High Performance Electron Negative Resist, Chloromethylated Polystyrene. A Study on Molecular Parameters

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Synopsis

High sensitivity and high contrast electron negative resist, chloromethylated polystyrene (CMS) was developed for direct writing electron beam lithography with 1-μm resolution. The resist shows excellent lithographic performances such as high plasma-etching durability and negligible "post-polymerization effect." A series of CMS covering a wide range of $\overline{M}_w$, 6,800–560,000, were synthesized by the chloromethylation of nearly monodisperse polystyrenes. The effects of molecular parameters on sensitivity and resolution were investigated. The chloromethylation remarkably improved the reactivity of polystyrene, but which was saturated above 40% of chloromethylation ratio. About 100 times higher sensitivity could be achieved as compared with the starting material. As the increase of chloromethylation ratio (CR) gradually broadened the molecular weight distribution (MWD), the optimum CR was evaluated to be about 40%. In the above range of $\overline{M}_w$, the sensitivity varies from 39 to 0.4 μC/cm, whereas the γ-value varies from 3.0 to 1.4. A sharp edge profile was obtained in developed pattern of CMS resist because of its relatively high glass-transition temperature (68–115°C) compared with commercial resists and the suitable selection of a developer. The resolution of CMS was compared with the structually related polymers synthesized from polystyrene with a broader MWD or vinylbenzylchloride and poly(chloroethylvinylether) (CEVE). These polymers show significantly lower resolution than CMS, which indicates the importance of MWD and T_g in electron negative resist.

INTRODUCTION

The electron-beam direct-writing method is one of the very promising technologies to fabricate VLSI with a pattern less than 1 μm. A resist used for this technology requires high dry etching durability, which is essentially demanded for submicron pattern fabrication, as well as high sensitivity and high resolution to the electron beam. Although the electron negative resist loses its resolution because of the swelling of the crosslinked polymer during development, the negative type is much easier for designing high sensitivity and high dry-etching durability than the positive type. Aromatic structure is effective for adding dry-etching durability to polymer resist because of its stability against plasma etching reaction and its high glass transition temperature (T_g). Since the incorporation of aromatic structure generally depresses the sensitivity of the resist, the polymer needs a proper reactive substitute to reach a lithographically useful sensitivity. As far as the resist reaction mainly involves the crosslinking of polymer chains, it is theoretically showed that the contrast (γ) is improved by narrowing the molecular weight distribution (MWD) of the negative resist.[1] Thus, a properly substituted aromatic polymer with narrow molecular weight distribution could be one of the best resists for electron beam lithography.

Journal of Applied Polymer Science, Vol. 27, 937–949 (1982)
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CCC 0021-8995/82/030937-13$01.30

Lithographic performances were presented with several aromatic polymers such as copolymers of styrene and glycidylmethacrylate,[2] iodinated polystyrene,[3] and related aromatic polymers,[4] which show moderate resolution maybe due to their broad molecular weight distribution. In the previous note, one of us reported the brief results about the new electron negative resist, chloromethylated polystylene (CMS).[5] This high sensitive and high resolution resist has excellent dry-etching durability and negligible "post-polymerization," which is continuous crosslinking after irradiation *in vacuo*. As the bond strength of Cl—C in the chloromethyl group especially attached to the aromatic ring is relatively weak, the chloromethylation of polystyrene attributes a great enhancement in sensitivity. This type of enhancement is also observed in other resists containing chloromethyl groups such as poly(vinylethers)[6] and polyacrylates.[7] In order to get very narrow molecular weight distribution with CMS, nearly monodisperse polystyrene was used. These polystyrenes were proved to have high contrast but extremely low sensitivity.[8] Recently, Feit and Stillwagon synthesized high contrast resist, chlorinated polystyrenes by direct chlorination of nearly monodisperse polystyrenes, the sensitivity of which is slightly less than that of CMS.[9]

In this paper, we describe lithographic performances of CMS by monitoring the contents of the chloromethyl group, molecular weight, and its distribution and exposure characteristics by comparing the results with poly(chloroethylvinylethers) (CEVE) and poly(vinylbenzylchloride) (PVB) which are prepared by additive polymerization. Factors influencing both design and processing of the resists are also discussed, with special attention to the molecular parameters. Recently CMS was successfully used for electron-beam direct-writing fabrication of 256-Kbit MOS Random Access Memory with a minimum pattern width of 1 μm.[10]

EXPERIMENTAL

Polymer Preparation

CMS was prepared from polystyrene and chloromethylmethylether using $SnCl_4$ catalyst.[11] Living-polymerized polystyrenes with very narrow MWD (M_w/M_n = 1.01–1.05), obtained from Toyo Soda Co., Ltd., were used as well as an ordinary available polystyrene (Wako Pure Chemicals) with a broader MWD. Chloromethylation was carried out under a nitrogen atmosphere. The polymers were obtained by pouring reaction solution into aqueous methanol and purified by repeated reprecipitations with acetone-aqueous methanol system.

Poly(vinylbenzylchloride) (60%/40% mixture of *o*- and *p*-isomers) was commercially available from Polyscience Inc. CEVE polymers were prepared by $BF_3(C_2H_5)_2O$-initiated cation polymerization of 2-chloroethylvinylether (Tokyo Chemical Industries) in toluene at −60–−70°C under a nitrogen atmosphere. The polymers were isolated by pouring solution into methanol, washed with methanol repeatedly, and purified by reprecipitation with toluene–methanol system.[12]

Characterization

Molecular weight ($\overline{M}_w$ and $\overline{M}_n$) and MWD were determined using gel permeation chromatography with a Hitachi Model 635 GPC equipped with microstyragel columns (Shodex A-803, A-804, and two A-806). The eluting solvent was methylethylketone. Chloromethylation ratio (CR) of CMS was calculated on the basis of chlorine content measured by the elemental analysis of polymers. The Glass transition temperature (T_g) was determined with Rigaku Differential Thermal Analysis Units.

Resist Working

Polymers were dissolved in xylene for CMS and PVB or in a xylene–methylethylketone mixture solvent for CEVE and then spincoated onto a silicon wafer with SiO_2 to a thickness 5000–8000 Å. Prebaking and postbaking were carried out under a nitrogen atmosphere, taking account of the glass transition temperature. The sensitivity of resist to electron beam was examined by exposing in computer-controlled scanning electron microscope JEOL Model JSM-35 with test patterns that contain a series of rectangles covering a wide range of exposure times. The electron energy was 20 kV. The exposure was controlled by the signal from secondary electron detector after calibration using a Faraday cup to measure the beam current. The resist films were developed by dipping in acetone or methylethylketone–isopropanol mixed solution for CMS and *n*-amylacetate for CEVE before rinsing in isopropanol. The resist film thickness before and after development was measured with Talystep. The sensitivity of resists was expressed as $D_{0.5}$ and D_0, which are defined as the dose to crosslink the resist such that the normalized resist thickness is 0.5 and as the minimum dose required to form the insoluble gel. The γ-value is defined as the slope of the extrapolated linear portion of the dose-thickness curve.[13]

RESULT AND DISCUSSION

Glass Transition Temperature (T_g)

Table I summarizes T_g of polymers as well as $\overline{M}_w$, MWD, sensitivity, and contrast (γ). Chloromethylation elevated T_g of CMS by 30–40°C as compared with corresponding starting material, polystyrene. This is mainly due to the steric effect of chloromethyl group introduced in benzene ring. At room temperature, CMS and PVB have glassy state, but CEVE is rubbery.

Molecular Weight Parameters and Chloromethylation

As the lithographic performances, details of which are presented in later sections, are greatly influenced by molecular weight parameters and CR, the effect of CR on $\overline{M}_w$ and MWD was examined.

In the Friedel–Crafts reaction of polystyrene with chloromethylmethylether, the chloromethylation is not the only reaction, but a crosslinking reaction between benzene rings and chlorobenzyl groups which were formed in the earlier stage of reaction is inevitable. Although an uncontrollable reaction easily resulted in the gelation of polymers, we could obtain CMS, having expected mo-

TABLE I
Molecular Parameters and Characteristics of Polymers

Polymer	$\overline{M}_w$ ($\times 10^{-4}$)	$\overline{M}_w/\overline{M}_n$	T_g (°C)	CR	Sensitivity ($\mu C/cm^2$) D_0	$D_{0.5}$	γ-value
CMS-1	0.68	1.05	68	0.79	27	39	3.0
CMS-2	1.4	1.03	98	0.46	8.9	15	2.2
CMS-3	1.5	1.03	98	0.53	8.8	14	2.2
CMS-4	9.1	1.1	105	0.98	1.3	2.2	1.8
CMS-5	14.5	1.1	110	0.43	0.71	1.3	1.7
CMS-6	56.0	1.1	115	0.42	0.18	0.4	1.4
CMS-7	53.0	3.3	112	0.95	0.17	0.75	1.0
PVB	9.6	1.8	110	1.0	1.3	2.5	1.5
PST-1	43.0	1.05	88	0	12.2	22.7	2.2
PST-2	23.0	2.6	85	0	23.0	42.0	1.8
CEVE	37.0	2.1	−12		0.79	2.3	1.1

$\overline{M}_w$ = weight-average molecular weight.
$\overline{M}_n$ = number-average molecular weight.
T_g = glass transition temperature.
CR = chloromethylation ratio calculated by the following equation: $CR = (A \times C \times 1/100)/[(A - B) r \times C \times 1/100 + D]$, where A is unit molecular weight of polystyrene, B is unit molecular weight of monochloromethylated polystyrene, C is chlorine content (%) determined elemental analysis, and D is atomic weight of chlorine.
CMS = chloromethylated polystyrene.
PVB = poly(vinylbenzylchloride).
PST = polystyrene.
CEVE = poly(2-chloroethylvinylether).

lecular weight parameters and the CR values by controlling the catalyst concentration and molecular weight parameters of the mother polymer, and keeping the reaction solution cool below −20°C.

In Figure 1 the molecular weight of various CMS synthesized is plotted against their CR for three kinds of starting polymers with different molecular weights. The linear dotted lines in this figure show the ideal molecular weight of CMS calculated on the assumption that there is no other reaction than the chloromethylation. The variation of GPC curves indicating the MWD is depicted with CR in Figure 2. As CR was increased, the deviation of CMS's molecular weight from the calculated line in Figure 1 became evident, and a new peak in GPC curve appeared clearly in the higher molecular weight region in Figure 2. These results indicate the existence of side reaction.

Figure 3 shows the variation of MWD with CR. Though, in a higher molecular weight polymer, MWD tends to broaden with CR, no significant broadening of MWD was observed until about 50% of CR.

Electron Beam Sensitivity

The variation of electron beam sensitivity of CMS with its CR is illustrated in Figure 4. The sensitivity was remarkably improved by introducing chloromethyl groups into polystyrene. This increase in sensitivity was quite large in the initial stage of CR, and then became gradually moderate with CR above 40%. Eventually, CMS with almost 100% of CR is about 100 times more sensitive than its starting material.

In order to evaluate the reactivity of CMS to electron beam, the contribution

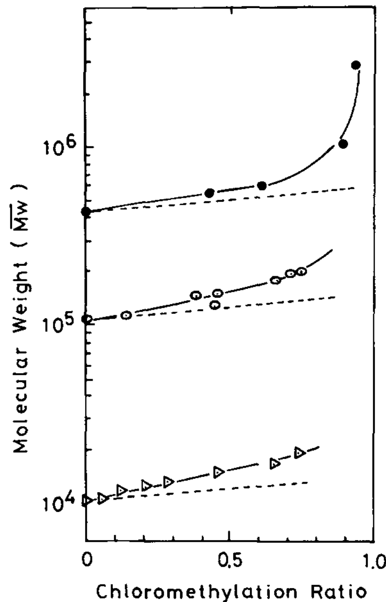


Fig. 1. Relationship between $\overline{M}_w$ and CR for CMS. The linear dotted lines show ideal molecular weight of CMS calculated on the assumption that there is no other reaction than the chloromethylation of the benzene ring. $\overline{M}_w$ of PST: (●) 4.3×10^5; (○) 1.1×10^5; (▷) 9.8×10^3.

of molecular weight to the sensitivity must be eliminated, because a higher molecular weight results in a higher sensitivity in electron negative resists. It is recognized that the product of D_0 and $\overline{M}_w$, which is almost constant for a particular polymer[14] regardless of its molecular weight, gives the best measure of polymer reactivity. Figure 5 shows the relationship between $D_0 \times \overline{M}_w$ and CR replotted from Figure 4. The reactivity of polystyrene abruptly jumped by a small degree of chloromethylation, and increases gradually with CR. Above 40% of CR, further chloromethylation had no effect in the enhancement of polymer reactivity, and CMS followed the relation $D_0 \times \overline{M}_w$ = const. Figure 6 shows the relationship between sensitivity $D_{0.5}$, D_0, and $\overline{M}_w$ for CMS with above 40% of

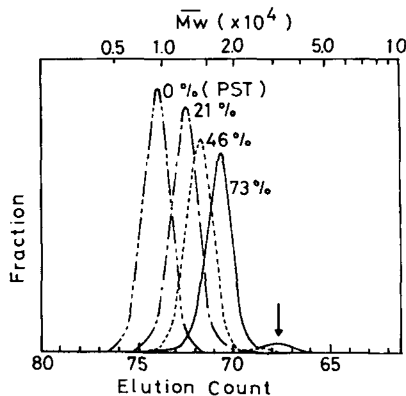


Fig. 2. The variation of GPC curve with CR. The arrow indicates the peak caused by side reaction in chloromethylation. $\overline{M}_w$ and $\overline{M}_w/\overline{M}_n$ of polystyrene are 9,800 and 1.01.

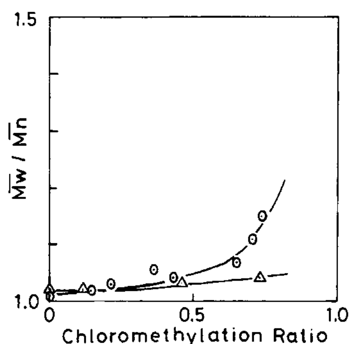


Fig. 3. The variation of MWD with CMS. $\overline{M}_w$ of PST: (△) 9.8 × 10^3; (○) 1.1 × 10^5.

CR and for CEVE. Once the reactivity of polymer saturates, the sensitivity of CMS simply depends on $\overline{M}_w$. By contrast, the reactive group such as the epoxy or vinyl group increases the polymer sensitivity linearly with its content in polymer.[15] The result that the saturation of polymer reactivity with reactive group content is also observed in iodinated polystyrene (IPS) suggests the same type of reaction mechanism involved in CMS as in IPS.[3]

The reactivity expressed by $D_0 \times \overline{M}_w$ is listed for various electron negative resists in Table II. An excellent value obtained with PGMA is attributed to the chain reaction of the epoxy group. As halogenated polymers have no unsaturated group, the crosslinking occurs mainly via stepwise reaction, presumably, a coupling reaction of two radicals formed by electron beam exposure. This type of reaction is preferable for giving high resolution rather than high sensitivity. CMS has the highest reactivity among halogenated polymers listed in Table II.

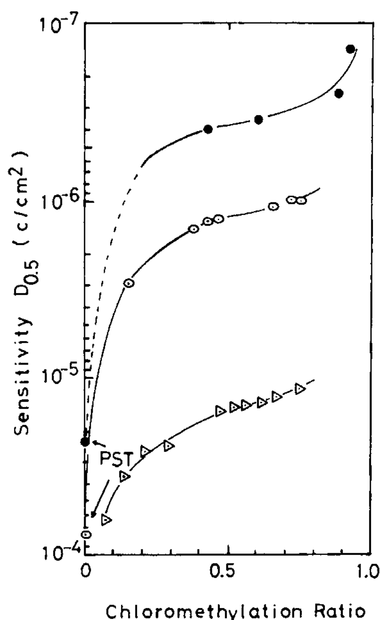


Fig. 4. The variation of electron beam sensitivity of CMS with CR. $D_{0.5}$ of polystyrene ($\overline{M}_w$ = 9,800) does not appear in the figure. $\overline{M}_w$ of PST: (●) 4.3 × 10^5; (○) 1.1 × 10^5; (▷) 9.8 × 10^3.

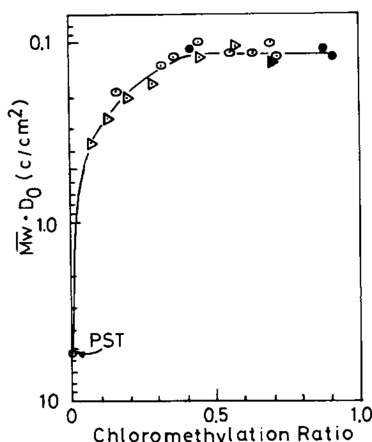
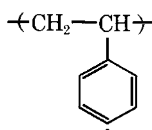


Fig. 5. The relationship between $D_0 \times \overline{M}_w$ and CR. $\overline{M}_w$ of PST: (●) 4.3×10^5; (○) 1.1×10^5; (△) 9.8×10^3.

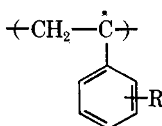
This could be due to the feasibility of the C—Cl bond dissociation in the chloromethyl group because of the high stability of the benzyl radical.

The crosslinking mechanism for CMS is proposed as in Scheme I where R is H or CH_2Cl.

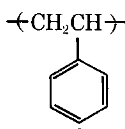
This reaction scheme is almost identical with one proposed by Shiraishi et al.[3] for IPS except X_2 (X=Cl or I) formation by coupling reaction of two X radicals, which can be also negligible in CMS because of the high reactivity of the Cl radical and much higher concentration of hydrogen available for hydrogen subtraction by the Cl radical than the Cl radical concentration for the Cl_2 formation. To interpret the relationship between the sensitivity of IPS and iodination ratio (IR), Shiraishi et al. assumed that the recombination rate of

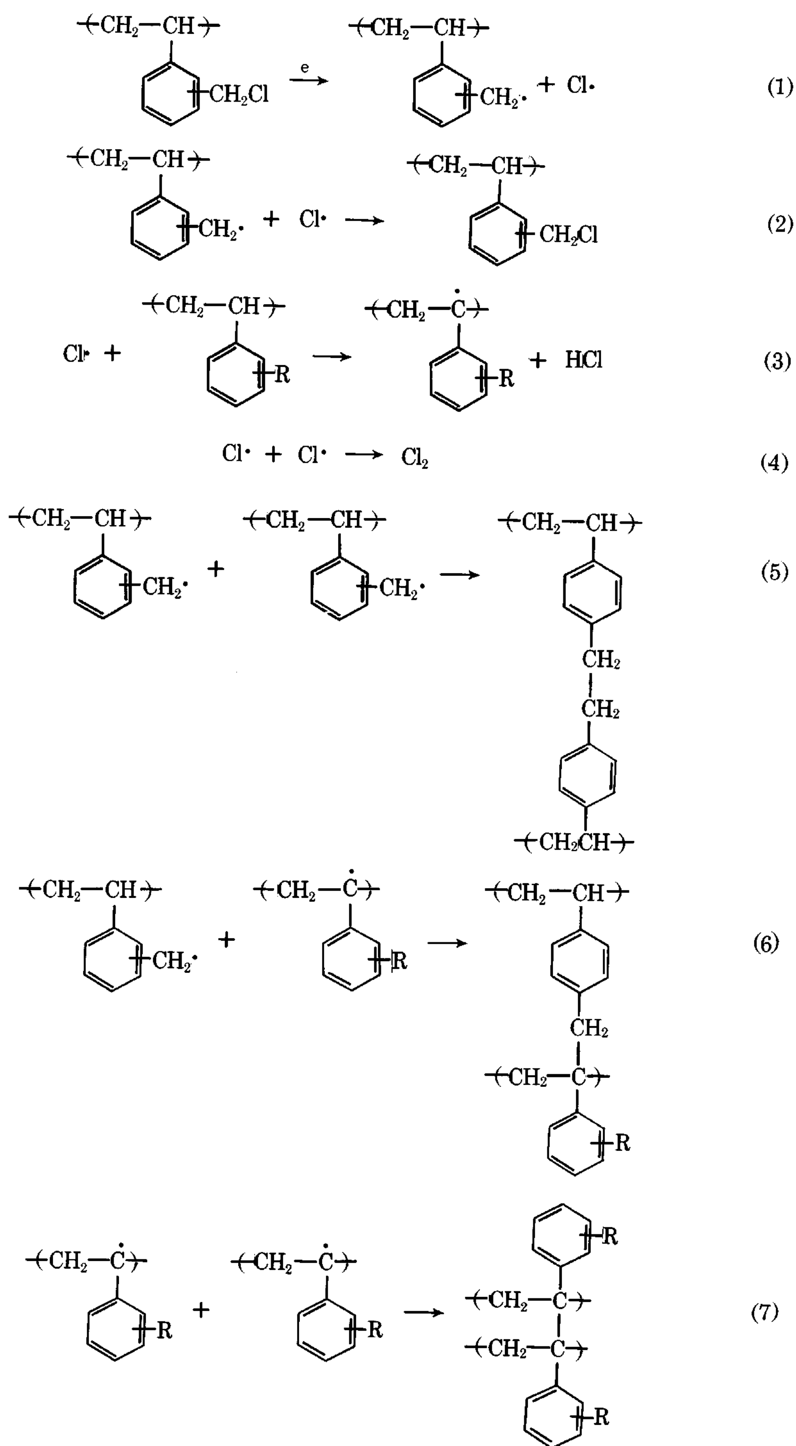


radical and I· radical is propotional to IR and that



where R=H or I formed via hydrogen subtraction by the I· radical freely reacts with the





Scheme I. Proposed crosslinking mechanism for CMS.

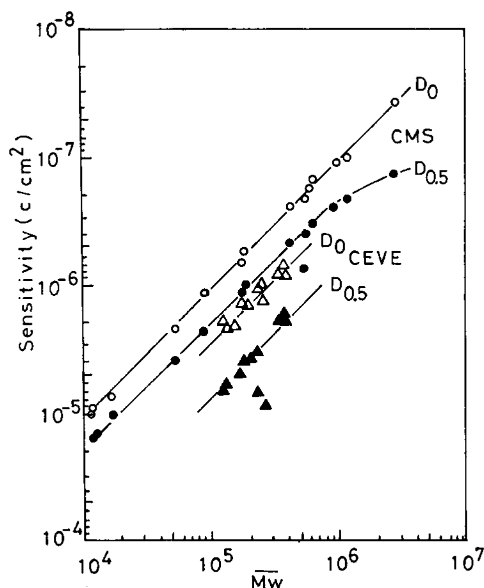
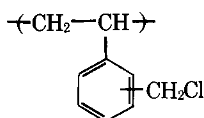


Fig. 6. The relationship between sensitivity and $\overline{M}_w$ for CEVE and CMS with above 40% chloromethylation.

radical. It seems to be, however, more plausible to assume that the reaction rate of crosslinking [reactions (5), (6), and (7)] is significantly lowered with the increase of halogenation because of the steric effect by a bulky chloromethyl group in CMS or the iodine atom in IPS. The effect could make an average distance between



and nearest

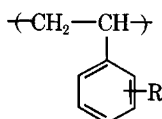
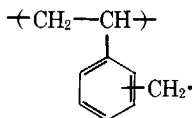


TABLE II
Reactivity Expressed by $D_0 \times \overline{M}_w$ of Various Negative Resists

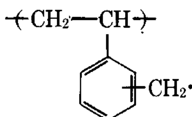
Resists	$D_0 \times \overline{M}_w$	Reference
CMS	0.13	This paper
PVB	0.12	This paper
	0.078	4
IPS	0.42	3
CPS	0.28	9
PGMA	0.028	15
CEVE	0.36	This paper

IPS = iodinated polystyrene.
CPS = poly(3-chlorostyrene).
PGMA = poly(glycidylmethacrylate).

groups, gradually longer with CR. This means that as CR is increased, the ratio of



groups available for crosslinking becomes smaller, despite the increase of total number of the



radical. High T_g of CMS or IPS would prevent radicals from moving about to react to each other. This assumption can explain qualitatively the saturation of polymer reactivity with CR and the fact that the saturation in IPS occurs at a relatively low IR (about 10%) because of a larger volume of iodine atom than the chloromethyl group. Preliminary electron spin resonance (ESR) study, in which a considerable amount of polymer radicals were detected in CMS samples after Co^{60} γ-ray or deep UV light irradiation, supports our assumption. Details of ESR studies will be reported elsewhere. The lack of post-polymerization effect in CMS, in spite of many radicals remaining alive, could be achieved by a high T_g of CMS.

Contrast and Resolution of CMS

Contrast (γ-value) generally depends on molecular weight parameters for electron negative resist. The sensitivity curves of CMS-3 and PVB which have almost the same $\overline{M}_w$ are shown in Figure 7. Although both polymers have the same D_0, the γ-value of CMS-3 was higher than that of PVB. CMS-7 synthesized from polystyrene with a broader MWD also showed a considerably lower γ-value than CMS-6 obtained from monodisperse polystyrene. These results

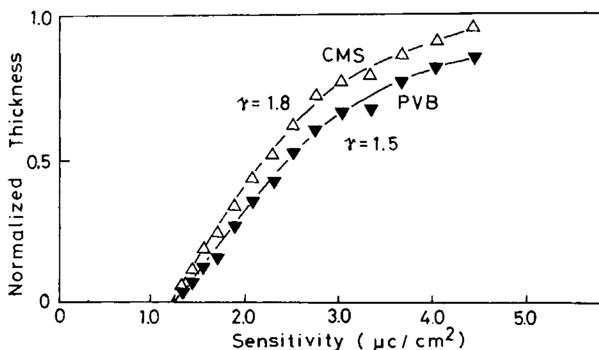


Fig. 7. The sensitivity curves of CMS-4 and PVB. $\overline{M}_w$ of CMS and PVB are 91,000 and 96,000, correspondingly.

indicate the importance of MWD and the utility of nearly monodisperse polystyrene as the starting material to design electron negative resist. The effect of a high γ-value of CMS is ascertained by pattern delineation. Developed resist pattern of CMS-3 was compared with that of PVB in Figures 9 and 10. CMS

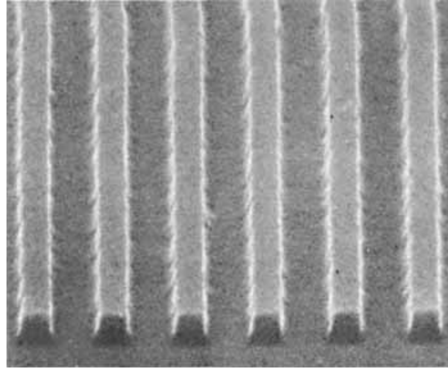


Fig. 8. The developed resist patterns of CMS-3 with 1 μm line and space. Patterns were delineated in 0.7-μm-thick resist prebaked at 105°C for 20 min, developed in methylethylketone–isopropanol mixed solution for 20 s, and rinsed in isopropanol.

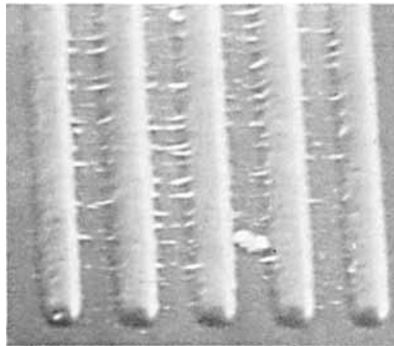


Fig. 9. The developed resist patterns of PVB with 1 μm line and space. The processing condition is the same with that of CMS.

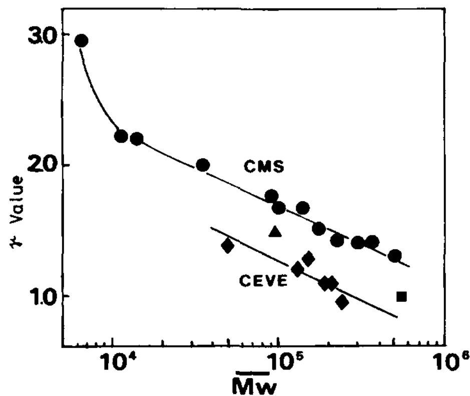


Fig. 10. The variation of γ-values with $\overline{M}_w$ for CMS and CEVE systems. ▲ and ■ indicate the values of PVB and CMS-7 obtained from polystyrene with a broad MWD.

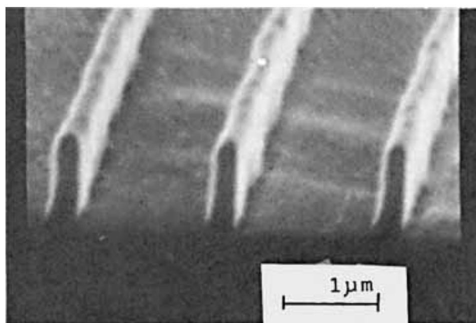


Fig. 11. The line patterns of CMS delineated by scanning single pass of focussed electron beam. The processing condition is same with that of CMS-3 in Figure 8.

resolved 1 μm line and space bar patterns which were not resolved on PVB resist.

The molecular weight of polymer also affects, γ-values, which is illustrated in Figure 10 for CMS and CEVE systems. Low molecular weight CMS-1 ($\overline{M}_w$ = 6800) had a quite high γ-value, 3.0. The reason for this high γ-value is not clear, but may be explained by the enhancement of the γ-value by development. The γ-value was gradually lowered as $\overline{M}_w$ was increased, but CMS with $\overline{M}_w$ = 145,000 ($D_{0.5}$ = 1.3 μC/cm^2) still had a relatively high γ-value, 1.7. The γ-values of CEVE were much lower than those of CMS and PVB. This could be caused by the broader MWD and the increase of chain reaction in CEVE because of its low T_g. It is interesting that both systems have almost the same slope in M_w dependence on the γ-value in Figure 10, despite a large difference in γ-value. The reason for this effect has not yet been well understood.

To evaluate the edge profile of the developed pattern, line patterns of CMS and CEVE were delineated by a scanning single pass of a focussed electron beam. As shown in Figure 11, the edge of developed CMS resist pattern is sharp and aspect ratio is quite high. On the other hand, Figure 12 indicates broadened deteriorated patterns in CEVE which suggest a large degree of swelling during development. Higher T_g value of CMS seems to be effective in minimizing the swelling of resist.

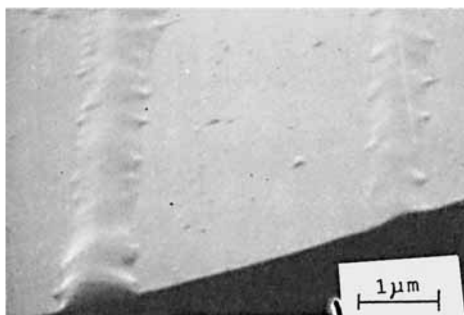


Fig. 12. The line patterns of CEVE delineated by scanning single pass of focussed electron beam. Patterns were delineated in 0.6-μm-thick prebaked at 50°C for 20 min, developed in *n*-amylacetate–isopropanol mixed solution for 20 s, and rinsed in isopropanol.

CONCLUSION

CMS resists were synthesized by chloromethylation of nearly monodisperse polystyrene. Molecular parameters affecting lithographic performances were investigated, of which results can be summerized as follows,

(1) Chloromethylation is the most effective method so far to sensitize the reactivity of polystyrene to electron beam.

(2) As CR is increased, the reactivity of CMS is greatly improved but saturates above 40% of CR, whereas increase of CR makes MWD gradually broader. Eventually, CMS with 40–50% of CR is the most practical as highly sensitive and high resolution resist.

(3) As starting material, a nearly monodisperse polystyrene is useful for designing high contrast negative resist with aromatic structure which can improve dry-etching durability and "post-polymerization effect" in negative resist.

The authors are grateful to K. Matsuyama, J. Shimada, K. Murase, O. Kogure, M. Kakuchi, K. Sukegawa, K. Miyoshi, and H. Sato for their helpful discussions. Thanks are also due to Dr. H. Katsuragi, Dr. T. Kitayama, T. Ogawa, K. Hirata, H. Sakakibara, and T. Kobayashi for their helpful discussions.

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Received May 5, 1981
Accepted August 6, 1981