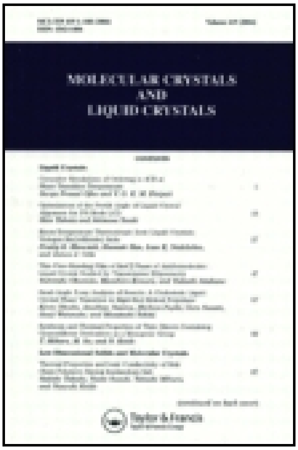

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Seong-Ju Kim [a], Ji-Hong Kim [a], Dae-Youp Lee [a], Young-Hoon Ko [a], Byung-Sun Park [b] & Chun-Geun Park [c]

[a] Korea Kumho Petrochemical Co., Ltd., Yeocheon, 555-210, Korea

[b] Electronics and Telecomunications Research Institute, Daeduk, 305-606, Korea

[c] Samsung Electronics Co., Ltd., Suwon, 440-600, Korea

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PHOTORESIST MATERIALS BASED ON ORGANOMETALLIC-CONTAINING POLYSULFONES

SEONG-JU KIM, JI-HONG KIM, DAE-YOUP LEE, YOUNG-HOON KO, BYUNG-SUN PARK[1], AND CHUN-GEUN PARK[2]
Korea Kumho Petrochemical Co., Ltd., Yeocheon 555-210, Korea; [1]Electronics and Telecomunications Research Institute, Daeduk 305-606, Korea; [2]Samsung Electronics Co., Ltd., Suwon 440-600, Korea.

Abstract Soluble 1:1 alternating copolymers of *p*-*tert*-butylstyrene, *p*-(trimethyl silyl)styrene, *p*-(trimethylgermyl)styrene, and 3-vinylbenzyltrimethylsilane with sulfur dioxide have been synthesized by *tert*-butylhydroperoxide-initiated copolymerization at T < -60°C. Oxygen plasma etch resistance of poly[*p*-(trimethyl germyl)styrene sulfone] resist is higher than that of poly[*p*-(trimetylsilyl)styrene sulfone] resist by a factor of 4.5, and that of cresol-novolac by a factor of 9. Among the polysulfone resists, poly[*p*-(trimethylgermyl)styrene sulfone] shows the best lithographic characteristics.

INTRODUCTION

Poly(olefin sulfone) resists such as poly(1-butene sulfone)(PBS) have been used for electron-beam lithographic fabrication of chromium photomasks because of their excellent sensitivity and resolution(0.8 $\mu C/cm^2$ at 10kV).[1] However, poly(olefin sulfone) resists are generally unstable in various plasma environments, in particular, during reactive-ion etching, which has limited their use in direct device processing. On the other hand, 2:1 poly(styrene sulfone)(2:1 PSS) shows high dry etch resistance because of the high content of aromatic groups. In general, the incorporation of aromatic groups into a resist system offers the increase of dry etch resistance. However, the 2:1 PSS is relatively less sensitive resist requiring exposure greater than 10^{-5} C/cm^2.[2] Another limitation of PSS is that alternating PSS is insoluble in the usual organic solvents, leading to a difficulty in use for the resist material. Recently one approach to overcome these difficulties was made by Matsuda *et al.* for silicon-containing polysulfones.[3,4] They found that alternating poly[(trimethylsilyl) styrene sulfone] and poly[(pentamethyldisilyl)styrene sulfone] are not only soluble to the usual organic solvents by incorporation of trimethylsilyl and pentamethyldisilyl groups, but also highly sensitive to electron beam and, excellently resistive to oxygen plasma etching.

On the other hand, PBS, although this is a sensitive positive tone electron beam resist, does not absorb above 200 nm, and the sensitization has not been successful.[5] Incorporation of pendant aromatic rings into the polysulfone structure extends the photosensitivity to the deep-UV and mid-UV regions. Effective spectral range of 2:1 PSS lies 240 nm ~ 280 nm, however, the sensitivity is very low(1000 mJ/cm^2 at 265 nm).[5] Alternating poly[(trimethylsilyl)styrene sulfone] and poly[(pentamethyldisilyl) styrene sulfone] show high electron beam and deep-UV sensitivities of 3 μC/cm^2 at 20 kV and 0.1 mJ/cm^2, respectively,[6] in spite of the excellent dry etch durability.[3]

This paper is intended to investigate the lithographic properties of some alternating silicon and germanium-containing polysulfones.

EXPERIMENTAL

Materials. *p*-(Trimethylsilyl)styrene(TMSS) and *p*-(trimethylgermyl)styrene(TMGS) monomers were synthesized as described previously.[7] 3-vinylbenzyltrimethylsilane (VBTMS) was synthesized from trimethylchlorosilane and 3-vinylbenzyl chloride by means of Grignard reaction and allyltriphenylsilane(ATPS) could also be synthesized from triphenylchloro silane and allylmagnesium chloride. *p-tert*-Butylstyrene(PTBS) was purchased from Polysciences, Inc., PA, U.S.A. The UV absorption data of the monomers were shown in Table I.

TABLE I λ_{max} and ε_{max} values of the monomers.

Monomers	λ_{max} (nm)	ε_{max} (L/mol cm)
PTBS	254	17,350
TMSS	257	20,990
TMGS	256	20,540
VBTMS	253	12,590
ATPS	223	23,970

(Solvent : 1,2-dichloroethane, Conc. : 3.3 x 10^{-5} mol/L)

Copolymerizations were carried out in a pressure-resistant glass vessel. The required amounts of *tert*-butyl hydroperoxide(*t*-BuOOH) and monomer were degassed by freeze-pump-thaw cycles, and liquid sulfur dioxide(SO_2) was introduced by vacuum-line techniques. The vessel was placed in a temperature-controlled bath which was cooled to -60°C. After the required copolymerization time elapsed, the resulting semisolid reaction mass was diluted with acetone, precipitated in hexane/methanol, and dried under vacuum at room temperature.

Characterization Methods. Compositions of the polysulfones were determined by the elemental microanalysis of carbon content. Molecular weights were determined by gel permeation chromatography(GPC) in THF using a TOSOH HLC-8020 instrument equipped with a refractive index detector. Infra-red(IR) spectra were obtained from a BIO-RAD FTS-65 spectrometer using thin polymer films cast on NaCl substrates. Ultraviolet(UV) absorption spectra were recorded on a Shimazdu UV-2100S UV/VIS spectrometer.

Lithographic Evaluation. The resist solutions of the polysulfones were prepared by dissolving the polymers in cyclohexanone. The solutions were filtered more than 2 times through a 0.2 μm pore size filter. Resist films of ca. 0.6 μm thickness were spin-coated onto silicon substrates at 1500 rpm, which were baked after coating at 130°C for 90 seconds on a MTI hot plate. Film thicknesses were measured using a Tencor Alpha Step 200 profilometer.

X-ray(λc form the bands=18.5 Å) exposures were done using a Karl Suss XRS 200 X-ray stepper. Electron beam exposures were performed on a LEICA EBML 300 at 30 kV. Lithographic imaging was carried out on KrF excimer laser stepper of Nikon(NA=0.45).

The exposed wafers were developed by immersing in 30/70 v/v mixture of toluene/isopropyl alcohol for 60 seconds at room temperature, and rinsed for 20 seconds in isopropyl alcohol. A JEOL JSM-5400 scanning electron microscope(SEM) at 255 kV was used to take photomicrographs of developed resist images.

Oxygen reactive-ion etching(O_2 RIE) was done in a BRANSON/IPC etcher. The etch conditions were as follows: Oxygen pressure 200 mTorr at a flow rate of 750 sccm, RF power of 800 W

RESULTS AND DISCUSSION

Materials Synthesis and Characterization. TBS,[8] TMSS,[9] TMGS, VBTMS, and ATPS were selected as comonomers of SO_2 because the polysulfones which were formed from the monomers incorporating pendant aromatic rings with organometallic groups are expected to show good durability to O_2 RIE and applicability to deep-UV resist. All of the monomers, except ATPS, are copolymerized with SO_2 at $T < -60°C$, to form 1:1 alternating polysulfones. The ATPS was scarcely formed copolymer with

SO_2 under our experimental conditions. Synthetic conditions to prepare the polysulfones are given in Table II.

TABLE II Synthesis of Polysulfones

Monomers	Temp. (°C)	Time (hr)	Yield (%)	Mn ($x10^{-4}$)	Mw/Mn
TBS	-60	19	50	44	2.3
TMSS	-60	18	16	1.3	4.0
TMGS	-60	18	20	2.3	4.8
VBTMS	-60	18	21	10.3	4.5

Monomers(0.06 mol), SO_2(0.12 mol) and a 3M solution in 2,2,4-trimethylpentane of *t*-BuOOH(0.18 mol/L) were used in each run.

UV-VIS spectra for 1:1 alternating polysulfones are shown in Figure I. Their λ_{max} and ε_{max} values are listed in Table III.

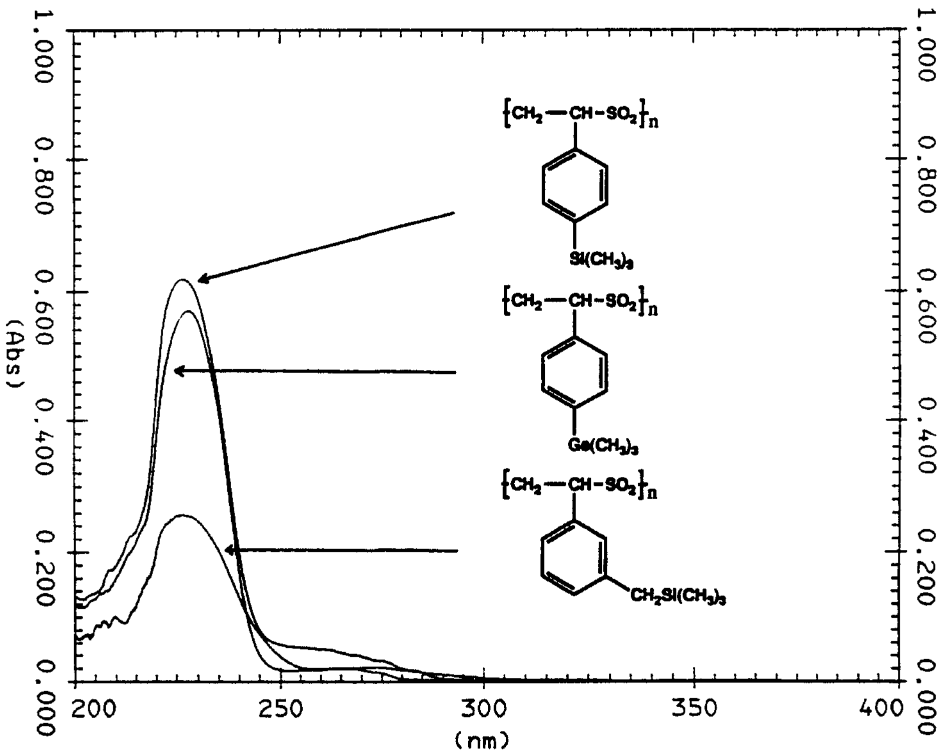

FIGURE 1 UV/VIS spectra of the polysulfones.

TABLE III The values of λ_{max} and ε_{max} of the polysulfones

Monomers	λ_{max} (nm)	ε_{max} *
Poly(TMSS Sulfone)	226.5	18,751
Poly(TMGS Sulfone)	227.8	16,700
Poly(VBTMS Sulfone)	226.5	9,640

* L/mol cm of vinyl monomer unit.

Irradiation Effect. Decomposition behavior of alternating poly(VBTMS sulfone) by the irradiation was monitored by a IR spectrometric technique(Figure 2).

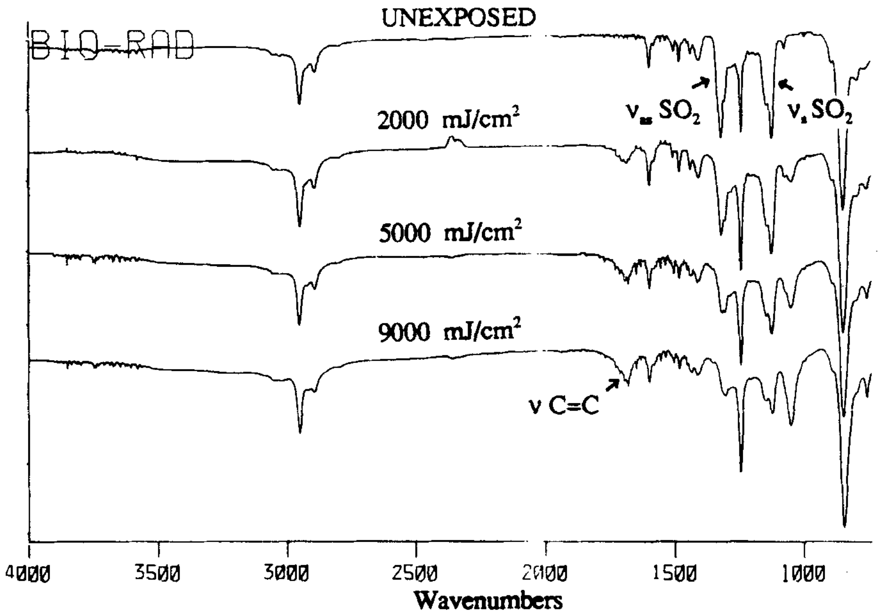

FIGURE 2 IR spectrum changes of poly(VBTMS sulfone) upon irradiation.

The typical strong two bands(1130 cm^{-1}, 1330 cm^{-1}) corresponding to sulfonyl group $>SO_2$ were declined upon the irradiation with Xenon lamp followed by the appearance of bands corresponding to C=C double bond at 1685 cm^{-1}. This evidently shows that the scission of C-S bond and the formation of C=C double bond are simultaneously happened upon irradiation. According to the mechanism of the photodegradation of poly[(pentamethyldisilyl)styrene sulfone]s, using flash photolysis technique proposed by Matsuda *et al.*[4], *p*-(pentamethyldisilyl)styrene is produced by extrusion of SO_2 by photolysis owing to the fast decomposition of the benzylsulfonyl radical.

Oxygen Plasma Stability. The results of O_2 RIE of four polysulfones are shown in Table IV, and compared with that of cresol-novolac resin.

TABLE IV Eech rate of alternating polysulfones and cresol-novolac resin

Polymers	Etch Rate (Å/min)	Etch Rate Ratio (Cresol-Novolac/Polysulfone)
Poly(TBS Sulfone)	940	2
Poly(TMSS Sulfone)	940	2
Poly(TMGS Sulfone)	230	9
Poly(VBTMS Sulfone)	920	2
Cresol-Novolac (Mw=9,200)	2,100	-

Etch conditions : Oxygen pressure 200 mTorr at a flow rate of 750 sccm, RF power of 800 W

Oxygen plasma etch rate of poly(TMGS sulfone) is slower than that of poly(TMSS sulfone) by a factor of 4.5. This may be explained by the fact that germanium-containing species have higher boiling point than silicon-containing species under oxygen reactive ion etching environment.

Preliminary Lithographic Evaluation. The lithographic performance of poly(TMGS sulfone) resist was examined briefly by electron-beam, X-ray, and KrF excimer laser exposures. Figure 3 shows positive tone resist pattern of poly(TMGS sulfone) resist achieved by the method mentioned above experimental section. Even though poly (TMGS sulfone) has almost no absorbance at 248 nm in Figure 1, it is noteworthy for poly(TMGS sulfone) to be sensitive to KrF excimer laser.

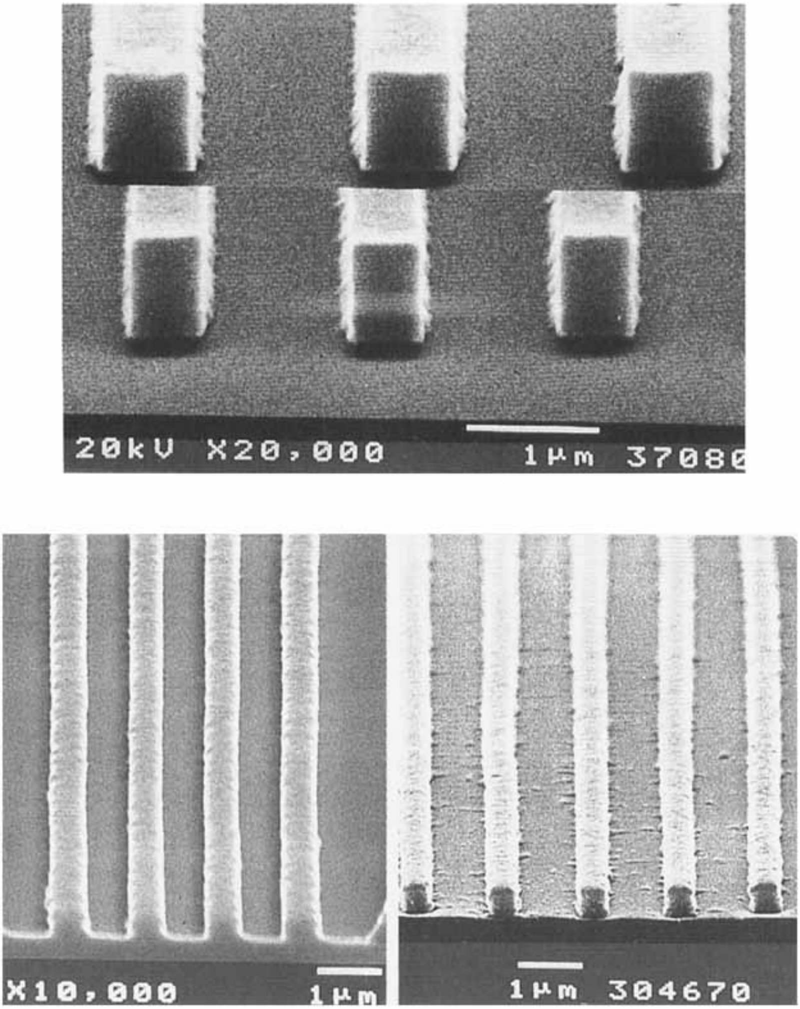

FIGURE 3 SEM photographs of poly(TMGS sulfone).
X-ray pattern(above), electron-beam pattern using 10 μC/cm^2 (left), and KrF excimer laser pattern using 46 mJ/cm^2.

REFERENCES

1. M. J. Bowden, R. F. W. Pease, L. D. Yau, J. Frakoviak, L. F. Thompson and J. G. Skinner, in Microcircuit Engineering, H. Ahmed and W. C. Nixon, Eds., Cambridge University Press, Cambridge (1980).
2. M. J. Bowden and L. F. Thompson, J. Electrochem. Soc., 121 (12), 1620 (1974).
3. A. S. Gozdz, H. Ono, S. Ito, J. A. Shelburne III, and M. Matsuda, Proc. SPIE-Int. Soc. Opt. Eng., 1446, 200 (1991).
4. A. Watanabe, T. Sakakibara, S. Ito, H. Ono, Y. Yoshida, S. Tagawa and M. Matsuda, Macromolecules, 25, 692 (1992).
5. T. Iwayanagi, T. Ueno, S. Nonogaki, H. Ito and C. G. Willson, in Materials and Processes for Deep-UV Lithography, M. J. Bowden and S. R. Turner, Eds., ACS Symposium Series 218, American Chemical Society, Washington, DC (1988).
6. S. Ito, H. Ono, S. J. Kim and M. Matsuda, IUPAC 32nd International Symposium on Macromolecules, Kyoto, Japan, 542 (1988).
7. S. J. Kim, B. S. Park and H. W. Lee, SPIE-Advances in Resist Technology and Processing IX, 1672, 477 (1992).
8. T. Sakakibara, M. S. Dissertation, Tohoku University, Sendai, Japan (1990).
9. S. J. Kim, S. Ito, H. Ono and M. Matsuda, IUPAC 32nd International Symposium on Macromolecules, Kyoto, Japan, 218 (1988).