

Silylated Poly(4-hydroxystyrene)s as Negative Electron Beam Resists

TSUTOMU SHINODA,¹ MITSUhide YOSHIKAWA,¹ TOHRU NISHIWAKI,¹ HARUO INOUE²

¹ Electronic Group, Tokyo Metropolitan Industrial Technology Research Institute, 3-13-10 Nishigaoka, Kita-ku, Tokyo 115-8586, Japan

² Department of Applied Chemistry, Graduate Course of Engineering, Tokyo Metropolitan University, 1-1 Minami-osawa, Hachioji, Tokyo 192-0364, Japan

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ABSTRACT: Silylated poly(4-hydroxystyrene)s and radical polymerized 4-*tert*-butyldimethylsilyloxystyrene (TBDMSOSt) were examined as electron beam resists. Commercial poly(4-hydroxystyrene) (PHS) with $M_w = 1.69 \times 10^4$ and $M_w/M_n = 5.41$ was silylated with 1-(trimethylsilyl)imidazole and *tert*-butylchlorodimethylsilane. Both silylation reactions proceeded quantitatively to afford trimethylsilylated PHS with $M_w = 3.93 \times 10^4$ and $M_w/M_n = 4.91$, and *tert*-butyldimethylsilylated PHS with $M_w = 4.08 \times 10^4$ and $M_w/M_n = 3.81$. These 2 silyl ether polymers acted as a negative working resist to electron beam (EB) exposure. Sensitivity and contrast of *tert*-butyldimethylsilylated PHS were not affected by prebake temperature around its T_g of 97°C, while those of PHS were dependent on prebake temperature around its T_g of 160°C. At a prebake temperature of 125°C, the sensitivity parameter $D_g^{0.5}$ and the contrast γ value were obtained as follows: $3.93 \times 10^{-4} \text{ C cm}^{-2}$ and 0.91 for PHS; $1.49 \times 10^{-4} \text{ C cm}^{-2}$ and 1.06 for trimethylsilylated PHS; $1.84 \times 10^{-4} \text{ C cm}^{-2}$ and 1.44 for *tert*-butyldimethylsilylated PHS. The silylation procedures obviously improved the sensitivity of PHS. TBDMSOSt was polymerized in bulk at 60°C with 2,2'-azobisisobutyronitrile (AIBN) as an initiator. The resultant poly(TBDMSOSt) possessed $M_w = 3.01 \times 10^5$ and $M_w/M_n = 1.92$ and exhibited a sensitivity $D_g^{0.5}$ of $1.60 \times 10^{-5} \text{ C cm}^{-2}$ and a γ value of 1.47. More than 10 times enhancement of sensitivity was observed compared with *tert*-butyldimethylsilylated PHS. Such a high sensitivity is probably due to the high molecular weight of the bulk polymerized material. Poly(TBDMSOSt) resolved an isolated line of 0.20 μm width and 0.5 μm line and space patterns. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 1151–1157, 1998

Key words: silylated poly(4-hydroxystyrene)s; poly(4-*tert*-butyldimethylsilyloxystyrene); radical polymerization; gel permeation chromatography; electron beam resists

INTRODUCTION

Short wavelength (190–250 nm) photolithography and electron beam (EB) lithography are

both leading technological alternatives to conventional i- and g-line photolithography (350–450 nm).¹ Silylated poly(4-hydroxystyrene)s have been investigated for short wavelength photolithography because of their acid labile silyl ether groups.^{2,3} A dry-developed resist process of utilizing vapor phase silylation of poly(4-hydroxystyrene) combined with oxygen reactive

Correspondence to: T. Shinoda (shinoda.tsutomu@iri.metro.tokyo.jp).

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ion etching (O_2 RIE) has also been proposed.⁴ However, the silyl ether polymers of poly(4-hydroxystyrene) have not yet been examined for EB lithography.

The authors have studied the application of silylated 4-hydroxystyrene monomers to micro-lithography resists.⁵ This article describes the behavior of poly(4-*tert*-butyldimethylsilyloxystyrene) to EB exposure and evaluation as a resist, compared with silylated materials of commercial poly(4-hydroxystyrene).

EXPERIMENTAL

Material Preparation

Poly(4-hydroxystyrene) (PHS) was obtained from Maruzen Petrochemical Company (Tokyo, Japan) and was purified twice by the following reprecipitation procedure. PHS was dissolved in 2-butanone, precipitated into hexane, and dried at room temperature under vacuum.

Trimethylsilylated PHS was prepared by silylating PHS with 1-(trimethylsilyl)imidazole in 1,4-dioxane. The reaction mixture was stirred at room temperature for 24 h. Precipitation into ice water gave pale brown powders. The yield was 90%.

Poly(4-*tert*-butyldimethylsilyloxystyrene) was prepared by 2 methods. One was silylation of PHS, and the other was the free radical polymerization of 4-*tert*-butyldimethylsilyloxystyrene (TBDMSOSt). Silylation of PHS was carried out in 1,4-dioxane with *tert*-butylchlorodimethylsilane in the presence of imidazole. The reaction was continued at room temperature for 40 h. Precipitation into ice water gave pale brown powders in an 87% yield.

The synthesis and polymerization of TBDMSOSt was as follows. Both 2.9 g (42 mmol) of imidazole and 2.0 g (17 mmol) of 4-hydroxystyrene, which was synthesized by the previously described procedure,⁶ were dissolved in 3.0 mL of *N,N*-dimethylformamide (DMF). The solution was added dropwise under nitrogen atmosphere at room temperature to a solution of 2.7 g (18 mmol) of *tert*-butylchlorodimethylsilane dissolved in 4.0 mL of DMF. After addition of water, the reaction mixture was extracted with petroleum ether. The solvent was evaporated, and vacuum distillation in the presence of hydroquinone gave 3.1 g of colorless liquid TBDMSOSt (bp 24–25°C/6

$\times 10^{-2}$ Pa). The yield was 75%. The silylated monomer was polymerized in bulk at 60°C for 16 h with 1.0 wt % of 2,2'-azobisisobutyronitrile (AIBN) as an initiator. The reaction was once quenched by cooling to -196°C (liquid N_2) and the product was dissolved in 1,4-dioxane. Precipitation into ice water gave poly(TBDMSOSt) as a white resin in a 93% yield.

Gel permeation chromatographic analysis was performed to determine molecular weight and molecular weight dispersity with a Tosoh Model 8120 chromatograph equipped with 3 TSKgel SuperHM-M columns and a refractive index detector. A 0.1 w/v % sample solution was injected in a volume of 20 μL . The eluting solvent was reagent-grade tetrahydrofuran at a flow rate of 0.6 mL min^{-1} . The retention times were calibrated against nearly monodispersed polystyrene standards (PS-oligomer kit, Tosoh Co., Ltd., Tokyo, Japan). All molecular data were reported as polystyrene-equivalent molecular weights.

The silylated materials were examined by ^1H nuclear magnetic resonance ($^1\text{H-NMR}$), ^{13}C nuclear magnetic resonance ($^{13}\text{C-NMR}$), and Fourier transform infrared (FTIR) spectroscopy to determine the extent of silylation. NMR spectra were recorded on a JEOL EX-400 spectrometer at a resonance frequency of 400 MHz for proton and 100 MHz for carbon-13. Acetone- d_6 was used to observe the $^1\text{H-NMR}$ spectra of PHS and trimethylsilylated PHS, while chloroform- d was employed for *tert*-butyldimethylsilylated PHS and poly(TBDMSOSt). The chemical shifts were referred to the solvents and converted to the tetramethylsilane (TMS) scale (acetone- d_6 , 2.00 ppm; chloroform- d , 7.26 ppm). FTIR spectra were obtained on a JEOL JIR-5500 spectrophotometer.

Glass transition temperature (T_g) for the series of materials was determined with a Shimadzu DSC-50 differential scanning calorimeter. Samples were encapsulated in aluminum pans in the mass range of 3 to 4 mg. Each sample was heated from 40 to 250°C at a heating rate of 20°C min^{-1} under nitrogen gas flow of 50 mL min^{-1} . Thermogravimetric analysis (TGA) of polymers was carried out with a Shimadzu TGA-50 instrument at a heating rate of 10°C min^{-1} under nitrogen gas flow of 50 mL min^{-1} .

Lithographic Evaluation

Resist solutions were prepared in 4–5 w/v % concentrations. PHS was dissolved in 2-methoxy-

ethyl acetate, and silicon-containing polymers were in toluene. The solutions were filtered with 0.45- μm pore-sized filters and spin-coated onto polished silicon substrates to 0.1–0.4 μm thickness. The coated substrates were prebaked at an appropriate temperature for 20 min in a convection oven.

Electron beam exposure characteristics were examined with an Elionix ELS-3300 computer-controlled EB lithography system. An accelerating voltage was 20 kV, and a beam current was adjusted to 1.0×10^{-10} A at a beam size of 35 nm diameter. After the EB exposure, wafers were developed by dipping into the following developers for 2 min at room temperature. PHS was developed with a 1.0 wt % aqueous solution of tetramethylammonium hydroxide (TMAH) and rinsed with deionized water, while silicon-containing polymers were developed with toluene and rinsed with 2-propanol. After drying, film thickness was measured with a Kosaka Laboratory SE-30K profilometer. A tip radius was 2 μm , and a stylus force was 0.7mN.

RESULTS AND DISCUSSION

Polymer Synthesis

In order to obtain silyl ether polymers with similar molecular weights and molecular weight dispersities, commercial PHS was silylated. Both trimethylsilylation and *tert*-butyldimethylsilylation resulted in complete disappearance of O—H stretching vibrations around 3370 cm^{-1} in the infrared (IR) spectrum of PHS. Trimethylsilylated PHS exhibited strong absorptions at 1252, 918, and 845 cm^{-1} , and *tert*-butyldimethylsilylated polymer had at 1255, 916, and 839 cm^{-1} due to aromatic alkylsilyl ethers instead. In the $^1\text{H-NMR}$ spectra of silylated polymers, no phenolic protons were observed, and protons of trimethylsilyl groups at 0.19 ppm or those of *tert*-butyldimethylsilyl groups at 0.16 and 0.98 ppm appeared. The relative intensities of proton resonances revealed that phenolic hydroxyl groups of PHS were silylated quantitatively in both silylation reactions.

Radical polymerized TBDMSOSt (poly(TBDMSOSt)) closely resembled *tert*-butyldimethylsilylated PHS in the IR spectrum and exhibited absorptions at 1255, 916, and 837 cm^{-1} . Their ^1H - and ^{13}C -NMR spectra also showed marked simi-

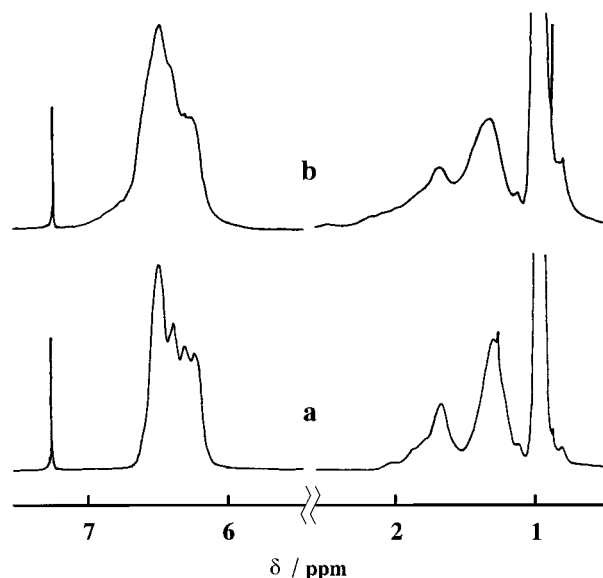


Figure 1 Aromatic, methine, and methylene proton resonances in the $^1\text{H-NMR}$ spectra of (a) poly(TBDMSOSt) and (b) *tert*-butyldimethylsilylated PHS.

larities to each other, except that the proton resonance peaks of poly(TBDMSOSt) were sharper, as shown in Figure 1. This sharpness was considered to reflect the narrower molecular weight dispersity of the polymer.

Gel permeation chromatograms of the starting polymer and silylated products are shown in Figure 2. Molecular weight and molecular weight dispersity of the starting polymer, commercial PHS, were determined as $M_w = 1.69 \times 10^4$ and $M_w/M_n = 5.41$. The profile of GPC chromatogram of trimethylsilylated PHS was similar to that of the starting polymer, and the chromatogram was shifted to the higher molecular weight, which corresponded to $M_w = 3.93 \times 10^4$ and $M_w/M_n = 4.91$. *tert*-Butyldimethylsilylated PHS possessed $M_w = 4.08 \times 10^4$ and $M_w/M_n = 3.81$. The relatively narrow dispersity was caused by the disappearance of lower molecular weight components.

Radical polymerized TBDMSOSt exhibited $M_w = 3.01 \times 10^5$ and $M_w/M_n = 1.92$, much higher molecular weight, and much narrower dispersity than *tert*-butyldimethylsilylated PHS, as shown in Figure 2.

Glass transition temperatures (T_g s) of each polymer were observed to be 160, 59, 97, and 107°C for PHS, trimethylsilylated PHS, *tert*-butyldimethylsilylated PHS, and poly(TBDMSOSt),

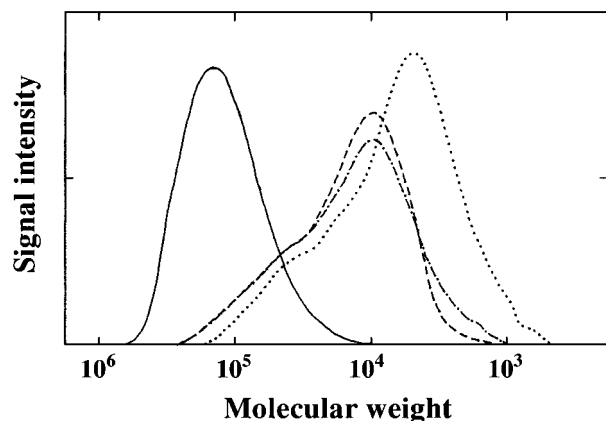


Figure 2 Gel permeation chromatograms of polymers: (-----) PHS, (-----) trimethylsilylated PHS, (-----) *tert*-butyldimethylsilylated PHS, and (——) poly(TBDMSOSt).

respectively. Figure 3 shows the results of thermogravimetric analysis for the polymers. Temperatures at 5% weight loss and weight fractions of nonvolatile residue at 450°C were observed as follows: 347°C and 14% for PHS; 366°C and 8% for trimethylsilylated PHS; 361°C and 13% for *tert*-butyldimethylsilylated PHS; and 315°C and 0% for poly(TBDMSOSt). Both trimethylsilylation and *tert*-butyldimethylsilylation retarded the initial weight loss of PHS. The weight fraction of nonvolatile residue at 600°C for PHS, 11%, was

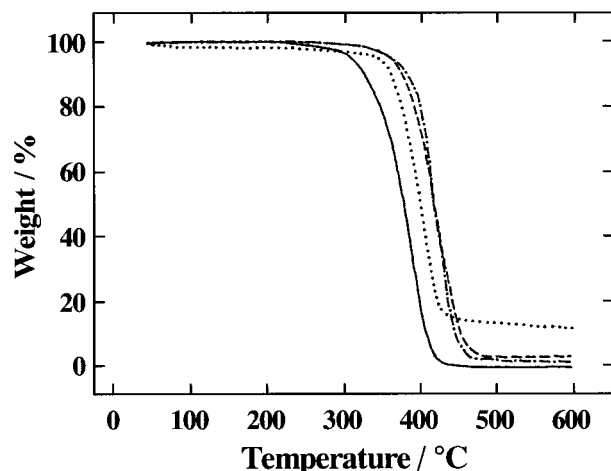


Figure 3 TGA curves for polymers in nitrogen atmosphere (heating rate = $10^\circ\text{C min}^{-1}$): (-----) PHS, (-----) trimethylsilylated PHS, (-----) *tert*-butyldimethylsilylated PHS, and (——) poly(TBDMSOSt).

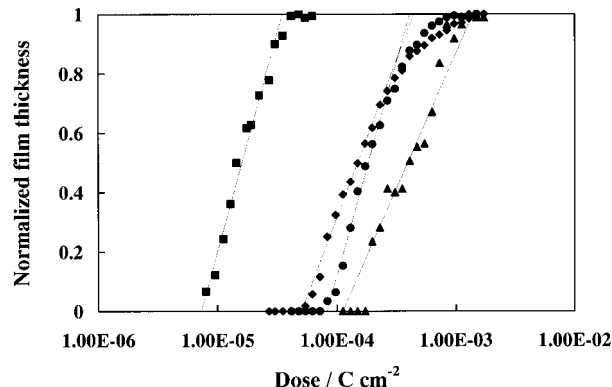


Figure 4 Sensitivity characteristic curves for polymers as EB resists: (\blacktriangle) PHS, (\blacklozenge) trimethylsilylated PHS, (\bullet) *tert*-butyldimethylsilylated PHS, and (\blacksquare) poly(TBDMSOSt).

also decreased by silylation, that is, 1% for trimethylsilylated PHS and 2% for *tert*-butyldimethylsilylated PHS. Silylation of phenolic hydrogens enhanced the heat resistance of PHS and altered the polymer more depolymerizable.

Poly(TBDMSOSt) was decomposed at much lower temperature than *tert*-butyldimethylsilylated PHS by 46 degrees. In general, chain branching reduces thermal stability of polymers. But the relative intensities of methine and/or methylene protons in the $^1\text{H-NMR}$ spectrum indicated that the extent of chain branching of poly(TBDMSOSt) was not larger on the basis of monomeric unit than that of *tert*-butyldimethylsilylated PHS. On the other hand, as shown in Figure 1, poly(TBDMSOSt) exhibited a small sharp peak at 1.3 ppm in its $^1\text{H-NMR}$ spectrum, which could be assigned to the methyl protons of isobutyronitrile end groups of the polymer. No corresponding peak was observed in the spectrum of *tert*-butyldimethylsilylated PHS. And commercial PHS is considered to be produced by thermal polymerization. The discrepancy in thermal stability between poly(TBDMSOSt) and *tert*-butyldimethylsilylated PHS might be attributed to the difference in end groups.

Lithographic Properties

Figure 4 shows characteristic curves toward EB exposure at a prebake temperature of 125°C on silicon wafer. As to PHS, a curve was obtainable only in a thin film of about $0.1\ \mu\text{m}$ thickness. When an initial film thickness was larger, resist peeled off in comparatively small doses.

Table I Characteristics of Poly(TBDMSOSt), PHS, and Silylated PHSs as EB Resists

Polymer		M_w	M_w/M_n	$T_g/^\circ\text{C}$	Prebake/ $^\circ\text{C}$	$D_g^{0.5}/\text{Ccm}^{-2}$	γ
Poly(TBDMSOSt)	On Si wafer	3.01×10^5	1.92	107	125	1.60×10^{-5}	1.47
	On polyimide				125	1.95×10^{-5}	1.65
Commercial PHS		1.69×10^4	5.41	160	125	3.93×10^{-4}	0.91
					150	5.07×10^{-4}	1.44
					175	3.49×10^{-4}	1.26
					200	4.45×10^{-5}	0.71
Trimethylsilylated PHS		3.93×10^4	4.91	59	125	1.49×10^{-4}	1.06
<i>tert</i> -Butyldimethylsilylated PHS		4.08×10^4	3.81	97	75	1.96×10^{-4}	1.46
					100	2.03×10^{-4}	1.42
					125	1.84×10^{-4}	1.44
					150	2.14×10^{-4}	1.53

With increasing exposure dose, the remaining film thickness increased. The results indicated that 3 silicon-containing polymers all acted as a negative working resist, as well as PHS, which was reported by Horibe et al.⁷ Lithographic properties were determined from the curves and summarized in Table I. Sensitivity $D_g^{0.5}$ is the dose required to effect 50% film thickness remaining after development, and contrast γ is determined from the slope of linear portion of the curve. At a prebake temperature of 125 $^\circ\text{C}$, both silylations improved the sensitivity of PHS, and trimethylsilylated PHS became more sensitive than *tert*-butyldimethylsilylated PHS. Sensitivities were improved in the order of decreasing T_g . This agreed with the result reported by Nagasaki et al.⁸ that a good correlation existed between T_g and sensitivity in silicon-containing polymers. Mobility of polymers is supposed to play an important role for the intermolecular coupling reaction.

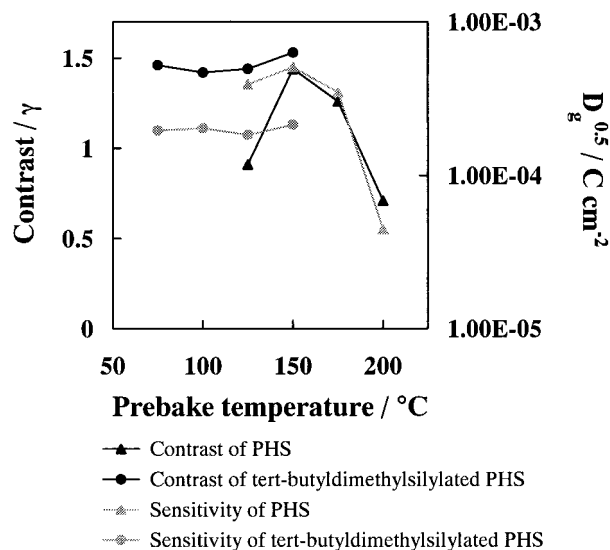
tert-Butyldimethylsilylated PHS exhibited a higher γ value than trimethylsilylated PHS. *tert*-Butyldimethylsilyl ether groups are much less labile to hydrolysis than trimethylsilyl ones.⁹ TBDMSOSt was thus adopted as a monomer for radical polymerization.

Poly(TBDMSOSt) possessed a γ value of 1.47, which was almost the same value as that of *tert*-butyldimethylsilylated PHS. Its sensitivity parameter $D_g^{0.5}$ was estimated to be $1.60 \times 10^{-5} \text{ C cm}^{-2}$. Radical polymerized TBDMSOSt was over 10 times more sensitive than *tert*-butyldimethylsilylated PHS. Such a high sensitivity is probably due to the high molecular weight of poly(TBDMSOSt), as reported in the case of PHS.⁷

The effects of prebake temperature on $D_g^{0.5}$ and γ were examined for PHS and *tert*-butyldimethylsilylated PHS. Temperature was varied around

T_g of each polymer, as shown in Figure 5. The sensitivity and contrast of PHS were altered with prebake temperature around its T_g (160 $^\circ\text{C}$). 2-Methoxyethyl acetate still slightly remained in PHS after prebaking at 125 $^\circ\text{C}$ for 20 min, while stains appeared on the surface of silicon substrate after development at a prebake temperature of 200 $^\circ\text{C}$. On the contrary, *tert*-butyldimethylsilylated PHS exhibited virtually invariant values of $D_g^{0.5}$ and γ around its T_g (97 $^\circ\text{C}$).

Poly(TBDMSOSt) is expected to show high resistance to O_2 RIE because of its high silicon content calculated to be 12.0 wt %. The polymer may be applied to bilevel lithographic processing as a top imaging resist. Polyimides are frequently

**Figure 5** Prebake temperature dependence of sensitivity and contrast.

employed as a bottom layer in the fabrication. Therefore, resist properties of poly(TBDMSOSt) were further examined on polyimide. By use of Semicofine SP-710 from Toray Industries (Tokyo, Japan), a polyimide layer of 4 μm thickness was prepared on a polished silicon substrate according to a prescription.¹⁰ As can be seen from Table I, poly(TBDMSOSt) film possessed similar sensitivity and contrast on polyimide to those on silicon wafer. Figure 6 shows isolated lines of 0.26 and 0.20 μm widths on a silicon wafer and on a polyimide layer, respectively. Zigzag line patterns were observed on a silicon wafer, which might have occurred through poor adhesion of the resist to the substrate. Poly(TBDMSOSt) resolved 0.5

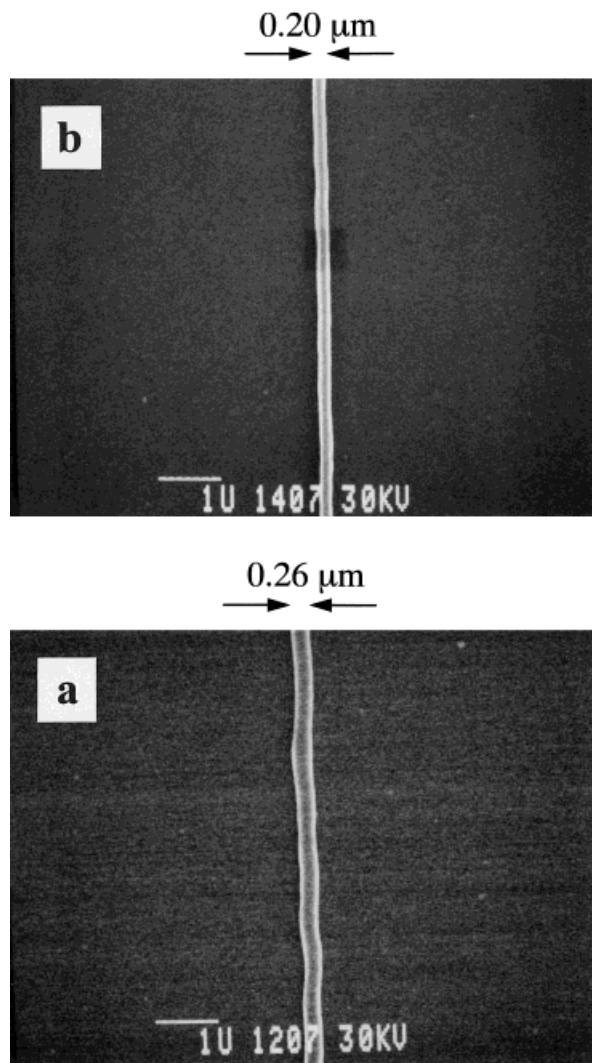


Figure 6 An isolated line of poly(TBDMSOSt) on (a) a silicon wafer, and on (b) a polyimide layer.

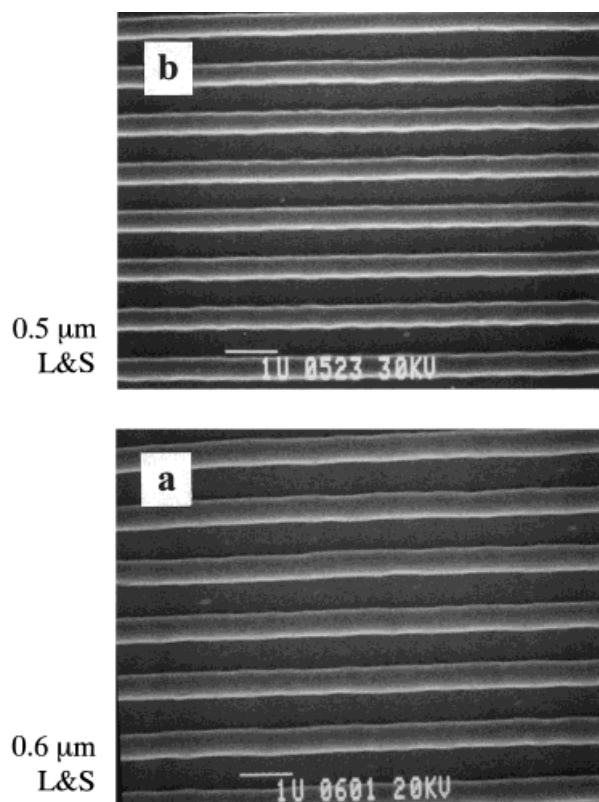


Figure 7 Line and space patterns of poly(TBDMSOSt) on (a) a silicon wafer and on (b) a polyimide layer.

and 0.6 μm line and space patterns on these substrates, as shown in Figure 7. Higher resolution was achieved on polyimide layer.

CONCLUSIONS

Both trimethylsilylated and *tert*-butyldimethylsilylated PHSs acted as a negative working resist to EB exposure. The sensitivities of these 2 silyl ether polymers were higher than that of a starting material of PHS. Radical polymerized TBDMSOSt possessed $M_w = 3.01 \times 10^5$ and $M_w/M_n = 1.92$ and exhibited a γ value of 1.47 and a sensitivity parameter $D_g^{0.5}$ of $1.60 \times 10^{-5} \text{ C cm}^{-2}$. Poly(TBDMSOSt) was over 10 times more sensitive than *tert*-butyldimethylsilylated PHS, which had $M_w = 4.08 \times 10^4$ and $M_w/M_n = 3.81$, while they possessed nearly the same γ values. Such a high sensitivity of poly(TBDMSOSt) was attributed to the high molecular weight of the polymer. The resist resolved an isolated line of 0.20 μm width and 0.5 μm line and space patterns.

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