

Plasma-Developable Photoresist Systems Based on Chemical Amplification

Scott A. MacDonald,* Hubert Schlosser,[†] Hiroshi Ito, Nicholas J. Clecak, and C. Grant Willson

IBM Research Division, Almaden Research Center, 650 Harry Road,
San Jose, California 95120-6099

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This paper reports work on two chemically amplified resist systems that can be developed in an oxygen plasma environment. These systems are based on the catalytic photogeneration of functional groups within the resist film that react, in a subsequent step, with a silylating agent that is delivered in the gas phase. As a result, the organosilicon species is selectively and covalently incorporated into the exposed regions of the resist film. When the silylated film is exposed to an oxygen plasma, the regions that do not contain the organosilicon species are etched to the substrate, whereas those areas containing silicon are not etched. This generates a negative tone relief image. The chemical mechanisms and lithographic properties of these systems will be discussed.

Introduction

In the traditional lithographic sequence, a substrate is coated with an organic photoresist and exposed to radiation through a mask. The exposed resist film is then developed in solvent to produce a three-dimensional relief replica of the mask pattern. In a subsequent step, the image in the resist is transferred into the underlying substrate by immersing the system in a solvent-based etching bath. Over the years, investigators have worked to replace these conventional, liquid-based substrate etching systems with a variety of plasma (dry) etch processes.^{1,2}

Given the several advantages that dry etching offers over solution etching, in particular the anisotropic nature of the etch, several groups have sought to bring these same advantages to the resist development step. In 1975, Penn and co-workers successfully demonstrated this concept by fabricating an active semiconductor integrated circuit using a plasma-developable resist system and all dry processing.³ More recently, Garza⁴ discussed the manufacturing issues associated with a commercially available, plasma-developable resist, while Nichols and co-workers^{5,6} described using this same resist system to fabricate a 0.5- μm n-MOS device. A large body of literature describing various dry-develop resist schemes exists. The advantages of a plasma developable resist system, along with reviews of the pertinent literature have been published by Taylor,⁷ Willson and Bowden,^{8,9} and Iwayanagi et al.¹⁰

For any resist to be developed in a plasma environment, the exposed and the unexposed regions must etch at different rates. One way to obtain this etch rate differential is to incorporate an appropriate inorganic component into one of these two areas.⁷ This approach is based on the considerable literature associated with the use of organometallic polymers as oxygen etch barriers in multilayer resist (MLR) systems.^{11,12} Silicon-containing materials such as poly(siloxane),¹³ poly(silane),¹⁴ poly[(trimethylsilyl)styrene],^{15,16} and poly[(trimethylsilyl)methyl methacrylate]¹⁷ have all been shown to exhibit resistance to degradation by an oxygen plasma. ESCA studies have demonstrated that oxygen plasma treatment converts the top surface of these organometallic polymers into a thin layer of nonvolatile silicon oxide. This in situ generated oxide layer then functions as the oxygen etch barrier.

er.^{15,16,18-20} These groups have also shown that an organosilicon polymer containing only 10-15% silicon by weight etches, in an oxygen plasma, at only 1/15th the rate of the hydrocarbon analogue. Silicon-containing materials have been extensively investigated as etch barriers, but other inorganic elements have also been shown to provide

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* Current address: Hoechst AG Corporate Research, Frankfurt am Main, Germany.

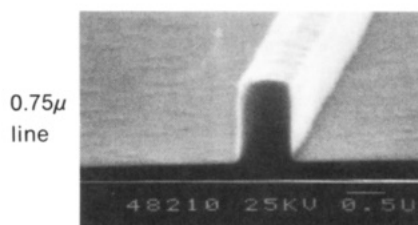
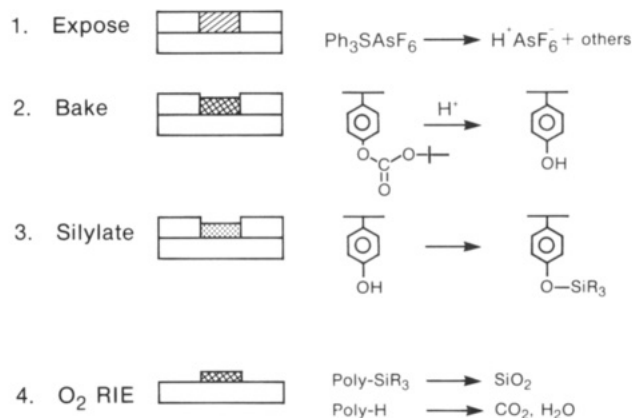
etch resistance by the same mechanism. For example, the properties of polymeric materials containing tin,²¹ iron,²² or germanium^{23,24} have been reported.

Two basic design approaches have been used to formulate organometallic-based plasma developable systems. One approach involves starting with an organic film containing a uniform distribution of an organometallic species, exposing the film to radiation, and in a subsequent process step removing the inorganic component selectively from either the exposed or the unexposed regions of the film. Taylor and co-workers have described several negative tone resist systems that consist of a monomeric organosilicon species dispersed within a hydrocarbon-derived polymeric matrix.^{25,26} Upon radiolysis, the monomeric organosilicon component becomes "fixed" within the exposed areas. In the next step, the films are heated so that the volatile, un-cross-linked organometallic component is expelled from the unexposed areas. When these films are then treated with an oxygen plasma, the organosilicon species in the exposed areas is converted to SiO₂, which behaves as an etch barrier. The regions that do not contain the organometallic species are etched to the substrate, forming a negative tone image of the mask. Meyer and co-workers have described a positive tone, plasma-developable resist that starts with a uniform distribution of silicon within the film.²⁷ This specific resist consists of an acrylic copolymer with pendant silicon side groups that can be cleaved and expelled from the film by UV light and heat.

Another approach to designing plasma-developable resists involves coating the substrate with an organic film that lacks an organometallic component and, in a subsequent step, introducing an element that forms a refractory oxide into regions of the film. A conceptually simple example of this approach used a focused beam of indium,²⁸ gallium,²⁹ or silicon³⁰ ions to write a pattern directly onto the surface of an organic polymer. When the patterned resist was subjected to oxygen RIE, the surface of the ion-implanted regions was oxidized to the corresponding oxide, which functioned as an etch barrier. The areas of the film that were not implanted etched rapidly to substrate, generating a negative tone image. While direct writing with inorganic ions is a straightforward way to generate an etch differential within an organic film, the technique does not hold immediate promise for VLSI production. In 1984 Taylor and co-workers published a process in which a bisazide/isoprene cross-linking resist was exposed to UV light and, in a subsequent step, treated with the vapor of an inorganic halide such as SiCl₄.^{31,32}

Scheme I

Dry Develop Process



Silicon diffused more rapidly into the un-cross-linked regions of the film, and accordingly this system yielded a positive tone image when developed in an oxygen plasma.

In 1985, we presented our initial findings on the dry develop resist system design shown in Scheme I.^{33,34} This approach starts with a resist film that does not contain an inorganic species and is inert toward reaction with organometallic reagents. This film does contain functional groups that, upon acid-catalyzed thermolysis, are transformed into a functionality that reacts with organometallic reagents. The inorganic component in this scheme is selectively and covalently introduced into the exposed regions of the film by a chemical reaction, thereby generating a large etch rate differential between the exposed and the unexposed areas. Hence, this is a negative tone resist.

In Scheme I, silicon is selectively introduced into the exposed regions of the film by allowing the phenolic hydroxyl groups that are generated by exposure to react with common silylating agents delivered in the gas phase. Within the past 5 years, several other dry developing resist systems involving the silylation of phenolic films have been published. The volume of literature associated with these systems is quite large. Therefore, as a review of all publications is beyond the scope of this paper, only the major contributions will be discussed. In 1986, Coopmans and Roland described the gas-phase silylation of a proprietary diazonaphthoquinone/phenolic matrix resin formulation yielding a negative tone, oxygen-plasma-developable resist.³⁵ This negative system (often referred to as DESIRE) is commercially available, has been evaluated for device fabrication,⁴⁻⁶ and has been subjected to fundamental mechanistic studies.³⁶ Also, it is possible to convert this

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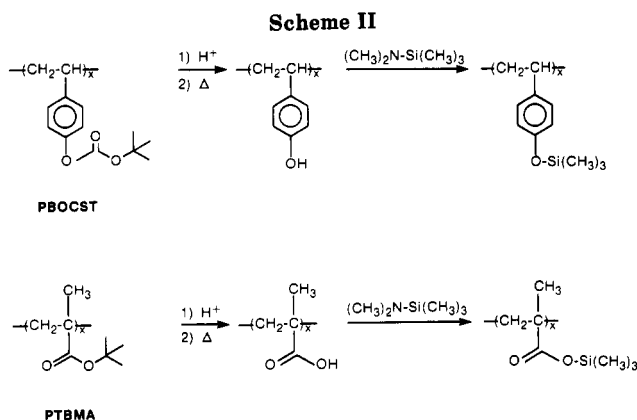
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negative tone system to a positive working resist by using a 193-nm exposure source³⁷ or a two-step exposure process.³⁸ A positive tone, dry developable system involving the gas-phase silylation of a three-component (phenolic resin/photoacid generator/cross-linking agent) resist has been described by two groups.^{39,40} Finally, silylating the phenolic matrix resin film can be accomplished in solution, as described by Yang.^{41,42}

The key step in Scheme I is the reaction of the silylating agent with the photogenerated phenol to selectively introduce silicon into the exposed regions of the film. Silylating agents (such as hexamethyldisilazane), which react with phenolic compounds to form silyl ethers, are also known to react with carboxylic acids to form silyl esters. So, on the basis of the chemistry shown in Scheme I, one should obtain a plasma-developable resist from a polymeric system that photogenerates carboxylic acid groups. Scheme II outlines the central steps for dry development of systems based on photogeneration of a phenol or photogeneration of a carboxylic acid. This paper describes the chemistry and lithographic properties of two negative tone oxygen-plasma-developable resist systems, poly[4-((*tert*-butyloxycarbonyl)oxy)styrene] (PBOCST) and poly(*tert*-butyl methacrylate) (PTBMA). These polymers are shown in Scheme II.

For this study the resist formulation and image-processing parameters were held constant, allowing a direct comparison of the chemistry of the two systems to be made. However, this experimental approach does not allow us to compare the ultimate imaging potential of these systems, as the process parameters were not optimum for either.

Experimental Section

Materials. 4-((*tert*-Butyloxycarbonyl)oxy)styrene (BOCST) was prepared by the procedure of Fréchet et al.⁴³ *tert*-Butyl methacrylate (TBMA) was purchased from Aldrich. Both mo-

nomers were distilled under reduced pressure prior to polymerization. 2,2'-Azobis(isobutyronitrile) (AIBN) was purchased from Kodak.

Polymerizations. Poly[4-((*tert*-butyloxycarbonyl)oxy)styrene] (PBOCST): A solution of 20.0 g (90.80 mmol) of BOCST in 20 mL of tetrahydrofuran (THF) containing 0.1 g (0.42 mmol) of AIBN was refluxed for 22 h under nitrogen to give 19.4 g (97%) of PBOCST as a white solid after precipitation in 1600 mL of methanol and drying. GPC: $\bar{M}_n = 46\,474$; $\bar{M}_w = 87\,400$; $\bar{M}_z = 139\,199$.

Poly(*tert*-butyl methacrylate) (PTBMA): A solution of 10.0 g (70.32 mmol) of TBMA in 25 mL of THF containing 0.03 g (0.13 mmol) of AIBN was refluxed for 40 h under nitrogen to give 9.4 g (94%) of PTBMA as a white solid after precipitation into 1000 mL of methanol/water (3:2) and drying. GPC: $\bar{M}_n = 30\,097$; $\bar{M}_w = 73\,916$; $\bar{M}_z = 135\,516$.

Resist Formulation and Processing. The polymer solutions in cyclohexanone (15 wt %) containing triphenylsulfonium hexafluoroarsenate (3 mol % to polymer repeating units) were spin-coated for 30 s at 3000 rpm onto three substrates: (1) silicon wafers for lithography, oxygen-reactive ion etching (O₂ RIE), and Rutherford backscattering (RBS) experiments, (2) sodium chloride plates for IR experiments, and (3) quartz plates for UV spectroscopy. Resist films measured 0.9–1.1 μm after drying at 90 °C for 4 min. Imagewise exposures of the resist films at 240–270 nm were conducted with a Perkin-Elmer Micralign 500 projection printer using a narrow-bandwidth UV-2 filter. All other exposures were carried out with an Optical Associates Inc. (OAI) illuminator through a 254-nm bandpass filter in the contact mode. Exposed wafers were postbaked at 100 °C for 1 min. Silylation of the resist films was carried out in a modified Yield Engineering Systems Inc. oven at 100 °C by evacuating and refilling the oven with (dimethylamino)trimethylsilane (DMATMS) vapor to 200 Torr. The temperature was monitored by a thermocouple attached to a silicon wafer placed next to the samples, and the oven pressure was measured with a capacitance manometer. The Plasma-Therm reactive ion etcher used for O₂ RIE of the resist films was run at 0.25 W/cm² power density, 30 mTorr of O₂ pressure, 40 scc/min O₂ flow, and –125 V bias. The O₂ RIE rates of the unexposed resist films recorded under these conditions are 0.076 μm/min for PBOCST and 0.249 μm/min for PTBMA. In lithography and sensitivity/contrast experiments the resist films were subjected to a 20% overetch.

Measurements. IR spectra were measured on an IBM IR/32 FT spectrometer. UV spectra were measured on a Hewlett-Packard Model 8450A UV-vis spectrophotometer. Molecular weight determinations were made by gel permeation chromatography (GPC) using a Waters Model 150-C chromatograph equipped with four Polymer Laboratories Inc. gel columns packed with cross-linked polystyrene (3.9 mm × 30 cm; 10⁶, 10⁵, 10⁴, 10³ Å) at 40 °C in THF. The molecular weights reported in the experimental section are relative to polystyrene standards (8000000 to 480 molecular weight). Thermal analyses were performed on a Du Pont 1090 thermal analyzer at a heating rate of 5 °C/min for TGA and 10 °C/min for DSC under nitrogen atmosphere. Film thickness was measured on a Tencor Alpha-Step. Exposure doses were measured with an Optical Associates Inc. 355 exposure monitor. Scanning electron micrographs were recorded with a Philips SEM 505. RBS experiments were performed with a 2.3-meV He⁺ beam and a detector angle of 170°.

Results and Discussion

Side-Group Cleavage and Silylation. Scheme II shows the two dry developable, chemically amplified resist systems that will be discussed in this paper. The reaction sequence for these systems consists of three steps: photogeneration of acid, catalytic thermolysis, and silylation. The first step, photogeneration of acid in a polymeric film, has been studied earlier⁴⁴ and will not be discussed in this paper. The combination of the first two steps (photogeneration of acid, followed by acid-catalyzed thermolysis)

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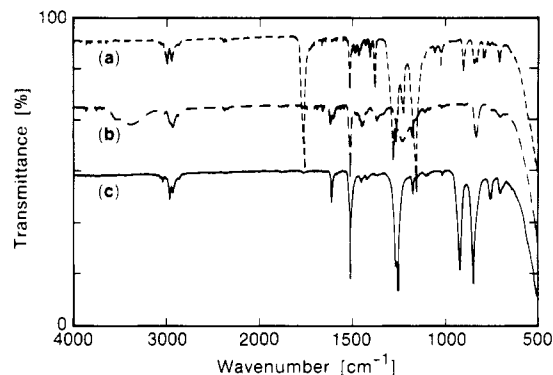


Figure 1. IR spectra of the PBOCST/Ph₃SAsF₆ dry-develop resist: (a) starting film; (b) after UV exposure (10 mJ/cm² at 254 nm) and postbake; (c) after treatment with DMATMS vapor for 5 min at 100 °C/200 Torr.

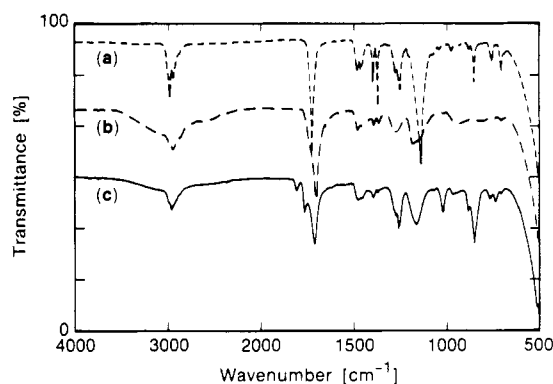


Figure 2. IR spectra of the PTBMA/Ph₃SAsF₆ dry-develop resist: (a) starting film; (b) after UV exposure (100 mJ/cm² at 254 nm) and postbake; (c) after treatment with DMATMS vapor for 20 min at 100 °C/200 Torr.

is the foundation of chemically amplified resist systems as described in 1982 by Ito et al.⁴⁶⁻⁴⁸ The details of the methacrylate system have been described by Ito and Ueda.⁴⁹ This general approach of side group cleavage is used in our dry development process and will be discussed. Finally, the last step, gas-phase silylation of the photo-generated phenol or carboxylic acid, is a key reaction in this resist scheme and will be discussed.

IR spectroscopy can be used to follow both the side-group cleavage reaction and the silylation step. Figure 1a shows the IR spectrum of the starting PBOCST/onium salt film. Figure 1b shows the IR spectrum of the film after being exposed to 10 mJ/cm² of 254-nm radiation and baked. Note that the carbonate C=O absorbance at 1757 cm⁻¹ completely disappears at this exposure dose. Figure 1c shows the IR spectrum of the film after treatment with (dimethylamino)trimethylsilane (DMATMS) vapor (200 Torr/5 min). Note the appearance of the characteristic CH₃-Si stretching bands at 1251 and 846 cm⁻¹ as well as the Ph-O-Si stretch at 918 cm⁻¹. Also note the disappearance of the broad phenolic OH band (3400 cm⁻¹) that is present in Figure 1b. This implies that, under these conditions, essentially all of the *tert*-butylcarbonate groups

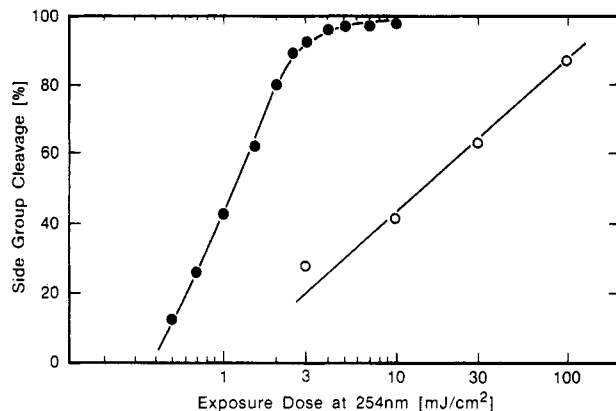


Figure 3. IR study of side-group deprotection as a function of exposure dose. (●) PBOCST/Ph₃SAsF₆ resist after UV exposure and postbake (100 °C/1 min) monitoring the carbonate absorbance at 1757 cm⁻¹. (○) PTBMA/Ph₃SAsF₆ resist after UV exposure and postbake (100 °C/1 min) monitoring the *tert*-butyl absorbance at 1368 cm⁻¹.

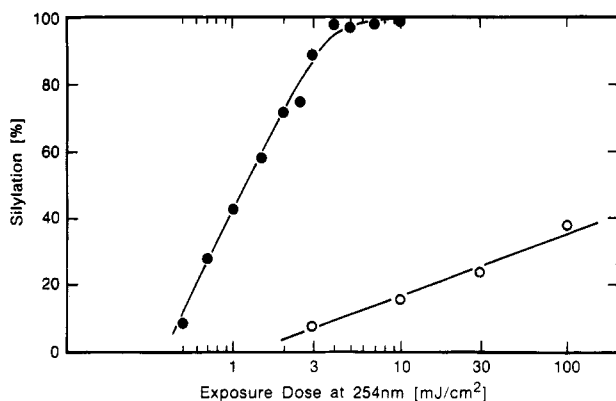


Figure 4. IR study on silicon uptake as a function of exposure dose. The vapor silylation was performed at 100 °C with 200 Torr of DMATMS for 5 min. (●) PBOCST/Ph₃SAsF₆ resist after UV exposure, postbake, and treatment with DMATMS vapor; monitoring absorbance at 918 cm⁻¹. (○) PTBMA/Ph₃SAsF₆ resist after UV exposure, postbake, and treatment with DMATMS vapor; monitoring absorbance at 848 cm⁻¹.

have been cleaved, and the resulting phenolic hydroxyl groups have been completely silylated. If all the phenolic hydroxyls have been silylated, then silicon should be uniformly distributed throughout the bulk of the film.

The IR spectroscopy of the PTBMA/onium salt system (Figure 2) is not as clean as that exhibited by the carbonate in Figure 1, but the chemistry that occurs is equally efficient. The complicating feature of the *tert*-butyl ester system is that all three spectra have a carbonyl absorbance. Figure 2a,b shows IR spectra of the film before and after UV exposure and baking. We have used the disappearance of the *tert*-butyl band (1368 cm⁻¹) to follow the ester cleavage reaction. Figure 2c shows the spectrum after treatment with DMATMS vapor. Note the appearance of the general alkyl-Si band at 848 cm⁻¹.

Figure 3 shows the dependence of carbonyl cleavage on incident exposure dose for both systems. At this postexposure bake temperature, the *tert*-butyl ester system requires approximately 100 times more exposure dose than the *tert*-butyl carbonate system to achieve 100% removal of the side groups. Figure 4 shows the results of allowing these exposed and baked films to stand in DMATMS vapor (200 Torr for 5 min). Comparing the data in Figure 4 with the curves in Figure 3 is very revealing. The two curves for the *tert*-butyl carbonate system are superimposable, while those for the *tert*-butyl ester are not. The

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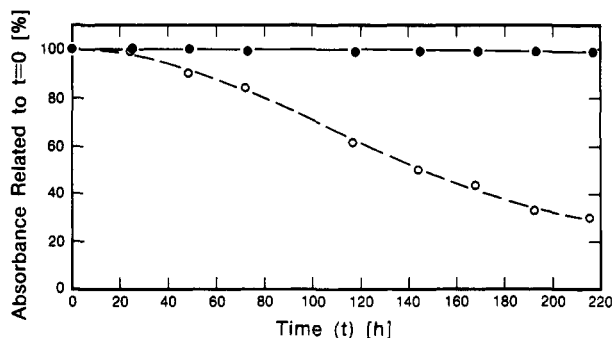


Figure 5. IR study on long-term stability of silylated resist films to ambient conditions. (●) PBOCST/ Ph_3SAsF_6 system after UV exposure (10 mJ/cm^2), postbake, and treatment with DMATMS vapor for 5 min. Monitoring absorbance of Ph-O-Si at 918 cm^{-1} . (○) PTBMA/ Ph_3SAsF_6 system after UV exposure (100 mJ/cm^2), postbake, and treatment with DMATMS vapor for 20 min. Monitoring absorbance of alkyl-Si at 848 cm^{-1} .

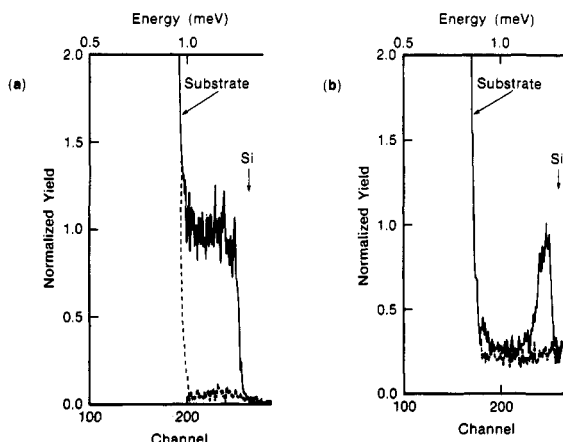


Figure 6. Rutherford backscattering spectra: (a) PBOCST/ Ph_3SAsF_6 resist film; (b) PTBMA/ Ph_3SAsF_6 resist film. (---) unexposed and treated with DMATMS for 5 min. (—) Exposed with 254-nm light (5 mJ/cm^2 for PBOCST, 30 mJ/cm^2 for PTBMA), baked, and treated with DMATMS for 5 min.

fact that the carbonate curves are identical implies that all of the photogenerated phenols are silylated during the 5-min vapor treatment. This result is completely consistent with our previously published work on BOCST/styrene copolymers.⁵⁰ The *tert*-butyl ester system is very different. Here less than half of the photogenerated carboxylic acid groups are silylated under these conditions. For example, Figure 3 shows that an exposure dose of 30 mJ/cm^2 cleaves approximately 63% of the *tert*-butyl ester groups, while Figure 4 shows that only 23% of carbonyl units are converted to silylester.

IR spectroscopy was also used to determine the hydrolytic stability of the silylated films. Trimethylsilyl ethers and trimethylsilyl esters are well-known to undergo facile hydrolysis in solution, and the humidity in our laboratory is about 50%. If rapid hydrolysis occurs in the film, then one would form a volatile silicon species that could evaporate from the resist film during normal handling. This is not desirable, as the silicon was intentionally placed into the film to act as an oxygen RIE barrier. Accordingly, silylated films were allowed to stand in the laboratory for 9 days, and the IR spectrum was recorded on a daily basis. Figure 5 shows that the phenolic silyl ether film is stable over this time period, while the aliphatic silyl ester is not.

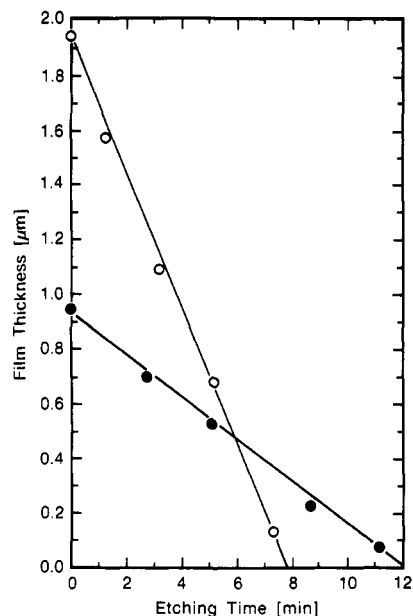


Figure 7. Film thickness remaining vs time in O_2 RIE for unprocessed films: (●) PBOCST/ Ph_3SAsF_6 ; (○) PTBMA/ Ph_3SAsF_6 .

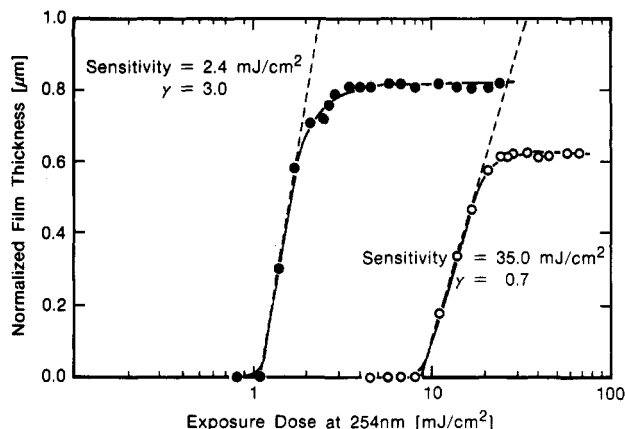


Figure 8. Sensitivity curve at 254 nm for both dry-develop systems. Films were postbaked at 100°C for 1 min and treated with 200 Torr of DMATMS at 100°C for 5 min. O_2 RIE development parameters are listed in the Experimental Section. (●) PBOCST/ Ph_3SAsF_6 ; (○) PTBMA/ Ph_3SAsF_6 .

Therefore, for consistency, all of the oxygen RIE work and Rutherford backscattering analyses were performed on freshly silylated films.

We used Rutherford backscattering analysis (RBS) to directly investigate the silicon distribution within these silylated films. Traditionally, RBS has been used to probe the distribution of inorganic elements within inorganic films. Recently, several groups have used this technique to study the distribution of inorganic elements within organic films, especially the distribution of silicon atoms within a phenolic matrix resin.^{6,36,37,40} The results of the RBS analysis of the PBOCST/onium salt system are shown in Figure 6a. This figure shows that the exposed and silylated film contains a uniform distribution of silicon from the resist-air interface down to the resist-substrate interface. This observation is in full agreement with the previously discussed IR data contained in Figure 1. Figure 6a also shows the RBS analysis of a film that was not exposed to UV light but was subjected to the vapor silylation treatment. This control film sample, which represents the unexposed regions of the resist, does not contain measurable amounts of silicon. RBS analysis of the

(50) Spence, C. A.; MacDonald, S. A.; Schlosser, H. *Advances in Resist Technology and Processing VII, Proc. SPIE 1990, 1262, 344-357.*

tert-butyl ester system is shown in Figure 6b. Figure 6b shows that the silicon in the exposed and silylated film is not uniformly distributed but is confined to the resist-air interface. This figure also shows the RBS analysis of a film that was not exposed to UV light but was subjected to the vapor silylation treatment. Again, this control film does not contain measurable amounts of silicon. In summary, the RBS analyses show that under UV exposure and subsequent vapor silylation, both polymeric systems selectively incorporate silicon into the exposed regions and not into the unexposed areas. Furthermore, the two polymeric systems exhibit different depth distributions of silicon within the exposed regions.

Lithographic Evaluation. The oxygen plasma development process is a critical step in the processing of any plasma developable resist. Therefore, the specific RIE parameters (rf power, pressure, flow) will strongly influence the quality of the final image.^{4,51} In this study, standard RIE process parameters were used to allow a direct comparison of the chemistry of the two polymeric systems. Figure 7 shows the etch rate of the unexposed films under the conditions listed in the Experimental Section. As expected, the aliphatic polymer etches faster (3×) than the aromatic polymer. The contrast curves for these two systems, under the silylation and etch conditions listed in the Experimental Section, are shown in Figure 8. Both resists are negative tone systems, with the PBOCST/onium salt being about 10 times more sensitive than the PTBMA system. This difference in lithographic sensitivity between the two systems should be compared to the previously discussed side-group removal study (Figure 3). In the side-group removal study, the PBOCST/onium salt system was approximately 100 times more sensitive than the PTBMA system. The difference between these two studies can be readily accounted for. In these plasma-developable resist systems, a relief image is obtained when there is sufficient silicon at the resist-air interface to form an etch barrier, and a silicon-rich layer can be produced at the surface as soon as there are sufficient reactive groups in the area. This condition can occur well before all of the reactive groups have been liberated.

Figure 9 shows relief images generated in these two polymeric systems by using the unoptimized lithographic process described in the Experimental Section. The SEM in Figure 9b shows a small amount of residue located between the relief images and on the silicon substrate. A slight substrate residue is often observed after oxygen plasma development, and it can be easily removed by rinsing the etched sample with 6:1 buffered HF for a few seconds. While the exact cause of this residue is not known, we have observed that the specific oxygen RIE conditions used to develop the image have a profound effect on the quantity and location of this residue. The scanning electron micrographs in Figure 9 demonstrate the utility of this dry develop resist concept but do not address the ultimate lithographic capability of either system. For example, the submicron relief images, shown in Figure 10, were readily obtained by optimizing the PBOCST formulation.

It is interesting to compare the data in Figures 3, 4, and 8 at the UV dose used for the RBS analysis. In the case of the PBOCST system, a 5 mJ/cm² dose was used to prepare the RBS sample. From Figure 8, this dose is just sufficient to retain the maximum film thickness after etching. The RBS data in Figure 6a show that silicon is

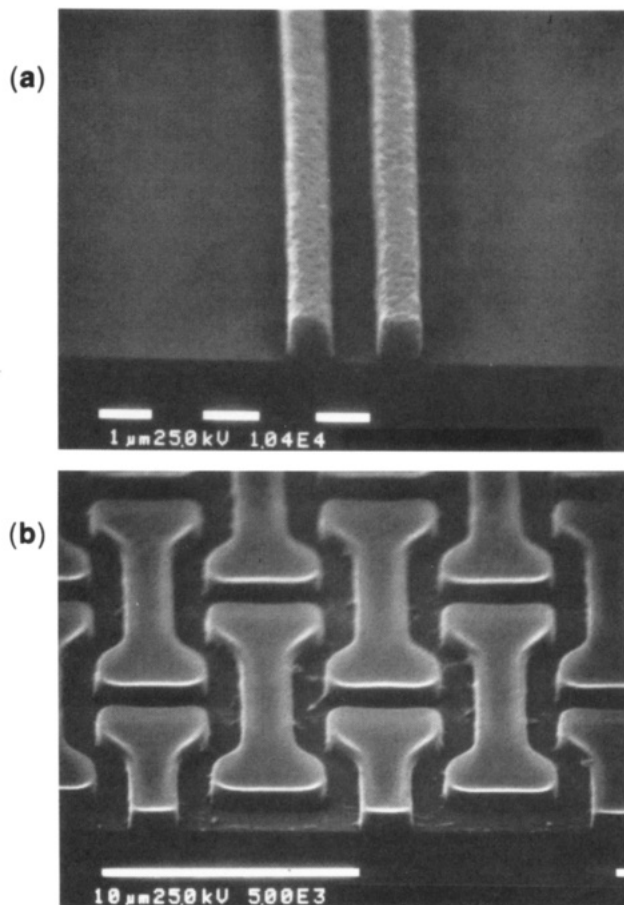


Figure 9. Scanning electron micrographs of images created with the dry-develop system. Both resists were processed under the conditions described in the Experimental section. (a) PBOCST/Ph₃SAsF₆ exposed on a Perkin-Elmer Micralign 500, with approximately 10 mJ/cm². (b) PTBMA/Ph₃SAsF₆ exposed on same Micralign 500 with approximately 48 mJ/cm².

uniformly distributed throughout the film. Figure 3 shows that all of the carbonate groups have been converted to phenolic hydroxyls, and Figure 4 shows that all of these phenols have been silylated.

In the case of the PTBMA system, a dose of 30 mJ/cm² was used to prepare the RBS sample. This dose is just sufficient to retain the maximum film thickness after etching and is at approximately the same point on the contrast curve as that used in the PBOCST experiments. The RBS data in Figure 6b show that silicon incorporation is confined to the resist-air interface. Figure 3 shows that only about 60% of the *tert*-butyl ester groups have been converted to carboxylic acid functionality, and Figure 4 shows that less than half of these carboxylic acid groups have been silylated.

Silylation Rate of PBOCST System. The data presented in Figures 4 and 6a show that all of the photo-generated phenolic groups are silylated under our experimental conditions (5 min, 200 Torr, 100 °C in a modified Yield Engineering Systems oven). Therefore, it is reasonable to ask whether a shorter reaction time, lower reaction pressure, or lower reaction temperature would also achieve 100% silylation. The rate of silylating exposed PBOCST films with HMDS vapor has been studied by using a quartz crystal microbalances.⁵² The rate of silylating the DESIRE system has been investigated by both

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Figure 10. Scanning electron micrographs of images generated in a modified PBOCST/ Ph_3SAsF_6 formulation exposed on a 0.35 NA, 1X, UltraStep X-248E step-and-repeat projection system built by Ultratech. The dose was approximately $8 \text{ mJ}/\text{cm}^2$.

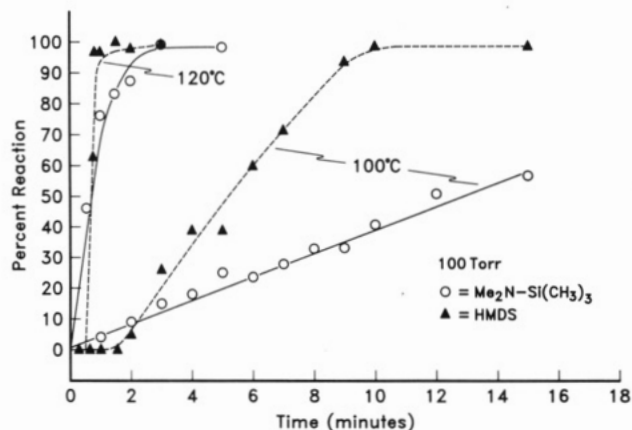


Figure 11. IR study of silicon incorporation by exposed PBOCST/ Ph_3SAsF_6 films using a single-wafer silylation tool built by Monarch Systems. Growth of the Ph-O-Si absorbance at 918 cm^{-1} was monitored. The study was run at two temperatures (100 and 120°C) and with 100 Torr of silylating agent: (O) DMATMS; (\blacktriangle) HMDS.

IR^{36} and laser interferometry.³⁸ We have followed the rate of silylating photogenerated phenols by monitoring the growth of the 918-cm^{-1} (Ph-O-Si) absorbance in the IR. These studies were carried out using a Monarch single-wafer silylation tool rather than the modified Yield Engineering oven. The results of this study are shown in Figures 11 and 12.

For these studies, the PBOCST film was exposed to $5 \text{ mJ}/\text{cm}^2$ and then baked to convert all of the carbonate

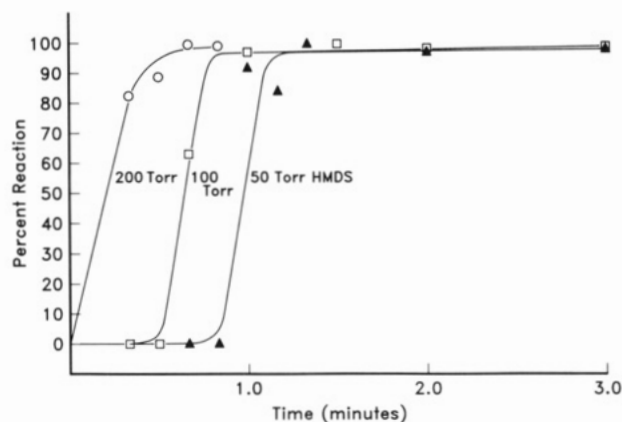


Figure 12. IR study of silicon incorporation by exposed PBOCST/ Ph_3SAsF_6 films using a single-wafer silylation tool built by Monarch Systems. Growth of the Ph-O-Si absorbance at 918 cm^{-1} was monitored. This study was run at 120°C with three pressures of HMDS: (\blacktriangle) 50 Torr; (\square) 100 Torr; (O) 200 Torr.

groups to reactive phenolic functionality. Figure 11 shows the rate of silyl ether formation using two different silylating agents. At 100°C and 100 Torr, HMDS achieves 100% silylation after 10 min, and DMATMS yields only 50% reaction after 13 min. When the reaction temperature is increased to 120°C , both reagents achieve 100% reaction in less than 2 min. Figure 12 shows the rate of silyl ether formation at three reaction pressures. As expected, the higher pressure increases the reaction rate. The data in Figures 11 and 12 demonstrate that the silylation time is compatible with single-wafer-processing schemes using a reasonable reaction temperature and pressure.

Conclusion

This paper describes a design for negative tone dry developable resists. In this design, a film that is initially unreactive toward silylating agents is rendered reactive by exposure and baking. As a result, upon treatment with an appropriate silylating agent silicon is incorporated exclusively into the areas of the film that have been exposed. No silicon (within the limits of RBS detection) is incorporated into the unexposed areas of the film. The system is black and white (digital) in its response to the silylating agent. The approach described in this paper is fundamentally different from systems that function on the basis of photoreactions that modulate the diffusion rate of the silylating agent as exemplified by the DESIRE process. These systems are gray scale (analog) in their response to silylating agents, and while it is possible through judicious choice of processing conditions to minimize silicon incorporation into unexposed areas, some undesirable silylation inevitably occurs.

Two examples of this design have been studied. Both use acid-catalyzed thermolysis to provide for high sensitivity through chemical amplification. Combining chemical amplification with selective silylation provides very sensitive, oxygen-plasma-developable resists. The systems studied undergo photoinduced changes in reactivity that arise from local generation of two classes of reactive groups, phenols and carboxylic acids. IR studies confirmed that silylation of these groups gives rise to silyl ethers and silyl esters respectively. RBS studies confirm that silylation occurs only in the exposed regions of the film. While this study focused on the photogeneration of phenols and carboxylic acid groups from *tert*-butyl carbonates and *tert*-butyl esters, this design concept is not limited of these two reactive species. A variety of chemical species are

known to react with organometallic reagents, and the synthetic chemical literature abounds with examples of removable protecting groups.

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Registry No. PBOCST, 87261-04-9; PTBMA, 25189-00-8; BOCST, 87188-51-0; TBMA, 585-07-9; DMATMS, 20839-91-2; Ph₃SAsF₆, 57900-42-2; O₂, 7782-44-7.

Surface Reaction of Poly[bis(trifluoroethoxy)phosphazene] Films by Basic Hydrolysis

Harry R. Allcock,* J. Steven Rutt, and Richard J. Fitzpatrick

Department of Chemistry, The Pennsylvania State University,
University Park, Pennsylvania 16802

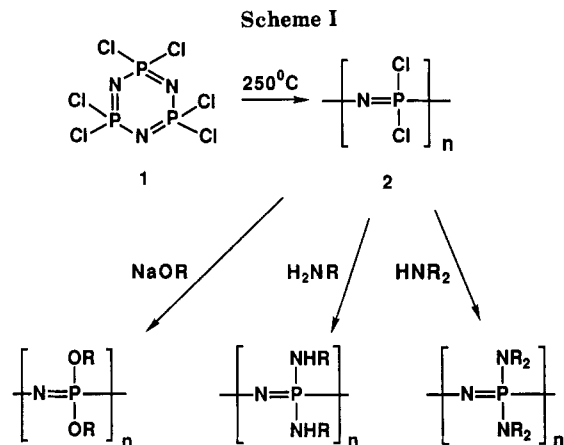
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A novel surface reaction of a fluoroalkoxyphosphazene polymer is reported. Films of poly[bis(trifluoroethoxy)phosphazene], [NP(OCH₂CF₃)₂]_n, underwent surface hydrolysis when treated for 0–15 min with 8 M aqueous sodium hydroxide in the presence of 0.05 M tetra-*n*-butylammonium bromide as a phase-transfer agent. This reaction converted a hydrophobic surface to one with hydrophilic and adhesive character. No surface reaction by NaOH solutions was detected in the absence of Bu₄NBr. On the basis of a series of surface analytical data, the principle chemical reaction was found to be a replacement of P–OCH₂CF₃ side groups at the polymer surface by P–O[−]NBu₄⁺ units. The modified surfaces were found to possess anionic sites, since an exchange reaction with the cationic dye methylene blue took place readily at the surface. No exchange occurred with the anionic dye Biebrich scarlet. Microscopic examination of the dyed films allowed the depth of the surface reaction to be measured. Contact-angle analysis showed that the surface of the polymer became progressively more hydrophilic as the reaction progressed. No significant changes in surface texture were detected. Surface reactions were also carried out with a commercial mixed-substituent fluoroalkoxyphosphazene elastomer. After extensive surface hydrolysis, films of [NP(OCH₂CF₃)₂]_n retained their solubility in organic solvents, in which they were analyzed by ³¹P, ¹³C, ¹H, and ¹⁹F NMR spectroscopy. The NMR analysis also suggested the presence of –O[−]NBu₄⁺ units. GPC analysis of an extensively modified material indicated that some cleavage of the phosphazene backbone may have occurred. The hydrolysis process was monitored by the reaction of solutions of [NP(OCH₂CF₃)₂]_n with NaOH in the presence of Bu₄NBr in refluxing THF. The mechanism of adhesion is discussed.

Introduction

A need exists to understand more fully the physical and chemical processes that are responsible for polymer adhesion and biocompatibility.^{1,2} It is known that fluorinated polymers such as poly(tetrafluoroethylene) or poly(chlorotrifluoroethylene) are difficult to bond to other materials because of their hydrophobic surfaces. Surface reactions of fluoropolymers to enhance adhesion have been studied extensively.^{3,4} In most cases, it is critical that the surface reaction should not affect the bulk properties of the polymer and that the depth of the reaction zone can be controlled easily.

Poly(organophosphazenes)^{5–8} are a relatively new class of polymers that are of increasing scientific and technological interest. A typical two-step synthesis of a poly(organophosphazene) is illustrated in Scheme I. It involves a ring-opening polymerization of hexachlorocyclo-



triphosphazene (1) at 250 °C to form poly(dichlorophosphazene) (2). Polymer 2 functions as a macromolecular intermediate. The high reactivity of the P–Cl bonds allows the polymer to undergo facile nucleophilic substitution reactions with sodium aryl oxides or alkoxides or with primary or secondary amines. The resultant poly(organophosphazenes) are usually stable to air and moisture. A wide variety of different types of side groups can be incorporated into the polymer structure, with the bulk and surface properties being dependent on the side groups present. The reactions and structures of cyclic phosphazene molecules such as 1 are useful models for the reactions and structures of the analogous macromolecules.⁹ Despite their technological utility, the surface chemistry

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