Gas-Phase Modification of Polymer Coatings: The Use of Gas-Phase Silylation for Image-Tone Reversal of Chemically Amplified Photoresists Based on Electrophilic Addition Reactions

S. Ming Lee, Stephen Matuszczak, and Jean M. J. Fréchet*

Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853-1301

Chester Lee and Yosef Shacham-Diamand

School of Electrical Engineering, Phillips Hall, Cornell University, Ithaca, New York 14853

Received April 5, 1994. Revised Manuscript Received June 6, 1994[⊗]

Image-tone reversal has been demonstrated with two chemically amplified resists through gas-phase silylation and dry development with oxygen plasma etching. Selective silylation of the radiation-exposed or unexposed portions of the resists has been achieved by two different approaches: (a) controlling the availability of the reactive groups; (b) varying the permeability of the resist material to the silylating reagent. Those areas of the resist films that are silylated resist oxygen plasma etching. This provides access to high-resolution images with the high sensitivity of the chemically amplified resists. Techniques useful to monitor the silylation process and factors affecting the silylation and etching processes are discussed.

Introduction

Fifteen years ago, Fréchet et al. pioneered the design of chemically amplified resist materials, based on the thermolysis of poly(*p*-[((*tert*-butyloxy)carbonyl)oxy]styrene)[1,2] and on the depolymerization of poly(phthalaldehyde).[3,4] Since then, chemically amplified resists that use photogenerated acid have attracted much attention because of their extremely high sensitivities and versatility to the radiation sources. A large selection of new resists systems based on acid-catalyzed chemistry have emerged in the past decade.[5–11]

Recently, this laboratory has designed a variety of chemically amplified resists based on the generation of reactive carbocationic intermediates.[12–14] These resists have demonstrated extremely high sensitivities to deep-UV, E-beam as well as X-ray radiation while allowing aqueous base development. Two representative designs of resists based on the same concept of acid catalyzed electrophilic reaction, but that provide complementary image tones, resists A and B, are shown in Schemes 1 and 2 respectively.

Positive resist A exploits the isomerization of an *O*-alkylated benzyl phenyl ether to the corresponding *C*-alkylated phenol as the imaging process (Scheme 1).[13] Therefore, polymer **1** is mixed with triphenylsulfonium hexafluoroantimonate as a two-component resist. Upon exposure to radiation, a strong acid is generated in the polymer matrix. During postbaking, the protonated benzyl ether **2** rearranges to the *C*-alkylated phenol **3**. The process of *C*-alkylation of the aromatic ring proceeds with the release of a proton providing for chemical amplification. Since a phenol is produced in the exposed areas of the film, a positive tone image may be obtained by aqueous base development. High sensitivities of the order of 2 mJ/cm^2 have been obtained using this approach with exposure at 254 nm.

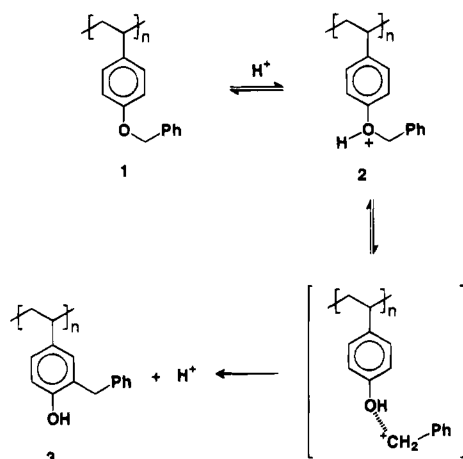
The three-component negative resist B contains triphenylsulfonium triflate as the photoacid generator, poly(4-hydroxystyrene) and a polyfunctional cross-linker **4**.[13] The benzylic hydroxyl groups of **4** act as latent electrophiles. The onium salt decomposes photochemically to release triflic acid that protonates the hydroxyls of **4**. Upon heating, the protonated hydroxyls eliminate water and the resulting benzylic carbocationic intermediates such as **5** are consumed in an electrophilic aromatic

⊗ Abstract published in *Advance ACS Abstracts,* July 15, 1994.

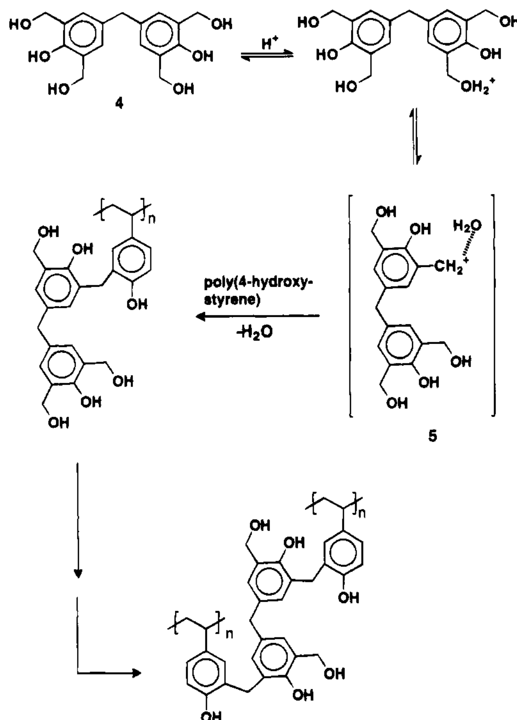
(1) Fréchet, J. M. J.; Ito, H.; Willson, C. G. *Proc. Microcircuit. Eng.* **1982**, 260. MacDonald, S. A.; Willson, C. G.; Fréchet, J. M. J. *Acc. Chem. Res.* **1994**, *27*, 151.
(2) Fréchet, J. M. J.; Eichler, E.; Willson, C. G.; Ito, H. *Polymer* **1983**, *24*, 995.
(3) Willson, C. G.; Ito, H.; Fréchet, J. M. J. *Proc. Microcircuit. Eng.* **1982**, 261.
(4) Ito, H.; Willson, C. G. *Polym. Eng. Sci.* **1983**, *23*, 1012.
(5) (a) Willson, C. G.; Ito, H.; Fréchet, J. M. J.; Tessier, T. G.; Houlihan, F. M. *J. Electrochem. Soc.* **1986**, *133*, 181. (b) Fréchet, J. M. J.; Bouchard, F.; Eichler, E.; Houlihan, F. M.; Iizawa, T.; Kryczka, B.; Willson, C. G. *Polym. J.* **1987**, *19*, 31.
(6) (a) Schwalm, R. *Polym. Mater. Sci. Eng.* **1989**, *61*, 278. (b) O'Brien, M. J.; Crivello, J. V. *Proc. SPIE* **1988**, *920*, 42. (c) O'Brien, M. J. *Polym. Eng. Sci.* **1989**, *29*, 846.
(7) Feely, W. E.; Imhof, I. C.; Stein, C. M.; Fisher, T. A.; Legenza, M. W. *Polym. Eng. Sci.* **1986**, *16*, 1101.
(8) Reichmanis, E.; Houlihan, F. M.; Nalamasu, O.; Neenan, T. X. *Chem. Mater.* **1991**, *3*, 394.
(9) (a) Tarascon, R. G.; Reichmanis, E.; Houlihan, F. M.; Shugard, A.; Thompson, L. F. *Polym. Eng. Sci.* **1989**, *29*, 850. (b) Nalamasu, O.; Cheng, M.; Kometani, J. M.; Vaidya, S.; Reichmanis, E.; Thompson, L. F. *Proc. SPIE* **1990**, *1262*, 32. (c) Houlihan, F. M.; Chin, E.; Nalamasu, O.; Kometani, J. M. *Polym. Mater. Sci. Eng.* **1992**, *66*, 38.
(10) (a) Schlegel, L.; Ueno, T.; Shiraishi, H.; Hayashi, N.; Iwayanagi, T. *Chem. Mater.* **1990**, *2*, 299. (b) Hattori, T.; Schlegel, L.; Imai, A.; Hayashi, N.; Ueno, T. *Proc. SPIE* **1993**, *1925*, 146.
(11) (a) Uchino, S.; Iwayanagi, T.; Ueno, T.; Hayashi, N. *Proc. SPIE* **1991**, *1466*, 429. (b) Uchino, S. I.; Katoh, M.; Sakamizu, T.; Hashimoto, M. *Microelectron. Eng.* **1992**, *17*, 261.
(12) Fréchet, J. M. J.; Matuszczak, S.; Reck, B.; Stöver, H. D. H.; Willson, C. G. *Macromolecules* **1991**, *24*, 1746.
(13) Fréchet, J. M. J.; Matuszczak, S.; Lee, S. M.; Fahey, J. T.; Willson, C. G. *Polym. Eng. Sci.* **1992**, *32*, 1471.
(14) Fahey, J. T. Ph.D. Thesis, Cornell University, 1991.

0897-4756/94/2806-1796$04.50/0 © 1994 American Chemical Society

Scheme 1



Scheme 2



substitution process involving the phenolic moieties of the polymer (Scheme 2). Negative-tone images are obtained by developing in aqueous base because the cross-linked (exposed) material has reduced solubility. This highly sensitive deep-UV resist has a sensitivity of about 0.2 mJ/cm^2.

An alternate approach to aqueous base development involves the dry development of a latent resist image by reactive ion etching (RIE).[15,16] To achieve this goal, an etch rate differential in oxygen plasma between the radiation-exposed and unexposed areas of the resist film is required. This can be achieved by incorporating an oxygen etch resistant element into selected parts of the resist.[17-27] Typically, following the imaging process, the patterned resist is selectively silylated with a silylating agent in either the liquid[18,19] or the vapor phase.[20-27] In the subsequent oxygen plasma etching, a thin coating of refractory silicon dioxide is formed at the surface of the silylated resist, protecting the underlaying material from oxidation. The unsilylated areas are etched away in the form of water vapor and carbon dioxide, ultimately leading to the dry-developed image. In general, dry development provides images with excellent line profile and high aspect ratio that are difficult to obtain with wet development.

Top surface imaging (TSI) makes use of silylation and dry development to eliminate image distortion caused by irregular substrate topography in single-level resists. In addition, through creative chemistry and design, schemes exploiting silylation and dry development of resists have been developed to produce negative-tone images in positive photoresists and vice versa.[17-27] Such image-tone reversal processes, in which the tone of the dry-developed image is reversed relative to the image obtained by wet development, greatly increase the versatility of the resists. This paper reports the development of image reversal processes for resists A and B.

Experimental Section

Materials. Poly(4-hydroxystyrene) was obtained from IBM Corp. GPC analysis: $M_w = 31\,000$; $M_n = 12\,100$. The onium salts, triphenylsulfonium hexafluoroantimonate, and triphenylsulfonium triflate, were provided by IBM Corp. Cross-linker **4** is prepared by hydroxymethylation of phenol with formaldehyde in the presence of sodium hydroxide.[28] (*N,N*-Dimethylamino)trimethylsilane (DMATMS), the silylating reagent, was purchased from Aldrich Chemical Co., Inc., and was used without further purification.

Preparation of 4-(Benzyloxy)styrene. Methyltriphenylphosphonium bromide (24.9 g, 0.070 mol) was placed in a 250-mL three-neck round-bottom flask equipped with a condenser, nitrogen gas inlet, dropping funnel, thermometer and a magnetic stirrer. THF (80 mL) dried by distilling from LAH was added to the flask. Potassium *tert*-butoxide (7.8 g, 0.069 mol) was then added, and a canary yellow suspension was formed. The mixture was stirred for 1 h at room temperature. 4-(Benzyloxy)benzaldehyde (12.1 g, 0.057 mol) dissolved in anhydrous THF (60 mL) was added dropwise to the flask with the reaction mixture temperature maintained below 25 °C. On

(15) Mucha, J. A.; Hess, D. W. In *Introduction to Microlithography: Theory, Materials and Processing*; Thompson, L. F., Willson, C. G., Bowden, M. J., Eds.; ACS Symposium Series 291; American Chemical Society: Washington, DC, 1983; pp 215–286.
(16) Coburn, J. W. *Plasma Etching and Reactive Ion Etching*; American Vacuum Society, Monograph Series; American Institute of Physics, Inc.: New York, 1982.
(17) Taylor, G. N.; Stillwagon, L. E.; Venkatesan, T. *J. Electrochem. Soc.* **1984**, *131*, 1658.
(18) Hartney, M. A.; Kunz, R. R.; Eriksen, L. M.; LaTulipe, D. C. *Proc. SPIE* **1993**, *1925*, 270.
(19) Yang, B.-J. L.; Yang, J.-M.; Chiong, K. N. *J. Vac. Sci. Technol.* **1989**, *B-7*, 1729.
(20) Thackeray, J. W.; Bohland, J. F.; Pavelechek, E. K.; Orsula, G. W.; McCullough, A. W.; Jones, S. K.; Bobbio, S. M. *Proc. SPIE* **1989**, *1185*, 2.
(21) Spence, C. A.; MacDonald, S. A.; Schlosser, H. *Proc. SPIE* **1990**, *1262*, 344.
(22) Coopmans, F.; Roland, B. *Proc. SPIE* **1986**, *631*, 34.
(23) MacDonald, S. A.; Schlosser, H.; Ito, H.; Clecak, N. J.; Willson, C. G. *Chem. Mater.* **1991**, *3*, 435.
(24) Fréchet, J. M. J.; Fahey, J. T.; Lee, S. M.; Matuszczak, S.; Shacham-Diamand, Y.; MacDonald, S. A.; Willson, C. G. *J. Photopolym. Sci. Technol.* **1992**, *5*, 17.
(25) MacDonald, S. A.; Schlosser, H.; Clecak, N. J.; Willson, C. G.; Fréchet, J. M. J. *Chem. Mater.* **1992**, *4*, 1364.
(26) Willson, C. G.; Cameron, J. F.; MacDonald, S. A.; Niesert, C.-P.; Fréchet, J. M. J.; Leung, M. K.; Ackman, A. *Proc. SPIE* **1993**, *1925*, 354.
(27) MacDonald, S. A.; Larson, C. E.; Schlosser, H.; Brock, P. J.; Clecak, N. J.; Fréchet, J. M. J. *Proc. SPIE* **1993**, *1925*, 279.
(28) Mitsui Petrochemical Industries, Ltd. Jpn. Kokai Tokkyo Koho 80 64,537, 1980; *Chem. Abstr.* **1977**, *93*, 204258v.

completing the addition, the reaction mixture was left stirring at room temperature for 24 h. Removal of the solvent by evaporation under reduced pressure left a brown solid which was dissolved in dichloromethane (250 mL). The solution was washed with water (4 × 80 mL) and then with brine (80 mL). The solution was dried ($MgSO_4$) and evaporated to dryness to afford a light yellow solid. The crude product was dissolved in pentane and the insoluble triphenylphosphonium oxide removed by filtration. Further purification by flash column chromatography (ethyl acetate–hexane, 1:4) afforded the pure product as a white crystalline solid (82%): mp 69.0–71.0 °C (hexane) (lit.[29] 69.0–70.0 °C); ^{1}H NMR ($CDCl_3$) δ 5.07 (s, CH_2, 2H); 5.11 (dd, CH, 1H); 5.15 (dd, CH, 1H); 6.66 (dd, CH, 1H); 6.93 (dq, ArH, 2H); 7.32–7.45 (m, ArH, 7H); ^{13}C NMR ($CDCl_3$) δ 70.0, 111.7, 114.9, 127.38, 127.43, 128.0, 128.6, 130.7, 136.2, 136.9, 158.5; IR (KBr) 3092, 3067, 3038, 2928, 2901, 2859, 1627, 1611, 1574, 1245, 1025 cm^{-1}.

Polymerization of 4-(Benzyloxy)styrene. A mixture of 4-(benzyloxy)styrene (10 g, 0.048 mol), AIBN (0.091 g, 0.557 mmol) in toluene (20 mL) was stirred under nitrogen for 1 h. The solution was then heated at 75 °C for 21 h. After dilution with toluene (40 mL), the solution was precipitated into hexane and the product collected by filtration. A second precipitation from toluene into hexane followed by drying under vacuum afforded the pure product as a white powder (74%): T_g 68 °C; ^{1}H NMR ($CDCl_3$) δ 1.30 (s, CH_2, 2H); 1.80 (s, CH, 1H); 4.90 (s, CH_2, 2H); 6.30–6.80 (br m, ArH, 4H); 7.27 (s, ArH, 5H); ^{13}C NMR ($CDCl_3$) δ 39.5, 44.1, 69.9, 114.2, 127.4, 127.8, 128.4, 137.2, 138.6, 156.7; IR (KBr): 3089, 3062, 3032, 2922, 2863, 2737, 1609, 1583, 1242, 1026 cm^{-1}; GPC (universal calibration) M_w = 74 000; M_n = 46 000.

Instruments. Infrared spectra were obtained on a Nicolet FTIR/44 spectrometer. ^{1}H NMR spectra were recorded on a Bruker WM-300 300 MHz spectrometer with the solvent proton signal as standard. ^{13}C NMR spectra were recorded on a Bruker WM-300 spectrometer at 75 MHz with the solvent carbon signal as standard. Differential scanning calorimetry was done on a Mettler DSC 30 instrument. Size-exclusion chromatography was carried out on a Nicolet 9560 liquid chromatograph using THF at 30 °C as the mobile phase at a flow rate of 1.0 mL/min (3 PL Gel columns: 500 Å, 1000 Å, and mixed bed). Molecular weight of poly(4-(benzyloxy)-styrene) was measured using universal calibration (in line viscosity detector from Viscotek, and refractive index detector) based on polystyrene standards. Resist film thickness was measured on a Tencor Alpha-Step 200 surface profiler. Deep-UV exposures were performed by contact printing either using a Canon HTG Systems III Contact Aligner or an Optical Associates Inc. exposure system comprising of a low-pressure mercury lamp with a shutter system, an intensity controller, and an exposure timer. Photon flux was measured using an Optical Associates Inc. 354 exposure monitor. The output of the mercury lamp was filtered through a 254-nm narrow bandwidth interference filter from Oriel Corp. Varying dosages of light for deep-UV sensitivity measurement were obtained with a Series 1 Multidensity resolution target, Ditric Optics Inc. Sensitivities reported are accurate to ±0.05 mJ/cm^2. E-beam exposures of the resist films were conducted with a Cambridge Instruments Electron Beam Microfabricator 10.5/CS. Scanning electron micrographs are recorded on a Cambridge Instruments Stereoscan 200 microscope.

The silylation reactions were carried out in a custom-made gas-phase functionalization chamber. Reactive ion etching was conducted with a Materials Research Corp. Model 720 magnetron ion etcher. Rutherford backscattering measurements were performed on a 1.7 MW Tandetron accelerators with a 2.7 MeV He^+ beam and a detector angle of 170°.

Resist Formulation and Processing. *Resist A.* Poly(4-benzyloxy)styrene) (0.7 g) and triphenylsulfonium hexafluoroantimonate (0.037 g) are dissolved in cyclohexanone (2.9 g) and filtered through a 0.45 μm filter. Spin-coating onto silicon wafers at 4400 rpm for 30 s followed by heating at 110 °C for 2 min gives 1.0 ± 0.05 μm films. All samples, unless otherwise stated, are postbaked at 110 °C for 2 min.

(29) Majumdar, D.; Ratner, B. D. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *26*, 1991.

Table 1. Experimental Conditions for Image Reversal of Resists A and B

		resist A	resist B
deep-UV exposure	dosage, mJ/cm^2	6.0	5.0
silylation	reaction temp, °C	70	110
	DMATMS gas pressure, Torr	200	100
	reaction time, min	20	2
reactive ion etch	O_2 flow rate, sccm/min	30	30
	pressure, mTorr	30	5
	power, W/cm^2	0.25	0.25
	bias voltage, V	600	50
	duration (30 s intervals between)	10 × 20 s	5 × 30 s

Resist B. Poly(4-hydroxystyrene) (0.51 g, 74 wt %), the cross-linker (0.1 g, 15 wt %) and triphenylsulfonium triflate (0.07 g, 10 wt %) are dissolved in diglyme (2.3 g) and filtered through a 0.45 μm filter. Spin-coating onto silicon wafers at 3700 rpm for 30 s followed by heating at 110 °C for 2 min gives 1.0 ± 0.05 μm films. All samples, unless otherwise stated, are postbaked at 120 °C for 3 min.

Gas-Phase Silylation. (*N,N*-Dimethylamino)trimethylsilane (DMATMS) was used as the silylating reagent. In a typical process, the exposed wafer is secured onto the heated base of the silylation chamber by vacuum suction. After evacuation, the system is allowed to reach thermal equilibrium before the silylation reagent is introduced at the appropriate pressure. Once the silylation reaction is complete, the chamber is evacuated and purged three times with nitrogen. The treated wafer is then removed for examination or dry-development in an oxygen plasma etcher.

The specific conditions used to obtain the scanning electron micrograph samples are listed in Table 1.

Results and Discussion

Resists A and B can readily be adapted to the process of image reversal through silylation. The literature contains many precedents for the silylation of phenolic resins such as poly(4-hydroxystyrene) using a gaseous silylating reagent such as HMDS or (*N,N*-dimethylamino)trimethylsilane (DMATMS) to afford poly(4-((trimethylsilyl)oxy)styrene) (Scheme 3).[20–27]

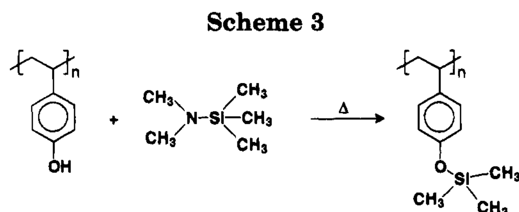
(A) Image Reversal of Resist A. Silylation in resist A depends on the availability of phenolic hydroxyl groups. These functional groups are only present in the radiation-exposed parts of the resist, where the acid catalyzed rearrangement reaction has occurred.[23] Since the unexposed areas have no phenolic hydroxyl groups available for silylation, they will be etched away by oxygen RIE to afford the negative tone image.

Deep-UV Exposure. An organosilicon polymer containing 10–15% silicon by weight is etched at one-fifteenth the rate of a hydrocarbon analog in an oxygen plasma.[23,30,31] For resist A, the radiation induced rearrangement reaction proceeds to 85% conversion (as measured by NMR spectrometry) and is followed by quantitative silylation of the liberated phenolic hydroxyl groups to afford a calculated silicon content of 8.8 wt %. This is expected to provide a certain degree of etching selectivity between the radiation-exposed and unexposed areas.[31] In this work, an exposure dose of 6 mJ/cm^2 was used because quantitative ^{1}H NMR studies

(30) Watanabe, F.; Ohnishi, Y. *J. Vac. Sci. Technol.* **1986**, *B4(1)*, 422.

(31) MacDonald, S. A.; Ito, H.; Willson, C. G. *Microelectron. Eng.* **1983**, *1*, 269.

Scheme 3



showed that when combined with an appropriate postexposure bake process, it leads to about 85% conversion of the *O*-alkylated into the *C*-alkylated phenol.

Gas-Phase Silylation. In a gas-phase silylation reaction, the three main factors affecting the conversion are (a) the reaction temperature, (b) the amount of silylating reagent, which is related to the pressure of the silylating gas in the reaction chamber, and (c) the duration of the reaction. In general, an increase in any one of these three variables will increase the extent of silylation, though the correlation is not linear.[14] Control of the reaction temperature is particularly critical as it directly affects the image resolution. While poly[(4-benzyloxy)-styrene] has a low T_g of 68 °C, the rearranged product, poly[(3-benzyl-4-hydroxy)styrene], is expected to have a T_g above 150 °C. However, upon silylation, the glass transition temperature of the polymer is again reduced to ca. 70 °C. Therefore, a low reaction temperature has to be maintained throughout the process to avoid softening and flowing of the printed image. DMATMS is the preferred silylating reagent for the resists described in this work because of its higher volatility and reactivity when compared to HMDS. In addition, because a decrease in the reaction temperature lowers the pressure at which a substance condenses from the vapor phase to the liquid phase, the higher volatility of DMATMS allows the use of a higher pressure, thereby shortening the reaction time. For resist A, all silylations were performed at 70 °C and 200 Torr of DMATMS.

To determine the optimum reaction time, the amount of silicon uptake was monitored by three different means: (a) film thickness measurements; (b) FT-IR; (c) Rutherford backscattering (RBS). The photoresist solution was spin-coated onto a silicon wafer polished on both sides that was then cleaved into small pieces. Each resist-coated piece was silylated for a different period of time and then analyzed by each of the 3 methods.

The increase in silicon content in resist A is accompanied by a significant increase in film thickness (Figure 1). Surprisingly, this swelling appears to affect only the vertical dimension since the image suffers no loss in lateral resolution.

Figure 2, parts a and b, shows the IR spectra of resist A before and after irradiation. The conversion into poly-[(3-benzyl-4-hydroxy)styrene] is indicated by the appearance of the phenolic hydroxyl peak and the concurrent decrease in the ether C−O−C stretching band at 1240 cm^{-1}. Upon silylation (Figure 2c), the hydroxyl peak disappears and the characteristic trimethylsilyloxy absorption bands appear at 1250 cm^{-1} ($\delta_S CH_3$ in the trimethylsilyl group), 920 cm^{-1} (ν_{Si-O}), and 849 cm^{-1} (ν_{C-Si}). The amount of silicon uptake is proportional to the areas under these absorption peaks. Figure 3 shows the changes in the peak areas of the O−H and Si−O stretching bands. On the basis of this quantitative IR study, a silylation reaction time of 20 min was chosen for the imaging experiments. This is estimated to bring about approximately 95% functionalization of the phe-

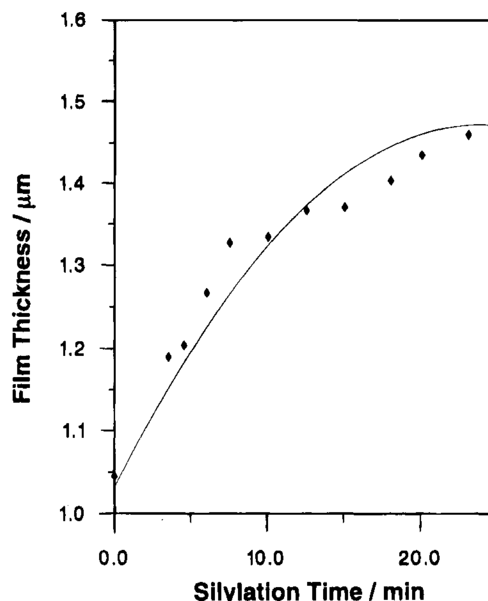


Figure 1. Film thickness of radiation-exposed samples of resist A as a function of the duration of the silylation reaction.

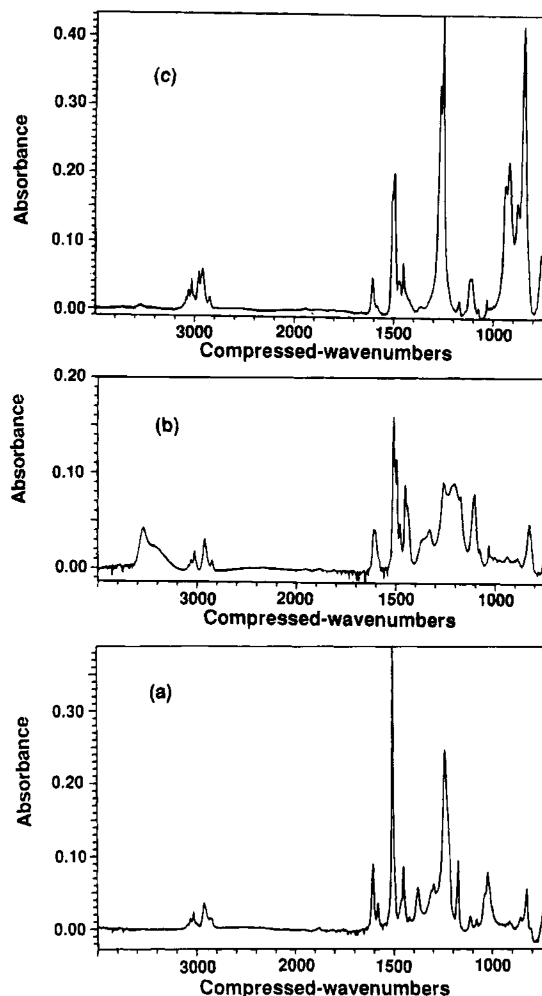


Figure 2. Infrared spectra of resist A samples: (a) radiation unexposed; (b) exposed to 6.0 mJ/cm² radiation at 254 nm; (c) exposed to 6.0 mJ/cm² radiation at 254 nm followed by reaction with 200 Torr of DMATMS for 20 min at 70 °C.

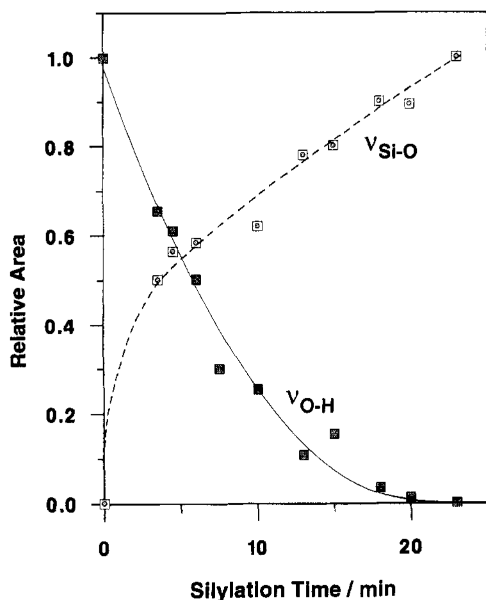


Figure 3. Changes in IR peak areas for radiation-exposed resist A samples silylated under 100 Torr of DMATMS at 110 °C.

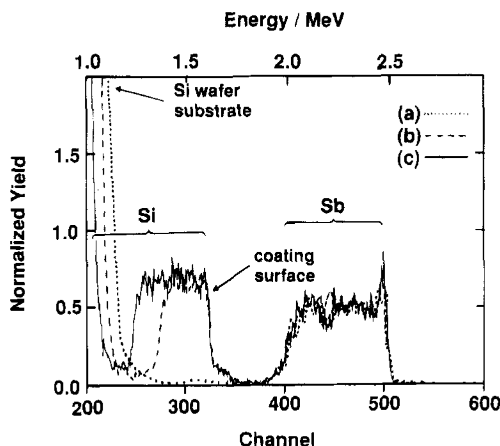


Figure 4. Rutherford backscattering spectra of radiation-exposed samples of resist A: (a) unsilylated; (b) 4.5 min silylated; (c) 7.5 min silylated.

nolic hydroxyl groups present in the resist film. Because the content of silicon in poly[3-benzyl-4-((trimethylsilyl)oxy)styrene] is less than 10 wt %, it is anticipated that the silylated material might still be etched away at a significant rate. MacDonald[31] and Reichmanis[32] have shown that a high degree of silylation is required to form a thick silicon-containing layer that withstands the etching process without appreciable erosion.

While quantitative FT-IR provides an overall estimation of the functionalization of the phenolic hydroxyl groups, Rutherford backscattering (RBS) reveals the distribution of silicon within the sample. Figure 4 shows the RBS spectra of the radiation-exposed but unsilylated material and of two samples with different extents of silylation. The incorporated silicon is not distributed uniformly within the entire depth of the resist. Instead, a localized silicon-containing zone grows from the top of the resist film downward toward the substrate. This indicates that the rate of silylation is

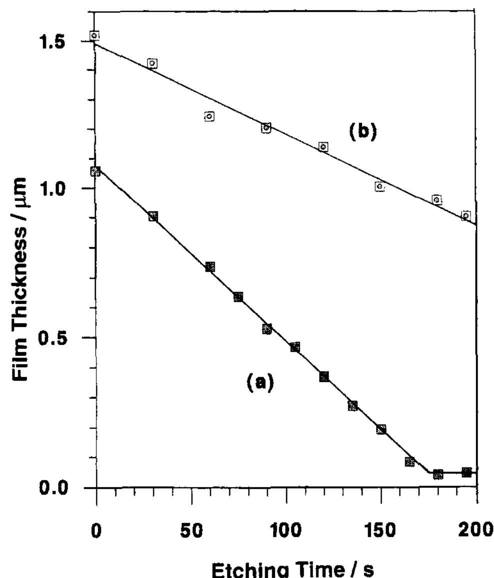


Figure 5. Comparison of oxygen reactive ion etching rates of radiation-exposed samples of resist A: (a) unsilylated; (b) 20 min silylated.

limited by the diffusion rate of the silylating agent into the polymer matrix. Because the thickness of the resist film increases during silylation, the signal from the helium ions scattered by the substrate shifts in position as the reaction proceeds.

Reactive Ion Etching with Oxygen Plasma. Figure 5 shows a comparison between the oxygen plasma etching rates of an unsilylated sample (curve a) and a sample silylated for 20 min (curve b) etched under identical conditions. The unsilylated and silylated resist materials have etching rates of 6.0 and 3.8 nm/s, respectively. Because of its insufficient silicon content (8.8 wt %) the silylated material does not have enough resistance to oxygen ion etching. This is due to the formation of relatively porous silicon dioxide protective layer that is not dense enough to shield the bulk of the polymer from the bombarding ions.[30-32]

The etching process is accompanied by some heat evolution that may cause melting and flowing of the silylated resist material if adequate heat transfer between the sample and the substrate is not achieved. Therefore, the etching was done using short pulses of 20 s duration, followed by 20 s intervals designed to allow sufficient time for sample cooling.

The sensitivity curve for the overall silylation-etching process is shown in Figure 6. Resist A has a sensitivity of 1.1 mJ/cm^2 and a contrast value of 3.3. Figure 7a shows the scanning electron micrograph of a contact-printed deep-UV image with feature size of 1.0 μm. The silicon dioxide protective layer has a rough surface due to its highly porous structure. The small amount of residue on the silicon wafer substrate is believed to be an inorganic oxide resulting from the oxidation of the antimony-based onium salt or the result of sputtered silicon oxide.

(B) Image Reversal of Resist B. Selective silylation in resist B is achieved as a result of a different process. The gas-phase silylation of polymers involves two distinct steps:[33] (a) diffusion of the silylating gas into the polymer film; (b) reaction of the silylating gas

(32) Reichmanis, E.; Smolinsky, G. *Proc. SPIE* **1984**, *469*, 38.

(33) Brust, T. B.; Turner, S. R. *Proc. SPIE* **1987**, *771*, 102.

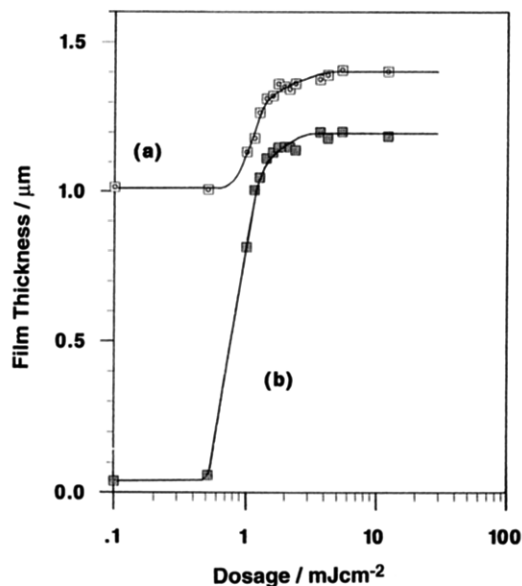


Figure 6. Sensitivity curves of radiation-exposed resist A: (a) after reaction with DMATMS; (b) after silylation and reactive ion etching.

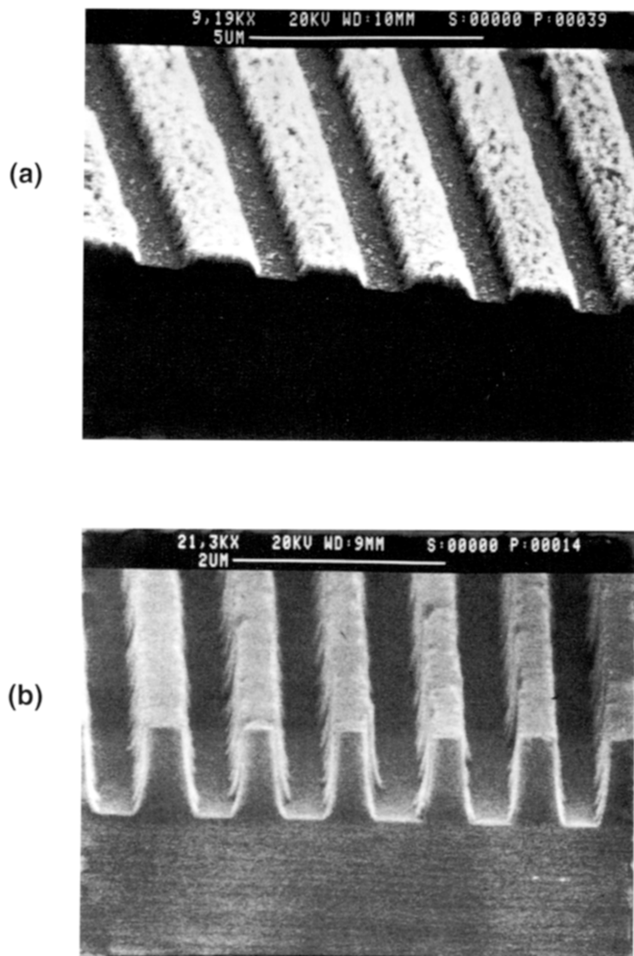


Figure 7. Scanning electron micrographs of images created with dry-develop systems. Both resists were processed under the conditions listed in Table 1. Deep-UV irradiation at 254 nm done with a contact-printer: (a) resist A; (b) resist B.

with certain functional groups on the polymer chains. The overall rate of the silylation process is controlled by the slower of these two steps. The rate of diffusion of the silylating gas into the polymer film depends on the mobilities of the polymer chains. In turn, the mobilities of the chains are related to the temperature at which the silylation reaction is performed. In negative-tone cross-linking resist systems, cross-linking increases the glass transition temperature of the polymer matrix and reduces the mobilities of the polymer chains. The concentration of the silylating gas is much lower in the cross-linked areas as the permeability of the resist film to the silylating reagent is lowered. Therefore, the silylation reaction is kinetically favored in the uncross-linked parts of the resist and a high selectivity between the radiation-exposed and unexposed areas can be achieved through a suitable choice of reaction conditions.[13,20,27] The subsequent oxygen RIE removes the radiation-exposed areas forming the positive tone image.

Deep-UV Exposure. Resist B has a high sensitivity of 0.2 mJ/cm^2 with deep-UV radiation and aqueous base development. However, because of its low degree of cross-linking, a resist sample exposed to such a low radiation dose is still highly permeable to the silylating gas under the silylating conditions used. Therefore, a much higher extent of cross-linking in the resist matrix is required to effectively stop the diffusion of DMATMS into the radiation exposed portions of the resist. With a relatively high exposure dosage of 5.0 mJ/cm^2, selective silylation of the unexposed areas of the resist can be achieved.

Gas-Phase Silylation. Resist B, based on a poly(4-hydroxystyrene) matrix has a much higher glass transition temperature (near 160 °C) than resist A. Therefore, the silylation reaction can be performed at a much higher temperature. A reaction temperature of 110 °C with 110 Torr of DMATMS provides the most efficient and selective silylation of the radiation unexposed resist. The presence of cross-linker **4** is only expected to have a minor influence on the overall silylation process.

The gas-phase silylation process is readily monitored by the techniques used previously for resist A. Incorporation of the trimethylsilyl group is reflected by a decrease in the phenolic hydroxyl stretching band at 3380 cm^{-1}, as well as increases in the absorbances of the Si−C and Si−O bands at 850 and 920 cm^{-1} (Figure 8). Because of the higher reaction temperature and the less sterically crowded environment of the hydroxyl group in poly(4-hydroxystyrene), a higher reaction rate is observed when compared to resist A.

RBS measurements provide results similar to those for resist A. They confirm the presence of a localized silicon-containing zone at the surface of the resist film that progresses further into the bulk of the coating as the silylation reaction proceeds. Poly(4-[(trimethylsilyl)-oxy]styrene) has a calculated silicon content of 15 wt % that is expected to provide ample resistance to oxygen plasma etching.[31] Hence, unlike resist A, a relatively thin layer of silylated material will be sufficient to protect the underlying hydrocarbon polymer. A silylation reaction time of 2 min that leads to 25−35% conversion, is used in the imaging experiments.

Reactive Ion Etching with Oxygen Plasma. Because of its high silicon content, silylated resist B shows a much higher resistance to oxygen plasma than the unsilylated resist, with etching rates of 0.35 and 7.88 nm/s, respectively. For the reasons stated earlier, the etching process was carried out in short 30 s pulses, allowing time (30 s) for heat transfer from the resist to the substrate holder. Although similar results were

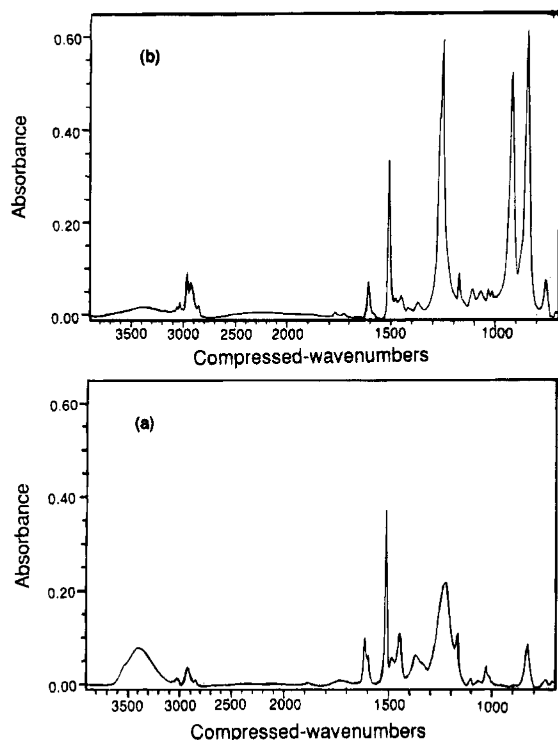


Figure 8. Infrared spectra of resist B samples: (a) radiation-unexposed and unsilylated; (b) radiation-unexposed and treated with 100 Torr of DMATMS at 110 °C for 15 min.

observed using both 600 and 50 V bias voltages, a low sheath voltage of 50 V was used to prevent radiation damage to the resist surface. The use of higher bias voltage results in sputtering of material from the resist surface by the high energy gas phase ions.

Figure 7b shows the scanning electron micrograph of 0.4 μm lines printed with a simple contact printer. The resist thickness is about 1.0 μm. The definition of the lines is excellent with nearly equal dimensions for the lines and spaces, and no residue is observed in the spaces because an onium salt free of inorganic element, triphenylsulfonium triflate, was used in these experiments.

Conclusions

By gas-phase silylation of phenolic hydroxyl groups, image-tone reversal has been achieved with both a direct positive-tone and a direct negative-tone chemically amplified resist. The key step is the selective silylation of the relief image obtained after the radiation exposure and baking processes. In the positive-tone resist A, the phenolic hydroxyl groups are generated as a result of the irradiation process. Silylation is restricted to the radiation-exposed areas. In the negative-tone resist B, radiation causes cross-linking of the polymer matrix in the exposed areas. The cross-linked material has a lower permeability to the silylating agent, demonstrated by selective silylation occurring only in the unexposed areas. While the silicon content in resist A is not high enough to resist the oxygen plasma etching, the higher percentage of silicon in resist B provides sufficient resistance. With simple deep-UV contact printing, reversed-tone images with high resolution have been obtained for both resists.

Acknowledgment. Thanks are due to Dr. P. Revesz of the Materials Science Center, Cornell University for measuring the RBS samples. The authors would like to thank Dr. C. G. Willson and Dr. S. A. MacDonald at IBM Almaden Research Center for helpful discussions. Financial support of this research by the Semiconductor Research Corporation and IBM Corp. is acknowledged with thanks. This work was performed in part at the National Nanofabrication Facility which is supported by the National Science Foundation under Grant ECS-8619049, Cornell University and industrial affiliates.