Chem. Mater. **1992,** *4,* 1364–1368

A Positive Tone Plasma-Developable Resist Obtained by Gas-Phase Image Reversal

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

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

Jean M. J. Frêchet

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

Received July 7, 1992. Revised Manuscript Received September 15, 1992

This paper describes a gas-phase image reversal process that generates a positive tone, plasma-developable image from a chemically amplified photoresist system. This system is based on the catalytic photogeneration of phenolic hydroxyl groups within the resist film that react, in subsequent steps, with either a silylating agent or an isocyanate that is delivered in the gas phase. This forms silyl ethers and carbamates within the polymeric film. The regions of the film containing the organosilicon species are not etched in an oxygen plasma environment. Correspondingly, the carbamate regions of the film are rapidly etched in an oxygen plasma. The overall process results in a positive tone image after development in an oxygen plasma.

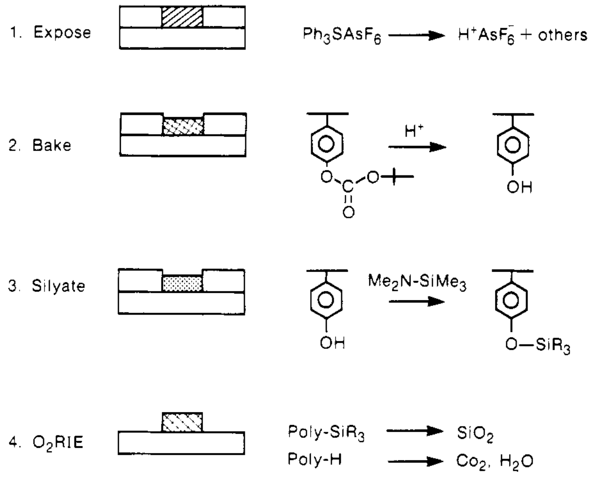
Introduction

Plasma-developable resist systems have been an active area of research for several years. While there are a variety of schemes used to obtain plasma-developable resists, the predominant approach involves a hydrocarbon polymer film containing an inorganic component.[1] When placed into an oxygen plasma environment, the hydrocarbon regions etch to substrate while the inorganic component (such as silicon,[2] tin,[3] germanium,[4] or titanium[5]) is converted into a nonvolatile oxide. This nonvolatile oxide significantly retards the oxygen etch rate, and hence the resist regions containing the inorganic component remain after oxygen plasma development.

For this approach to work, it is necessary to define within the polymer film regions containing the inorganic component and, correspondingly, regions lacking the inorganic species. A very attractive way to accomplish this is to expose the polymeric film to UV light and, in a subsequent step, treat the film with an inorganic reagent (such as diborane,[6] tin(IV) chloride,[7] hexamethyldisilazane,[8] or bis(triethylgermyl)amine[9]) to selectively incorporate the inorganic species into the film. While this general process can be applied to a variety of polymers and inorganic reagents, most of the published work deals with phenolic hydroxyl-containing films that react with a silylating agent to yield the corresponding silylether. A key feature in these systems is the way in which the UV exposure alters film reactivity toward the silylating reagent.

For example, we have described a positive tone system consisting of a phenolic polymer, photoacid generator, and acid-activated cross-linking agent.[10] In this system, UV exposure and heating cross-link the exposed regions, reducing the rate at which hexamethyldilsilazane (HMDS) can diffuse into these areas. Hence, when the exposed film is treated with HMDS vapor, the silylating agent diffuses more rapidly into the un-cross-linked region of the film, reacts with the phenolic hydroxyl group to form a silyl ether, and yields a positive tone image when developed in an oxygen plasma. Workers at Philips Research,[11] Shipley Co.,[12] Lincoln Laboratories,[13] and IBM[14] have also described positive tone systems derived from radiation-induced cross-linking of phenolic films.

Scheme I. Negative Tone Dry Develop Process



One can also obtain negative tone, dry-developable systems based on altering the diffusion rate of a phenolic

---

* To whom correspondence should be addressed.

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

[1] Taylor, G. N.; Wolf, T. M.; Stillwagon, L. E. *Solid State Technol.* **1984,** *Feb,* 145–155.

[2] MacDonald, S. A.; Ito, H.; Willson, C. G. *Microelectron. Eng.* **1983,** *1,* 269–293.

[3] Labadie, J. W.; MacDonald, S. A.; Willson, C. G. *J. Imag. Sci.* **1986,** *30,* 169–173.

[4] Fujioka, H.; Nakajima, H.; Kishimura, S.; Nagata, H. Advances in Resist Technology and Processing VII. *Proc. SPIE* **1990,** *1262,* 554–563.

[5] Nalamasu, O.; Baiocchi, F. A.; Taylor, G. N. In *Polymers in Microlithography: Materials and Processes; ACS Symposium Series, No. 412;* Reichmanis, E., MacDonald, S. A., Iwayanagi, T., Eds.; American Chemical Society: Washington, DC, 1989; pp 189–209.

[6] Taylor, G. N.; Stillwagon, L. E.; Venkatesan, T. *J. Electrochem. Soc.* **1984,** *131,* 1658–1664.

[7] Wolf, T. M.; Taylor, G. N.; Venkatesan, T.; Kraetsch, R. T. *J. Electrochem. Soc.* **1984,** *131,* 1664–1670.

[8] MacDonald, S. A.; Ito, H.; Hiraoka, H.; Willson, C. G. *Proceedings of SPE Regional Technical Conference;* Mid-Hudson Section, Society of Plastic Engineers: Ellenville, NY, 1985; pp 177–196.

[9] Yoshida, Y.; Fujioka, H.; Nakajima, H.; Kishimura, S.; Nagata, H. *J. Photopolym. Sci. Technol.* **1991,** *4,* 497–507.

[10] Frêchet, J. M. J.; Fahey, J.; Lee, S. M.; Matuszczak, S.; Shacham-Diamand, Y.; MacDonald, S. A.; Willson, C. G. *J. Photopolym. Sci. Technol.* **1992,** *5,* 17–30.

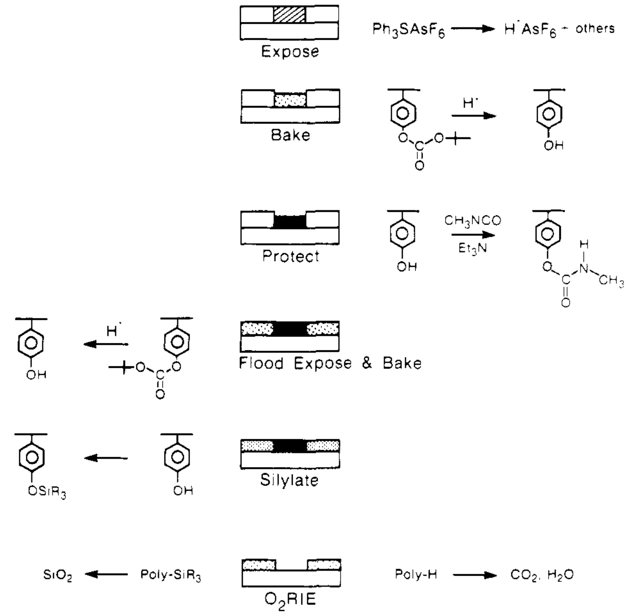
[11] Schellekens, J. P. W.; Visser, R.-J. Advances in Resist Technology and Processing VI. *Proc. SPIE* **1989,** *1086,* 220–228.

[12] Thackeray, J. W.; Bohland, J. F.; Pavelechek, E. K.; Orsula, G. W.; McCullough, A. W.; Jones, S. K.; Bobbio, S. M. Dry Processing for Submicrometer Lithography. *Proc. SPIE* **1989,** *1185,* 2–11.

[13] Hartney, M. A.; Johnson, D. W.; Spencer, A. C. Advances in Resist Technology and Processing VIII. *Proc. SPIE* **1991,** *1466,* 238–247.

0897-4756/92/2804-1364$03.00/0 © 1992 American Chemical Society

Scheme II. Positive Tone Dry Develop Process



film. Coopmans and Roland described the gas-phase silylation of a proprietary diazonaphthoquinone/phenolic matrix resin formulation yielding a negative tone, oxygen-plasma-developable resist.[15] This negative tone system (often referred to as DESIRE) is commercially available, has been evaluated for device fabrication,[16-18] and has been subjected to fundamental mechanistic studies.[19]

Our approach to obtaining a negative tone, oxygen-plasma-developable resist system has been to have the exposing radiation alter the chemical reactivity of the polymeric film, rather than only alter the diffusion properties of the film.[20,21] This concept is outlined in Scheme I using poly(4-((*tert*-butyloxycarbonyl)oxy)styrene) (PBOCST) as the polymeric system. In this approach, UV exposure and heating initiate the well-studied, acid-catalyzed thermolysis of this *tert*-butyl carbonate to a phenolic hydroxyl group.[22,23] As silylating agents (such as HMDS or (dimethylamino)trimethylsilane (DMATMS)) are known to react with phenolic hydroxyl groups and correspondingly to not react with *tert*-butyl carbonates, treating the exposed film with DMATMS vapor selectively and covalently incorporates an organosilicon species into the exposed regions of the film. When the silylated film is placed into an oxygen plasma, the regions of the film which do not contain the organosilicon species etch to substrate, while those areas containing silicon are not etched. As shown in Scheme I, this overall process generates a negative tone relief image.[21]

Scheme I yields a negative tone relief image because the UV exposure generates phenolic hydroxyl groups; these phenolic hydroxyl groups react with the silylating reagent and these regions do not develop in an oxygen plasma. In short, Scheme I describes a negative tone system because the organosilicon species is incorporated into the UV-exposed regions. With these concepts in mind, we have developed an image-reversal process to generate a positive tone, dry-developed image from the system shown in Scheme I. This positive tone process is outlined in Scheme II.[24] In the approach shown in Scheme II, the phenolic hydroxyl groups that are produced by the image exposure react with an organic reagent (that must not contain Si, Ge, Ti, etc.) to form a product that is thermally stable and unreactive toward silylation. Flood exposure and baking convert the remaining PBOCST to poly(4-hydroxystyrene) (PHOST). As in Scheme I, these phenolic hydroxyl groups react with the silylating agent to selectively incorporate silicon. When the processed film is exposed to an oxygen plasma, the regions that do not contain the organosilicon species are etched to substrate, while those areas containing silicon are not etched. Since the region which does not contain silicon is the area exposed in the imaging step, the process described in Scheme II generates a positive tone relief image. This paper will discuss the details of this positive tone, plasma-developable resist system.

Experimental Section

Materials. Poly[4-((*tert*-butyloxycarbonyl)oxy)styrene] was prepared as previously described by radical polymerization of 4-((*tert*-butyloxycarbonyl)oxy)styrene.[25] Triphenylsulfonium hexafluoroarsenate was purchased from Eastman Kodak. Methyl isocyanate (MIC), triethylamine (TEA), and (dimethylamino)trimethylsilane were purchased from Aldrich.

Imaging. A solution of PBOCST in cyclohexanone (15 wt %) containing triphenylsulfonium hexafluoroarsenate (3 mol %) was spin-coated for 30 s at 3000 rpm onto two different substrates: (1) silicon wafers for lithography and oxygen reactive ion etching (O_2 RIE) experiments and (2) sodium chloride plates for IR experiments. The resulting resist films measured 0.77–0.97 μm after drying at 90 °C for 4 min. The variation in film thickness was caused by using different batches of PBOCST which had different molecular weights. Imaging 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. All exposed wafers (both the image exposure and the flood exposure) were postbaked at 100 °C for 1 min. Carbamate formation experiments described in Figures 3–5 were performed in a Monarch Universal Process Module (100 °C wafer temperature, 35 °C chamber temperature), with a 2:1 mixture of methyl isocyanate and triethylamine. The reaction pressure was monitored with a capacitance manometer. Carbamate formation experiments described in Figure 2 were performed in a small laboratory vacuum oven (100 °C in center of chamber with 100 Torr of N_2) with a 4:1 mixture of methyl isocyanate and triethylamine. 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 DMATMS vapor to 200 Torr for 5 min. The temperature in the Yield Engineering Systems oven 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 etch machine used for O_2 RIE of the resist films was run at 0.25 W/cm^2 power density, 30 mTorr of O_2 pressure, 40 scc/min O_2 flow and −240-V bias.

---

(14) Yang, B.-J. L.; Yang, J.-M.; Chiong, K. N. *J. Vac. Sci. Technol.* **1989**, *B7*, 1729–1733.

(15) Coopmans, F.; Roland, B. Advances in Resist Technology and Processing III. *Proc. SPIE* **1986**, *631*, 34–39.

(16) Garza, C. M.; Misium, G.; Doering, R. R.; Roland, B.; Lombaerts, R. Advances in Resist Technology and Processing VI. *Proc. SPIE* **1989**, *1086*, 229–237.

(17) Nichols, D. N.; Goethals, A. M.; De Geyter, P.; Van den hove, L. *Microelectron. Eng.* **1990**, *11*, 515–520.

(18) Goethals, A. M.; Nichols, D. N.; Op de Beeck, M.; De Geyter, P.; Baik, K. H.; Van den hove, L.; Roland, B.; Lombaerts, R. Advances in Resist Technology and Processing VII. *Proc. SPIE* **1990**, *1262*, 206–218.

(19) Visser, R.-J.; Schellekens, K. P. W.; Reuhman-Huisken, M. E.; Van Ijzendoorn, L. J. Advances in Resist Technology and Processing IV. *Proc. SPIE* **1987**, *771*, 111–117.

(20) Ito, H.; MacDonald, S. A.; Miller, R. D.; Willson, C. G. U.S. Patent No. 4,552,833, 1985.

(21) MacDonald, S. A.; Schlosser, H.; Ito, H.; Clecak, N. J.; Willson, C. G. *Chem. Mater.* **1991**, *3*, 435–442.

(22) Ito, H.; Willson, C. G. *Polym. Eng. Sci.* **1983**, *23*, 1012–1018.

(23) Ito, H.; Willson, C. G.; Fréchet, J. M. J. U.S. Patent No. 4,491,628, 1985.

(24) Fréchet, J. M. J.; Ito, H.; MacDonald, S. A.; Willson, C. G. U.S. Patent No. 4,657,845, 1987.

(25) Fréchet, J. M. J.; Eichler, E.; Ito, H.; Willson, C. G. *Polymer* **1983**, *24*, 995–1000.

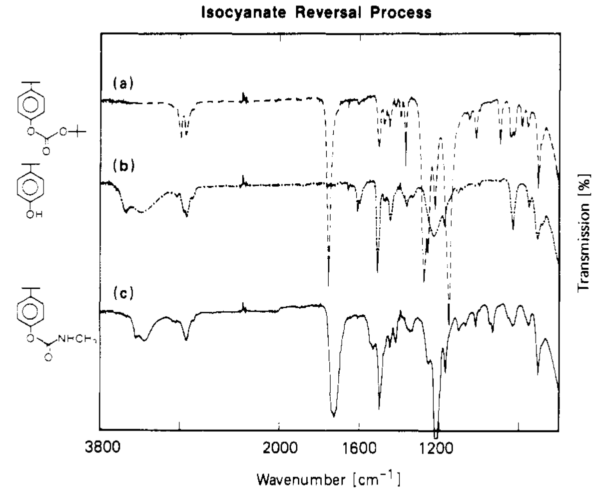


Figure 1. IR spectra of the isocyanate image reversal sequence described in Scheme II: (a) starting film of PBOCST/Ph_3SAsF_6; (b) after UV exposure (10 mJ/cm^2 at 254 nm) and postbake; (c) after treatment with MIC/TEA vapor for 20 min at 100 °C/300 Torr.

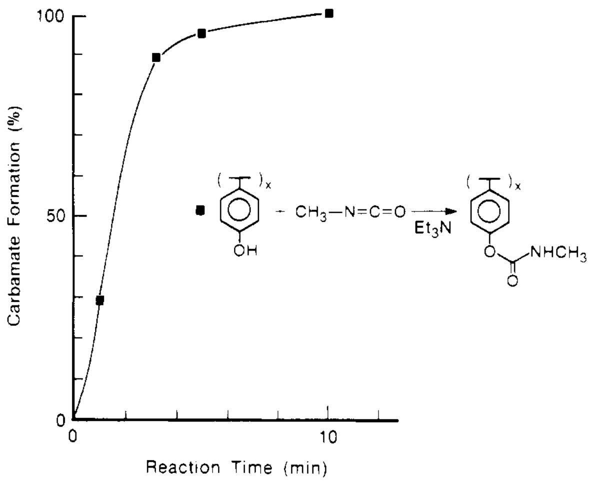


Figure 2. IR study on carbamate formation (monitoring absorbance at 1720 cm^{-1}) in a modified laboratory vacuum oven. The PBOCST/Ph_3SAsF_6 film was exposed to 10 mJ/cm^2 and baked at 100 °C. Films were treated with MIC/TEA (4:1) vapor at 100 Torr.

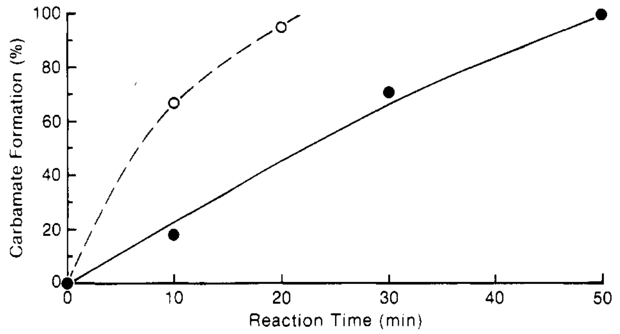


Figure 3. IR study on carbamate formation (monitoring absorbance at 1720 cm^{-1}) in a Monarch Universal Processing Module. The PBOCST/Ph_3SAsF_6 film was exposed to 10 mJ/cm^2 and baked at 100 °C. Films were treated with MIC/TEA (2:1) vapor at two pressures: ● = 200 Torr, ○ = 300 Torr.

The O_2 RIE rate of the carbamate region was 0.12 μm/min. In lithographic 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. 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.

Results and Discussion

Chemistry of Reversal Process. In comparing the negative tone, dry-develop process shown in Scheme I with the positive tone, image reversal process shown in Scheme II, one can see that the most of the chemical reactions are the same. The key difference between the two is the protection of the phenolic hydroxyl group that occurs in the reversal process. The reagent used for this protection step must meet several requirements: (1) it must react with phenolic hydroxyl groups to yield a product that is photochemically stable and inert toward silylation; (2) it must not contain silicon, tin, germanium, or any other element that forms a refractory oxide; (3) it must be volatile to allow for gas-phase delivery. While there are a variety of protection schemes that fulfill these general requirements (such as acylation or alkylation), we have used carbamate formation to accomplish this goal. As outlined in Scheme II, this image reversal process is based on the base-catalyzed reaction of a phenolic hydroxyl group with methyl isocyanate vapor. Methyl isocyanate vapor is toxic and should be handled with care.[26] Please see the Merck Index citation[26] prior to running the image reversal process described in Scheme II.

IR spectroscopy can be used to follow the catalytic photoregeneration of phenolic hydroxyl groups within the thin polymeric film and the subsequent reaction with methyl isocyanate. The IR spectra shown in Figure 1 provide spectroscopic support for the first three steps of the reversal process described in Scheme II. 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/cm^2 of 254-nm light and baked. Note the complete disappearance of the carbonate C=O absorbance at 1757 cm^{-1} and the appearance of the broad phenolic OH band (3400 cm^{-1}). Figure 1c shows the IR spectrum of the film after treatment with methyl isocyanate/triethylamine vapor. Note the appearance of the characteristic carbamate C=O absorbance at 1720 cm^{-1}. The IR spectra presented in Figure 1 are consistent with the events proposed in Scheme II.

IR spectroscopy was used to study the rate of carbamate formation in these thin polymer films. For these studies the PBOCST film was exposed to 10 mJ/cm^2 and baked to convert all of the carbonate groups to phenolic functionality. Figure 2 shows the rate of carbamate formation when the exposed and baked film was treated with methyl isocyanate/triethylamine vapor (100 Torr at 100 °C) in a modified vacuum oven. The data in Figure 2 show that 90% of the phenolic hydroxyl groups are converted to the corresponding carbamate after 3 min of reaction time.

While carbamate formation in this oven was quite rapid, this specific oven was not compatible with processing the 125-mm wafers required to perform lithographic evaluation of the image reversal process. Hence, the rate of carbamate formation was studied using the same single-wafer vapor delivery system (Monarch) that was used in our previously published vapor silylation studies.[21] Figure 3 shows the rate of carbamate formation when the exposed and baked film was treated with MIC/TEA vapor at 200 and 300 Torr in the Monarch system. For this study the Monarch hot plate (which holds the 125-mm wafer) was set at 100 °C, while the surrounding chamber was at room temperature. The data in Figure 3 show that even at 300 Torr, 18 min of reaction time is required to convert 90% of the phenolic

---

[26] *The Merck Index*, 11th ed.; Merck & Co., Inc.: Rahway, NJ, 1989; 6004.

Table I[a]

carbamate reaction conditions			after flood exposure and vapor silylation[e]	
pressure (Torr)	time (min)	carbamate[c] formed (%)	carbamate[c] remaining (%)	silyl ether[d] formed (%)
200	10	18	18	2
200	30	71	72	0
200	50	100	97	0
300	10	67	67	0
300	20	95	93	0
300[b]	20[b]	0	0	90

[a] All films, except the control film, were exposed with 10 mJ/cm^2 (254 nm) and baked for 60 s at 100 °C, liberating all of the phenolic hydroxyl groups. [b] A control film of unexposed PBOCST/onium salt. [c] Based on IR analysis of absorbance at 1720 cm^{-1}. [d] Based on IR analysis of absorbance at 918 cm^{-1}. [e] Flood exposure: 20 mJ/cm^2 at 254 nm, 100 °C/60 s postexposure bake. Vapor silylation: 5 min at 100 °C, 200 Torr of DMATMS.

hydroxyl groups to the corresponding carbamate. Obviously, the Monarch System was not optimized for this reaction. However, on the basis of the vacuum oven experiments that were discussed in the previous paragraph, carbamate formation can rapidly occur within the polymeric film.

The gas-phase protection reaction, used in the lithographic experiments to be discussed in the next section, was run for 20 min at 200 Torr in the Monarch system. Interpolation of the data in Figure 3 shows that these conditions should not lead to 100% protection of the phenolic hydroxyl groups but rather result in 45% carbamate formation. It would be most undesirable if these unreacted phenolic hydroxyl groups were to react with the silylating agent used in the next step, as this would introduce silicon into the regions that must be etched. The IR analysis shown in Table I demonstrates that these phenolic groups are not silylated as rapidly as the hydroxyl groups found in PHOST (generated from PBOCST). In this study, the films used for Figure 3 (containing varying amounts of unprotected phenolic hydroxyl groups) were subjected to a UV flood exposure and vapor silylation treatment to simulate the final lithographic process steps. Table I shows that only one of these films, the film containing the greatest number of unprotected phenolic hydroxyl groups, incorporated silicon. And in that film, only 2% of the available phenolic functionality underwent silylation. This implies that while it is possible to carry the carbamate formation reaction to completion, it is not necessary to do so for the image reversal process to function.

As a control, a film of unexposed PBOCST/onium salt was treated with MIC/TEA vapor, flood exposed, and subjected to the vapor silylation treatment. Table I shows that this film underwent significant silylation (90%). This demonstration is important, since the liberation of the phenolic hydroxyl group is an acid-catalyzed reaction and one might anticipate (prior to running the experiment) that residual triethylamine would prevent this process from occurring. Furthermore, we have previously reported that ppb levels of organic base in room air degrade the performance of acid-catalyzed, chemically amplified photoresist systems.[27] Therefore, it was reasonable to assume that the final deprotection step might not work at all.

There are at least two reasons why the final, acid-catalyzed cleavage of the *tert*-butyl carbonate can occur even after treatment with MIC/TEA. First, most of the triethylamine is removed from the film under vacuum prior to the flood exposure step. After the wafer is treated with MIC/TEA, that mixture is pumped out of the reaction chamber and the wafer stands under vacuum for 5 min before the UV flood exposure step occurs. Second, the high dose (in the flood exposure step) generates more than enough acid to cleave all carbonate units, and hence this reaction can still reach completion even if some acid molecules are neutralized by residual triethylamine. The UV flood exposure dose used in Scheme II is relatively high (20 mJ/cm^2), whereas the UV dose used for solvent development (in the case where we reported the ppb level contamination with amine) was in range 1–5 mJ/cm^2. While the IR data in Table I demonstrate the viability of Scheme II, it does not address the issue of image size control. No attempt was made to determine line-width control for the isocyanate reversal process.

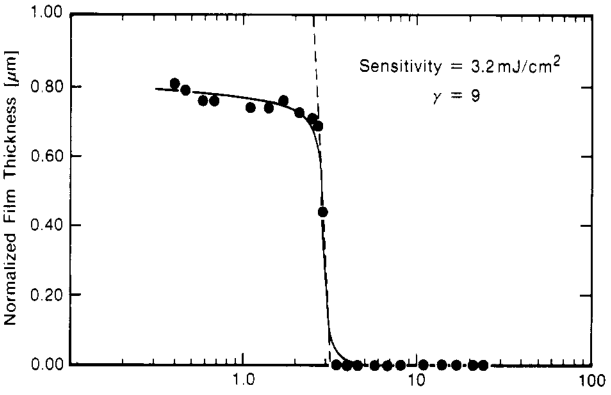


Figure 4. Sensitivity curve at 254 nm for the isocyanate reversal process described in Scheme II. PBOCST/Ph_3SAsF_6 films were postbaked at 100 °C for 1 min and treated with MIC/TEA vapor (20 min at 100 °C/200 Torr). The films were flood exposed (20 mJ/cm^2), baked (1 min at 100 °C), and silylated with DMATMS vapor (5 min at 100 °C/200 Torr). The films were developed with O_2 RIE.

The data in Table I also confirm that the carbamate functional group meets the previously discussed requirements of thermal stability, photostability, and lack of reactivity toward the silylating agent. Note that the percentage of carbamate within the films is not altered by the flood exposure and vapor silylation sequence.

Lithographic Evaluation of Reversal Process. The contrast curve for the dry-develop image reversal process outlined in Scheme II is shown in Figure 4. This figure is a plot of resist film thickness remaining after plasma development versus the image exposure dose, holding the conditions in the other processing steps constant. In this study, the imaged film was treated with MIC/TEA vapor (20 min at 200 Torr), flood exposed with 20 mJ/cm^2 (254 nm), treated with DMATMS vapor (5 min at 200 Torr), and developed with O_2 RIE. Figure 4 demonstrates that this scheme generates a positive tone, dry-develop system with a defined sensitivity of 3.2 mJ/cm^2 (at 254 nm) and a contrast of 9. The sensitivity of this image reversal process compares favorably with the previously reported value of 2.4 mJ/cm^2 for the negative tone system shown in Scheme I.[21]

Figure 5 shows the relief image generated by the dry-develop image reversal process outlined in Scheme II, when exposed with approximately 15 mJ/cm^2 on a Perkin-Elmer Micralign 500. All of the other processing conditions used to generate this relief image were the same as those used to produce the contrast curve shown in Figure 4. The scanning electron micrograph in Figure 5 demonstrates the

---

(27) MacDonald, S. A.; Clecak, N. J.; Wendt, H. R.; Willson, C. G.; Snyder, C. D.; Knors, C. J.; Deyoe, N. B.; Maltabes, J. G.; Morrow, J. R.; McGuire, A. E.; Holmes, S. J. Advances in Resist Technology and Processing VIII. *Proc. SPIE* **1991**, *1466*, 2–12.

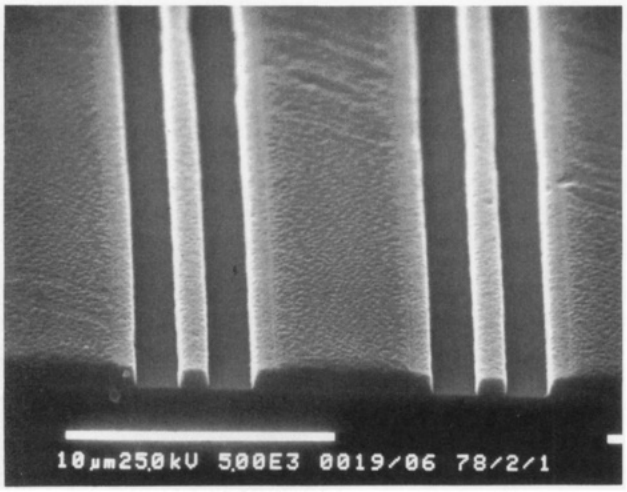


Figure 5. Scanning electron micrograph of images generated by the isocyanate reversal process described in Scheme II. The imaging exposure was performed on a Perkin-Elmer Micralign 500 with approximately 15 mJ/cm^2. Sample was rinsed with 6:1 buffered HF for 2 s after etching.

viability of this approach but does not address the ultimate resolution capability of this image reversal scheme. The resolution limits of this dry-develop image reversal process have not been studied.

Concluding Remarks

Two key features underlie the approach to plasma developable resists outlined in Schemes I and II. The first is the photochemical generation of reactive functional groups within a polymeric film, and the second is the reaction of these functional groups with the proper chemical reagent to ultimately obtain the desired oxygen plasma etch properties. If one desires an oxygen plasma etch barrier, then the chemical reagent should contain silicon, tin, germanium, or some other element that forms a refractory oxide. Correspondingly, if one desires the regions to be removed by etching, then one should use a chemical reagent composed of elements which form volatile oxides. The work described in this paper has used the acid-catalyzed generation of phenolic hydroxyl groups and the subsequent reaction with (dimethylamino)trimethylsilane or methyl isocyanate vapor to demonstrate this concept. However, the design concept contained in Schemes I and II should not be limited to just this small set of compounds. The synthetic chemical literature contains a variety of organometallic reagents, volatile organic reagents, and schemes designed to photochemically remove protecting groups.

In Schemes I and II, we have shown that the PBOCST/onium salt chemically amplified resist system can be dry-developed in an oxygen plasma to generate either a negative or a positive tone relief image. Previously, our laboratories have reported that the PBOCST/onium salt chemically amplified resist system can be developed with solvent to generate either a negative or positive tone relief image.[22,23] Thus, the PBOCST/onium salt chemically amplified resist system is a remarkably versatile imaging system as it can be plasma developed, as well as solvent developed, to yield images of either tone.

Acknowledgment. We thank J. T. Hucko for editorial assistance and N. K. Voke for technical assistance.

Registry No. MIC, 624-83-9; TEA, 121-44-8; O$_2$, 7782-44-7; poly[4-((*tert*-butyloxycarbonyl)oxy)styrene], 87261-04-9; triphenylsulfonium hexafluoroarsenate, 57900-42-2; (dimethylamino)trimethylsilane, 2083-91-2.

Synthesis and Characterization of Two New Quaternary Chalcogenides, CaYbInQ$_4$ (Q = S and Se), with an Olivine-Type Structure[†]

James D. Carpenter and Shiou-Jyh Hwu[*]

Department of Chemistry, Rice University, P.O. Box 1892, Houston, Texas 77251

Received July 24, 1992. Revised Manuscript Received September 18, 1992

Two new quaternary chalcogenide compounds, CaYbInQ$_4$ (Q = S and Se), were synthesized using a eutectic halide flux. The preliminary results from infrared spectroscopy experiments, using both DRIFTS and single-crystal transmittance methods, show no strong absorption bands in an extended infrared region (2–25 µm). These phases were structurally characterized by a single-crystal X-ray diffraction method. They crystallize in an orthorhombic crystal system with space group *Pnma* (No. 62) and $Z = 4$. The cell dimensions are $a = 13.639$ (2) Å, $b = 7.926$ (2) Å, $c = 6.503$ (2) Å, $V = 703.1$ (5) Å^3 for the sulfide compound and $a = 14.282$ (3) Å, $b = 8.247$ (2) Å, $c = 6.776$ (1) Å, $V = 798.1$ (5) Å^3 for the selenide compound. The single-crystal structure solutions of these chalcogenide analogues show that they adopt an olivine-type structure (Mg_2SiO_4). Structure refinements and chemical analysis suggest nonstoichiometry, which can possibly be attributed to cation mixing in an indium rich phase. The synthesis, structure characterization, and spectroscopy of the title compounds are discussed in this paper.

Introduction

The search for new materials with desirable optical properties has become important in recent years. In particular, a need has emerged for compounds that are candidates for use as long-wavelength infrared (LWIR) window materials, e.g., 8–12 µm (a transparent region in the earth's atmosphere).[1,2] It is apparent that there is a

---

[†] Presented at the inorganic chemistry poster session during the American Chemical Society Meeting, New York, NY, August 25–30, 1991.

[*] To whom correspondence should be addressed.

(1) (a) *Infrared Technology Fundamentals*; Spiro, I. J., Schlessinger, M., Eds.; Marcel Dekker, Inc.: New York, 1989. (b) Window and Dome Technologies and Materials I. Klocek, P., Ed.; *Proc. SPIE* **1989**, *1112*, and references therein. (c) Window and Dome Technologies and Materials II. Klocek, P., Ed.; *Proc. SPIE* **1990**, *1326*, and references therein.

0897-4756/92/2804-1368$03.00/0 © 1992 American Chemical Society