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Electron Irradiation of Poly(olefin Sulfones). Application to Electron Beam Resists

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Synopsis

All the poly(olefin sulfones) examined degraded rapidly under electron irradiation. The dose required to effect a molecular weight distribution completely separated from the original distribution as required for fractional solution development was similar for all polymers, viz., $1\text{–}2 \times 10^{-6}$ coulomb/cm^2. This indicates that they all have similar values for G(scission). The film thickness of the exposed area decreased at a rate dependent on olefin structure and temperature. This process, termed vapor development, has been attributed to concurrent chain scission and depolymerization. Factors determining the rate of depropagation are discussed.

INTRODUCTION

Electron beam lithography has continued to gain increasing importance in recent years in the fabrication of microelectronic devices where factors such as high resolution (0.5–3 μ) are of importance.[1] This technique includes the delineation of specific patterns in conducting or insulating layers of material. The substrate to be pattern delineated is covered with a polymeric film (termed an electron resist) which is selectively irradiated by a focused beam of 5–20 kV electrons. Under such ionizing radiation, polymers predominantly crosslink or degrade. The latter process leads to enhanced solubility of the irradiated regions which may be "developed" by fractional solution (a technique which dissolves the degraded fragments while leaving the remaining film intact), leaving a positive image in the resist film. This pattern may now be repeated in the substrate by etching away the unprotected regions. Likewise, a crosslinking polymer will give rise to a negative image in the resist film through which the substrate can subsequently be etched. For a general discussion of lithographic techniques in microcircuit fabrication, see Glang and Gregor.[2]

The ultimate success of a polymer as a resist depends on parameters such as film-forming properties, chemical resistance to etching solutions, sensitivity, and adhesion. While several crosslinking polymers with adequate sensitivity are known,[3,4] only a few polymers, notably poly(methyl methacrylate) (PMMA), are known to degrade under electron irradiation and to have physical properties suitable for resist application. The

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sensitivity of PMMA[5] is $\sim 5 \times 10^{-5}$ coulomb/cm^2, too low for economic large-scale fabrication of devices.

The low sensitivity of existing positive resists is related to their low G(scission), the number of main chain fractures per 100 eV of energy absorbed; G(scission) for poly(methyl methacrylate)[6] is about 2. It has recently been reported that poly(butene-1 sulfone) and poly(hexene-1 sulfone), which are alternating copolymers of the respective olefin with SO_2, can be readily degraded either in air or in vacuo with γ-rays. They exhibit a G(scission) in vacuo[7] of 10–12, far higher than most other degrading polymers. This suggests a possible application of these materials as electron beam resists.

This paper describes the preparation of several poly(olefin sulfones), their subsequent behavior to electron irradiation, and evaluation as resists.

EXPERIMENTAL

Polymer Preparation

The following Phillips pure or research-grade olefins were used: propylene, butene-1, pentene-1, hexene-1, octene-1, 2-methylpentene-1, *cis*- and *trans*-butene-2, hexene-2 (mixture of cis and trans isomers), cyclopentene, and cyclohexene.

Heptene-2 (mixture of cis and trans isomers) and 2-methylbutene-1 were obtained from Chemical Samples Co. Allyl alcohol and methyl vinyl ketone were obtained from Aldrich Chemical Co.

The olefins were distilled from $LiAlH_4$ to remove peroxides. Sulfur dioxide was admitted to the vacuum line, dried by passage over P_2O_5, and stored at $-80°C$. Mixtures were made up with molar volume of SO_2 to olefin ranging from 1:1 to 4:1 and degassed to about 10^{-3} mm Hg.

The poly(olefin sulfones) were prepared either by initiation with *t*-butyl hydroperoxide at $-80°C$ or by UV irradiation at 0°C from a medium-pressure Hg lamp. The former method of initiation was preferred for those olefins whose ceiling temperature (T_c) for copolymerization with SO_2 was $<0°C$ (the ceiling temperature is that temperature above which it is impossible to form long-chain polymer and is a consequence of the reversibility of the propagation reaction).[8] Chemical initiation at $-80°C$ was also preferred for materials whose rate of UV polymerization was slow, e.g., cyclohexene. Certain olefins, e.g., octene-1, tended to give crosslinked products at high conversion. This problem could be eliminated either by stopping the reaction at low conversion or adding a chain-transfer agent such as bromotrichloromethane.

Following polymerization, the polymers were dissolved in a suitable solvent, precipitated into methanol, and dried for 24 hr at 40°C in vacuo.

Microanalysis determination for C, H, and S was made on several of the polysulfones. Results confirmed that all polymers were 1:1 copolymers of SO_2 with the respective olefin. The presence of the sulfone group

was confirmed by IR spectra of cast films using a Perkin-Elmer Model 21 infrared spectrometer.

The molecular weights of three polysulfones were determined by dilute-solution viscometry. Viscosity-average molecular weights so determined were about 10^6 in all cases. Viscosity parameters are listed elsewhere.[12]

Evaluation as an Electron Resist

To evaluate a material as an electron resist the sensitivity, etch resistance, adhesion, resolution, and edge acuity must be studied. The materials were exposed to electron irradiation using a modified Cambridge Mark II scanning electron microscope (SEM) (Fig. 1). The beam was programmed with a Hewlett Packard Model HP function generator.

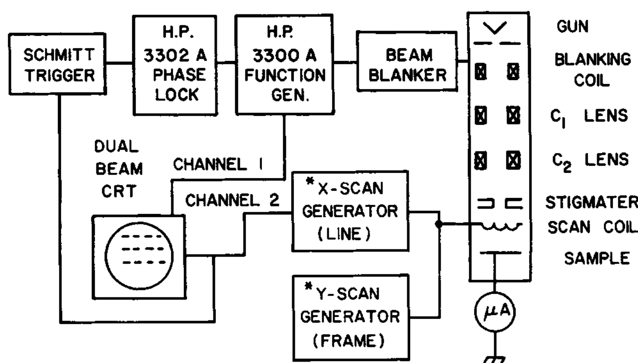


Fig. 1. Block diagram of the electron beam pattern generator used in conjunction with a used scanning electron microscope for resist evaluation.

Sensitivity is defined as the lowest dose of electrons (expressed in units of coulomb/cm^2) required to develop an image suitable for use as an etching mask. The exact technique is described elsewhere.[9] The substrates were spin-coated with the polymer from a filtered solution using a Headway Research Model EC-101 spinner. After exposure, the resist was developed using a 15-sec spray with the developer given in Table I. The strength of the developer (fraction of good solvent) required to dissolve the irradiated areas of the polymer film was strongly a function of molecular weight and baking schedule. Two substrate materials, SiO_2 and tungsten, were used in this evaluation. The SiO_2 was thermally grown in a steam furnace and etched with a buffered HF solution (etch rate ~100 nm/min). The tungsten was deposited from WF_6 using chemical vapor deposition and etched with $K_3Fe(CN)_6$/KOH solution (etch rate ~50 nm/min).

The adhesion and etch resistance were qualitatively evaluated by writing high-resolution patterns in resist films spun on 200 nm of SiO_2 and 100 nm of tungsten and subsequently etching the patterns. If several large

TABLE I
Evaluation Parameters of Polysulfone Electron Beam Resists[a]

Resist	Code number	T_c, °C [M][SO]$_2$ = 27 mole^{2}l^{-2}	Solvent	Developer[b]	Sensitivity,[b] coulomb/cm^2	Comments
Poly(propylene sulfone)	PPrS-M1	90	DMSO			Does not spin a film from DMSO at room temperature. Polymer is insoluble in all other solvents.
Poly(butene-1 sulfone)	PBS-M2	64	MEK	60% MEK 40% 2-PrOH	1-2×10^{-6}	Spins excellent films although preferably from less volatile solvents than MEK. Behaves as an excellent etch mask when prebaked at ≥100°C. Does not readily depolymerize, i.e., very little evidence of vapor development below 10^{-5} C/cm^2. Similar in this regard to PMMA
	PBS-M20	64	MEK 60% cyclohexanone 40%	85% MEK 15% 2-PrOH	1-2×10^{-6}	
Poly(pentene-1 sulfone)	PPS-M1	63	MEK	50% MEK 50% 2-PrOH	1-2×10^{-6}	Similar to PBS
Poly(hexene-1 sulfone)	PHS-M4	60	MEK	35% xylene 65% 2-PrOH	1-2×10^{-6}	Xylene preferred spinning solvent. Partially vapor develops at these doses. Erosion of the resist during etching was sometimes observed.
	PHS-M14	60	xylene	35% xylene 65% 2-PrOH	1-2×10^{-6}	
Poly(octene-1 sulfone)	POS-M1		MEK	60% heptane 40% 2-PrOH	1-2×10^{-6}	Poor etch mask. Partially vapor develops.
Poly(*cis*-butene-2 sulfone)	Pc-B-2S-M1	46	dioxane	60% dioxane 40% 2-PrOH	2-4×10^{-6}	The 2-butenes do not spin good films from dioxane.
Poly(*trans*-butene-2 sulfone)	Pt-B-2S-M1	38	dioxane	60% dioxane 40% 2-PrOH	2-4×10^{-6}	

Poly(butene-2 sulfone)	PB-2S-M1		dioxane	60% dioxane 40% 2-PrOH	$2\text{-}4\times10^{-6}$	
Poly(hexene-2 sulfone)	PH-2S-M1		MEK	50% MEK 50% 2-PrOH	$1\text{-}2\times10^{-6}$	Poor etch mask when film thickness is <200 nm. Can be completely vapor developed at $2\text{-}4\times10^{-6}$ C/cm^2 for film thickness <150 nm.
Poly(heptene-2 sulfone)	PHp-2S-M1	−39	MEK	20% xylene 80% 2-PrOH	$1\text{-}2\times10^{-6}$	Poor etch mask. Completely vapor develops at $1\text{-}2\times10^{-6}$ C/cm^2 for film thickness <150 nm.
Poly(cyclopentene sulfone)	PcycloPS-M1	102.5	dioxane	60% dioxane 40% 2-PrOH	$2\text{-}3\times10^{-6}$	No evidence of depolymerization at exposures $<10^{-5}$ C/cm^2. Does not spin good films from dioxane. Improved by spinning from dioxane/chlorobenzene. Poor etch mask.
Poly(cyclohexene sulfone)	PcycloHS-M1	24	dioxane	60% dioxane 40% 2-PrOH	$1\text{-}2\times10^{-6}$	Chlorobenzene preferred spinning solvent. Partially vapor develops at these doses. Completely vapor develops at 5×10^{-6} C/cm^2 for film thickness <150 nm. Good etch mask.
	PcycloHS-M1	24	chlorobenzene	60% dioxane 40% 2-PrOH	$1\text{-}2\times10^{-6}$	
Poly(2-methylpentene-1 sulfone)	PMPS-M3	−34	xylene	15% xylene 85% 2-PrOH	$1\text{-}2\times10^{-6}$	Excellent etch mask. Can be completely vapor developed at film thickness <150 nm with sensitivities of 5×10^{-7}–1×10^{-6} C/cm^2.
Poly(2-methyl butene-1 sulfone)	PMBS-M1		MEK dioxane			Material spins poor films from both solvents.

[a] All materials were prebaked and postbaked at ≥110°C for ≥0.5 hr.

[b] The polysulfones exhibit very sharp contrast between the irradiated and unirradiated sections which requires careful adjustment of the developer for each polysulfone in order to maximize sensitivity. The developer solutions listed represent the average of several samples.

(1 mm^2) areas of high resolution patterns were defect free, the etch resistance and adhesion were considered satisfactory.

Film thickness was determined by standard interferometric techniques using a polarizing interferometer.

RESULTS AND DISCUSSION

Physical and Chemical Properties of Polysulfone Resists

A positive electron beam resist is a chemically resistant, film-forming polymer which undergoes a marked increase in solubility owing to degradation on exposure to electron irradiation.

All the poly(olefin sulfones), hereafter abbreviated to polysulfone, formed uniform films by the spin-coating technique. Choice of spinning solvent was limited by the solubility characteristics of each polysulfone. The nature of the olefin markedly determines the range of solvents in which the respective polysulfone is soluble.[10] Film thickness was governed by solution viscosity (a function of solids content and molecular weight) and spinning speed.

The polysulfones are relatively unstable to heat, a factor which has precluded industrial application of these materials, e.g., decomposition of poly(butene-1 sulfone) as determined by thermogravimetric analysis commenced at 130°C. It is advantageous to prebake resists at temperatures above the glass transition temperature.[11] This procedure removes the stress created in the film during spin coating, removes excess solvent, and promotes adhesion. The glass transition temperatures of the polysulfones usually lie above room temperature, as indicated by their heat distortion temperatures, and below their decomposition temperature.[12] In general, the films were prebaked and postbaked at temperatures in the range of 100–110°C for 0.5–1 hr. This treatment did not cause any deterioration of the polymer films. Lower temperatures resulted in poor adhesion to the substrate.

The polymers were resistant to the chemical etching solutions studied, viz., buffered HF (to etch SiO_2) and $K_3Fe(CN)_6$/KOH (to etch W). They are known to be stable to acids but are degraded by hot alkali solutions.[12] No deleterious effects were observed using the chemical solutions and etch times described above.

Electron Irradiation of Polysulfone Films

The films, 300–500 nm thick, were irradiated with a focused beam of electrons over a range of energies from 5 to 20 kV and beam doses ranging from 5×10^{-7} to 5×10^{-6} coulomb/cm^2. *All* the polysulfones described in this report behaved as positive resists, indicating that main-chain scission is the principal reaction occurring upon electron irradiation. Further, the sensitivity as determined in solution development was of the order of 1–2×10^{-6} coulomb/cm^2 at 5 kV for all these polysulfone resists, independent of the nature of the olefin. Details are listed in Table I.

Solution development requires that the molecular weight distribution of the irradiated material be well separated from that of the original polymer, i.e., the fracture density p_s (number of main-chain bonds broken per monomer unit) must be large enough to effect this separation in molecular weight distributions.

For a system undergoing only random scission, the dose Q required to effect the necessary fracture density is given[11] by the equation

$$Q = \frac{p_s 100 q \rho z N}{E G(s) Mo} \tag{1}$$

where q = electron charge, ρ = density, z = film thickness, N = Avogadro's number, E = energy absorbed in the film per incident electron, $G(s) = G$(scission), and Mo = molecular weight of a monomer unit. The fact that all the polysulfone resists exhibit similar sensitivities Q indicates that they all have essentially the same G(scission) since none of the other materials-dependent terms in eq. (1) would be expected to change significantly for each polymer. The results of Brown and O'Donnell[7] would put the value of G(scission) in the range of 10–12. The similarity of the G(scission) values does not seem unreasonable since all the polymers contain the weak C–S bond in the main chain.

Some typical micrographs of test patterns etched through polysulfone masks are shown in Figures 2A, 2B, and 2C.

It was observed that the film thickness of the exposed area decreased with irradiation time. Thus, under certain conditions it was possible to "develop" the image without recourse to a solution development process. we have termed this process vapor development. A micrograph of a test pattern etched through a vapor-developed polysulfone mask is shown in Figure 2D. It can be seen that factors such as edge acuity and resolution are enhanced over solution-developed patterns. Plots of film thickness versus dose for five different polysulfones are shown in Figure 3, where it may be noted that the initial rate of vapor development for each material decreases in the same order as the ceiling temperature for formation of the polysulfone in the liquid state.

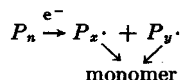
One means of achieving a vapor development process is to attain a fracture density of unity, the monomer fragments being removed by the vacuum system. Substitution of this value into eq. (1) predicts a sensitivity of about 10^{-4} coulomb/cm^2 (again assuming only random scission occurs). Further, the film thickness should not decrease from the onset of irradiation but should remain essentially constant, drastically decreasing only as the total dose approaches 10^{-4} coulomb/cm^2 (where monomer fragments are being produced). However, the film thickness decreased from the onset of irradiation for the majority of the polysulfones (Fig. 1). For initial film thickness <150 nm, several polysulfones could be etched at sensitivities $>5 \times 10^{-6}$ coulomb/cm^2 (Table I) indicating values of $p_s \ll 1$. Obviously, then, some process must be acting which enhances the reversion

(A) 6 μ (B) 4 μ

(C) 2 μ (D) 4 μ

Fig. 2. SEM micrographs of patterns etched through electron beam-delineated polysulfone masks. (A), (B), and (C) were etched through solution-developed masks; (D) was etched through a vapor-developed mask. Substrates are (A) 100 nm CVD tungsten, (B) and (D) 200 nm SiO_2, (C) 600 nm SiO_2.

of a fractured chain to individual monomer. This may be represented by the following:



$$P_n \xrightarrow{e^-} P_x\cdot + P_y\cdot \rightarrow \text{monomer}$$

Such a process will occur if (1) the polymer radicals are thermodynamically unstable with respect to the monomer, and (2) a kinetic pathway exists between the two states.

Thermodynamic analysis of a typical exothermic polymerization process predicts that for a given monomer concentration there exists a temperature known as the ceiling temperature (T_c) above which polymerization will

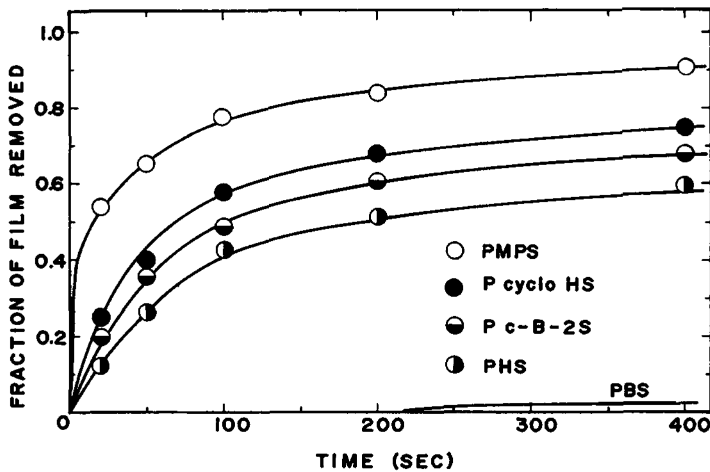
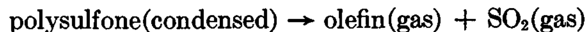


Fig. 3. Plots showing fraction of film removed as a function of time for five polysulfone resists. Initial film thickness, 500 ± 50 nm; I, 5×10^{-10} amp. See Table I for explanation of legend.

not take place.[8] As mentioned previously, this can be understood kinetically in terms of the reversibility of the propagation reaction. The converse of this statement was pointed out by Ivin,[12] viz., that at any temperature there will be an equilibrium monomer concentration which is independent of the amount of polymer in the system. The attainment of this equilibrium requires that there be a continuous supply of polymer radicals. The existence of such an equilibrium has been demonstrated for poly(methyl methacrylate)[13] and recently for poly(butene-1 sulfone).[7,14] A straightforward depolymerization mechanism provides the kinetic pathway.

In the present experiments, the vapor development process refers to the reaction



$$\text{polysulfone(condensed)} \rightarrow \text{olefin(gas)} + SO_2\text{(gas)}$$

Radicals are being continually formed during electron irradiation and the product gases are continually removed by the vacuum system. Hence, equilibrium will not be attained and the reaction moves entirely to the right. We may then see the vapor development process as one of initial chain scission followed by depolymerization of the fractured chain ends.

Such a process should be highly sensitive since, in principle, only one fracture per chain need occur to "develop" that particular chain whereas a large number of fractures must ordinarily be made to fracture a chain sufficiently for solution development. However, two factors operate to invalidate this argument. Firstly, the reduction in sheet density (ρz) with time leads to a decreasing rate of energy absorption.[15] Secondly, side reactions leading to chain termination will interrupt the depolymerization process. Termination is taken to include radical

processes such as abstraction which kill the active chain so that the number of successive depropagation steps is not necessarily large. Both these factors act to decrease sensitivity. The former is a natural consequence of the vapor development process. It seems probable, though, that the latter process is related to the rate of depropagation since the faster a chain unzips, the less likely secondary reactions will terminate the depropagating chain.

One way of increasing the depropagation rate would be to increase the temperature, and it can be seen in Table II that, in the case of PBS, increasing the temperature from 20° to 140°C increased the sensitivity from 2×10^{-4} to 6×10^{-6} coulomb/cm^2. An increase in rate can also be accomplished by lowering the activation energy for depropagation E_d. This may be the reason for the observed dependence of the rate of vapor development on olefin structure (Fig. 3), viz., that the magnitude of E_d is determined by the olefin structure. There is evidence to suggest that the observed variation of T_c with olefin structure in the liquid-phase copolymerization is due to changes in the heat of polymerization ΔH_p.[16,17] Application of thermodynamic additivity principles would predict similar changes in the heat of polymerization $\Delta H'_p$ for polymerization in the gas phase. The activation energy for the depropagation reaction is given by $E_d = E_p - \Delta H'_p$.[18] Therefore, assuming the magnitude of E_p is relatively unaffected by changes in olefin structure, the variation of ΔH_p (and hence $\Delta H'_p$) with olefin structure would be reflected in E_d predicting rates of vapor development in agreement with the order shown in Figure 3.

TABLE II

Effect of Temperature on the Vapor-Developed Sensitivity of a 75 nm PBS Film

Temperature, °C	Sensitivity, C/cm^2
21	3×10^{-4}
58	2.1×10^{-4}
140	6×10^{-6}

However, such an argument does not explain the wide difference in vapor development rates between, for example, PBS and PHS whose ceiling temperatures for polymerization in the liquid state (and hence E_d's) differ by only a few degrees. It might alternatively be argued that the rate-determining step in the vapor development process is the rate of chain termination and that this is determined by olefin structure.

In order to maximize the rate of vapor development, the results in Figure 3 suggest using an olefin whose T_c for copolymerization with SO_2 is as low as possible. However, this has the effect of making synthesis of the particular polysulfone more difficult; e.g., Cook et al.[16] reported that T_c for the formation of polymer from 2-ethylbutene and SO_2 is less than -80°C. Its preparation has not been reported in the literature although possible synthetic routes have been discussed by Ivin and Rose.[11]

CONCLUSIONS

The poly(olefin sulfones) are all readily degraded by 5–20 kV electrons. They exhibit similar rates of degradation indicating that *G*(scission) is the same for all materials. Comparison with γ-irradiation studies would put this value of *G*(scission) at 10–12. High sensitivity coupled with their attractive physical and chemical properties should make this family of polymers excellent electron beam resists for use in the fabrication of microelectronic devices by electron beam lithography.

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