Experimental Techniques for Detection of Components Extracted from Model 193 nm Immersion Lithography Photoresists

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Extraction of small molecule components into water from photoresist materials designed for 193 nm immersion lithography has been observed. Leaching of photoacid generator (PAG) has been monitored using three techniques: liquid scintillation counting (LSC); liquid chromatography mass spectrometry (LCMS); and scanning electrochemical microscopy (SECM). LSC was also used to detect leaching of residual casting solvent (RCS) and base. The amount of PAG leaching from the resist films, 30−50 ng/cm^2, was quantified using LSC. Both LSC and LCMS results suggest that PAG and photoacid leach from the film only upon initial contact with water (within 10 s) and minimal leaching occurs thereafter for immersion times up to 30 min. Exposed films show an increase in the amount of photoacid anion leaching by upward of 20% relative to unexposed films. Films pre-rinsed with water for 30 s showed no further PAG leaching as determined by LSC. No statistically significant amount of residual casting solvent was extracted after 30 min of immersion. Base extraction was quantified at 2 ng/cm^2 after 30 s. The leaching process is qualitatively described by a model based on the inhomogeneities in resist films.

Introduction

Immersion lithography is an adaptation of traditional semiconductor microlithography where space between a photoresist coated silicon wafer and the final lens element of a lithographic exposure tool is filled with a liquid medium, which has a refractive index higher than air.[1] The higher refractive index of the liquid results in a larger process window in terms of depth of focus. The high-index fluid allows for the design of lenses with very high numerical apertures, thus providing higher resolution than would be possible with a dry system.[2,3] First proposed in the 1980s,[1−3] immersion lithography was not seriously considered until recently,[4] but has now become the primary technology plan for reaching the 45 nm node of the International Technology Roadmap for Semiconductors.[5,6] Water has been proposed as the ideal immersion fluid to be coupled with current 193 nm lithography technology because of its compatibility with current manufacturing techniques, its low absorbance ($\alpha_{193} = 0.036$ cm^{-1} base 10),[7] and high refractive index ($n_{193} = 1.437$).[8]

One of the initial concerns about incorporating water into the lithographic process was the potential effects of direct contact between the water and a photoresist film.[4] These effects included photoresist performance degradation from the dissolution of vital resist components into water, resulting in changes in the optical properties of the resist film and the water, and contamination of the lens system by the extracted components. The components of concern included residual casting solvent (RSC), photoacid generators (PAG), and base quenchers. Since the extraction of photoresist components posed such a serious concern, methods to detect the amounts of extracted material were needed. To detect the small quantities of material expected to be found in water samples from immersion experiments,[9] three different measurement techniques were proposed: liquid chromatography/mass spectrometry (LCMS), scanning electrochemical microscopy (SECM), and liquid scintillation counting (LSC).[10,11]

Due to concerns regarding the long-term effects of perfluorinated sulfonates on the environment, highly sensitive liquid LCMS analytical methods have been developed. Preliminary experiments[12] as well as those described here take advantage of these established techniques to measure the amount of perfluorobutane sulfonate (PFBS), a common anion used in photoacid generators (PAGs), that leaches from a photoresist into the immersion medium (IM). The second

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approach was to use several modes of SECM to monitor changes in pH and ion concentrations at the resist/IM interface. The final technique highlighted in this work is the use of radiochemical analysis in which ^{14}C-labeled versions of the photoresist components were synthesized and analyzed for leaching in immersion water.[11] LSC of ^{14}C-labeled materials is a useful technique for establishing the presence of a specific photoresist component in a film and accurately determining the amount of that component in the water as a function of different processing steps.[13] In this paper, the methodology, results, and limitations of these three techniques for the study of leaching processes at resist/IM interfaces are presented. From the available data, a qualitative model of the resist/IM interface is proposed.

Experimental Section

SECM/LCMS/XPS Experiments. Milli-Q water (18 MΩ cm) was used for all sample preparations and analyses. The scanning electrochemical microscopy setup and electrode fabrication have been described elsewhere.[14] Square wave voltammetry was performed using a CHI 600 electrochemical instrument (Austin, TX). The working electrode used in voltammetry experiments was a 25 μm diameter Hg drop plated onto a Pt microelectrode as described previously[15] and a Pt wire was used as a counter electrode. Potentials were referenced versus a Ag/AgCl electrode. pH measurements were made by measuring the potential between a Sb microelectrode (100 μm diameter) and a SCE using a high-input impedance potentiometer. Conductivity measurements were performed using a modification of the method originally described by Johnson and Enke[16a] and adapted by Calhoun et al.[16b] Data acquisition and pulse generation were accomplished using home-built software and electronics based on previous designs.[16] A more detailed description of the application of DC pulses to measure solution conductivity at solid/liquid interfaces is given elsewhere.[17] LCMS analysis of water samples was performed by Exygen Research (3058 Research Drive, State College, PA, 16801). X-ray photoelectron spectra were collected using a PHI 5700 ESCA system.

The cell used in this work has been described previously.[10] A 6.5 mm diameter hole was drilled in a Teflon well. A quartz plate was used as the bottom of the well, resulting in a cell volume of 100 μL and a surface area in contact with water of 0.33 cm^2. Samples were irradiated from below the quartz plate such that the incident light and the electrode were perpendicular to the substrate plane. 193 nm exposure was conducted using a Lambda Physik (Ft. Lauderdale, FL) excimer laser (26 kV, 120 mJ/cm^2, 10−50 ns pulse length, 1 to 10 Hz pulse rate). Light was directed through a fiber optic cable onto the underside of the conductivity cell, resulting in an average energy output per pulse ranging from 1 to 2 mJ/cm^2. Flood exposure was performed using a 3500 W unfiltered EXFO Novacure lamp (Mississauga, Ontario, Canada).

Synthesis of ^{14}C-Compounds. *Propylene Glycol Methyl Ether Acetate-Carbonyl-^{14}C (PGMEA) (Chart 1 **I**).*[13a,18] 1-Methyoxy-2-propanol (5.20 g, 57.7 mmol) and acetyl chloride (2.30 g, 29.3 mmol) were added to 50 mL of pentane in a 100 mL three-neck round-bottom flask with a condenser. Acetic chloride-carbonyl-^{14}C (Sigma Chemicals Corp., 500 μCi, specific activity (SA) 2.5 mCi/mmol) was cooled with a dry ice/2-propanol bath and washed with acetyl chloride (3.00 g, 38.2 mmol) in 7 mL of pentane. The washing was added to the flask and transfer was completed with two 5 mL pentane rinses. The flask was immersed in an ice bath and triethylamine (7.35 g, 72.6 mmol) was added dropwise with vigorous stirring. After complete addition of the base, the reaction was warmed to room temperature and stirred for 1 h. The resulting solution was washed with water (7.5 mL), saturated sodium dihydrogen phosphate solution (11.5 mL), and saturated sodium bicarbonate solution (11.5 mL). The aqueous layer was discarded and the organic layer was dried over anhydrous magnesium sulfate. Pentane was removed by distillation and nonlabeled PGMEA (8.04 g, 60.8 mmol) was added to the distillation flask. The product was collected at 143−147 °C. The yield was 63% and the purity was greater than 99% by gas chromatography. The specific activity (SA) was 35.65 ± 0.01 μCi/g.

*^{14}C-Ethyl Lactate (Chart 1 **II**).*[13a] Diethyl ether (10 mL) containing CuBr (0.17 g, 1.18 mmol) was transferred to a 50 mL round-bottom flask with a condenser. Dicyclohexylcarbodiimide (10.52 g, 51. mmol) was added to the flask and stirred. An ampule of ethanol-carbonyl-^{14}C (Sigma Chemicals Corp., 500 μCi, SA of 3.8 mCi/mmol) was cooled with dry ice/2-propanol and the contents was transferred with a solution of 3 mL of diethyl ether and 1 mL of ethanol followed by two washings (3 mL and 2 mL) of diethyl ether. The mixture was refluxed for 2 h. After cooling the mixture, 6.50 g of an aqueous 70.72 wt % lactic acid (4.60 g, 51.0 mmol) solution was added to the flask. Nonlabeled s(-)-ethyl lactate (8.00 g, 67.7 mmol) was transferred to the flask and the mixture was refluxed for 10 min, then cooled to room temperature, and dried over anhydrous magnesium sulfate at 5 °C for 12 h. Ether was removed by distillation and the resulting solution was cooled and pressure-filtered with nonlabeled s(-)-ethyl lactate (12.0 g, 102 mmol). The filtrate was distilled and the product collected at 150−155 °C. The distillation flask was washed with s(-)-ethyl lactate (5.00 g, 42.5 mmol) and the distillation was repeated. The yield of ethyl lactate was 71% and purity was greater than 99% by gas chromatography. The SA was 48.31 ± 0.01 μCi/g.

*^{14}C-Triphenylsulfonium Perfluorobutanesulfonate (TPS Nonaflate) (Chart 1 **III**).*[19,20] *(1) ^{14}C-Labeled Diphenyl Sulfoxide*. Break-seal ampules containing ^{14}C labeled benzene (Sigma-Aldrich, Inc., 1.4 mCi, SA of 10.3 mCi/mmol) were cooled in an ice bath. The ampules were ruptured and rinsed with 20 mL of benzene. The benzene was transferred to an oven-dried 100 mL three neck round-bottom flask under nitrogen. Thionyl chloride (0.6 mL, 8.2 mmol) was added and the flask was cooled to 0 °C before triflic acid (3.1 mL, 35.3 mmol) was added. The ice bath was removed after 1 h and the reaction stirred for 24 h at room temperature. The reaction was quenched by pouring the solution over ice and neutralizing with sodium bicarbonate. The neutralized solution was extracted with four 30 mL portions of methylene chloride. The combined organics were dried over magnesium sulfate. The solution was

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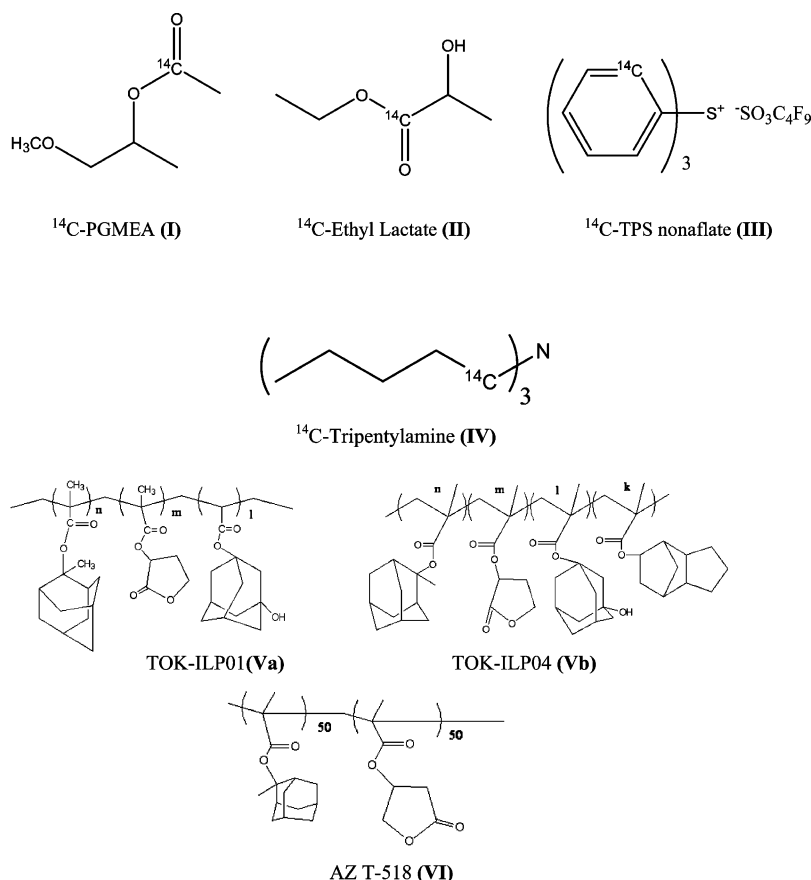
Chart 1



filtered to remove the magnesium sulfate and distilled to remove methylene chloride and benzene. The residue was dissolved in boiling hexanes and decanted away from the hexane insoluble yellow oil. The yellow oil was extracted with boiling hexanes once more. The combined hexanes solutions were cooled in an ice bath and diphenyl sulfoxide precipitated out as a white solid that was isolated by filtration and dried under vacuum. Yield: 1.32 g (80%). mp: 69−72 °C. ^{1}H NMR ($CDCl_3$, ppm): δ 7.4 (m, 6H), δ 7.6 (m, 4H).

(2) Triphenylsulfonium Bromide (^{14}C-TPS Bromide). A 875 mg (36 mmol) portion of powdered magnesium was suspended in 20 mL of dry diethyl ether in an oven-dried 500 mL three-neck flask equipped with a Teflon-coated stir bar, reflux condenser, and dropping funnel. A positive pressure of dry nitrogen was maintained throughout the reaction. The dropping funnel was charged with 5.9 g (37.5 mmol) of bromobenzene and 10 mL of diethyl ether, of which 1−2 mL was added immediately. An iodine crystal was added to initiate the reaction and the remaining bromobenzene solution was added dropwise at a rate to maintain reflux. The solution was allowed to stir overnight under a nitrogen atmosphere. The ether solvent was removed by heating in an 80 °C bath in vacuo with stirring for 2 h, giving a semisolid brown residue. Freshly distilled heptane, 50 mL, was added to the flask, which was removed by heating in an 80 °C bath in vacuo. This was repeated three times. Dry heptane, 100 mL, and 50 mL of dry benzene were added to the flask and the reaction was heated to reflux. A 1.32 g (6.5 mmol) portion of diphenyl sulfoxide was dissolved in 30 mL of freshly distilled benzene and added dropwise to the refluxing phenylmagnesium bromide mixture. After addition was complete, the mixture was maintained at reflux overnight, followed by cooling to 0 °C with an ice bath. HBr, 80 mL of 25%, was added slowly to maintain a temperature below 20 °C and allowed to stir overnight. The aqueous phase was collected and the organic phase washed with two 30 mL portions of 5% HBr. The combined aqueous phases were extracted with four 30 mL portions of dichloromethane. The organics were dried over $MgSO_4$ and removed in vacuo to give a tan powdered product. Yield: 0.324 g (15%). mp = 284−286 °C. ^{1}H NMR ($CDCl_3$, ppm): δ 7.6 (m, 9H), δ 7.8 (m, 6H).

(3) Triphenylsulfonium Perfluoro-1-butanesulfonate (^{14}C-TPS Nonaflate). In a 100 mL round-bottom flask were placed 0.324 g (0.94 mmol) of TPS bromide and 0.319 g (0.94 mmol) of potassium perfluoro-1-butanesulfonate. To this mixture were added 10 mL of deionized water and 10 mL of nitromethane. After the mixture was stirred vigorously for 1 h, the phases were separated and the organic phase extracted 3 × 30 mL of deionized water followed by drying over $MgSO_4$. Removal of solvent in vacuo gave a viscous oil. After the oil was extracted with ice cold diethyl ether several times, a crystalline product was isolated. Filtration gives the desired product as a white solid. Yield: 0.23 g (43%). mp = 88−89 °C. ^{1}H NMR ($CDCl_3$, ppm): δ 7.6 (m, 9H), δ 7.8 (m, 6H). ^{19}F NMR ($CDCl_3$, reference = $CFCl_3$, ppm): δ −80.8 (3F, CF_3), −114.4 (2F, $CF_3\mathbf{CF_2}CF_2CF_2SO_3^-$), −121.1 (2F, $CF_3CF_2\mathbf{CF_2}CF_2SO_3^-$), −125.6 (2F, $CF_3CF_2CF_2\mathbf{CF_2}SO_3^-$). The SA was 8.60 ± 0.02 μCi/g.

^{14}C-Tripentylamine (Chart 1 ***IV****). (1) Tosylation of ^{14}C-Labeled 1-Pentanol.* A break-seal ampule containing ^{14}C-labeled 1-pentanol (American Radiolabeled Chemicals, Inc., 1 mCi, SA of 5 mCi/mmol) was cooled in a dry ice-isopropyl alcohol bath. The ampule was ruptured and rinsed with 2.5 mL of 1-pentanol. The 1-pentanol (2.5 mL, 23 mmol) was distilled from calcium hydride directly into the oven-dried three-neck round-bottom flask used for the tosylation reaction. Dichloromethane (20 mL) and pyridine (2.3 mL, 28 mmol) were added to the flask. The flask was cooled in an ice bath before

tosyl chloride (4.83 g, 25.3 mmol) was added. The reaction was warmed to room temperature and stirred overnight and then filtered through a Celite plug to remove the pyridinium chloride that formed. The solution was then extracted with water (3 × 15 mL) and once with 20 mL of brine solution. The organic layer was dried over $MgSO_4$ and removed in vacuo to give a clear oil. The oil was used for the next reaction without any further purification.

(2) ^{14}C-Tripentylamine. The oil from the tosylation reaction was added to a 100 mL round-bottom flask with dipentylamine (14.1 mL, 69 mmol) and K_2CO_3 (6.36 g, 46 mmol). The flask was heated and held at 100 °C overnight, then cooled, and filtered through a Celite plug to remove any solids. The plug was then rinsed with ethyl acetate. The organics were dried over $MgSO_4$ and the ethyl acetate was removed in vacuo. The unreacted dipentylamine was removed by vacuum distillation at 37 °C at 540 mTorr. The tripentylamine (2.4 g, 46% yield) was isolated at 66−69 °C at 540 mTorr. ^{1}H NMR ($CDCl_3$, ppm): δ 2.4 (t, 6H), 1.2−1.5 (m, 18H), 2.4 (t, 9H). The SA was 49.8 ± 0.1 μCi/g.

Resist Formulation/Film Preparation. Model 193 nm photoresist materials were provided by Tokyo Ohka Kogya (TOK) Co. (Japan) and AZ Electronic Materials (Somerville, NJ). The TOK resists, TOK-ILP01 and TOK-ILP04, were formulated from acrylic ter-polymer and tetra-polymer resins, Chart 1 **Va** and **Vb**, TPS nonaflate and triethanolamine, obtained from Acros Co. (Morris Plains, NJ), which were dissolved in a 60/40 mixture of PGMEA and ethyl lactate. The AZ formulation, T-518, included an acrylate polymer, Chart 1 **VI**, TPS nonaflate and diethanolamine dissolved in ethyl lactate. Additional unlabeled PGMEA and ethyl lactate were obtained from Aldrich Co. (Milwaukee, WI).

The resists were formulated with a 6 wt % total solids concentration, a PAG loading of 5 wt % of the polymer, and a base loading of 0.3 wt % of the polymer for a total mass of 20 g. Three samples of each resist were made, one with an aliquot of ^{14}C-labeled casting solvent, one with ^{14}C-TPS nonaflate, and the last with ^{14}C-tripentylamine replacing the above-mentioned bases. The TOK resists had 0.5 g of ^{14}C-PGMEA; the resulting SA of the PGMEA in the TOK resists was 1.54 μCi/g. The same amount of ^{14}C-ethyl lactate was added to the Clariant resist for a final ethyl lactate SA of 1.31 μCi/g. For the other samples only radiolabeled PAG and base were used in the formulations. Unlabeled resist formulations were prepared in a similar manner with appropriate materials.

Resist films were cast onto 2 in. silicon wafers using a Headway Research, Inc. EC101DT spin coater at a speed of 2000 rpm for 30 s. The films were then subjected to a post apply bake for 90 s at 115 °C, resulting in a film thickness of approximately 150 nm. Film thickness was measured using a J. A. Woollam M-2000 variable angle spectroscopic ellipsometer. Ellipsometric data were collected over a spectral range of 400−1000 nm and fit using WVASE32 software from Woollam.

^{14}C-Component Extraction Experiments. Wafers coated with resists containing radiolabeled components were placed into a 2 in. glass Petri dish lid and covered with a 7 mL puddle of deionized (DI) water for contact times ranging from 30 s to 30 min. The water was then transferred to a scintillation vial containing 12.5 mL of Scintiverse BD scintillation cocktail (Fisher Scientific Co., Hampton, NH) and decay events were counted over 20 min using a Beckman 1801 liquid scintillation counter for the RCS and PAG samples. A Beckman LS 6500 counter was used to count the base samples for 4 to 5 h. The scintillation counter also measured the extent to which the signal from the decay events was quenched by components in the vials. A sample of scintillation cocktail containing 7 mL of DI water was also counted to determine the level of background radiation present. To measure the amounts of radiolabeled components remaining in the films after immersion, the film was dissolved in 5 mL of unlabeled casting solvent. The wafer and Petri dish were rinsed two times with 5 mL and one time with 4.5 mL of casting solvent to complete transfer of the sample into a scintillation vial and counted as described above.

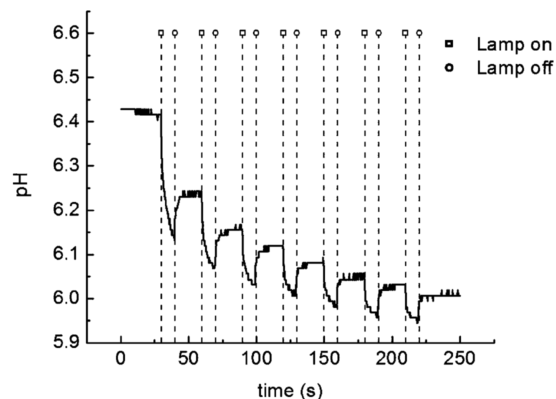


Figure 1. pH measurements of liquid layer above a film of **Va**. A decrease in pH occurs when Hg lamp is turned on and the pH increases upon shutting the lamp off.

The PAG extraction experiment on **Va** was repeated twice with slight variations. First, a 248 nm excimer laser was used to flood expose the resist films immediately after immersion. In the second repetition, a 30 s prerinse immersion was performed before immersing four films from 30 s to 5 min. The prerinse on **Va** was also performed for the base extraction. Thickness dependence on PAG and base leaching was measured using films of **Vb** with thicknesses ranging from approximately 140−50 nm that were immersed for 30 s. A custom-built polycarbonate immersion cell based on a previously published design was used to improve time resolution to 10 s.[5] A 4 mL aliquot of DI water was injected into the 2 mm high space in the cell over films of **VI** and was allowed to sit for a specified time before being collected with a 10 mL syringe.

Results

Scanning Electrochemical Microscopy. Three modes of scanning electrochemical microscopy (SECM)—potentiometric, voltammetric, and conductometric—were used to analyze the diffusion of photoacid and photoacid generator from a photoresist into a water layer. In SECM, the response of an ultra-microelectrode is monitored as a function of distance from a substrate where the species of interest is being generated. In the potentiometric mode, an antimony fiber with a diameter of 100 μm was sealed in glass and used to measure changes in pH close to a resist-coated wafer submerged in water. The use of antimony as a pH-sensitive electrode is well-established and Sb microelectrodes have been used previously in SECM methodology.[21] pH measurements of water in contact with **Va** containing 5 wt % PAG are shown in Figure 1. The Sb microelectrode was positioned approximately 50 μm above the resist and the pH was measured as a function of time and UV exposure. Upon flood exposure using a Hg lamp, the pH of the water layer decreases. The solution pH increases slightly when the lamp is turned off, indicating that the acidic species generated during exposure are diffusing away from the electrode. The

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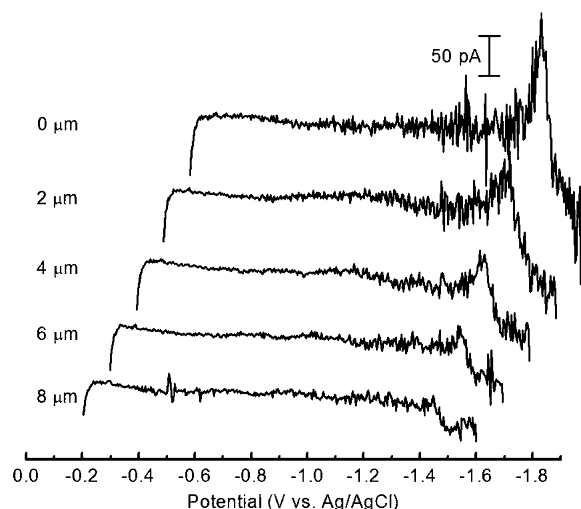

Figure 2. Square wave voltammograms at a Hg hemisphere microelectrode above a film of **Va**. The peak at −1.45 V vs Ag/AgCl is the reduction of triphenylsulfonium. The distance between the electrode and the film is noted in the legend.

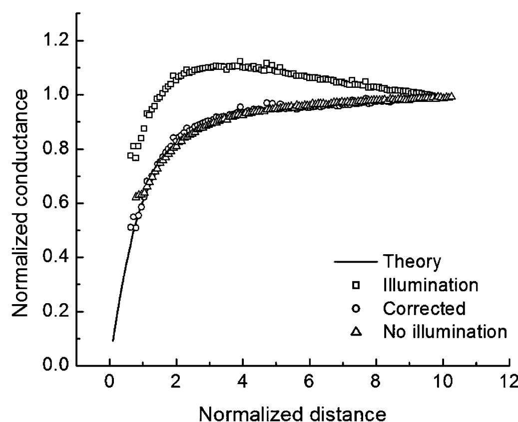

Figure 3. Conductivity approach curves of 4% PAG loaded **VI** immersed 18 MΩ cm water. Triangles denote approach in the dark. Squares denote raw approach curve under illumination with 193 nm light (1 Hz pulses, 1.5 mJ/cm^2). Circles denote approach under illumination after correction for conductivity increase due to background. Solid line is theory for negative feedback.

fact that the pH of the exposed solution does not return to its original value suggests that the photoacid generator is present in the water layer by the time the cell is exposed to UV light. Repeat experiments show the same qualitative behavior but have varying initial pH values, which is most likely due to difficulties in measuring the pH of pure, unbuffered water accurately. The transient nature of this experiment and fluctuating background make precise pH measurements difficult and the determination of moles of H^+ hard to quantify.

In the voltammetric SECM mode, the solution concentration of photoacid generator was measured by triphenylsulfonium cation (TPS) reduction at a Hg drop microelectrode. The electrochemistry of TPS has been reported previously[22] and a reduction wave occurs at −1.45 V versus a Ag/AgCl reference electrode. Square wave voltammograms of water in contact with a wafer coated with **Va** and PAG (5%) are shown in Figure 2, where the Hg drop microelectrode was positioned at various distances from the wafer surface. As the microelectrode approaches the surface, the reduction wave for TPS grows. While the voltammograms are a qualitative confirmation that TPS is leaching from the resist, it is difficult to quantify the amount for two reasons: the current due to TPS reduction is only slightly larger than the background current and the true geometry of the Hg drop is not known. At the distance marked 0 μm, it is not clear whether the tip of the Hg hemisphere is touching the surface or if the drop has been compressed between the glass of the microelectrode and the wafer, which could result in a larger current since a larger area of the wafer would be probed. Despite the inability to obtain quantitative data, both pH and voltammetric measurements clearly show the presence of PAG and/or photoacid in the IM.

Both transient and steady-state conductometric SECM modes were used to investigate changes in ion concentration at the resist/IM interface. In the steady-state measurements, the solution conductivity was measured as a function of distance from the surface. Figure 3 shows an approach curve where the conductance is normalized by the conductance remote from the surface and the distance is normalized by the radius of the tip (in this case 12.5 μm). The theoretical response (solid line) for conductance approach curves has been previously shown to follow the expected feedback for an approach to an insulating surface.[23] As the microelectrode approaches an insulating surface, the surface blocks diffusion and migration pathways to the tip, minimizing the conductance measured at the tip. In an inhomogeneous solution, such as when ions would leach from the surface, the increase in local conductance around the tip would result in a normalized conductance that is higher than the theory predicts. Approaching films of **VI** with 4% PAG loading follows the theory until the tip is approximately 10 μm from the film. This abrupt, distance independent, conductivity is due to geometric effects, where the microelectrode plane is not parallel to the substrate plane. In this case, the glass sheath of the microelectrode touches the glass substrate, limiting the distance of closest approach. The squares in Figure 3 show an approach curve recorded while the cell was exposed to 1.5 mJ/cm^2 193 nm light pulses at a rate of 1 Hz. There is a clear increase in conductance as the electrode approaches the film. If the electrode is placed remote from the film, however, and the solution conductance is monitored as a function of time, it increases under these exposure conditions. The source of this increase is unclear but is likely due to the geometry of the experimental setup, where the laser beam is incident on the electrode surface. Excitation of the platinum electrode surface may induce photoemission and water electrolysis can occur, resulting in what appears to be a conductance change.[24] A background scan was obtained by performing an approach curve remote from any surface, such that only the time-dependent behavior would be recorded. Correcting the approach curve for this background effect, one finds that even under illumination the

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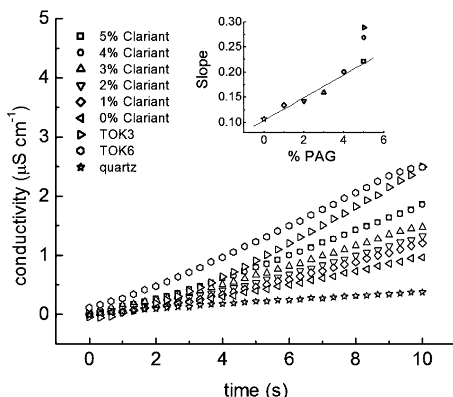

Figure 4. Change in conductivity of 18 MΩ cm water over various substrates as indicated in the legend. A 100 μm diameter Pt electrode was positioned 100 μm from the substrate and the cell was irradiated with 190 mJ/cm^2 of 193 nm light over 10 s. BICON conditions: $E_{app} = 0.5$ V, $\tau_p = 40$ μs, $R_f = 96$ MΩ. Inset is plot of the slopes of the conductivity versus time plot.

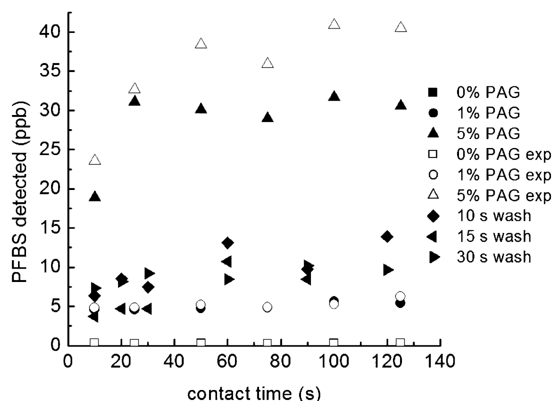

Figure 5. Amount of perfluorobutanesulfonate detected in 100 μL drops in contact with films of **VI**. PAG loading, exposure, and rinse time are shown in the legend.

approach follows the theory for a homogeneous solution (circles in Figure 3).

Transient conductance measurements were used to monitor changes in ion concentration in the water layer during exposure of the resist to 193 nm light. A 100 μm diameter Pt electrode was placed at a fixed distance (100 μm) from the surface and conductance was measured as a function of time. Under these conditions, and assuming a limiting molar conductivity of 100 S cm^2 mol^{-1},[25] the minimum detection limit of TPS nonaflate is on the order of 1 μM. Conductance measurements of water in contact with unexposed resist films with PAG loading are not statistically different from similar measurements over resist films with no PAG. Note that the time required to position the microelectrode, which in this case is 30 s, determines the earliest point at which a conductance measurement can be made. Figure 4 shows the conductance response when various resist formulations were irradiated with 190 mJ/cm^2 of 193 nm light over 10 s (10 Hz pulse rate). Greater PAG loading yields a higher conductance during exposure and slopes of the solution conductance versus time plots follow a linear dependence with PAG loading in the film (Figure 4 inset). The two TOK films, **Va** and **Vb**, with 5% PAG loading, have similar slopes that are approximately 30% higher than the corresponding 5% AZ formulation.

LCMS Analysis. The dependence of PAG and photoacid leaching on resist/IM contact time was analyzed using LCMS detection of the nonaflate anion. Aliquots of water, 100 μL, were left in contact with exposed and unexposed films of **VI** with PAG loadings of 0−5% from 10 to 120 s (Figure 5). As expected, no nonaflate was observed in the water samples that were in contact with films containing no PAG. The amount of nonaflate in the water was dependent on the resist formulation and a nearly five times increase in nonaflate was observed between the 1% and 5% PAG loaded films. The 5% PAG formulation displayed an increase in PAG concentration until a near steady-state value was obtained after a contact time of 30 s. One cannot observe a significant difference between the exposed and unexposed 1% PAG-loaded films; however, the amount of nonaflate leached from the exposed 5% film was approximately 20% higher than the corresponding unexposed film. To confirm that PAG was leaching out of the film only during the first few seconds of contact with water, resist-coated wafers were bathed in deionized water for 10 to 30 s and air-dried prior to performing the water contact/leaching experiment. As shown in Figure 5, washing unexposed wafers for 10 s decreases the amount of nonaflate detected by approximately 80%. Within the accuracy of this measurement, increasing the wash time to 30 s does not reduce the amount of PAG leached form the film any further.

Liquid Scintillation Counting. Liquid scintillation counting was used to provide quantitative information regarding leaching of components from photoresists. Unlike the previous methods described, detection by LSC is limited not by the physiochemical properties of the analyte or the establishment of well-defined procedures but rather by the facility with which one can synthesize a radioactive form of the analyte. For this study, liquid scintillation counting was used to measure the number of radioactive decay events from ^{14}C-labeled photoresist components leached into immersion water.[26] The mass in grams of labeled material in a sample was determined using eq 1

$$Mass = \left(\frac{CPM - CPM_b}{Efficiency}\right)\left(\frac{1\ \mu\text{Ci}}{2.22 \times 10^6\ \text{DPM}}\right)/SA \qquad (1)$$

where *CPM* is the counting rate per minute of decay events, CPM_b is the level of background radiation, *Efficiency* is determined from the amount of quenching measured by the LSC instrumentation, and the specific activity, *SA*, is given in μCi/g.[27,28]

LSC measurements of the amount of residual casting solvent in films of **Va** cast onto 2 in. wafers had an average

(25) An estimate of 100 S cm^2 mol^{-1} for the limiting molar conductivity of TPSPFBS was determined by comparing the conductivity response of TPSPFBS solutions to that of KCl solutions under identical conditions. The limiting molar conductivity of KCl in water is known; see Lind, J. E., Jr.; Zwolenik, J. J.; Fuoss, R. M. *J. Am. Chem. Soc.* **1959**, *81*, 1557.

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(28) Horrocks, D. L. In *Liquid Scintillation, Science and Technology*; Academic Press: New York, 1976.

of 424 ± 27 CPM with a counting efficiency of 93%. This corresponded to an average RCS mass of 177 ± 12 μg. For the amount of PAG in **Va** on a 2 in. wafer, an average of 473 ± 10 CPM with an efficiency of 88% was obtained, which corresponds to 25 ± 0.5 μg of PAG in the film. Measurements of the amount of base in **Va** resulted in an average *CPM* value of 179 ± 5 with an efficiency of 90% for a total of 1.48 ± 0.04 μg of tripentylamine in the films.

The leaching of RCS was determined from LSC measurements of immersion water. For extraction times from 30 to 1800 s, no statistically detectable amount of RCS was seen in the immersion water from any of the formulations tested. A detection limit for each was determined by eq 2

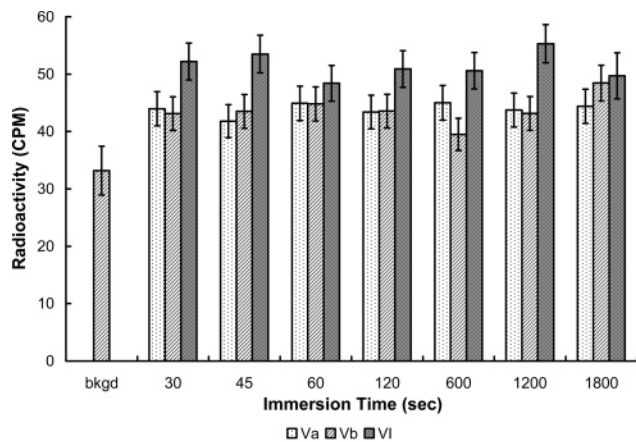
$$Mass_{\min} > \left(\frac{2\sqrt{CPM_b \times t}}{t}\right)\left(\frac{1\,\mu\text{Ci}}{2.22 \times 10^6\,\text{DPM}}\right)/SA \quad (2)$$

where t is the total time in minutes that the background level was counted and the first term on the right-hand side is the 95% error limit of the CPM_b measurement.[26,29] Under the conditions of these experiments, no more than 0.8 μg of RCS could have been extracted from a 2 in. wafer. Normalized to surface area, this corresponds to a limit of 40 ng/cm^2. An increase in the sensitivity of these measurements by an order of magnitude would require either an equal increase in the magnitude of the SA of the radiolabeled casting solvent or a sample counting time of approximately 33 h.

The results of the ^{14}C-PAG extraction experiments from unexposed films of all three resists showed a significant signal in each of the immersion water samples. Figure 6a shows that, after only 30 s of immersion, a statistically significant amount of ^{14}C-PAG was detected. The amount of PAG extracted from each resist then remained essentially constant after 30 s for increasing immersion times up to 30 min. Figure 6b shows leaching from **VI** occurring primarily in the first 10 s of immersion. For a counting efficiency of 91%, the amounts of PAG extracted from films of **Va** and **Vb**, averaged over immersion time, was determined to be 30 ng/cm^2. Under the same conditions, 52 ng/cm^2 of PAG leached from the **VI**. Detection limits for the PAG extraction experiments were determined from eq 2 to be 7 ng/cm^2.

Figure 7 compares leaching of PAG and photoacid from unexposed and exposed samples of **Va** with 5% PAG loading, respectively, as determined by LSC. Contrary to LCMS measurements, no statistically significant difference between the amount of PAG extracted from the exposed resist and that extracted from the unexposed samples was observed using LSC, but it should be noted that LCMS could detect only the anion and LCS could detect only the benzene ring on the cation. Accurate measurement of photoacid leaching using this method would require the synthesis of a PAG with a radiolabeled anion. Several films of **Va** were also subjected to a 30 s prerinse before immersion. Figure 8 shows that the LSC measurements of the prerinse water reported radioactivity levels comparable to those reported for the initial PAG extraction experiments, but the activity level of the immersion water was no greater than background.

(29) Personal communication with Dr. Lorenzo Sadun, Department of Mathematics, The University of Texas at Austin.



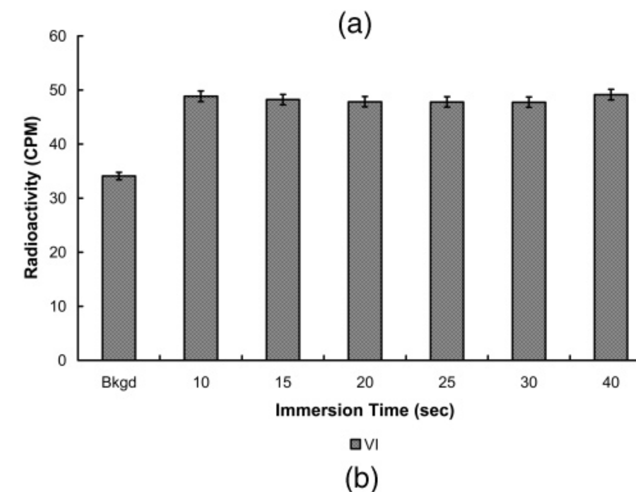


Figure 6. Radioactivity in CPM from LSC measurements of immersion water containing extracted ^{14}C-PAG vs immersion time.

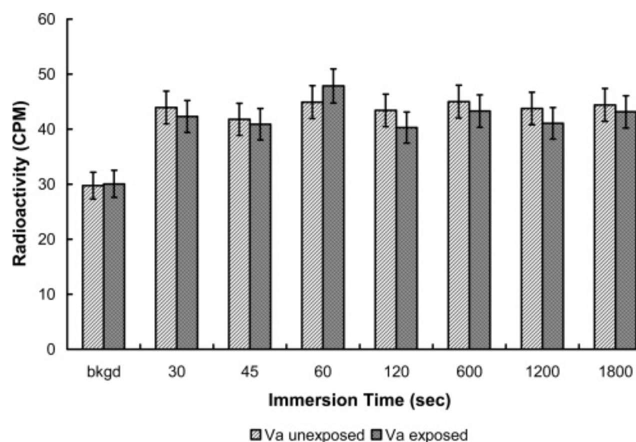


Figure 7. Radioactivity in CPM from LSC measurements of ^{14}C-PAG extracted from exposed and unexposed films of **Va** in immersion water vs immersion time.

This shows that essentially all the PAG that is extracted from a photoresist film is removed within the first 30 s of immersion. Figure 9 shows the thickness dependence of PAG extraction from films of **Vb**. The radioactivity levels in the immersion water stay constant with decreasing film thickness, indicating that PAG is only being extracted from the surface of the film.

The results of the ^{14}C-base extraction experiments are summarized in Figure 10. The radioactivity level in the immersion water shows that after 30 s of immersion a small, but detectable amount of base was extracted from each resist.

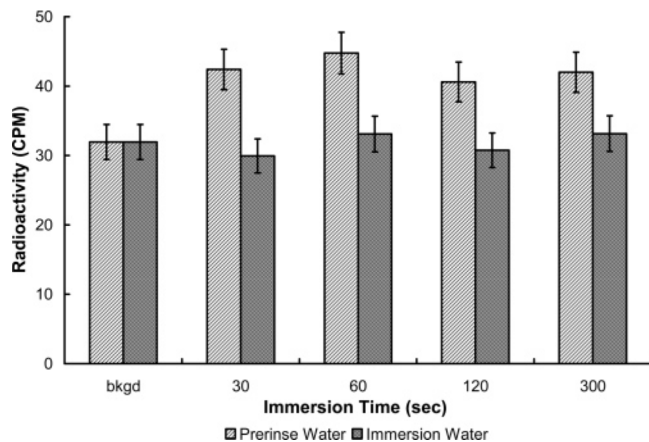


Figure 8. Radioactivity in CPM from LSC measurements of ^{14}C-PAG extracted from films of **Va** in 30 s pre-rinse water and immersion water vs immersion time.

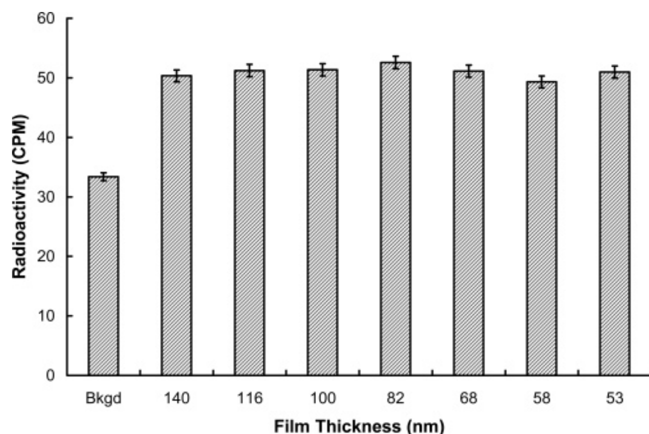


Figure 9. Radioactivity in CPM from LSC measurements of ^{14}C-PAG extracted from films of **Vb** over decreasing thickness during 30 s of immersion.

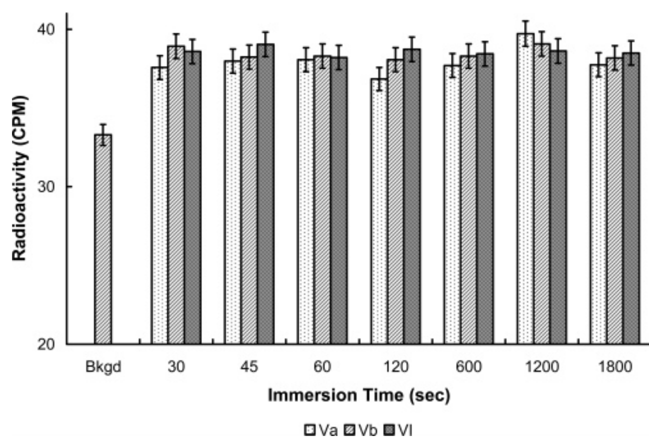


Figure 10. Radioactivity in CPM from LSC measurements of immersion water containing extracted ^{14}C-tripentylamine vs immersion time.

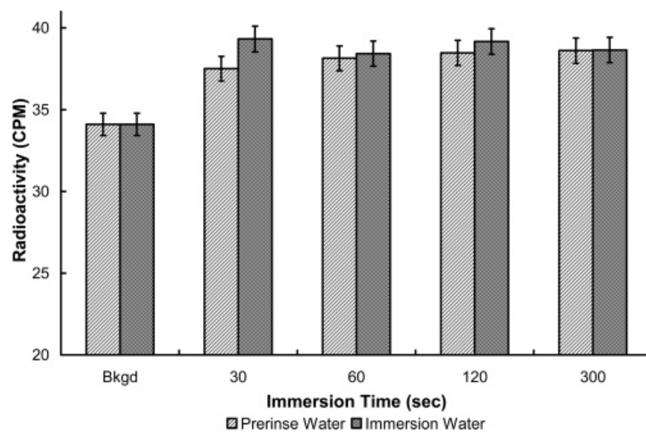
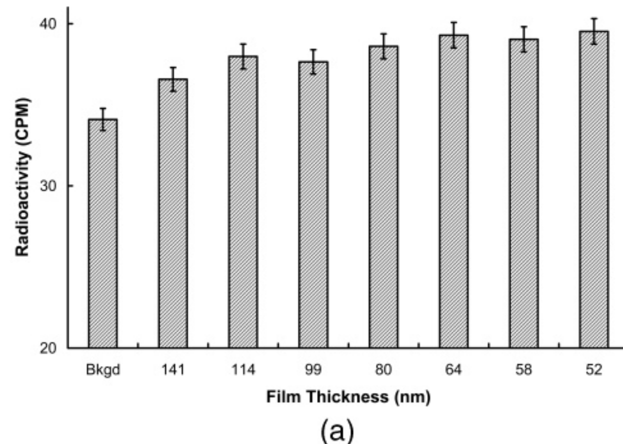


Figure 11. Radioactivity in CPM from LSC measurements of ^{14}C-tripentylamine extracted from films of **Va** in 30 s of pre-rinse water and immersion water vs immersion time.



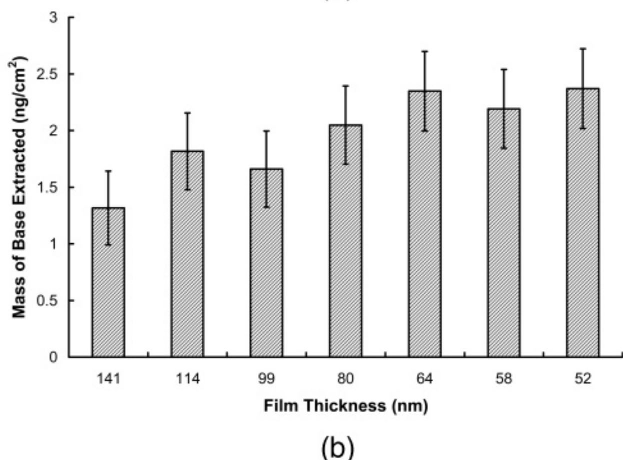


Figure 12. (a) Radioactivity in CPM from LSC measurements of ^{14}C-tripentylamine extracted from films of **Vb** vs film thickness during 30 s of immersion. (b) Mass per unit surface area of extracted base vs film thickness.

The level did not increase with immersion time, again indicating that the extraction is complete within 30 s. The amount extracted, with a counting efficiency of 96% and averaged over immersion time, was 0.04 μg or 2 ng/cm^2 of ^{14}C-tripentylamine from each resist. Sub-30 s measurements showed no detectable signal from labeled base in the immersion water until 25 s of immersion time.

Figure 11 shows that LSC measurements of prerinse and immersion water from films of **Va** had similar levels of radioactivity from extracted base. The level again did not increase with immersion time and was consistent with those shown in Figure 10. Figure 11 indicates that the base, unlike the PAG, will continue to be extracted from a film during subsequent immersion. This was confirmed by rinsing a film five times and detecting a level of extracted base consistent with the data in Figures 10 and 11 for each rinse. Results from thickness dependent base extraction measurements are shown in Figure 12. As the thickness of the **Vb** films decreased, the radioactivity level in the immersion water increased, Figure 12a, indicating that an increasing mass of tripentylamine was extracted, as shown in Figure 12b. This

is opposite to what one would expect for bulk diffusion of base through the film, suggesting the possibility of a thin film effect.

Discussion

The extraction of components from model 193 nm photoresists has been studied with three different analytical techniques. While each method provided qualitative evidence of extraction, quantification was made difficult by several factors. The SECM modes all allowed for real-time monitoring of the resist/IM interfacial region and, in combination, differentiated between the leaching of PAG, photoacid, and other photo products. However, the sensitivity limit of SECM is in the micromolar region, which is not sufficient for the samples measured. LCMS has parts per billion sensitivity limits for the PFBS anion, but is indifferent to the counterion and thus cannot differentiate between PAG and photoacid. LSC methods provide the opportunity to investigate multiple photoresist components, depending on synthetic capability and the availability of radiolabeled precursors. Detection limits are set by the amount of radiolabeled material used and the time invested in the counting procedure. Using highly radioactive samples and very long counting times provides very high, tunable sensitivity. However, the synthesis of ^{14}C-isotope labeled chemicals for LSC requires a significant commitment.

The challenge of accurate quantification becomes apparent when the results of LCMS are compared to those of LSC. The result from the former method, analyzing 100 μL drops, indicates that an order of magnitude less PAG was extracted from **Vb** than what was detected by the latter, analyzing 7 mL baths. To probe this discrepancy, several additional experiments were carried out. First, a nominally 100 ng/mL sample of radiolabled TPS nonaflate was prepared and analyzed by both LSC and LCMS. LCMS detected a concentration of 74 ng/mL and the concentration determined by LSC measurements was 105 ng/mL, demonstrating that the two techniques provide comparable results within about 20% accuracy. In the second experiment, an extraction was performed using the full wafer immersion procedure and this solution was analyzed using LCMS. The amount of extracted PAG detected was 30 ng/cm^2. In the last, 100 μL drops were analyzed by LSC. Samples containing just one drop showed no detectable signal from labeled PAG, but a sample containing six drops collected from different areas of the same film did. This amount was again consistent with the above measurements from LSC. This indicates an error in the analysis of extremely small samples and led to the use of LSC as the primary method of leaching quantification.

Results from previous studies[30] of concentration gradients and diffusion in photoresist films support the observations from this work. A modified Fujita-Doolittle solvent diffusion model developed to generate residual casting solvent concentration profiles in a resist film showed a significant decrease in the RCS concentration at the resist surface relative to the bulk value after post application bake (PAB) of a spin-coated wafer.[13a,31] This results in densification of the resist film which reduces the mass transport rate at the surface, leading to the expectation that very little RCS could be extracted from any resist film. A similar inhomogeneity has also been seen in the PAG concentration profile. The PAG concentration profile throughout the film depends on the nature of the resist and the physicochemical properties of the PAG. Early work showed that polar PAGs such as triphenylsulfonium hexafluoroantimonate tended to show a depletion at the surface of a resist film formulated with nonpolar polymers such as polystyrene.[32] More recent work using near edge X-ray absorption fine structure showed that ionic PAGs with high fluorine content tend to aggregate to the surface of resist films.[33] As the PAG used in this study is similar to those used in the latter work, it is expected to aggregate at the surface and be more susceptible to extraction. Also, the amounts of PAG extracted from the resists are consistent with what would be expected based on previously published values of diffusion coefficients for PAGs and photoacid generators.[34] By assuming a homogeneous distribution of PAG throughout the film, an upper limit of 4−6 nm is estimated for the depth from which PAG is leached.

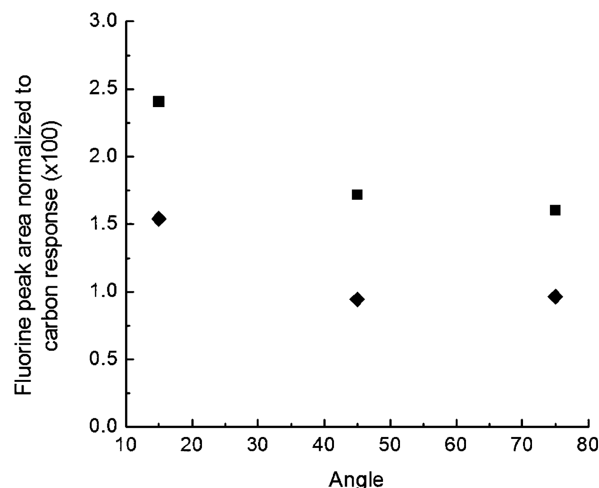


Figure 13. XPS analysis of fluorine content in wafers coated with **V** both washed (♦) and unwashed (■). The fluorine signal was normalized by the amount of carbon detected.

Preliminary studies using XPS are given in Figure 13. A film of **VI** with 5% PAG loading was coated onto a wafer which was split in half. One-half of the wafer was bathed in water for 30 s. Relative amounts of fluorine in the film were obtained by assuming a constant carbon concentration and normalizing the fluorine signal by the carbon signal. In both the washed and unwashed samples, the fluorine signal

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decreases with increasing angle, suggesting a higher fluorine concentration at the surface than in the bulk of the film. As expected, the washed sample displays lower fluorine signals at all angles relative to the unwashed sample.

Conclusions

Scanning electrochemical microscopy, liquid chromatography/mass spectrometry, and liquid scintillation counting were used to analyze leaching phenomena from model resists for 193 nm immersion lithography. Qualitative confirmation of PAG and photoacid leaching is observed using all techniques. While the LCMS technique was capable of providing quantitative results for PAG extraction, only the LSC method was able to do so for all three photoresist components studied. In the discrepancy between the two techniques, the LSC results showed greater PAG extraction. Therefore, the LSC results were used for quantification so that measurements of the amounts of each component extracted were consistent and would represent at least a worst case scenario among all of the results. As such, the amount of PAG leaching from a resist film was 30−50 ng/cm^2, depending upon formulation. Base leaching was also quantified at 2 ng/cm^2, independent of the formulation. No statistically significant residual casting solvent was seen to be extracted from the resists. The behavior of leaching as a function of immersion time suggests that PAG leaching occurs only at the surface and that, after a 30 s rinse of a film, no additional leaching is observed for upward of 30 min. Base leaching also occurs within the first 30 s of immersion, but unlike the PAG, it continues to be leached from the film during subsequent immersions. The differences in the behavior of the PAG and base leaching suggest that the base is extracted from these resist films through a more complex mechanism than simply being rinsed from the surface, as the PAG appears to be.

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