Synthesis and Lithographic Characterization of Block Copolymer Resists Consisting of Both Poly(styrene) Blocks and Hydrosiloxane-Modified Poly(diene) Blocks

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We investigated block copolymer resists consisting of both poly(styrene) blocks and hydrosiloxane-modified poly(diene) blocks which have good properties for use as negative tone, electron beam resists. The polymers were prepared by attaching hydrosiloxanes to the diene blocks of styrene–diene block copolymers using platinum divinyltetramethyldisiloxane complex. A resolution better than 0.1 μm for an isolated line, sensitivity of 30 $\mu C/cm^2$, and contrast of 2.8 were demonstrated using a block copolymer consisting of a poly(styrene) block and a pentamethyldisiloxane-modified poly(isoprene) block (PS-*b*-PDPI). Used in a bilayer resist scheme, PS-*b*-PDPI has an oxygen RIE selectivity ratio of 42 with respect to poly(imide). Oxygen RIE selectivity ratios with respect to poly(imide) as large as 54 were measured for other hydrosiloxane-modified block copolymers we prepared. In a bilayer resist system, using PS-*b*-PDPI as the imageable layer, patterns of 0.3-μm-wide lines and 1.5-μm-wide spaces were transferred through a 1.2-μm-thick poly(imide) planarizing layer.

Introduction

Silicon-containing block copolymers can offer many features desirable for high-resolution resist materials, especially when oxygen plasma etch resistance is required. However, the preparation of such polymers with controlled architectures provides many challenges. Modification of polymers allows one to obtain new polymers having special properties.[1-6] Polymers prepared by living polymerization methods may be modified to give large new families of monodisperse, controlled architecture polymers. These modified polymers often have structures that would be, at the very least, difficult to prepare by living polymerization of monomers. Catalytic hydrosilylation is the most common chemical reaction used to form a carbon–silicon bond. Along with the synthesis of small molecules,[7-9] hydrosilylation was used by past researchers in the modification of oligomers and polymers. The most commonly hydrosilylated oligomers[10,11] and polymers[6,12-14] are based on butadiene. In 1978, Ito et al. reported the hydrosilylation of 1,2-butadiene oligomers with various trialkylsilanes as well as hydrosiloxanes.[10] In 1985, Khananashivili et al. reported the kinetics of the hydrosilylation of butadiene oligomers using H_2PtCl_6.[11] More recently, Guo et al.[6,14] demonstrated the hydrosilylation of poly(butadiene) and copolymers of butadiene with styrene and acrylonitrile using the catalyst $RhCl(PPh_3)_3$.[7] However, to our knowledge, researchers have not previously studied either the hydrosilylation of poly(isoprene), except at high pressure,[15] or the modification of true block copolymers by hydrosiloxanes. We concentrated on attaching hydrosiloxanes to the diene blocks of both styrene–butadiene and styrene–isoprene block copolymers and using the modified polymers as electron beam resists.

We designed these block copolymer resists to have the qualities needed to reach the increasingly important goal of achieving features of 100-nm resolution in production. In many cases where the surface of a device or substrate is nonplanar, single-level resists are not able to image 100-nm features. In such cases multilayer resist systems are used.[16] Multilayer resist schemes use a nonimageable polymeric material to planarize the surface of a device. The simplest type of multilayer resist scheme is a bilayer resist, which tops the planarizing layer with an imageable layer.[17] Besides imageability, the imageable polymer of a bilayer resist scheme must fulfill two critical requirements. First, after development the imageable layer must

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be able to act as a mask to enable the pattern to be transferred through the underlying planarizing layer. This requires the imageable layer to have resistance to the etch used to remove the planarizing layer. Second, the imageable polymer should have a high enough glass transition temperature (T_g) to prevent blurring of submicron images during processing.[18]

The most common approach for accomplishing pattern transfer in a bilayer resist involves using a silicon-containing polymer for the imageable layer, an organic polymer for the planarizing layer, and an oxygen RIE (reactive ion etch) to etch through the planarizing layer.[19] When exposed to the oxygen plasma, the surface of the silicon-containing polymer can be transformed to silica.[20] After this transformation, the silicon-containing polymer is not chemically etched by the oxygen plasma but is sputtered due to high-ion-energy bombardment. The removal rate due to sputtering of the silicon-containing polymer is substantially lower than the removal rate of the organic planarizing layer.[21] If the etch rate of the planarizing polymer is at least 20 times greater than that of the imageable polymer, reproducible pattern transfer can be performed.[22]

Many groups have studied parameters that effect the microlithographic performance of silicon-containing resists. In general, the oxygen RIE resistance of a polymer increases with increasing content of silicon.[21] However, the incorporation of silicon into polymeric resists, especially in the form of siloxanes, generally decreases their T_g, which can lead to dimensional stability problems of imaged features.[23] Gokan et al. reported that low-T_g polymers offered higher oxygen RIE resistance than high-T_g polymers with the same concentration of silicon.[24] Thus, there are significant tradeoffs between oxygen RIE resistance and dimensional stability of the patterns during processing. In designing the imageable layer for a bilayer resist, a compromise is usually made. Thus, a random copolymer of a silicon-containing monomer and a "high-T_g" monomer is used. The properties of the resulting random copolymer resist, including T_g and oxygen RIE resistance, will be in-between the properties the silicon-containing homopolymer and "high-T_g" homopolymer.

By properly taking advantage of microphase separation and surface segregation, block copolymers can be designed to have properties which satisfy the requirements of both oxygen RIE resistance and dimensional stability. Block copolymers can offer these unique properties due to their composite-like behavior.[25] Hartney et al. first reported using silicon-containing block copolymers as microlithographic resists in 1985.[26] Both Jurek et al.[27] and DeSimone et al.[28] proposed that segregation of a silicon-containing block to the air-resist surface can increase the oxygen RIE resistance of a resist. Despite the studies mentioned above, block copolymers deserve further study as possible resist materials. We believe that block copolymers, applied as resist materials, can lead to a new generation of resists much in the same way as they resulted in a new generation of high impact strength resins.[29]

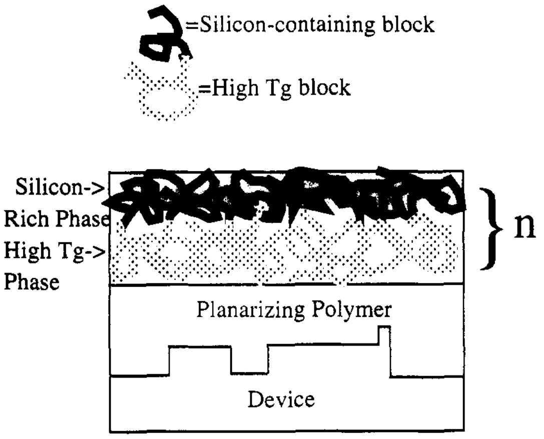

Figure 1. Schematic of a planarized device on which a block copolymer used as an imaging layer has undergone microphase separation. One lamella is shown, but there can be any number, *n*, of repeating lamellae.

The block copolymers we are studying for the imageable layer of a bilayer resist, consist of a high-T_g block and a low-T_g hydrosiloxane-modified diene block. The schematic of Figure 1 shows one possible configuration for a microphase separated symmetric block copolymer resist (one that forms lamellae). The high silicon concentration and the low T_g of the hydrosiloxane-modified diene phase of the resist potentially allow the block copolymer to provide better oxygen RIE resistance compared to the resistance provided by a random copolymer of the same chemical composition. The high-T_g phase serves as an anchor for the low-T_g phase, allowing patterns made in the resist to be dimensionally stable, during lithographic processing.

Surface energies should result in a hydrosiloxane-modified diene rich phase at the air-resist surface. With films of asymmetric block copolymers, the surface should still be enriched with silicon even though the bulk microstructure of the polymer might not be lamellar. This effect is due to spreading of the hydrosiloxane-modified diene block at the air-resist surface to form the silicon-enriched, low-energy surface. In addition to being useful electron beam resists, the poly(styrene) hydrosiloxane-modified poly(diene) block copolymers show promise for use as low-energy surfaces. For example, they are a potential replacement for the tributyltin based paints currently used to prevent fouling of ship hulls.[30]

Experimental Section

Modification of Block Copolymers. *Materials.* A mixture of poly(styrene-*b*-butadiene) and poly(styrene-*b*-butadiene-*b*-

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styrene) (SB 12.5-64) was obtained from The Shell Development Co. The styrene block had been prepared to have a theoretical number average molecular weight (M_n) of 12 500 g/mol. The butadiene blocks had been prepared to have a theoretical M_n of 64 000 and 128 000 g/mol for the diblock and triblock copolymers respectively. From GPC the diblock copolymer had a M_n of 110 000 and a polydispersity (P) of 1.07, while the triblock had a M_n of 350 000 and a P of 1.13. The isomeric composition of the butadiene block, determined by NMR, was 40% 1,2-butadiene and 60% 1,4-butadiene. Poly(isoprene) homopolymer, which had been prepared to have a theoretical M_n of 25 000 g/mol, was obtained from the Eastman Kodak Co. From GPC the polymer had a M_n of 38 500 g/mol and a P of 1.07. The isomeric composition of the isoprene units, determined by NMR, was 29% 1,2-isoprene, 68% 3,4-isoprene and 3% 1,4-isoprene. Poly(styrene-*b*-isoprene) was also obtained from the Eastman Kodak Co. The block copolymer had been prepared to have a theoretical M_n of 13 000 g/mol for each block. From GPC the diblock copolymer had a M_n of 25 800 g/mol and a P of 1.46. The isomeric composition of the isoprene block, determined by NMR, was 34% 1,2-isoprene and 66% 3,4-isoprene. All hydrosiloxanes were obtained from Hüls America Inc. and distilled prior to use. A 2% solution of platinum divinyltetramethyldisiloxane complex[31,32] in xylenes (Pt–DTD) was also obtained from Hüls America Inc. and used as received.

Characterization. M_n and P were found by GPC (THF) using a Waters Associates 510 pump, poly(styrene) standards, and both a 254-nm UV and a 410 refractive index detector. Samples for FT-IR were prepared by casting polymer films from chloroform or toluene solutions onto sodium chloride plates. NMR spectra, from $CDCl_3$ solutions, were obtained using a Varian XL-200 NMR spectrometer. T_g were measured with either a TA Instruments differential thermal analysis (DTA) unit or a Perkin-Elmer differential scanning calorimeter (DSC). Elemental analysis was performed by Galbraith Laboratories.

Addition of Pentamethyldisiloxane (PMDS) to SB 12.5-64. SB 12.5-64, 1.02 g (6.20 mmol of vinyl group) was dissolved, under nitrogen, in 50 mL of anhydrous toluene in a 100-mL three-neck round-bottom flask equipped with a septum and condenser. The solution was heated to 80–85 °C. After 1 h, 13.7 μL (4.6×10^{-4} mmol of Pt) of Pt–DTD was added. After an additional 30 min, 1.16 mL (5.90 mmol) of PMDS was added. The reaction was determined to be completed in 18 h, using gas chromatography. During the 18-h reaction period small black precipitates formed in the colorless solution. The solution was cooled, filtered, and concentrated to about 25 mL, followed by precipitation into 250 mL of anhydrous ethanol. The polymer (PS-*b*-PDPB) was redissolved in toluene, reprecipitated in ethanol, and then dried in vacuo for 24 h (1.65 g, 86.5%). The dried PS-*b*-PDPB was colorless and translucent. Analysis of PS-*b*-PDPB is shown in Tables 1–4.

Addition of 1,1,1,3,3,5,5-Heptamethyltrisiloxane (HMTS) to SB 12.5-64. SB 12.5-64 (0.50 g, 3.10 mmol vinyl group) was dissolved, under nitrogen, in 30 mL of anhydrous toluene in a 50-mL three-neck round-bottom flask equipped with a septum, a condenser, and a dropping funnel. The dropping funnel contained 0.85 mL (3.1 mmol) of HMTS and 10 mL of toluene. The solution, in the round-bottom flask, was heated to 90–95 °C. After 1 h, 6.0 μL (2.0×10^{-4} mmol of Pt) of Pt–DTD was added. After 30 min, the HMTS solution was added at a rate of 2 mL/min. The reaction was determined to be completed in 24 h, using FT-IR. The yellow tinged solution was then cooled and precipitated into 250 mL of anhydrous ethanol. The polymer (PS-*b*-HTPB) was redissolved in toluene, reprecipitated in ethanol, and dried in vacuo for 24 h (1.1 g, 91.6%). The dried PS-*b*-HTPB was colorless and translucent. Analysis of PS-*b*-HTPB is shown in Tables 1–4.

Addition of Bis(trimethylsiloxy)methylsilane (BTS) to SB 12.5-64. SB 12.5-64 (0.50 g, 3.10 mmol vinyl group) was dissolved, under nitrogen, in 70 mL of anhydrous toluene in a 150-mL three-neck round-bottom flask equipped with a septum, condenser, and dropping funnel. The dropping funnel contained 1.34 mL (5.0 mmol) of BTS and 15 mL of toluene. The solution, in the round-bottom flask, was heated to 85–90 °C followed by the addition of 15 μL (5.1×10^{-4} mmol of Pt) Pt-DTD. After 30 min, the BTS solution was added at a rate of 2 mL/min. The reaction was determined to be completed in 48 h, using FT-IR. The yellow tinged solution was then cooled and precipitated into 350 mL of anhydrous ethanol. The polymer (PS-*b*-BTPB) was redissolved in toluene, reprecipitated in ethanol, and dried in vacuo for 24 h (1.05 g, 88%). The dried PS-*b*-BTPB was colorless and translucent. Analysis of PS-*b*-BTPB is shown in Tables 1–4.

Table 1. Conversion of Double Bonds

polymer	$-C{=}CH_2$/SiH (molar ratio)	% conversion 1,2-units	% conversion 3,4-units	total conv 1,2- and 3,4 units (%)
PS-*b*-PDPB	1:0.95	87		87
PS-*b*-HTPB	1:1	92		92
PS-*b*-BTPB	1:1.5	91		91
PS-*b*-BTPB	1:1	75		75
PS-*b*-PDPI	1:0.67	72	28	43
HTPI	1:0.77	69	12	29

Table 2. Comparison of Elemental Composition Calculated from Both Elemental Analysis (E.A.) and NMR

	Si wt %		C wt %		H wt %	
polymer	NMR	E.A.	NMR	E.A.	NMR	E.A.
PS-*b*-PDPB	16.78	15.05	67.77	67.67	10.66	10.71
PS-*b*-HTPB	20.71	21.00	60.93	60.80	10.48	10.10
PS-*b*-BTPB[a]	20.61[b]	16.62	61.06[b]	63.56	10.48[b]	10.29
PS-*b*-BTPB[c]	19.20[b]	16.88	64.64[b]	64.35	10.68[b]	9.39
PS-*b*-PDPI[d]	10.57	9.07	76.62	77.81	9.78	9.07

[a] 91% conversion of 1,2-butadiene. [b] Calculated assuming BTS is the attaching hydrosiloxane. [c] 75% conversion of 1,2-butadiene. [d] This sample had a total conversion of 1,2- and 3,4-units of 35.7%.

Table 3. M_n and Polydispersity of Polymers (GPC)

polymer	M_n (diblock)	P (diblock)	M_n (triblock)	P (triblock)
SB 12.5-64	110 000	1.07	350 000	1.13
PS-*b*-PDPB	135 000	1.07	543 000	1.34
PS-*b*-HTPB	132 000	1.19	553 000	1.27
PS-*b*-BTPB[a]	123 000	1.08	497 000	1.64
PS-*b*-PI	25 800	1.46		
PS-*b*-PDPI	29 500	1.47		
PI[b]	38 500	1.07		
HTPI[b]	53 200	1.16		

[a] 91% conversion of 1,2-butadiene. [b] PI and HTPI are not block copolymers, but their M_n and P are reported in this table for completeness.

Addition of HMTS to Poly(isoprene). Poly(isoprene), (0.88 g, 13.0 mmol of vinyl and methyl vinyl group), was dissolved, under nitrogen, in 45 mL of anhydrous toluene in a 100-mL three-neck round-bottom flask equipped with a septum and condenser. The solution was heated to 80–85 °C. After 1 h, 10 μL (3.4×10^{-4} mmol of Pt) of Pt-DTD was added. After an additional 20 min, 2.74 mL (10 mmol) of HMTS was added. After 24 h the light yellow solution was cooled, filtered, and concentrated to about 15 mL and then precipitated into 200 mL of anhydrous methanol. The polymer (HTPI) was redissolved in toluene, reprecipitated in methanol, and then dried in vacuo for 24 h (1.50 g, 91%). The dried HTPI was colorless and translucent. Analysis of HTPI is shown in Tables 1–4.

Addition of PMDS of Poly(styrene-b-isoprene). Poly(styrene-*b*-isoprene) (2.0 g, 14.8 mmol of vinyl group and methyl vinyl group), was dissolved, under nitrogen, in 90 mL of anhydrous toluene in a 150-mL three-neck round-bottom flask equipped with a septum and condenser. The solution was heated to 80–85 °C. After 20 min, 20 μL (6.8×10^{-4} mmol Pt) of Pt-DTD was added. After an additional 30 min, 1.97 mL (10.0 mmol) of PMDS was added. After 24 h the light yellow solution was cooled, filtered, and precipitated into 350 mL of anhydrous ethanol. The polymer (PS-*b*-PDPI) was redissolved in toluene, reprecipitated in ethanol, and then dried in vacuo for 24 h (2.52 g, 85%). The dried PS-

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Table 4. Glass Transition Temperature of Polymers

polymer	T_g (°C) of diene/siloxane phase	T_g (°C) of styrene phase
SB 12.5-64	−65	106
PS-*b*-PDPB	−63	106
PS-*b*-HTPB	−74	
PS-*b*-BTPB[a]	−69	
PS-*b*-PI	8	106
PS-*b*-PDPI	−22	106
PI	−12	
HTPI	−23	

[a] 75% conversion of 1,2-butadiene.

Figure 2. Electron-beam exposure pattern. The pattern was either a series of single-scan, 0.1- and 0.2-μm linewidths with 1.8-, 1.7-, and 1.6-μm spaces or a series of single-scan, 0.3- and 0.5-μm linewidths with 1.8-, 1.5-, and 1.3-μm spaces.

b-PDPI was white and opaque. Analysis of PS-*b*-PDPI is shown in Tables 1–4.

Lithographic Processing. All resist processing was done in a class 100 clean room at The National Nanofabrication Facility (NNF) at Cornell. Film thicknesses were measured on a Tencor Instruments Alpha Step 200 profilometer. RIE was done in an Applied Materials parallel plate reactive ion etcher. A pressure of 30 mTorr, a power setting of 0.25 W/cm^2, and a self-bias of 510 V were used throughout this research for all RIE. A 5-min "cleaning" etch was used before any wafers were processed. An oxygen flow rate of 30 sccm was used for the "cleaning" etch.

Solutions (4 wt %) of both PS-*b*-HTPB and PS-*b*-PDPI in toluene were passed through 0.1-μm-pore-size Teflon filters. Films of the polymers were made by statically dispensing approximately 3 mL of resist solution onto either 3-in. silicon wafers or 3-in. silicon wafers coated with poly(imide), followed by spinning at 3000 rpm for 30 s. Resulting PS-*b*-HTPB and PS-*b*-PDPI films were 0.10 and 0.17 μm thick, respectively. When a poly(imide) planarizing layer was to be used, an adhesion promoter was first applied to a virgin silicon wafer. The adhesion promoter consisted of 1 part Ciba-Geigy QZ3289 concentrate and 9 parts Ciba-Geigy QZ diluent. Approximately 3 mL of adhesion promoter was statically dispensed onto a wafer followed by spinning the wafer at 5000 rpm for 20 s. Ciba-Geigy XU284 poly(imide) was then statically dispensed onto the wafer followed by spinning at either 2700 rpm for 30 s when a 2.4-μm film was required or 6500 rpm for 30 s when a 1.2 μm film was required. The poly(imide) film was then baked in air at 85 °C for 30 min, 150 °C for 15 min, and finally 240 °C for 15 min.

Electron beam exposures were made on a JEOL JBX-5DII electron beam lithography system using an accelerating voltage of 50 kV, a current of 1 nA, an e-beam diameter of 50 nm, and a dot-to-dot pixel spacing of 50 nm. Incident doses ranged between 20 and 160 μC/cm^2. The test pattern, shown in Figure 2, was exposed at each dose. The pattern had either a series of single-scan, 0.1- and 0.2-μm linewidths with 1.8-, 1.7-, and 1.6-μm spaces or single-scan, 0.3- and 0.5-μm linewidths with 1.8-, 1.5-, and 1.3-μm spaces.

Results and Discussion

Styrene–diene block copolymers have been shown to be effective negative-tone electron beam resists.[33] To prepare new electron beam resists with the added feature of high oxygen RIE resistance, we used catalytic hydrosilylation to modify styrene–diene block copolymers.[34–37] We chose to use the well-known reaction of catalytic hydrosilylation and the very common styrene–diene block copolymers so that the resulting resists would be industrially relevant and useful. Such a strategy proved to be very effective as described below.

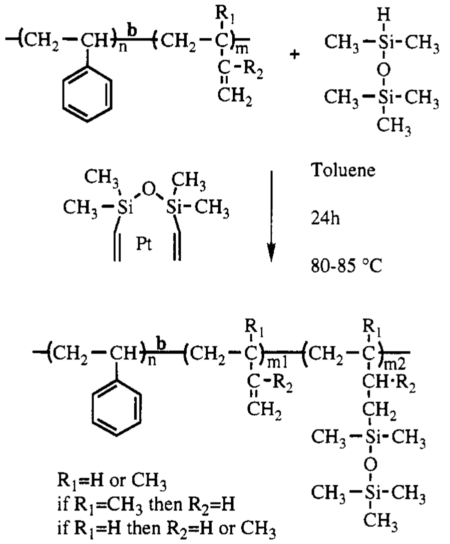

Figure 3. Hydrosilylation of a styrene–diene block copolymer with PMDS.

Hydrosilylation of Diene-Based Polymers. Using Pt–DTD as a catalyst, the hydrosiloxanes were efficiently attached to the side-chain double bonds of the diene polymers as shown in Figure 3. In Figure 3 and other figures where the chemical structures of the modified polymers are shown, the attachment of the hydrosiloxanes is arbitrarily drawn in the anti-Markovnikov configuration. This is only an assumption, and ^{13}C NMR analysis was not used for verification. To our knowledge, we are the first to demonstrate the hydrosilylation of poly(isoprene) at atmospheric pressure, although high-pressure hydrosilylation of isoprene oligomers was reported previously.[15] When attaching hydrosiloxanes to poly(butadiene), we have been able to use a ratio of Pt–DTD to 1,2-units of at least 1 order of magnitude less than the ratio of RhCl(PPh$_3$)$_3$ to 1,2-units that Guo et al. used.[6] The efficiency of hydrosilylation was not affected by antioxidants such as BHT.

The degree of hydrosilylation of 1,2- and 1,4-butadiene units as well as 1,2-, 3,4-, and 1,4-isoprene units was calculated from ^{1}H NMR spectra. The peaks associated with the protons of the siloxane moieties did not have quantitative integration because of their long relaxation times (T_1 = 2.34 s). Therefore, peaks associated with the double bonds were used in determining the conversions of the 1,2-, 1,4-, and 3,4-units of the diene blocks. The peaks associated with the phenyl groups of the styrene block were used as an internal reference when calculating these conversions. Analysis of the spectra shows that hydrosilylation of poly(dienes) is structurally selective, with the side-chain double bonds being attacked and the

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main-chain double bonds being unreactive. This result is in accordance with other studies, which used Rh or other Pt catalysts for the hydrosilylation of poly(butadiene).[6,11,14] The conversions, calculated from the NMR spectra, of the 1,2-butadiene units as well as 1,2- and 3,4-isoprene units are shown in Table 1.

Guo et al. reported that using $RhCl(PPh_3)_3$, the hydrosilylation of styrene–diene random copolymers proceeded with difficulty compared to the hydrosilylation of poly(butadiene) homopolymer.[14] However, we found that the conversion of the 1,2-butadiene units of SB 12.5-64 was high in the presence of Pt–DTD. Typically when using the hydrosiloxanes PMDS or HMTS in a 1:1 molar ratio to the 1,2-butadiene units of SB 12.5-64, the conversion was greater than 90%. However, when we used a 1:1 molar ratio of BTS to vinyl group, only 75% of the 1,2-butadiene units were converted. Longer reaction periods did not increase the conversion. Conversion of 91% of the vinyl groups was achieved when a 1.5:1 molar ratio of BTS to vinyl group was used.

The lower than usual conversion of the 1,2-butadiene units when using BTS, in a 1:1 molar ratio to the vinyl groups, can be explained by a rearrangement first reported by Stober et al.[38] They observed that BTS exchanged methyl and trimethylsiloxy groups when added to 2-hexene and the catalyst hexachloroplatinic acid. This resulted in a mixture of PMDS and tris(trimethylsiloxy)silane as well as unreacted BTS. They found that the tris(trimethylsiloxy)silane could not be attached to 2-hexene, presumably because of steric hindrance. We believe that a similar rearrangement occurs with BTS, SB 12.5-64 and Pt–DTD. Thus, when a BTS to vinyl group molar ratio of one is used, the effective ratio of hydrosiloxane to vinyl group is less than one because some of the BTS is converted to the nonreactive tristrimethylsiloxysilane.

The elemental analysis results for the hydrosiloxane-modified polymers are shown in Table 2. Overall, the elemental analysis results agree reasonably well with the elemental calculations from the NMR spectra. However, the substantially lower content of silicon measured by elemental analysis for the BTS modified polymers, is further evidence that the rearrangement of a portion of the BTS to reactive PMDS (two-thirds the amount of silicon compared to BTS) and nonreactive tristrimethylsiloxysilane occurs during hydrosilylation.

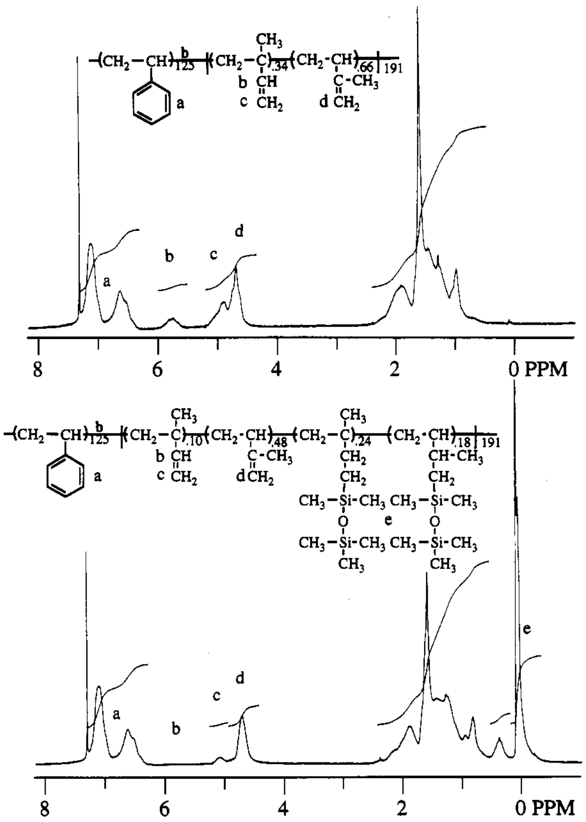

Figure 4. ^{1}H NMR of poly(styrene-*b*-isoprene) (A) and PS-*b*-PDPI (B).

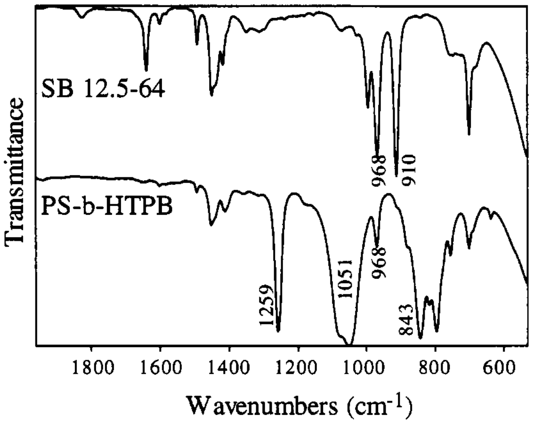

Figure 5. FT-IR spectra of SB 12.5-64 (A) and PS-*b*-HTPB (B).

Conversion of the 1,2- and 3,4-isoprene units was not complete. The NMR spectra of both poly(styrene-*b*-isoprene) and PS-*b*-PDPI are shown in Figure 4. Analysis of the NMR spectra leads to the structures shown and reveals that only 64% of the hydrosiloxane was incorporated into the polymer. Higher conversions were not observed even with fresh additions of catalyst and/or PMDS and longer reaction times. The decreased conversion of the 1,2-isoprene units compared to 1,2-butadiene units was probably due to steric effects. We expect that the conversion of 1,2-isoprene units can be as high as those achieved with 1,2-butadiene units if a poly(isoprene) with a ratio of main-chain to side-chain double bonds more similar to that of SB 12.5-64 is used. The main-chain double bonds are not reactive, so they do not have bulky siloxane groups attached. The space associated with the main-chain double bonds can therefore be used by the hydrosiloxanes to efficiently attack neighboring side-chain double bonds which are susceptible to hydrosilylation. Conversion of the 1,2-isoprene units was typically at least 2.5 times larger than conversion of the 3,4-isoprene units. The decreased reactivity of the of 3,4-isoprene units is attributed to steric hindrance. This result is consistent with similar small molecule cases.[8]

The FT-IR spectra of SB 12.5-64 and PS-*b*-HTPB are shown in Figure 5. The FT-IR spectrum of the PS-*b*-HTPB has the same general features as the spectra of PS-*b*-PDPB and PS-*b*-BTPB. The completion of the hydrosilylation reaction is shown by the substantial decrease in intensity of the characteristic absorbance of the vinyl $—CH{=}CH_2$ bond (910 cm^{-1}, out-of-plane bending of terminal vinyl group) relative to that of the main chain $—CH{=}CH—$ bond (968 cm^{-1}). In the modified polymer, peaks due to the siloxane are as follows: 1259 cm^{-1}, $Si–CH_3$ stretching vibration; 1051 cm^{-1}, very broad peak, Si–O stretching vibration; 843 cm^{-1}, $Si–CH_3$ bending. The

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(38) Stober, M. R.; Musolf, M. C.; Speier, J. L. *J. Org. Chem.* **1965**, *30*, 1651.

hydrosilylation of poly(isoprene)-based polymers can also be monitored with FTIR using the 1,2-isoprene peak at 910 cm^{-1} and the 3,4-isoprene peak at 887 cm^{-1}.

The polydispersities and number average molecular weights of the various polymers are reported in Table 3. The polydispersities of the poly(styrene-*b*-hydrosiloxane modified butadiene-*b*-styrene) were larger than that of the starting triblock. With some samples higher molecular weight peaks were evident. In these cases, the higher molecular weight peaks were included in the calculation of the molecular weight and polydispersity of the triblock. Branching of the modified SB 12.5-64 is suspected. By using dilute solution (2% or less) and thus decreasing the chance that one polymer chain will branch with another, the increase in polydispersity was minimized. However, even at 2% polymer concentration, hydrosilylation of SB 12.5-64 with BTS using Pt–DTD resulted in the formation of a gel during the hydrosilylation. With BTS, unless concentrations of less than 0.5% were used, additional higher molecular weight peaks appeared in the GPC traces of the resulting polymer along with broadening of the diblock and triblock peaks. The poly(styrene-*b*-isoprene) was modified with PMDS without increasing its polydispersity.

Both the HMTS-modified poly(isoprene) and the PMDS modified poly(styrene-*b*-isoprene) have remained soluble and have not changed color for more than 18 months. In contrast, all of the hydrosiloxane modified SB 12.5-64 samples formed gels after 1 month, even when stored at 0 °C. Also, the butadiene-based polymers were translucent and colorless after drying but gradually turned yellow, while remaining translucent, during storage at 0 °C for 1 year. The stability was not increased by the use of antioxidants. However, if the hydrosiloxane-modified SB 12.5-64 block copolymers were stored as a toluene solution, they showed no signs of cross-linking even after 2 years of storage. We suspect that the platinum catalyst is not completely removed during the precipitation of the polymer and that it is involved in the yellowing of the polymer. Coordination of the Pt to unreacted double bonds may prevent complete removal of the Pt during precipitation. The differences in stability currently observed between isoprene and butadiene based materials are limited to two specific polymers. Therefore, generalizations should not be made. The diene block of SB 12.5-64 is much longer and has a large number of main-chain double bonds compared to the isoprene based materials. These two factors probably play important roles in the stability differences that are currently observed between the isoprene- and butadiene-based polymers. This should be studied in the future, along with determining how the number of precipitations affects the stability of the hydrosiloxane-modified butadiene-based polymers.

Microphase separation of the block copolymers is expected to result in a two phase material exhibiting two T_g values. The T_g values for PS-*b*-PDPB, PS-*b*-HTPB, PS-*b*-BTPB, HTPI, and PS-*b*-PDPI are reported in Table 4. For the block copolymers PS-*b*-HTPB and PS-*b*-BTPB only one T_g was observed. This does not mean that microphase separation did not occur in these two cases, but rather than the DSC was not sensitive enough to measure the T_g of the minority, poly(styrene) phase. After attachment of the hydrosiloxanes, the −65 °C T_g of the poly(butadiene) phase of SB 12.5-64 changed less than 10 °C.

Oxygen RIE Resistance. To determine the feasibility of using PS-*b*-PDPI as the imageable layer of a bilayer resist scheme, its oxygen RIE resistance was compared to that of poly(imide), which is a good planarizing polymer. Both samples were simultaneously etched using an oxygen flow rate of 30 sccm. During a 10-min etch, poly(imide) etched at an average rate of 0.22 μm/min, and PS-*b*-PDPI etched at an average rate of 0.0053 μm/min, yielding an etch rate selectivity of 42:1. Using the same etching conditions, the etch rate selectivity between poly(imide) and PS-*b*-HTPB was 54:1. These etch selectivity ratios far surpass the ratio of 20:1 usually accepted as necessary for reproducible image transfer.[22] These high values may be attributed to the high content of silicon in the hydrosiloxane-modified diene-rich phase, as discussed in the Introduction. If composed entirely of hydrosiloxane-modified diene blocks, the phase will have a silicon concentration of 18.4 wt % for PS-*b*-PDPI and 22.7 wt % for PS-*b*-HTPB. This value compares with the overall silicon concentration of 12.1 wt % for PS-*b*-PDPI and 20.7 wt % for PS-*b*-HTPB.

Sensitivity and Contrast. PS-*b*-PDPI, was spun on top of a poly(imide)-coated wafer and then exposed at different doses. Development was done using a 1-min agitated dip in a mixture of toluene and acetone (99:1) followed by rinsing with isopropanol. A sensitivity of 30 $\mu C/cm^2$ and a contrast of 2.8 were calculated. For those applications where a sensitivity of 10 $\mu C/cm^2$ or lower is desirable, chloromethylating both the phenyl groups of the poly(styrene) block and unreacted double bonds of the poly(diene) block is a potential method for tuning the sensitivity of these block copolymers. Saeki et al. previously demonstrated that the sensitivity of a poly(styrene) based resist can vary from 0.26 to 10 $\mu C/cm^2$ depending on the degree of chloromethylation.[39] However, chloromethylation will complicate the preparation of the resist.

Electron-Beam Exposure in Single-Level Resist Scheme. PS-*b*-HTPB was found to be unsuitable as a resist material in the block ratio studied. When spun into a thin film, the stability problem of bulk PS-*b*-HTPB was magnified. No solvent was found that could remove PS-*b*-HTPB after it was coated on a wafer and allowed to sit at room temperature for 2 h. Thus, it was not possible to obtain acceptable, patterned images in either single-level or bilayer resist schemes using PS-*b*-HTPB.

In contrast to PS-*b*-HTPB, PS-*b*-PDPI was found to have many desirable properties. A 0.17-μm-thick PS-*b*-PDPI film was coated onto a 3-in. silicon wafer. Without annealing, the resist was exposed using the single-scan, 0.1- and 0.2 μm linewidth with 1.8-, 1.7-, and 1.6-μm space exposure pattern. The unexposed PS-*b*-PDPI was removed by a 1-min agitated dip in toluene, followed by an isopropyl alcohol rinse. The single-scan, 0.1- and 0.2-μm exposed lines were clearly apparent after development (Figure 6). The actual dimensions of the 0.2- and 0.1-μm exposed lines are 0.3 and 0.2 μm, respectively. The single-scan lines are on average 0.07 μm wide but have an uneven linewidth, as shown in the Figure 6B. We assume the increase and oscillation in linewidth is at least partially due to swelling, which is common in negative tone resists.[40]

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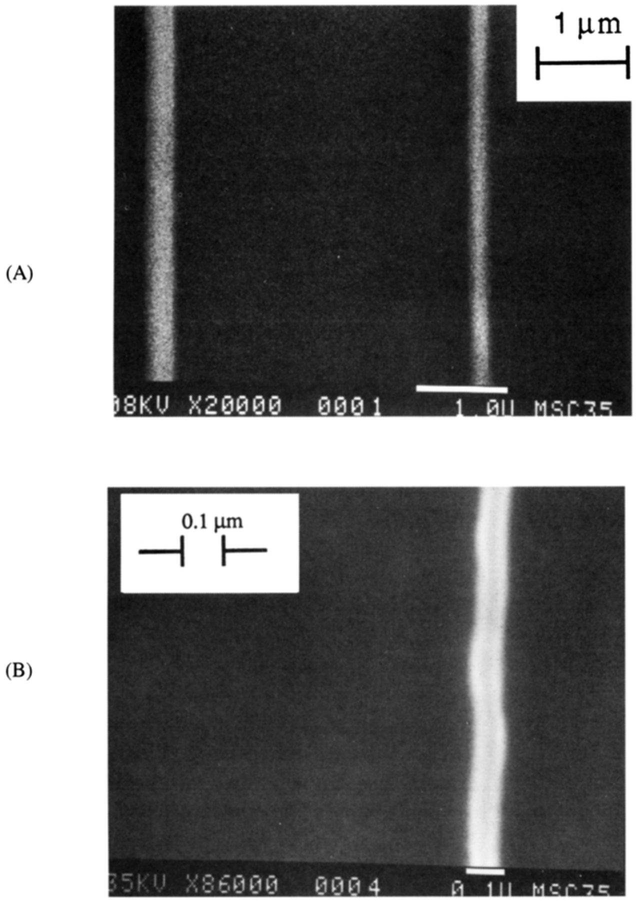

Figure 6. SEM-micrographs of 0.2- and 0.1-μm lines (A) and single-scan lines (B) imaged in PS-*b*-PDPI.

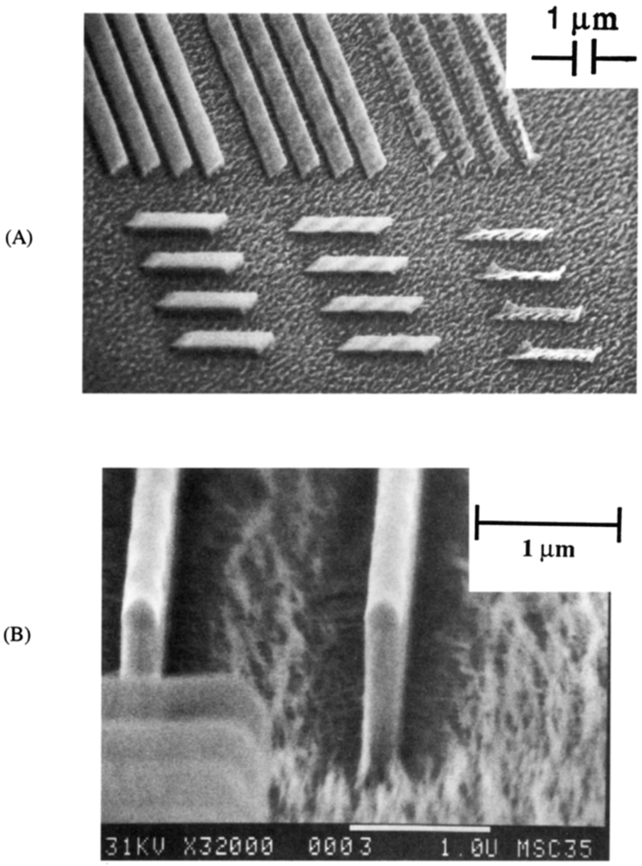

Figure 7. (A) SEM-micrograph of 0.5 and 0.3 μm and single-scan line pattern with grass after oxygen RIE. (B) SEM micrograph of 0.3 μm lines with substantially less grass in the region approximately 0.5-μm directly adjacent to the line.

Electron-Beam Exposure in Bilevel Resist Scheme. A 1.2-μm-thick poly(imide) film was coated onto a 3-in. silicon wafer. A 0.17-μm-thick PS-*b*-PDPI film was then coated on top of the poly(imide) film. The resist was exposed, using the single-scan, 0.3- and 0.5-μm linewidth with 1.8-, 1.5-, and 1.3-μm space exposure pattern. The unexposed PS-*b*-PDPI resist was then removed by a 1-min development, using either a mixture of toluene and acetone (99:1) or pure toluene, followed by an isopropyl alcohol rinse. Samples were etched, by oxygen RIE, using an oxygen flow rate of 30 sccm for 5.5 min. The samples had well-defined 0.5- and 0.3-μm-wide resist lines, while the single-scan lines were substantially degraded (Figure 7). The spaces, however, could not be completely cleared using oxygen RIE. A substantial amount of residue or "grass"[41–43] remained on the wafer, as shown in Figure 7A. Substantially less grass was observed in the region approximately 0.5 μm directly adjacent to the lines as shown in Figure 7B. When the wafer was subjected to additional oxygen RIE, the lines were degraded before the residue was removed.

Although grass will most likely not be a problem in etchers used in commercial production, especially as etchers with new designs are made commercially available,[44] we developed an alternative etching scheme to eliminate the residue in our etcher. Mele et al. reported grass formation when using poly(imide) in a trilayer resist scheme.[41] They reasoned that using only oxygen, RIE produced nonvolatile silica, which deposited nonuniformly in the spaces between the lines. By adding CHF_3 (6.25%) to the oxygen during RIE, Mele et al. eliminated the deposition of silica and obtained spaces free of grass, presumably because volatile halogenated silicon compounds were formed.

We modified the approach taken by Mele et al. and first etched through the majority of the poly(imide) and then removed the grass. A 5.5-min oxygen etch with a 30 sccm oxygen flow rate was used to partially etch the poly(imide). This step was followed by a 1-min CHF_3/oxygen etch using a flow rate of 30 sccm CHF_3 and 1 sccm oxygen. This approach resulted in the elimination of the grass (Figure 8). However, the single-scan lines were almost entirely removed. The 0.5- and 0.3-μm line had straight side walls and had aspect ratios as high as 4.5.

PS-*b*-PDPI has properties which make it attractive as a negative-tone electron beam resist, but its processing has not been refined enough to enable all of its attributes to be taken advantage of at the same time. For example, 0.3-μm lines transferred through the poly(imide) with pure oxygen RIE were smooth, as displayed in Figure 7B. However, the 0.3-μm-wide lines transferred through the poly(imide) with an oxygen RIE followed by a CHF_3/oxygen RIE were rough (Figure 8B). Thus, smooth lines were obtained although not consistently. Another example is the difference between the linewidth exposed and that observed using SEM. The lines imaged and transferred through the poly(imide) (Figure 7 and 8) do not differ

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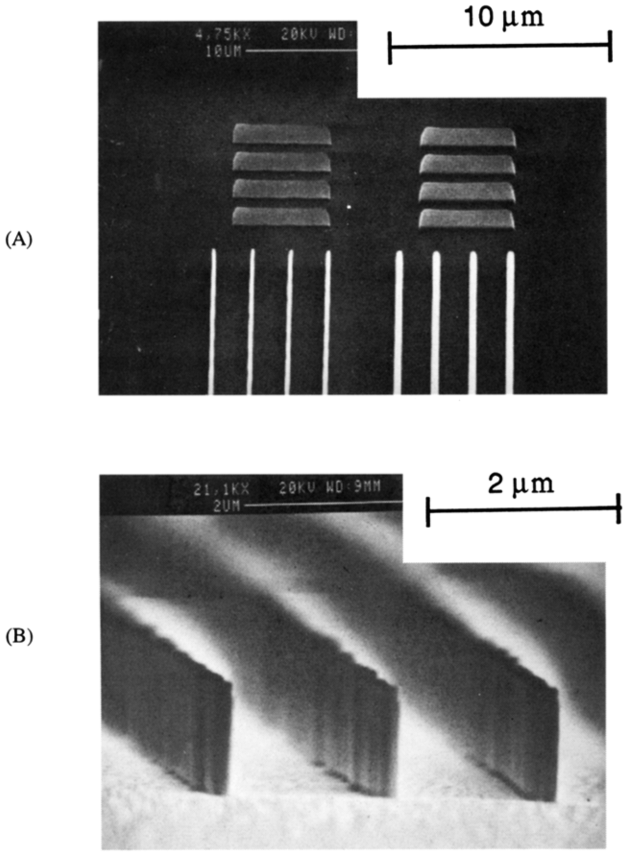

Figure 8. (A) SEM micrograph of 0.5- and 0.3-μm line pattern without grass after CHF_3/oxygen RIE. (B) SEM micrograph of 0.3-μm lines transferred thorough 1.2 μm of poly(imide).

significantly from the exposed linewidth. Thus, the increase in linewidth observed when PS-*b*-PDPI was imaged in the single level resist scheme is not an inherent property of the resist. We believe the variations between the imaged patterns result mainly from the lack of reproducibility associated with a manual process. Through automation of the development and optimization of the process, consistently straight and smooth lines of the desired width should be attainable using PS-*b*-PDPI.

Conclusions

We showed that resists based on readily available styrene–diene block copolymers exhibit properties that are in many ways better than the currently used, oxygen RIE resistant, negative-tone resists. Attachment of hydrosiloxanes to the diene block was successful using the catalyst platinum divinyltetramethyldisiloxane complex. The isoprene-based materials, including PS-*b*-PDPI, have good stability. However, the stability of the butadiene based materials is presently poor, preventing their use as resists. PS-*b*-PDPI has many properties, including exceptionally high oxygen RIE resistance and better than 0.1-μm resolution for an isolated line which make it an attractive electron beam resist. At this point, the processing of PS-*b*-PDPI needs to be optimized. Currently we are designing and preparing new block copolymers that will have other desirable properties, including deep UV imageability.

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