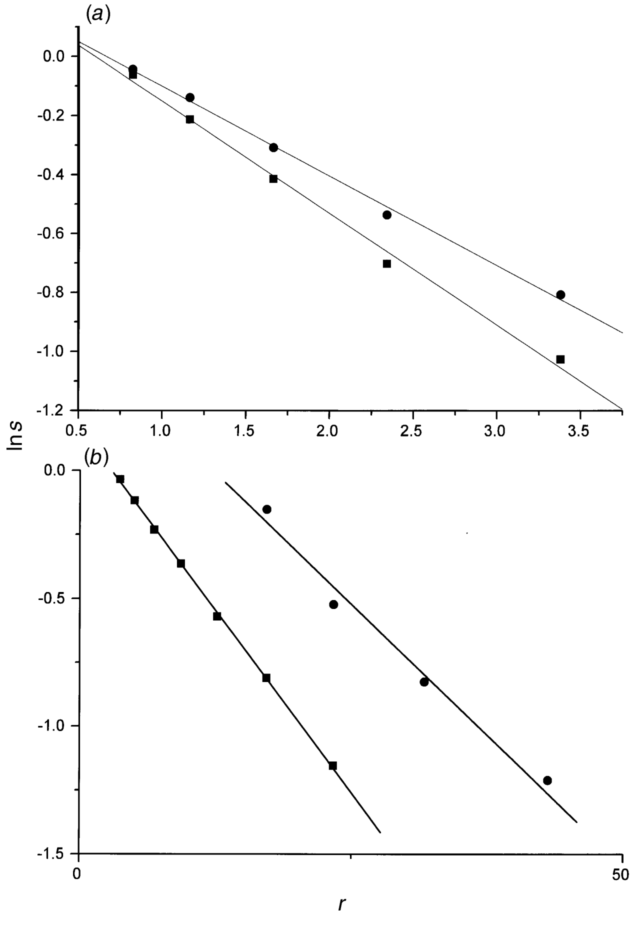

Fig. 6 Charlesby plots of data of contrast curves represented in Fig. 1

resist formulations P2 and P6. The curves are linear up to normalised thicknesses remaining in excess of 0.7, beyond which they show a positive deviation from linearity. The onset of this deviation generally appears at lower doses for the unbaked systems. It is attributed to localised reductions in epoxide groups to levels at which the active centres of crosslinking become effectively trapped at voids.

With the exception of the plot for the poly(4-epoxystyrene) homopolymer, P1, the plots for copolymers with epoxystyrene contents greater than 8% displayed small positive intercepts ranging from about 0.05 to *ca.* 0.25. Within this range there was no apparent order to indicate a correlation with the epoxystyrene content of the copolymers, but it can nonetheless be inferred that the model for the copolymers should be modified to accommodate a small correction factor, K, as shown in eqn. (4), the magnitude of which would be no greater than 1.5. The significance that can be attached to the need for this correction is that the apparent gel dose of the copolymer resists is marginally suppressed, an effect that can be attributed to the irregular distribution of crosslinking points along the polymer chain that results from a statistical copolymerisation process. The irregular distribution is itself a source of structural voids at which active centres might be trapped. This concept accords with the Charlesby models of radiation-induced crosslinking reactions in which the processes are eventually terminated at centres from which further growth is inhibited for any one of several reasons, and which are represented by the generalised formula of eqn. (4).

$$s = K\,\mathrm{e}^{-\alpha r} \tag{4}$$

For ease of reference whilst following the ensuing kinetic argument, an adaptation of Scheme 1 to represent radiation-induced crosslinking in the copolymer resists is shown in Scheme 3, within which **Ox** represents an oxirane group, $\mathbf{C}^+$ propagating carbonium ions and **i** is the associated extent of crosslinking, which in the limit assumes the average value n, *i.e.* $1 \leqslant \mathbf{i} \leqslant n$.

$$\mathrm{PAG} \xrightarrow{e^-} \mathrm{H}^+$$
$$\mathrm{H}^+ + \mathbf{Ox} \xrightarrow{G} \mathbf{C}_0{}^+$$
$$\mathbf{C}_{i-1}{}^+ + \mathbf{Ox} \longrightarrow \mathbf{C}_i{}^+$$

Scheme 3

Although values of G have not been determined it is reasonable to assume that they are proportional both to the PAG loading and to the concentration of epoxide groups since the addition of a proton to an oxirane has a significant energy of activation of 25 kJ mol^{-1}.[20] The PAG loadings have been maintained at 4% throughout the series of resists represented in Table 1. G is therefore proportional to the epoxystyrene content within the copolymers. The length of the ensuing chain crosslinking reaction, n, is again proportional to the concentration of epoxide groups. It follows that the product parameter, Gn, should vary linearly with the square of the mol fraction, x, of epoxystyrene in the copolymers, *i.e.* $Gn = kx^2$ where k is a proportionality constant.

Although the above conclusions can be applied directly to the values of Gn listed in Table 1 it is more informative to relate them back to the lithographic parameters. Thus, substituting $s = 0.5$ at $r = R^{0.5} = 2D^{0.5}$ into eqn. (4) and rearranging leads to eqn. (5).

$$D^{0.5} = \frac{\ln(0.5/K)}{2.08 \times 10^{-6} Gn} \tag{5}$$

If K is taken to be 1 then eqn. (5) reduces to eqn. (6).

$$D^{0.5} = 3.33 \times 10^5/Gn = (3.33 \times 10^5/k)x^{-2} \tag{6}$$

Eqns. (5) and (6) both indicate that the lithographic sensitivity, $D^{0.5}$, should vary inversely with the square of the epoxystyrene content of the copolymers. A linear regression analysis of the $\log_{10} D^{0.5}$ *vs.* $\log_{10} x$ plot of Fig. 7 reveals a slope of -1.99. The plot of $D^{0.5}$ *vs.* x^{-2} of Fig. 8 shows the accuracy of the correlation over the data points of lithographic interest.

It was previously shown that, according to the simple model represented by eqn. (1), the contrast, γ, should always be 0.8 whilst, at the same time, it was acknowledged that for the epoxy novolac systems this apparently represented a minimum value.[16] From Table 1 it is apparent that this same minimum value applies to these systems. However, it is clear that the epoxystyrene homopolymer is the only one to which the value 0.8 actually applies, and that with decreasing epoxystyrene content within the copolymers, the contrast steadily increases. If eqn. (4) is used as the premise for the derivation of an expression for contrast, taken to be the slope of the contrast curve at the dose required for 50% gelation, then it is readily shown that eqn. (7) holds.

$$\mathrm{d}g/\mathrm{d}\log_{10} r = 2.303\,K \alpha r\,\mathrm{e}^{-\alpha r} \tag{7}$$

By substituting $r = R^{0.5}$, it follows that contrast is given by eqn. (8).

$$\gamma = 0.8 + 1.15 \ln K \tag{8}$$

Comparison of eqn. (8) with Fig. 9, a plot of γ *vs.* the reciprocal of the mol fraction, x, of epoxystyrene in the copolymer, indicates that there is a rough correlation between K and composition. The slope of this plot when it is equated to 1.15 ln K leads to eqn. (9).

$$K = \mathrm{e}^{0.047/x} \tag{9}$$

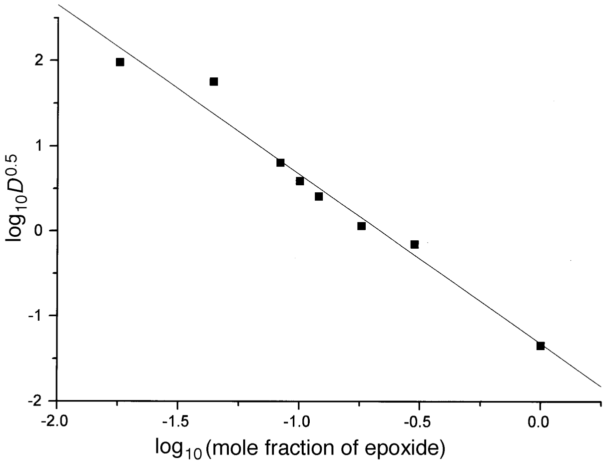

Fig. 7 Log–log plot of the variation of lithographic sensitivity with copolymer composition

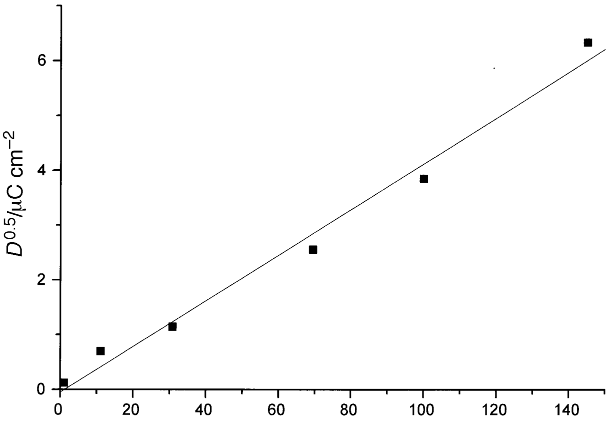

Fig. 8 Variation of lithographic sensitivity with copolymer composition plotted in accordance with the form of eqn. (6)

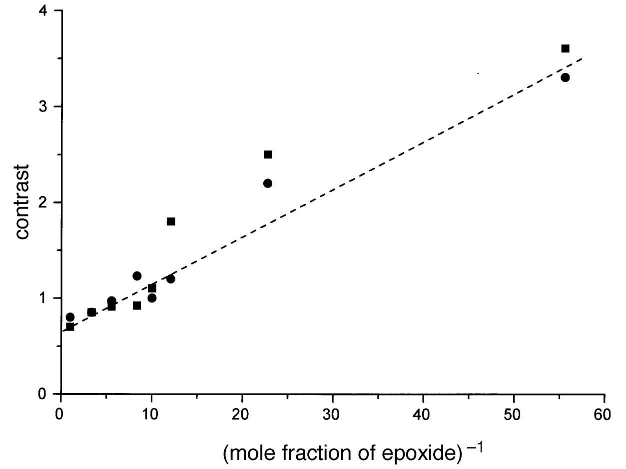

Fig. 9 Plot of the variation of contrast with the reciprocal of copolymer composition

For copolymers containing 8–30% of epoxystyrene, values of K calculated from eqn. (8) are of about the same magnitude as those estimated from the intercepts of the Charlesby model plots though, as the epoxystyrene content drops to lower values, the value of K, estimated from eqn. (9), increases by an order of magnitude. However, at such low contents of epoxystyrene it is arguable that the system bears little resemblance to the epoxy novolac system upon which it was modelled. Copolymers of $\bar{M}_n$ approximately 15 000 have degrees of polymerisation lying between 100 (epoxystyrene homopolymer) and 145 [poly(styrene)], corresponding to numbers of oxirane groups per molecule in the range 100 to 11 for copolymers in the lithographically interesting composition range. The remaining copolymers of the series, P7 and P8, contain even fewer oxirane groups, *ca.* 5 and 2 respectively. Not surprisingly these systems are likely to behave in a similar fashion to poly(styrene) for which sensitisation by a PAG is an irrelevance; indeed their lithographic parameters resemble those of low sensitivity single-stage crosslinking systems. From Table 2, it is evident that the resist based on copolymer P6 without the inclusion of PAG displays a greater sensitivity than either of these resists. The three resists actually make a series in which the sensitivities of the unbaked systems increase with increasing epoxystyrene content. Fig. 10 represents a plot of the contrast curve of Fig. 5, which is for the resist P6 without PAG, in accordance with the Charlesby model for a radiation-induced single-stage crosslinking reaction of a polymer with a normal molecular mass distribution.[19] The broken line represented in Fig. 5 applies to a system which undergoes a radiation-induced chain crosslinking process but which is of the same sensitivity. The more satisfactory fit of the data points to the former model than to the latter is clear.

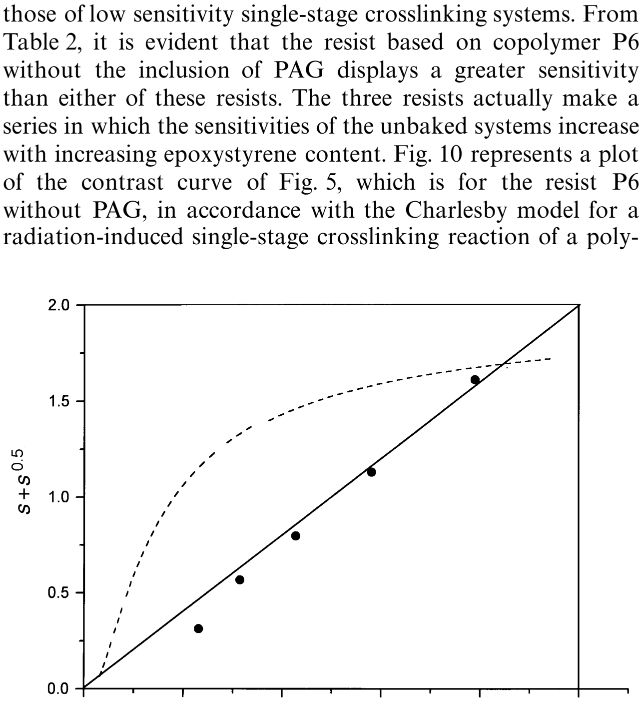

Fig. 10 Data taken from the contrast curve of Fig. 5 plotted in accordance with the Charlesby model for a single-stage crosslinking reaction (—) compared with a similar representation for a system of the same sensitivity which undergoes a chain crosslinking process (···)

Conclusions

It has been demonstrated that statistical copolymers of styrene and 4-epoxystyrene, in formulations with an onium salt photoacid generator, make very sensitive electron-beam resists, even when the epoxystyrene content of the copolymers is quite low. The mathematical model previously developed to correlate the lithographic data for the so-called 'Hatzakis' resist based on formulations of epoxy novolacs and a PAG has been extended for application to these systems and a possible explanation for contrast variations has followed. At one extreme of copolymer composition, the systems have been shown to behave as chemical amplification resists in an exactly analogous manner to the 'Hatzakis' systems, whilst at the other end of the composition scale, their lithographic performance is more in accordance with that of an unsensitised, single-step crosslinking system. The chemical amplification effect within those resists that are of lithographic interest is not as pronounced as has been observed for the 'Hatzakis' systems, an attractive feature with regard to the reproducibility of the effects of any post exposure bake that would be applied during processing. The wide potential for the further development of the resist has been demonstrated. The optimisation of its lithographic performance will need to take into account molecular mass considerations and the need to seek an appropriate solvent development system but through the present study it has again been shown that resists designed around copolymers offer a flexibility that cannot be obtained from homopolymer systems.

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