polymer papers

Electron-beam resists from Langmuir–Blodgett films of poly(styrene/maleic anhydride) derivatives

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A range of styrene/maleic anhydride polymer derivatives and some related polymers have been synthesized and their performance as electron-beam resists assessed, initially as spin-coated films and then as Langmuir–Blodgett (LB) films on silicon. The effects of molecular structure, molecular weight and packing have been investigated in designing materials for optimum sensitivity and resolution. The most promising materials contain vinyl or ethynyl crosslinking groups and are negative resists, resolution $\approx 0.25\,\mu m$ and gel dose in the range $1–40\,\mu C\,cm^{-2}$. Exposed and developed LB films only 50 layers (≈ 50 nm) thick have good plasma etch resistance, allowing the processing of tri-level resist structures (polyimide/Al/LB film) with little loss of resolution. This indicates that LB films based on poly(styrene/maleic anhydride) have the potential for the fabrication of submicrometre electronic devices.

(Keywords: poly(styrene/maleic anhydride); Langmuir–Blodgett films; electron beam; lithography; resist)

INTRODUCTION

Electron-beam lithography is currently the favoured technique for submicrometre device fabrication because of its direct writing capability, but it can only achieve its full potential if resist films of thickness comparable to the required resolution are used (reducing forward-scatter) and a suitable choice of beam energy and substrate is used (reducing backscatter)[1,2]. Spin-coated films relatively free from pinhole defects are now routinely available only 50 nm thick, giving resolutions of better than 100 nm for both positive and negative resists.

Langmuir–Blodgett (LB) films 50 nm thick or less are also relatively free from such defects; they may include a variety of moieties chosen for their sensitivity or etch resistance, and the molecular packing is usually well defined, which may enhance sensitivity. Polymerizable LB films were first investigated as possible electron-beam resists about a decade ago by Barraud *et al.*[3], and work up to 1983 has been reviewed by Peterson[4]. Barraud and coworkers[5,6] have used ω-alkenoic acid derivatives and alkadiynoic acid derivatives. The former were negative resists with good resolution (50 nm). Fariss *et al.*[7] obtained both positive and negative resists based on α-octadecylacrylic acid with resolutions of 100 nm and 50 nm, respectively, and Broers and Pomerantz[8] achieved the highest resolution reported to date (10 nm) for lines written in films of manganese stearate without, however, discussing the mechanism in any detail.

Despite these achievements, the only work on LB films that has seriously addressed the problem of dry etch resistance in subsequent processing as well as sensitivity and resolution has been that of Barraud and coworkers, who showed that 40 nm of resist could protect 150 nm of aluminium. Also, the range of chemical structures considered for LB films has been small compared with that available for microlithography in general[9]. For example, epoxide and halogen groups can be very efficient in promoting crosslinking in negative resists. Polymers of styrene that have been chlorinated, and especially chloromethylated, in various proportions are very good in terms of both sensitivity and dry etch resistance[10,11]. Copolymers of α-methylstyrene/maleic anhydride have greater sensitivity and contrast than α-methylstyrene homopolymers, but like most other positive resists the sensitivity is still only moderate[12].

We have reported extensively on copolymers of styrene/maleic anhydride used as LB films for various other purposes (see, for example, Hodge *et al.*[13]). These films combine the advantages of easy deposition, good quality, mechanical rigidity and adhesion, with the possibility of incorporating a variety of reactive moieties on both the main chain and on side chains. This has allowed us to carry out a systematic study of the factors involved in good electron-beam sensitivity and resolution in LB films and to design materials accordingly. We have also extended the processing to tri-level resist structures[14,15], indicating that LB films have all the necessary properties for submicrometre device fabrication.

EXPERIMENTAL

Polymer synthesis

The structures of the polymers studied in this project are summarized in *Table 1*. Polymers 1–6 were a gift from Dr E. Khoshdel and formed part of a series prepared in conjunction with another project[13]. Polymers 7–14 were prepared by reacting the appropriate alternating vinyl/maleic anhydride copolymers with the appropriate alcohols as indicated below.

The styrene/maleic anhydride copolymer ($M_n = 1600$) and the octadec-1-ene/maleic anhydride copolymer

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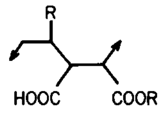
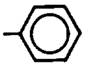
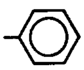
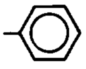
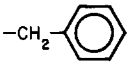
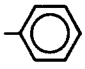
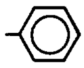
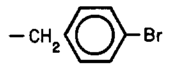
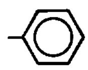
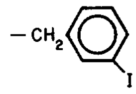
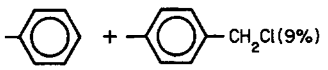
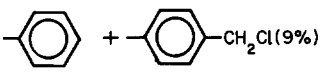
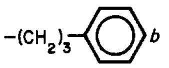
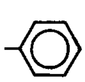
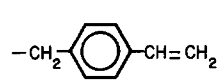
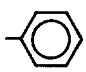
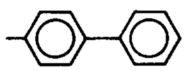
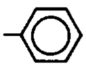
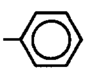
Table 1 Polymers used for electron-beam resist work

Structure



Polymer number	R	R'	$\bar{M}_n$[a]
1		$-H$	1600
2		$-CH_3$	1600
3			1600
4		$-CH_2(CF_2)_5CH_2F$	1600
5			1600
6			1600
7		$-CH_3$	1600
8			1600
9			1600
10		$-(CH_2)_9CH{=}CH_2$	[a]1600 [b]19000
11	$-(CH_2)_{15}CH_3$	$-(CH_2)_9CH{=}CH_2$	19000
12		$-(CH_2)_9CH{=}CH_2$	5000
13		$-(CH_2)_9C{\equiv}CH$	[a]1600 [b]19000
14		$-(CH_2)_9C{\equiv}C{-}C{\equiv}C(CH_2)_{11}CH_3$	1600

[a] These are the M_n of the intermediate vinyl-maleic anhydride copolymers

[b] Approximately 90% of these residues; the remainder are $-CH_3$ residues

($M_n = 19\,000$) were commercial samples. The 4-vinylbiphenyl/maleic anhydride copolymer ($M_n = 5000$) was a gift from Dr E. Khoshdel. The styrene/maleic anhydride copolymer ($M_n = 19\,000$) was prepared by copolymerization of styrene and maleic anhydride in carbon tetrachloride at 60°C initiated by AIBN (azobisisobutyronitrile): the M_n was determined by vapour pressure osmometry.

The chloromethylated styrene/maleic anhydride copolymer was prepared by treating the copolymer (5.0 g, $M_n = 1600$) with chloromethyl ether (12.5 ml) and boron trifluoride etherate (10 ml) in hexane (50 ml) at 35°C for 3 h. Precipitation into methanol and reprecipitation from tetrahydrofuran into methanol gave the chloromethylated product (2.5 g) with 1.47% Cl, equivalent to chloromethylation of 9% of the phenyl rings. The carbonyl region of the infra-red spectrum was essentially like that of the starting material.

3-Phenylpropanol and 10-undecenyl alcohol were commercial samples. The latter was converted into 10-undecynyl alcohol by the method of Jefferey and Vogel[16]. 4-Vinylbenzoic acid was prepared from 4-chlorostyrene as described by Leebrick and Ramsden[17]; reduction of the product with lithium aluminium hydride in ether gave 4-vinylbenzyl alcohol. Pentacosa-10,12-diynol was prepared by a similar reduction of the corresponding acid which was obtained from QMC Industrial Research Limited, London.

Polymers 7 and 8 were prepared by treating the chloromethylated styrene/maleic anhydride copolymer with the appropriate alcohol in tetrahydrofuran at reflux temperature for 2 weeks. Polymers 9–14 were prepared by treating the appropriate vinyl/maleic anhydride copolymer with sodium hydride and the appropriate alcohol in tetrahydrofuran at reflux temperature for 1–2 weeks. Except where indicated otherwise in *Table 1*, the infra-red spectra of the products indicated (carbonyl region) that the conversions of anhydride residues into the half-esters were 95–100% complete. In the one case indicated the ring opening was completed using methanol.

Substrates and LB film deposition

Substrates for spin-coating and LB film deposition were polished 3 inch n-type 1-1-1 orientated silicon wafers (Wacker Chemitronic GMBH) on which a 100 nm oxide layer had been thermally grown. They were treated in one of the following ways. (i) They were cleaned for 5 min at 40°C in an aqueous solution containing 2% w/v NaOH and 5% v/v of 30% H_2O_2, rinsed thoroughly in distilled water, dried in clean air, and made hydrophobic by overnight exposure to the vapour of 1,1,1,3,3,3-hexamethyldisilazane. (ii) They were cleaned by alkali as in (i), then coated with Al (75 nm ± 10%) by evaporation at a rate of $0.5\,\%\,s^{-1}$ at 10^{-5} Torr (for Al etching studies). (iii) They were spin-coated with 1.5 μm of polyimide (Hitachi PIQ) before aluminizing as in (ii) (for tri-level resist studies).

For spin-coating, polymers were dissolved in methanol, ethyl acetate or tetrahydrofuran (1 g/10 ml). Wafers were pre-baked at 130°C for 30 min, then 70°C for 30 min, then coated with 2 ml of the solution and spun at 5000 rpm, then baked again at 120°C for 30 min.

For LB film deposition, polymers were dissolved in ethyl acetate ($0.5\,mg\,ml^{-1}$) and filtered through 0.5 μm filters. The subphase was deionized, doubly distilled, millipore-filtered water at 20°C, pH 4.5–6.0. Film deposition was at a pressure of $30–40\,mN\,m^{-1}$ and a dipping speed of $8\,mm\,min^{-1}$ with 3 min drying time between dipping cycles. Fifty Y-type layers were routinely deposited. LB film deposition and all subsequent processing was carried out under clean room conditions and under yellow light (some of the polymers were u.v.-sensitive) and was completed within 1 week where possible.

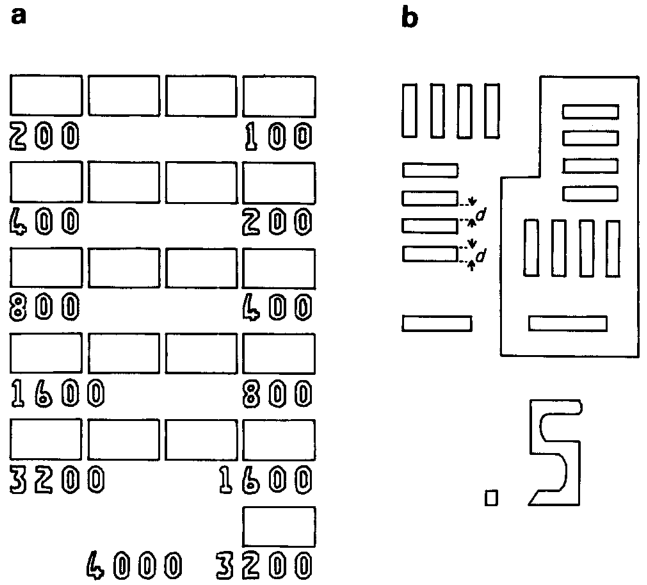


Figure 1 Electron-beam lithography test patterns. (a) Wedge pattern used for determining sensitivity and contrast. The dose received at any point on the wedge is inversely proportional to the beam incrementing rate, given (in kHz) by the figures. (b) Part of a bar and gap (EBT) pattern used for determining resolution. The number by the pattern gives the width of the bars and gaps (*d*) in micrometres

Electron-beam lithography

This was performed at RSRE Malvern on a Cambridge Instruments EBMF-2 microfabrication machine[14] at 20 kV accelerating voltage with beam currents in the range 0.1–4 nA and a spot size of 0.15–0.2 μm. The beam incrementing rate was in the range 25 kHz to 4 MHz, allowing standard wedge patterns with doses in the range 0.16–256 $\mu C\,cm^{-2}$ to be drawn for assessing the sensitivity and contrast of films (*Figure 1a*). Test patterns for resolution consisted of a series of gratings, spacing 0.125–2.0 μm, and a series of bar and gap (EBT) patterns, 0.25–10 μm (*Figure 1b*). The arrangement of test patterns on any wafer was fully programmable.

Development

Exposed wafers were immersed at 20°C in a non-solvent, then in two changes of a development solvent with agitation for 15–60 s, then in non-solvent again (avoiding reprecipitated polymer which may be difficult to remove) and finally blow-dried. The development solvents were normally mixtures of the non-solvent and a solvent and included benzene/propan-2-ol, benzene/chloroform, chloroform/propan-2-ol, chloroform/methanol and 4-methyl-2-pentanone. By varying the composition of the mixtures and the development times, suitable development conditions giving a clear background, good pattern contrast and the best resolution were found for each polymer.

Evaluation of resist parameters: sensitivity, contrast and resolution

Sensitivity was initially estimated for each polymer by noting the electron dose required to give just-detectable thinning (negative resists) or nearly complete film removal (positive resists) in developed wedge patterns. Small changes in thickness for films 50 layers (≈ 50 nm) thick on 100 nm oxide were easily detected by reflection microscopy as a change of interference colour. For negative resists more accurate thickness determinations were carried out by traversing gold-coated wedges with a Talystep mechanical stylus or by comparing interference colours in wedges with those in a specially fabricated LB wedge with four-layer steps. The two methods were in reasonable agreement but the stylus method was somewhat more accurate (±7% for 50 layers). Sensitivity, or gel dose, was taken as the dose at which the extrapolated middle portion of a plot of $\log_{10}$(dose) *versus* fractional thickness remaining intercepted the horizontal line corresponding to unit thickness. Contrast is defined as the slope of this linear middle portion.

Resolution was estimated by exposing grating and EBT patterns near to the gel dose determined previously from wedge patterns, developing, and viewing in an optical microscope. Patterns with a resolution better than the optical limit (0.37 μm) were viewed in a scanning electron microscope after coating with 10–20 nm of gold by sputtering or, for slightly better contrast, by angled evaporation.

Further device fabrication steps

Plasma etching of Al to transfer developed test patterns into the metal was carried out at RSRE Malvern in an Applied Materials 8130 metal etcher using a BCl_3/Cl_2 plasma (60/15 sccm flow) at 25 mTorr and 280 V bias. The process was monitored by reflectivity of a freshly exposed uniform metal surface. The etch time was 2.6–3.0 min followed by a 20% over-etch period.

For the tri-level structures, the Al etch was followed by polyimide etching in an O_2 plasma at 2 mTorr, −350 V d.c. bias and 250 W forward r.f. in an Applied Materials AME 8111 etcher. The etching (67 min, with no over-etch) was monitored by interferometry. The structures produced were viewed directly in the scanning electron microscope without metallization. The fabrication sequence is shown in *Figure 2.*

RESULTS AND DISCUSSION

Preliminary screening of polymers as spin-coats and LB films; effects of chemical structure and packing on sensitivity

Polymers 1–6 (*Table 1*) behaved as rather insensitive positive resists when spin-coated, exposed to standard wedge patterns and developed in benzene/chloroform mixtures (*Table 2*). It was expected that they might function as positive resists in a similar manner to poly(methyl methacrylate) (PMMA) but with better sensitivity because of the alternating structure and more radiation-sensitive groups[12], or that polymers 5 and 6 might crosslink to give negative resists. The initial trials were disappointing and were not extended to LB films.

The remaining polymers in *Table 1* (7–14) would be expected to crosslink on irradiation and therefore to serve as negative resists. All those with aromatic rings, and especially polymers 7–9, would also be expected to have good plasma etch resistance. Vinyl or acetylene groups (polymers 9–14) would be expected to have good sensitivity since on irradiation they could polymerize via a chain reaction, although if this process is carried too far it could lead to loss of resolution. Initial studies with some of these polymers (7, 10a, 11), spin-coated and developed in chloroform or benzene/propan-2-ol mixtures,

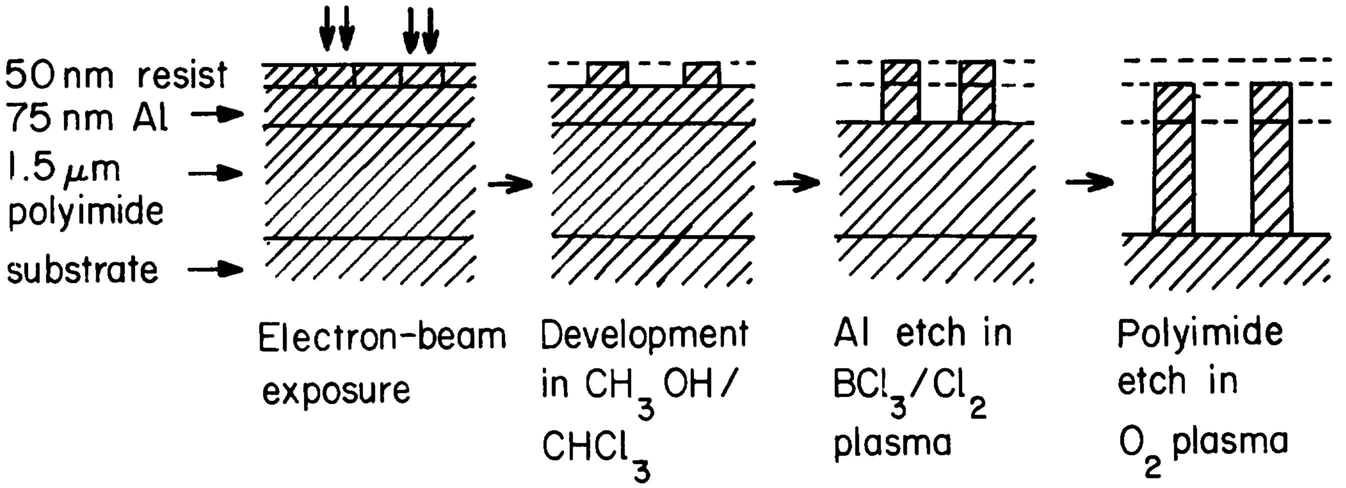


Figure 2 Fabrication sequence used for tri-level resist structures (schematic)

Table 2 Electron-beam sensitivity of polymers as spin-coats and as LB films

Polymer	Reactive group	$\bar{M}_n$	Gel dose (μC cm^{-2}) Spin-coat	Gel dose (μC cm^{-2}) LB film
1–6	Various	1600	100–1000^a	–
7	4-Chloromethylphenyl	1600	50	>100
8	4-Chloromethylphenyl	1600	–	>100
9	Styryl	1600	–	250
10a	Vinyl	1600	20	10
11	Vinyl	19000	10	>100
12	Vinyl	5000	–	400
13a	Ethynyl	1600	–	40
14	Diacetylene	1600	–	500

^{a} Positive resists

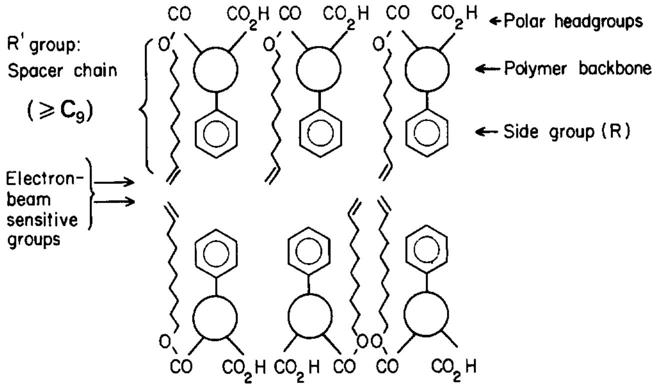


Figure 3 Model for the packing of poly(styrene/maleic anhydride) derivatives in LB multilayers, viewed end-on to the polymer backbones (schematic)

confirmed that they were negative resists and had much better sensitivity than the previous materials (*Table 2*).

Further results in *Table 2*, obtained with LB films, also illustrate the role of molecular structure and packing in determining sensitivity, and provide important guidelines for materials design. These are as follows.

(1) Polymer 10a, with the reactive vinyl group on a C_9 spacer chain and R as a phenyl group, is much more sensitive than polymers 11 and 12, where R is a long aliphatic chain or a relatively bulky aromatic group, despite the fact that polymers 11 and 12 had higher molecular weights which would normally improve sensitivity. This can be rationalized in terms of the model shown in *Figure 3* and originally proposed[13] to explain other observations on the packing of LB multilayers of poly(styrene/maleic anhydride) derivatives. The model indicates that if the spacer on R′ is less than C_8 the reactive moiety can only react with one suitably positioned neighbour, but if the spacer is $>C_8$ many more reactive moieties are accessible for crosslinking both within and between layers. Thus polymers 10a and 13a are reactive but in polymers 11 and 12 the relatively large R groups screen even a C_9 spacer group and the polymers are less reactive.

(2) Polymer 9, with a styryl crosslinking group, is less sensitive than expected, probably for the same reason, i.e. the spacer chain is too short and the reactive moiety is screened.

(3) Polymer 14 is also rather insensitive. Here the reasons are less well understood, but it may be that the rigid diacetylene moiety requires a spacer greater than the usual C_9 chain and/or the C_{11} chain seriously hinders crosslinking between layers.

(4) Polymers 7 and 8 have rather poor sensitivity, but the reason here is probably that the percentage of chloromethylated groups (9%) is statistically too small for a polymer of this low *MW* to form adequate crosslinks.

(5) Polymers 7 and 11 were less sensitive as LB films than as spin-coated films. Here the packing constraints imposed by LB films may have mitigated against reactivity in comparison with randomly oriented molecules, rather than providing the intended enhancement of reactivity. In polymer 8 it might be expected that the chloromethylated groups would be able to crosslink onto any phenyl ring and be less sensitive to packing than the other polymers.

Detailed studies on LB films of polymers containing vinyl and ethynyl crosslinking groups: effects of physical parameters on sensitivity, contrast and resolution

The most promising two polymers from a chemical point of view (10 and 13) were next studied in more detail

Table 3 Resist characteristics for LB films of polymers containing vinyl and ethynyl crosslinking groups

Polymer	$\bar{M}_n$	Gel dose (μC cm^{-2})	Contrast	Resolution at gel dose (μm)	
				Grating	EBT
10 (Vinyl)	19 000	~1.0	–	1.5	1.0
	1 600	10	0.6	0.62	0.25–0.5
13 (Ethynyl)	19 000	25	0.9	0.37	0.25
	1 600	40	1.0	0.37	0.25

in an attempt to optimize their performance as resists. The physical and physicochemical parameters that might affect this[1,2] include (i) molecular weight, (ii) dispersivity, (iii) film thickness, (iv) substrate properties, (v) dose, (vi) accelerating voltage and (vii) development conditions. Further instrumental limitations arise because of the finite spot size (0.15 μm) and the statistical nature of electron emission (apparent as 'shot noise' at doses $< 1 \mu$C cm^{-2}), and the ultimate performance will also depend on etching conditions if further processing is involved. In this work, (ii) and (vi) were not varied and (iv) was always the same except when further processing was carried out. Within these limitations, the effects of varying the remaining parameters on resist performance are described below.

Increasing the molecular weight from 1600 (polymers 10 a and 13a) to 19 000 (polymers 10b and 13b) improved the sensitivity as expected (*Table 3*). This was particularly the case for the more sensitive polymer with vinyl groups (10), but at some cost in terms of resolution, and polymer 10b was also difficult to handle because it became totally insoluble if accidentally exposed to u.v. light or traces of divalent metal ions during LB film deposition.

Development solvents could be varied within wide limits, with no significant effect on resolution and only small effects on contrast. For example, the gel doses and resolutions given in *Table 3* were hardly altered by varying the proportions of chloroform/propan-2-ol or chloroform/methanol in the solvent or by using pure 2-butanone or pure 4-methyl-2-pentanone as the solvent. The contrast, however, did vary somewhat with the strength of solvent. *Figure 4* shows dose–thickness curves used to determine contrast for the three polymers in *Table 3* for which a reasonable estimate is possible. The contrast increases with decreasing sensitivity as is usual for negative resists, but the best value obtained (~1.0) is rather lower than is generally considered necessary for good resolution in spin-coated negative resists.

The good resolution (in spite of the low contrast) and its relative insensitivity to development solvents must arise from the thinness of LB films compared with many spin-coated films. Normally the choice of solvent is critical because, if this is too strong, swelling of the gel occurs, resulting in loss of contrast and a low aspect ratio, i.e. steepness of sidewalls in written features. With LB films this can occur to some extent without affecting resolution because they are thin in comparison with the lateral size of features. The resolution will be limited instead by other factors, e.g. backscattering from the substrate. Nevertheless, it might still be advantageous to improve contrast. This might be done by decreasing the dispersivity, although for polymers 10b and 13b this is already reasonably low, or by reducing development times.

The effects of dose and thickness on resolution were investigated by depositing films on wafers in zones of different thickness (12, 26, 42, 60 layers) and exposing three bar and gap patterns on each thickness at different doses near to the gel dose previously determined. *Figure 5* shows the effect of dose on pattern quality in test patterns written in 60-layer films of polymer 10a at 0.25 and 0.5 μm resolution. At the optimum, bars and gaps should be equal in width, as seen in *Figure 5c* (16 μC cm^{-2}), with a minimum of gap infilling, indicating over-exposure, or wall erosion, indicating under-exposure. *Figure 6* shows a comparable result for polymer 13b at the exposure closest to the optimum (24 μC cm^{-2}).

The resolution (0.25 μm) is not significantly improved in thinner films. The granularity observed (~0.1–0.2 μm) might arise from the texture of the crosslinked polymer, but this only seems plausible for the higher molecular weight material. However, the machine spot size is also of this order. Thus either the lithographic facility or the film texture, rather than the film thickness, may be setting a limit to the best resolution obtainable.

Further processing; plasma etching and tri-level resist structures

In microelectronic fabrication the pattern written in the resist is transferred into a metal, oxide, or much thicker organic film, which then acts as the mask for subsequent processing of the semiconductor substrate (*Figure 2*). LB films are too thin to act as masks directly in most processes. For image transfer, the crosslinked film must resist a plasma metal etch and protect the metal below it for long enough to allow the unprotected metal to be completely removed.

LB films of polymers 10 and 13 (11, 25, 41 and 59 layers) were deposited on aluminium (75 nm), exposed to bar and gap patterns at doses near to the optimum, stored, and developed as before. Successful transfer of the patterns into the metal layer by plasma etching was achieved without severe loss of resolution and with good clearing of the unexposed areas, provided that the following conditions were obeyed.

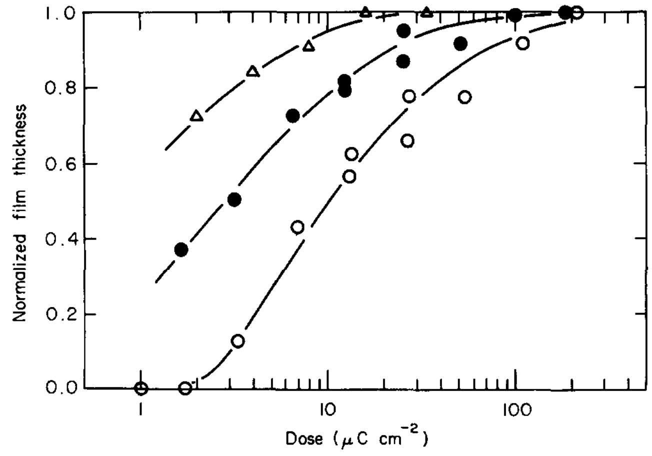


Figure 4 Log(dose) *versus* thickness curves obtained from developed wedge patterns using a mechanical stylus: ○, polymer 13a; ●, polymer 13b; △, polymer 10a. The original thickness was 50 layers (~46 nm) and the development solvent was chloroform/propan-2-ol

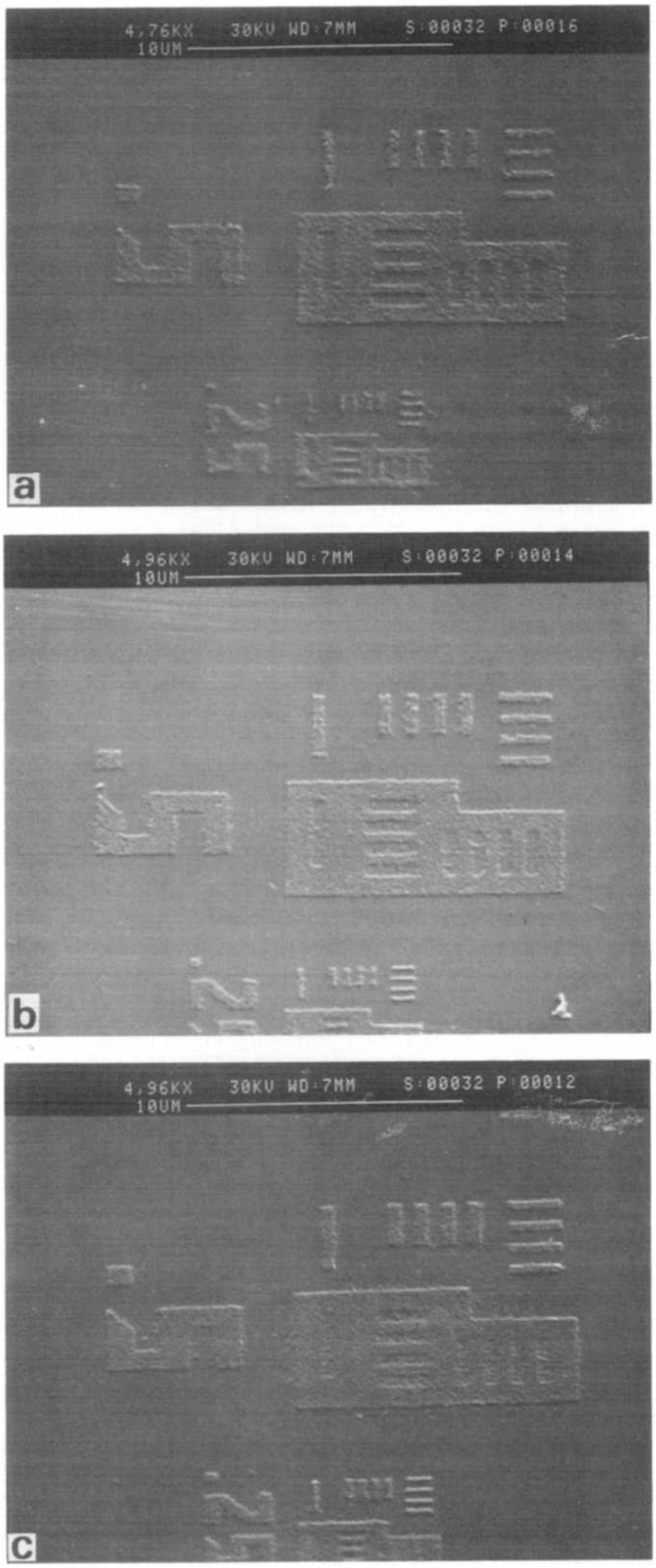


Figure 5 Electron micrographs of bar and gap test patterns (0.25 and 0.5 μm) exposed in polymer 10a (with reactive vinyl groups, $M_n = 1600$) and developed in chloroform/methanol. The doses were (a) 8 μC cm^{-2}, (b) 12 μC cm^{-2} and (c) 16 μC cm^{-2}

(i) The processing, from initial evaporation of aluminium to etching, must be completed in less than 1 week if possible to avoid ageing effects in the metal film, which led to loss of resolution and granular appearance of the metal under exposed resist.

(ii) The resist must be etched within a few hours of development to avoid contaminating the freshly exposed metal surface.

(iii) Over-exposure must be avoided, particularly for the more sensitive polymer 10, with vinyl groups, and similarly development must be effective because the masking effect of traces of incompletely removed resist during etching magnifies any defects in the earlier processing.

(iv) The etching time must be adequate for removal of metal from all unexposed areas after allowing for thickness variations.

The resolution of the resultant test patterns in the aluminium layer was ~ 0.5 μm, or slightly poorer than the values of 0.25–0.37 μm obtained for patterns in resist on silicon. As before, the effect of dose on resolution was observed for the thicker films (41, 59 layers) with the best resolution at 32 μC cm^{-2} for polymer 13a. Films of 11 and 25 layers had insufficient etch resistance fully to protect the underlying metal from thinning. There was some evidence for improved resolution in these thinner films, but the advantage was outweighed by the metal thinning.

In the final experiment, the complete tri-level resist structure (1.5 μm polyimide/75 nm Al/67 layers resist) was made using polymers 10a and 13b, and processed by exposure, development and aluminium etching as previously (*Figure 2*) before the final step of polyimide etching in an O_2 plasma. Tri-level systems are of particular value to LB films because the film only has to survive for long enough to transfer the image faithfully into the metal, the lower polyimide layer serving as the resist for any processing beyond that shown in *Figure 2*. Full advantage can be taken of the thinness of LB films in avoiding forward-scatter, while the resist structure should minimize backscatter by separating the film from the substrate. Furthermore, the polyimide acts as a planarizing layer, i.e. it provides a uniform surface for resist deposition, with good coverage over stepped structures in partially processed substrates, and the etching process has been well characterized and is highly anisotropic, resulting in faithful pattern transfer down to the substrate surface[14,15].

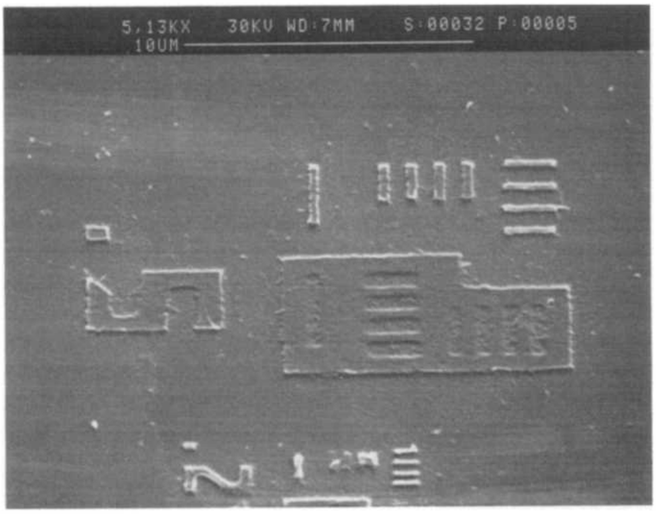


Figure 6 Electron micrograph of bar and gap test patterns (0.25 and 0.5 μm) exposed in polymer 13b (with reactive ethynyl groups, $M_n = 19\,000$) at 24 μC cm^{-2} and developed in chloroform/methanol

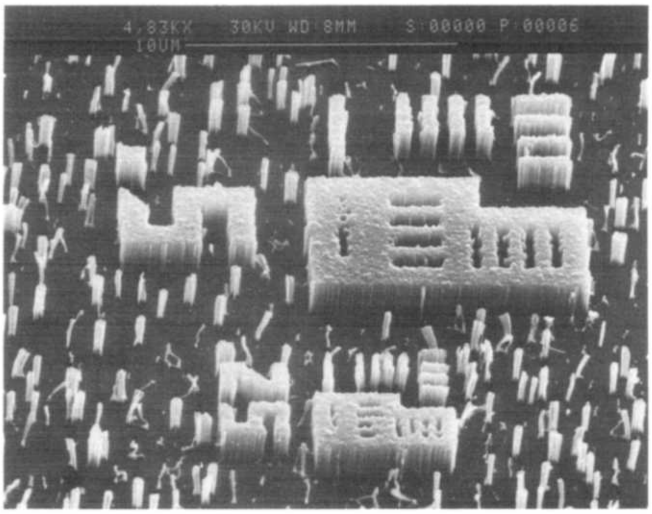


Figure 7 Electron micrograph of structures produced in polyimide after tri-level processing of bar and gap test patterns (0.25 and 0.5 μm) exposed in polymer 10a (with reactive vinyl groups, $M_n = 1600$) at 8 μC cm^{-2}

The structures produced were viewed directly in the scanning electron microscope and are shown in *Figures 7* and *8* for doses near to the optimum for resolution. Polymer 10a is slightly over-exposed at 8 μC cm^{-2} with some infilling of gaps (*Figure 7*) while polymer 13b is slightly under-exposed at 24 μC cm^{-2} with some wall erosion (*Figure 8*). In *Figure 7* the micro-masking effect of residual metal is apparent. This is due to some combination of over-exposure, imperfect development and insufficient metal etch time, and should be avoidable with more rigorous process control. In view of the preliminary nature of this trial the results, which indicate very little loss of resolution (0.25–0.5 μm) compared with single-layer resists, are very encouraging.

CONCLUSIONS

Sufficient studies have now been done by various workers to demonstrate beyond doubt that LB films have the potential to function as electron-beam resists with a resolution better than 0.1 μm. However, no single material has yet been shown to combine all the properties necessary (sensitivity, resolution, plasma etch resistance, low defect density) to perform to this level in a commercial process. This is in contrast with the much more extensive work on spin-coated resist films where gratings of spacing well below 0.1 μm can now be routinely written and subsequently processed to transfer the patterns into metal. This is achieved by utilizing the very thin resists now obtainable, multilevel structures, and very thin substrates[18], although comparable resolution has also been achieved with thick substrates[19].

In this work, we have demonstrated that LB films of poly(styrene/maleic anhydride) derivatives can serve as negative resists at a more moderate resolution (0.25 μm) and be compatible with the subsequent processing. A more specific comparison of LB film and spun resists is not possible on the basis of the present work since the means to obtain spin-coated films as thin as LB films was not available to us and resolution was not measured in spun films. Instead, we have chosen to compare the efficiency of different polymers as LB resists only. Polymers 10 and 13, containing vinyl or ethynyl crosslinking groups, were most effective, and other features identified as being useful to incorporate in the chemical structure were (i) a long ($>C_9$) spacer chain for attachment of the reactive group, (ii) aromatic groups for plasma etch resistance, and (iii) molecular weights of the order 20 000. In addition, although the low molecular weight prevented success in the present work, partially chloromethylated poly(styrene/maleic anhydride) is potentially a good resist material since in high molecular weight forms it functions well as a spin-coat[10,11], and similarly polymer 9 with a styryl crosslinking group might also be very effective in a high molecular weight version with a spacer chain.

The question of whether LB films are likely to offer any significant future advantage over spin-coated films as commercial electron-beam resists will only be resolved by further development and attention to process control. The thinness required for the highest resolution reduces the permitted margins of error, or processing latitude, in device fabrication steps such as plasma etching. The process of film deposition must be more rigorously controlled than is often the case at present to ensure reproducibility, large-area film uniformity and a low device failure rate. Unless use is to be restricted to specialized mask-making, speed of production must be greatly increased. At present, the performance of LB films has to be assessed using the fabrication technology developed to suit spin-coated films, but if investment in LB films is considered worth while the technology could instead be adapted to suit LB films and utilize their advantages, particularly thinness. This might involve, for instance, modified etching conditions, different accelerating voltages in electron guns, or even a shift in emphasis towards X-ray or ion-beam lithography.

As yet, no specific advantages can be claimed for LB films, since those films that rival spin-coated films in ultimate resolution (20 nm) have not been fully tested in device fabrication steps. In any case, optical and near-u.v. lithography appear to satisfy the resolution needs (0.5 μm) of the electronics industry in the short term and

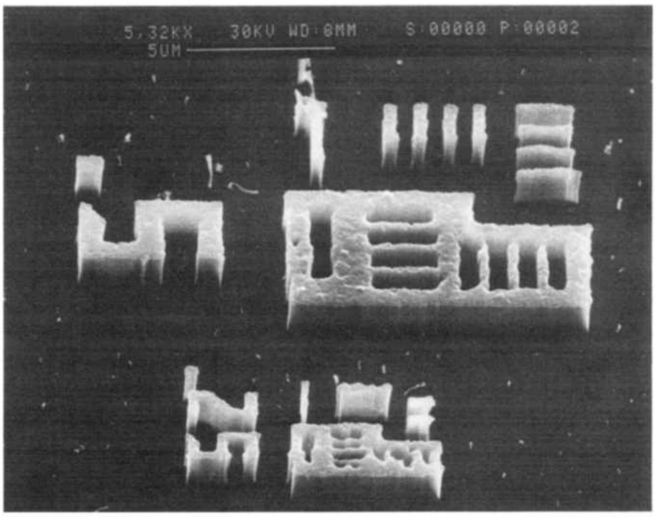


Figure 8 Electron micrograph of structures produced in polyimide after tri-level processing of bar and gap test patterns (0.25 and 0.5 μm) exposed in polymer 13b (with reactive ethynyl groups, $M_n = 19\,000$) at 24 μC cm^{-2}

both spun resists and LB resists can easily achieve this. Nevertheless, further research and development into LB films as resists ought to be pursued for the day when their ultimate resolution capability may be required in some device.

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