

Insolubilization Mechanism and Lithographic Characteristics of a Negative Electron Beam Resist Iodinated Polystyrene

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Synopsis

To elucidate the insolubilization mechanism of iodinated polystyrene (IPS) upon exposure to an electron beam and deep UV, the effects of additives on exposure characteristics of IPS and its parent polymer, polystyrene, are clarified. Results indicate the following mechanism. Iodine atoms produced by homolytic dissociation upon exposure undergo competitive reactions: the radical recombination which is the reverse of dissociation and the formation of other radicals that leads to insolubilization. The proposed reaction mechanism can explain the relationship between the sensitivity and degree of iodination. The G values for crosslinking of IPS, $G(X)$, are also obtained according to Charlesby's theory. The calculated lithographic characteristics on the basis of $G(X)$ are discussed.

INTRODUCTION

Electron beam resists such as poly(glycidyl methacrylate) (PGMA)¹ and poly(glycidyl methacrylate-co-ethyl acrylate)² have come to be widely used in mask making for semiconductor device fabrication. However, these resists are not durable against plasma- or ion-etching routinely utilized in direct semiconductor device fabrications.

Direct write-on-wafers in the electron beam lithography require resist materials with good dry-etch resistance and high resolution, as well as high sensitivity. Resists with highly aromatic characters are necessary for high dry-etch resistance. However, electron sensitivity of such aromatic polymers as polystyrene and poly(α -methylstyrene) is rather low^{3,4} due to the "sponge effect."⁵ Consequently, many attempts were made to sensitize polystyrenes by introducing radiation sensitive substituents into the phenyl groups of the polystyrenes. The following polymers have been investigated as negative electron resists; poly(vinyl benzyl azide),⁶ chloromethylated polystyrene,⁷ polychloromethylstyrene,⁸ poly(glycidyl methacrylate-co-chlorostyrene),⁹ homopolymers and copolymers of substituted styrene,¹⁰ chlorinated polystyrene,¹¹ a mixture of bisazide and polystyrene,¹² chloromethylated poly(α -methylstyrene),¹³ and other aromatic polymers.^{12,14,15} The fact that iodinated polystyrene (IPS)¹⁶ can also be a potential candidate for an electron beam resist used in direct device fabrication has already been reported.

Though there is some information on the radiation chemistry of polystyrene¹⁷ and the photochemistry of polyhalostyrene,¹⁸ little is known about the insolubilization mechanism of these polymer materials.¹⁹

This paper elucidates the insolubilization mechanism of IPS upon exposure. Crosslinking G values $G(X)$ of IPS are also obtained according to Charlesby's theory.⁵ Lithographic characteristics calculated on the basis of $G(X)$ are presented.

EXPERIMENTAL

Polymer Preparation. IPS was prepared by iodination of polystyrene using the previously described method.¹⁶ With the reaction vessel being kept at $90 \pm 2^\circ\text{C}$, polystyrene was dissolved in nitrobenzene. Iodine, iodine pentaoxides, carbon tetrachloride, and sulfuric acid were added to the polystyrene solution. Iodination degree of IPS was varied by changing the reaction time and/or iodine concentration.

Characteristics. Polymer structure was confirmed by measurement of infrared spectra using a Hitachi Perkin-Elmer Model 225 Spectrophotometer. Iodination degree was evaluated using elementary analysis with a Hitachi 026 CHN Analyzer. Polymer density was measured by Archimedes' method, where aqueous zinc chloride solution was used as a density-adjustable liquid medium. It was found that IPS density increases with iodination. Molecular weight and molecular weight distribution were determined by gel permeation chromatography (GPC) with a Hitachi 635 Liquid Chromatography System. Absorbance spectra were measured with a Hitachi 340 Spectrophotometer.

Sensitivity Measurement. The resist was spun cast onto a Si substrate from a chlorobenzene solution. Films were prebaked and exposed to an electron beam using a modified Hitachi Electron Microscope at 15 kV acceleration voltage. Developing was done using chlorobenzene and kerosene mixtures as developers. Thickness of the layer remaining on the exposed area was determined with an interferometer. For deep UV exposure, a Hanovia 600-W Xe-Hg lamp with a heat cutting filter was used as the light source. Exposure characteristic curves were obtained by plotting normalized film thickness against exposure dose. The normalized film thickness (gel fraction) is the ratio of the film thickness of polymer film remaining after development to the initial thickness.

Additives. Additives used in this experiment were 1,1-diphenyl-2-picrylhydrazyl (DPPH) (Eastman Kodak Co.) and 1,4-diiodobenzene (Tokyo Kasei Kogyo Co.).

Pattern Fabrication. Exposure patterns were defined with an electron beam drafting machine operated at 30 kV, specially designed by the Hitachi Central Research Laboratory.

RESULTS AND DISCUSSION

Exposure Characteristics

Electron beam exposure characteristics of IPS and its starting material, polystyrene, are shown in Figure 1. A plot of IPS sensitivity against iodination is shown in Figure 2. Sensitivity in Figure 2 is defined as a reciprocal value of the minimum irradiation dose needed to form the first insoluble gel. Error bars in Figure 2 show uncertainty induced by extrapolation of the exposure characteristic curves in Figure 1.

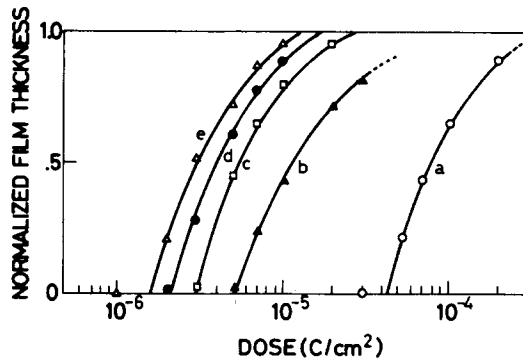


Fig. 1. Electron exposure characteristics for IPS and polystyrene. Degree of iodination: (a) 0; (b) 0.02; (c) 0.04; (d) 0.28; (e) 0.85.

The deep UV exposure characteristics of IPS and polystyrene are shown in Figure 3. The relationship between sensitivity and iodination in the deep UV exposure is shown in Figure 4. It was found that oxygen in air does not affect IPS and polystyrene exposure characteristics in the deep UV exposure. Polymer film thickness was $0.7\text{--}1.0\ \mu\text{m}$. In this range, the dependence of sensitivity on film thickness was not observed.

The relationship between sensitivity and iodination in electron beam exposure is almost the same as that in the deep UV exposure as shown in Figures 2 and 4. This indicates that the insolubilization mechanism for IPS in the electron beam exposure is quite similar to that in deep UV exposure. First, an attempt was made to elucidate the IPS reaction mechanism upon deep UV exposure as follows.

Effect of Additives

1,1-Diphenyl-2-Picrylhydrazyl (DPPH). The effect of adding of DPPH, a radical scavenger, on deep UV exposure characteristics was investigated to see

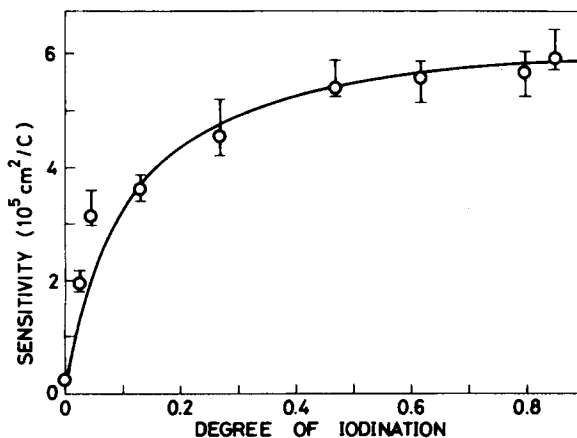


Fig. 2. Electron beam sensitivity as a function of iodination degree.

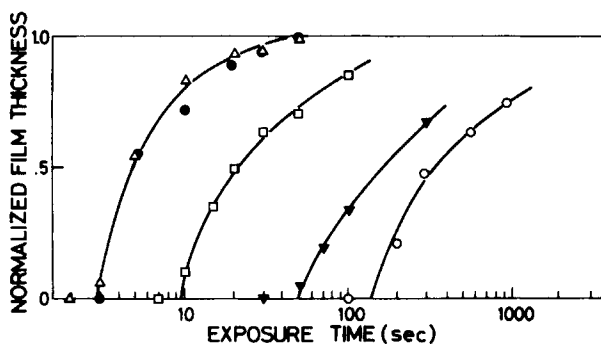


Fig. 3. Deep UV exposure characteristics of IPS and polystyrene. Degree of iodination: (○) 0; (▼) 0.02; (□) 0.04; (●) 0.28; (△) 0.85.

if the insolubilization is induced by radical reaction. The effect of DPPH on IPS and polystyrene exposure characteristics is shown in Figure 5. The DPPH concentration is 1 mol % for average monomer units of these polymers. Upon adding DPPH, the lower the iodination, the more pronounced the decrease in IPS sensitivity becomes. Since DPPH affects sensitivity of these polymers as shown in Figure 5, it is concluded that the insolubilization is induced by radical reactions.

Since DPPH has its optical absorption maximum, λ_{\max} , at 520 nm, and IPS shows no absorption in the visible region, the change of DPPH concentration in IPS before and after the deep UV irradiation was monitored by spectrophotometer. Absorption spectra for varied exposure times are shown in Figure 6. Results for IPS with various iodination are summarized in Figure 7. The DPPH concentration decreases linearly with exposure time, except in the small absorbance region where there are overlaps from other absorption bands. Slopes of these lines give radical production rates which are plotted as a function of iodination as shown in Figure 8. It is clearly demonstrated that the radical production rate increases with iodination.

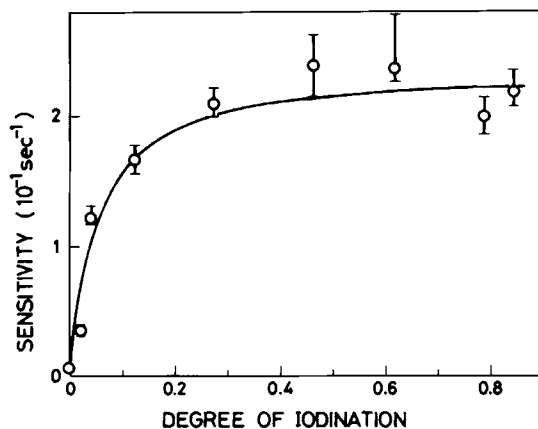


Fig. 4. Deep UV sensitivity as a function of iodination degree.

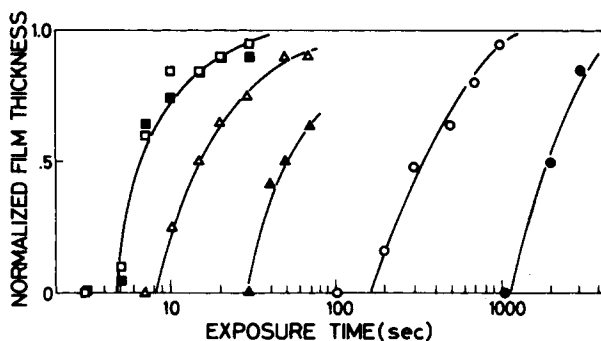


Fig. 5. Effect of DPPH on exposure characteristics of IPS and polystyrene. (O) polystyrene; (●) polystyrene with DPPH; (▲) IPS (iodination degree: 0.04); (▲) IPS (iodination degree: 0.04) with DPPH; (□) IPS (iodination degree: 0.85); (■) IPS (iodination degree: 0.85) with DPPH.

1,4-Diiodobenzene. To elucidate what kind of radical is responsible for the insolubilization, the effect of diiodobenzene on polystyrene sensitivity was investigated. The diiodobenzene concentration is 3 mol % for average monomer units of polystyrene. Polystyrene sensitivity with a diiodobenzene additive is about 10 times that without diiodobenzene as shown in Figure 9. Since the bond energy of C—I is about a half that of C—H, it is considered that deep UV exposure produces more radicals in the film with diiodobenzene by homolytic dissociation of the C—I bond than in the film without diiodobenzene. The photolysis study of iodoaromatic compounds²⁰ supports this assumption. These radicals may lead to crosslinking after successive reaction shown in Figure 10.

Insolubilization Mechanism

Additive effect on IPS and polystyrene exposure characteristics described in the preceding section are summarized as follows: (i) insolubilization is induced by radical reactions; (ii) radical production rate increases with IPS iodination; (iii) amount of radicals not contributing to insolubilization increases with iodination; (iv) radicals causing insolubilization are those produced by homolytic dissociation of the C—I bond under irradiation. From these results, the reaction

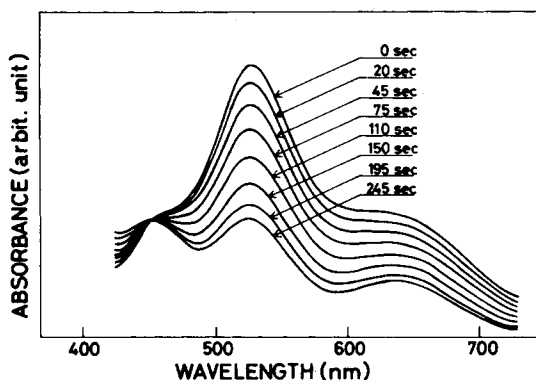


Fig. 6. Variation of DPPH spectra in IPS with deep UV irradiation times.

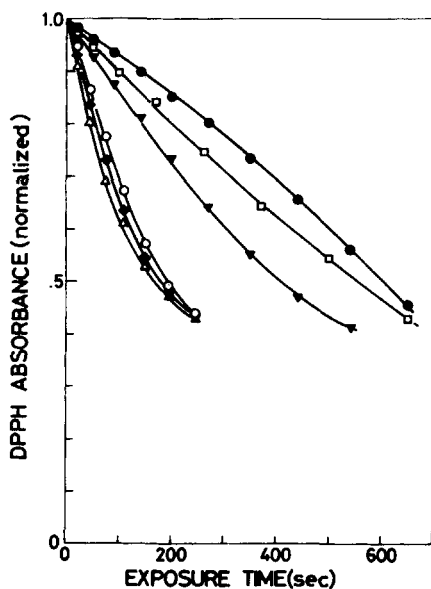


Fig. 7. Relationship between DPPH absorbance at 520 nm and deep UV irradiation times. Degree of iodination: (●) 0; (□) 0.02; (▼) 0.04; (○) 0.27; (◆) 0.47; (△) 0.61.

mechanism shown in Figure 10 is proposed. It is assumed that reactions in polystyrene do not affect the reaction mechanism shown in Figure 10. The parameter β is the homolytic dissociation rate under the irradiation and x is the iodination degree. The parameters k_1 and k_2 indicate the rate constants of the reactions in Figure 10, being described below in detail. Since glass transition temperature of IPS is high,¹⁶ it should be noted that the reaction occurs in the rigid polymer, where the radical mobility is low. Therefore, it is likely that there are competitive reactions between radical recombination and hydrogen abstraction in the neighborhood where homolytic dissociation occurs. Radicals produced by hydrogen abstraction reaction react with those produced by homolytic dissociation, causing crosslinking.

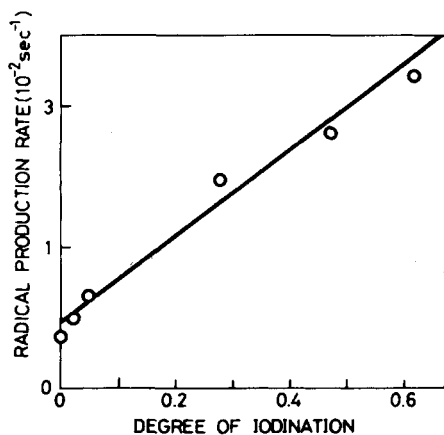


Fig. 8. Plot of radical production rate vs. iodination degree.

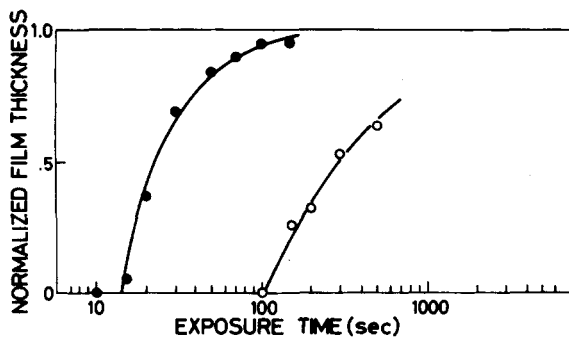
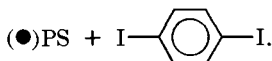


Fig. 9. Effect of diiodobenzene on exposure characteristics of polystyrene: (○) PS;



The homolytic dissociation rate can be described by βx , since the radical production rate increases with iodination as shown in Figure 8. The radical recombination rate is proportional to the phenyl radical concentration which is in proportion to iodination degree under irradiation. Therefore, the radical recombination rate can be described as $k_1 x [I]$, where $[I]$ is the iodine atom concentration and $k_1 x$ represents the product of the rate constant and phenyl radical concentration. Hydrogen abstraction rate can be described as $k_2 [I]$, where k_2 represents the product of the rate constant and IPS monomer unit concentration. In the competitive reactions between radical recombination and hydrogen abstraction, the proportion leading to crosslinking reaction is described by $k_2 / (k_1 x + k_2)$. Therefore, the sensitivity increase by iodination is expressed by $\beta x \cdot k_2 / (k_1 x + k_2)$. On the basis of the above, the sensitivity S is described by

$$S = S_0 + \frac{A\beta x}{1 + (k_1/k_2)x} \quad (1)$$

where S_0 represents polystyrene sensitivity and A is the constant value. Determining a set of values for S_0 , $A\beta$, and k_1/k_2 produces the solid curves of eq. (1) shown in Figures 2 and 4. The curves are in good agreement with the observed data. It is clear that eq. (1) derived according to the above reaction mechanism can explain the relationship between sensitivity and iodination.

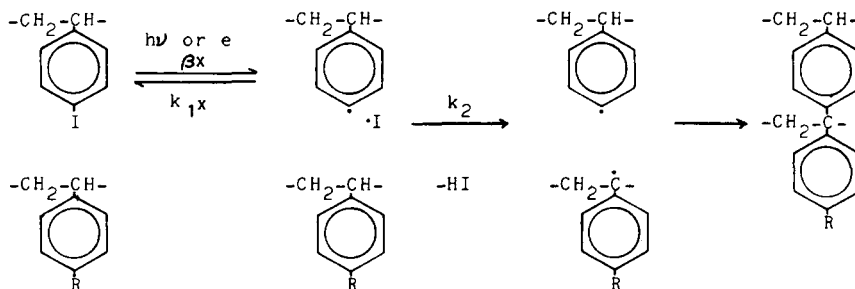


Fig. 10. Reaction mechanism of IPS under deep UV or electron beam irradiation: (R) H or I; (x) degree of iodination; $(k_1 x)$ rate of radical recombination; (k_2) rate of hydrogen abstraction.

TABLE I
 Crosslinking G Value, $G(X)$, and Other Related Values

Lot no.	Iodination degree	Resist thickness (μm)	Polydispersity (M_w/M_n)	Wt avg degree of polymerization	ΔE (eV)	$G(X)$
Polystyrene	0.00	0.61	2.53	2620	1070	0.04
IPS-010-1	0.02	0.69	2.08	2570	1220	0.23
IPS-010-2	0.04	0.66	1.87	2740	1160	0.30
IPS-010-3	0.85	0.64	1.93	2610	1350	0.38
IPS-011	0.61	0.66	1.92	2980	1310	0.39
IPS-012	0.47	0.66	1.91	2690	1270	0.40
IPS-013	0.79	0.64	1.94	2490	1330	0.41
IPS-014	0.27	0.59	1.89	2630	1090	0.38
IPS-015	0.13	0.63	1.94	2590	1120	0.38

G Value of Crosslinking

It is important to obtain the crosslinking G value, since there is a possibility of both crosslinking and degradation occurring in polymer upon electron beam irradiation. According to Charlesby's theory,⁵ the relation between solubility s and crosslinking G value $G(X)$ and degradation G value $G(S)$ is expressed by the following when molecular weight distribution is random:

$$s + \sqrt{s} = \frac{G(S)}{2G(X)} + \frac{100ldN_Ae}{2G(X)\Delta EM_n} \cdot \frac{1}{Q} \quad (2)$$

where $s = 1 - g$, g is the gel fraction: the normalized resist thickness, l is the film thickness, d is the IPS density, N_A is Avogadro's number, e is the electron charge, M_n is the number average of molecular weight, Q is the exposure dose, and ΔE is the electron energy loss when an electron passes through a polymer with a thickness of l obtained according to the Bethe equation.²¹ Equation (2) can be used only when the molecular weight distribution is random. The molecular weight distribution of IPS used in this experiment may be considered random because the polydispersity value is about 2, as shown in Table I. According to eq. (2), $s + \sqrt{s}$ is plotted as a function of $1/Q$ as shown in Figure 11. The plot for each iodination degree shows linear dependence of $s + \sqrt{s}$ on $1/Q$. The slope

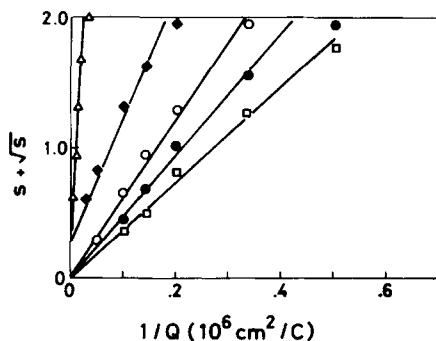


Fig. 11. Plot of $s + \sqrt{s}$ as a function of the reciprocal of electron dose, $1/Q$, according to eq. (3). Degree of iodination: (Δ) 0; (\blacklozenge) 0.02; (\circ) 0.04; (\bullet) 0.27; (\square) 0.79.

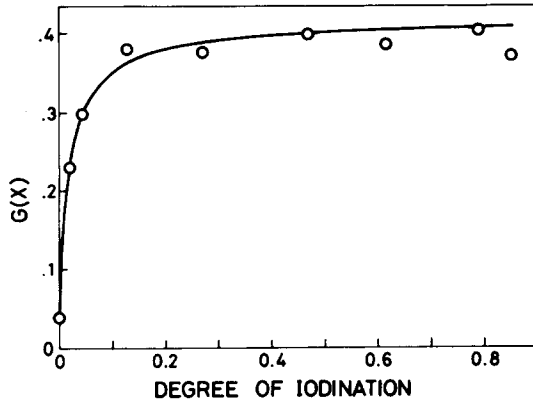


Fig. 12. Plot of $G(X)$ as a function of iodination degree.

of each line gives the $G(X)$ value and the intercept gives the $G(S)$ value. The $G(X)$ values are summarized in Table I. The plot of $G(X)$ against iodination is shown in Figure 12. The solid curve is calculated according to the following, which is equivalent to eq. (1):

$$G(X) = G_0(X) + \frac{A'\beta x}{1 + (k_1/k_2)x} \tag{3}$$

where $G_0(X)$ is the crosslinking G value for polystyrene and A' is the constant value. Since this dependence of $G(X)$ on iodination (Fig. 12) is quite similar to that of electron beam sensitivity on iodination degree (Fig. 2), it is concluded that IPS sensitivity reflects the crosslinking G value.

Exposure Characteristics Calculated from G Value

Dependence of Resist Thickness on Sensitivity. Exposure characteristics of IPS with resist thicknesses, 0.3, 1.0, and 1.5 μm , were calculated in Figure 13. Observed IPS exposure characteristics are shown in Figure 14. Calculated dependence of resist thickness on sensitivity is in good agreement with the experiments. Sensitivity slightly increases with resist thickness. This is due to

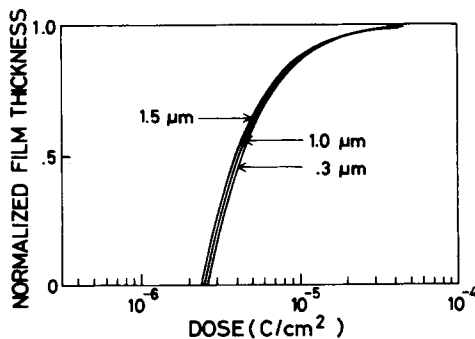


Fig. 13. Calculated exposure characteristics of IPS with 0.3, 1.0, and 1.5 μm resist thickness. Iodination degree = 0.13; electron acceleration potential = 15 kV.

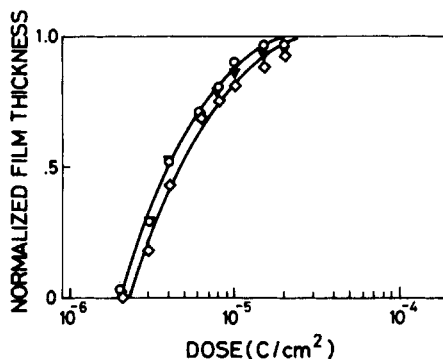


Fig. 14. Experimental exposure characteristics of IPS with various resist thicknesses: (\diamond) 0.5 μm ; (\circ) 1.0 μm ; (\blacktriangledown) 1.5 μm .

the increase in electron energy loss in passing through a resist with a larger thickness. However, the effect of resist thickness on sensitivity is small.

Dependence of Electron Energy on Sensitivity. It is known that sensitivity increases as electron acceleration potential decrease.²² The minimum irradiation dose necessary to form the first insoluble gel, Q_0 , is calculated for various electron energies, as shown in Figure 15. This figure shows Q_0 (the reciprocal of sensitivity) decreasing with electron energy. This is due to the increase in electron energy loss with the decrease in initial electron energy, which results in decreasing Q_0 .

Dependence of Molecular Weight Distribution on Exposure Characteristics. It is known that the lower the polydispersity the larger the γ -value (contrast) becomes.^{1,3,4,11} The exposure characteristic curve for IPS with uniform distribution $M_w/M_n = 1.0$ was also calculated according to Charlesby's theory.⁵ The calculated curve is shown in Figure 16, along with the curve for IPS with a random distribution. The curves in Figure 16 show that the γ value for uniform distribution is larger than that for random distribution. This result was confirmed by experimental results as shown in Figure 17. Although it is considered that the γ value is closely related to the resolution, swelling during

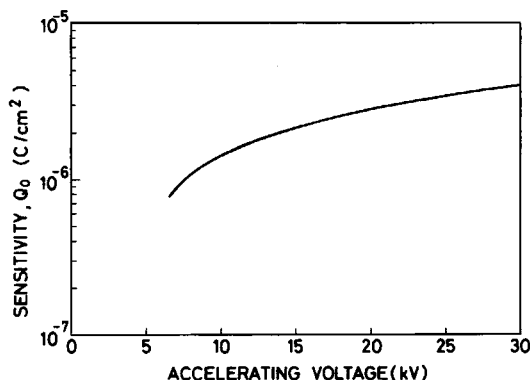


Fig. 15. Dependence of electron energy on sensitivity. Iodination degree of IPS = 0.13; resist thickness = 0.63 μm .

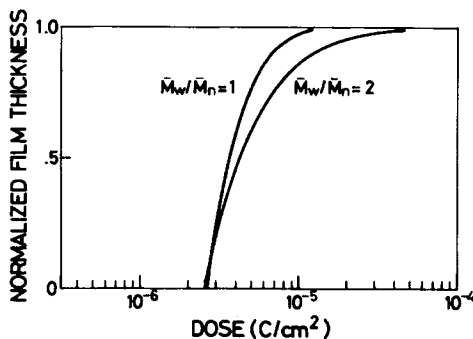


Fig. 16. Calculated exposure characteristics of monodispersed ($M_w/M_n = 1.0$) and random dispersed ($M_w/M_n = 2.0$) IPS. The thickness of IPS is $0.66 \mu\text{m}$; iodination degree is 0.13; and initial electron energy is 15 keV.

the development also limits resolution when the crosslinking reaction occurs upon electron beam irradiation.

Resist Resolution

Resist resolution was evaluated by writing resolution test patterns. Samples were flat Si wafers, coated with IPS resist $1 \mu\text{m}$ thick. Each sample was exposed with a $2.5 \mu\text{C}/\text{cm}^2$ dose using a 30-kV acceleration potential. An example of the fine pattern is shown in Figure 18. It reveals that IPS is capable of resolving $0.6\text{-}\mu\text{m}$ lines and $1.0\text{-}\mu\text{m}$ spaces.

CONCLUSION

It has already been reported that IPS is a negative resist suitable for direct wafer electron beam exposure.¹⁶ The mechanism of sensitization by iodination was clarified using the method of additives. The results are summarized as follows;

(i) IPS undergoes C—I fission upon irradiation of deep UV and electron beam forming a phenyl radical and an iodine atom, which leads to crosslinking.

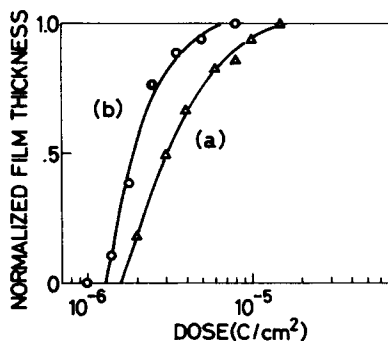


Fig. 17. Experimental exposure characteristics of a narrow molecular weight distribution IPS [$M_w/M_n = 1.03$ (a)] and a broad distribution [$M_w/M_n = 2.29$ (b)]. Weight average of polymerization degree of (a) is 2700 and that of (b) is 3200.

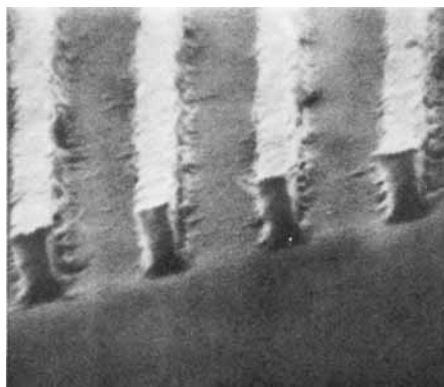


Fig. 18. SEM micrograph of typical resolution patterns of IPS.

(ii) The saturation of sensitivity with the increase in iodination is accounted for by the recombination reaction of radicals produced.

Crosslinking G-values of IPS were also calculated on the basis of Charlesby's theory. The following become evident:

- (iii) Dependence of resist thickness on sensitivity is small.
- (iv) Sensitivity increases with the decrease of electron acceleration potential.
- (v) The γ value (contrast) increases with the decrease of polydispersity.

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