Epoxidized Perfluoropolyethers: A Route to Hydrophobic, Negative-Tone Photoresists

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ABSTRACT: The synthesis, formulation, and wafer level processing conditions of a heavily fluorinated hydrophobic photoresist was demonstrated. The synthesis is based on terminal epoxy modification of commercially available perfluoropolyethers. Structural characterization shows that terminal epoxide can open during the synthetic process, but in a simple formulation has a negligible effect on photoresolution of the photoresist. Formulation into a traditional photoresist requires careful selection of appropriate cosolvents to ensure solubility of the hydrophobic epoxy and hydrophilic photoacid generator while attaining adequate coating quality. Formulation processing conditions are presented and the chemical resistance of the resist through aggressive processing steps is demonstrated. Wafer level patterning using traditional photolithographic tools illustrates the applicability of the formulation and process conditions for traditional resist or microfluidic applications. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 4636–4644, 2012

Key words: resists; lithography; fluoropolymer; hydrophobic

INTRODUCTION

Hydrophobic materials typically fall into the class of nonpolar materials including hydrocarbons, silicones, and fluorinated materials. These surfaces create a thermodynamically unfavorable interface for water causing it to interact more strongly with itself than the surface. This manifests itself in contact angle measurements where hydrophobic surfaces have static water contact angles of greater than 90°. Patterned hydrophobic materials can be used to control regional wettability of fluids which has been shown to aid in directed assembly of simple devices. For example, organic transistors can be made by spin coating an organic semiconductor solution in the presence of prefabricated nonwetting structures. In the nonwetting areas, the organic semiconductor fluid is forced to the wetting regimes, forming the desired semiconductor pattern.[1] Other demonstrated examples in device fabrication also use directed assembly techniques.[2–11]

Blanket hydrophobic films are common; however, it is more challenging to create patterned hydrophobic surfaces. Traditional photolithography is used to pattern metals, ceramics, and plastics in microelectronic device fabrication. Combining the patterning capability of photolithography with a blanket coated hydrophobic coating offers a simple route to creating a thick film (>500 nm), hydrophobic patterned surface. There are several commercially available options for blanket coated fluorinated surfaces from commercial vendors using spin coating.[12] To pattern this material, a resist is patterned over the fluoropolymer followed by a dry etch step to create a patterned hydrophobic surface.[13]

To maintain hydrophobicity after patterning, common processing conditions should be considered when choosing between silicones, hydrocarbons, or fluorinated materials. While silicones such as polydimethylsiloxane (PDMS) can also create hydrophobic surfaces, they become hydrophilic when exposed to an oxygen plasma. The oxygen plasma step is typical of photoresist processing and a hydrophilic SiO_2 surface is formed by plasma oxidation of the silicone.[14,15] This leaves fluorinated materials and hydrocarbons as more suitable candidate materials. Since fluorinated materials are more commonly used as chemically resistant, hydrophobic surfaces, our focus is directed towards this class of materials.

New materials allowing direct lithographic patterning could be developed by incorporating hydrophobic functionalities into resist materials. Examples include trifluoromethylation of bisphenol A derivatives[16] or 157 nm resists.[17] These materials are not considered due to insufficient fluorination necessary to create a robust, hydrophobic surface. An example of a heavily fluorinated resist has been reported and does not suffer from typical resist formulation issues such as component solubility.[18] However, in their system, resin curing was accomplished using scanning probe lithography rather than traditional photolithography precluding the use of hydrophilic onium photoacids.

Perfluoropolyethers are unique, commercially available starting materials with high fluorine content that can be converted into a photoresist by epoxidation of terminal alcohols. Unlike poly(tetrafluoroethylene)s, perfluoropolyethers are liquids and can be dissolved in many organic solvents, and compounded with organic polymers such as polyethers,[19] polyurethanes,[20] polyesters,[21] and polyolefins.[22] Previous work has shown the ability to create acrylate functionalized perfluoropolyethers, the ability to photocure and formulate with free-radical photoinitiators *en route* to microfluidics device fabrication.[23] We report herein the utilization of an epoxy functionalized perfluoropolyether, simple formulations, and photolithographic processing conditions. This report will discuss the challenges in utilizing perfluoropolyethers as traditional photoresists and how their properties are unique from typical photoresists.

EXPERIMENTAL

Chemicals

All chemicals were purchased from the vendors in parentheses and used without further purification unless otherwise noted: Fluorolink D (Solvay-Solexis, Brussels, Belgium), 1*M* potassium *tert*-butoxide in *tert*-butanol (Sigma-Aldrich, St. Louis, MO), *tert*-butanol (Sigma-Aldrich, St. Louis, MO), epichlorohydrin (Sigma-Aldrich, St. Louis, MO), 1,4-bis(trifluoromethyl)benzene (BTFB; TCI, Oakwood), H-Galden ZV60 (Solvay-Solexis, Brussels, Belgium), Galden ZT130 (Solvay-Solexis, Brussels, Belgium), α,α,α-trifluorotoluene (TFT; Sigma-Aldrich, St. Louis, MO), 3-(trifluoromethyl) acetophenone (Sigma-Aldrich, St. Louis, MO), α,α,α-trifluoro-*m*-tolunitrile (Sigma-Aldrich, St. Louis, MO), 1,3,5-tris(trifluoromethyl)benzene (Sigma-Aldrich, St. Louis, MO), 2-chlorobenzotrifluoride (Sigma-Aldrich, St. Louis, MO), 4-methylbenzotrifluoride (Sigma-Aldrich, St. Louis, MO), 2,5-bis(trifluoromethyl) bromoben- zene (Sigma-Aldrich, St. Louis, MO), 2-fluorobenzotrifluoride (Sigma-Aldrich, St. Louis, MO), 3-methylbenzotrifluoride (Sigma-Aldrich, St. Louis, MO), 1-hexanol (Sigma-Aldrich, St. Louis, MO), 1-pentanol (Sigma-Aldrich, St. Louis, MO), 1-butanol (Sigma-Aldrich, St. Louis, MO), and 2,2,3,4,4,4-hexafluorobutanol (HFB; Sigma-Aldrich, St. Louis, MO).

Triarylsulfonium hexafluoroantimonate (mixed salts, Aldrich) was vacuum distilled to a white solid to remove propylene carbonate and stored in the refrigerator to retard any thermal or photochemical degradation.

Synthesis

A solution of Fluorolink D (400 g), 1.0*M* potassium *tert*-butoxide in *tert*-butanol (440 mL, 1.5 equiv.), and *tert*-butanol (400 mL) was stirred at 40°C for 1 h under nitrogen. This solution was slowly added over the course of an hour to a stirring solution of epichlorohydrin (314 mL, 10 equiv.) and *tert*-butanol (200 mL) at 80°C under nitrogen. Following the addition, the reaction was allowed to proceed for 2–24 h under nitrogen. During this time, a salt precipitate formed. Once the reaction completed, the mixture was cooled, then filtered by decanting the solution onto a medium flow rate filter paper removing residual salt. The mother liquor was diluted with Freon 113 ($\sim$ 50% volume) and washed several times with water. The organic phase can then be passed through an alumina plug (activated, neutral, Brockmann 1, $\sim$ 150 mesh) using Freon 113 as the mobile phase. After reduction of the excess solvent by rotary evaporation, the product was filtered through a 0.45 μm polyethersulfone filtration disk yielding a slightly yellow oil (yields routinely range from 40 to 50%). This process was replicated for batches A and B.

For batch C, slight modifications to the workup procedure were made. First, before filtration through medium flow rate filter paper, the reaction mixture was allowed to separate into two distinct phases. The top phase (C-1) was an amber colored liquid. The bottom slurry (C-2) was lighter in color and also had the formed salt precipitate. Both phases could be diluted with Freon 113 ($\sim$ 50% volume) and passed through an alumina plug using Freon 113 as the mobile phase. Reduction of solvent and filtration through a polyethersulfone filter proceeded as previously mentioned.

Processing tools

All processing at the coupon level was done on one inch silicon coupons coated with SU8-5 (Microchem) and processed through postexpose bake according to recommended process conditions. For coating, we used a G3P-8 Spincoater (Specialty Coating Systems, Cookson Electronics). For softbake, post expose bake, and hardbake, a programmable VWR Hotplate/Stirrer was used. For expose, a Blak-Ray longwave UV lamp (Model B-100 AP/R) or an OAI Hybralign Series 200 aligner was used.

All processing at the wafer level was done on eight inch silicon wafers coated with SU8-5 (Microchem). For spin coating, a Laurell Model WS-400B-8NPP/Lite/HPD spincoater was used. For softbake and post expose bake, a Brewer Scientific hotplate (Model no. CEE-1110) was used. For expose, an OAI Hybralign Series 200 aligner was used. For hardbake a Blue M electric oven was used.
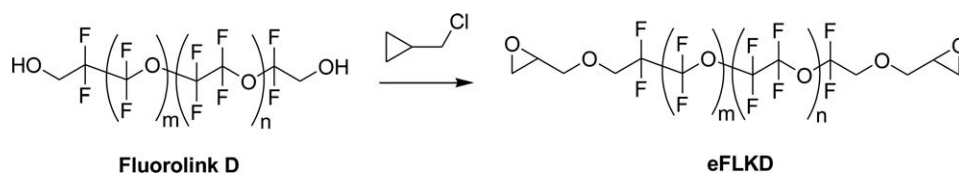
Formulation and processing conditions

eFLKD photoresist formulation

24.48 g 1,4-bis(trifluoromethylbenzene) (BTFB)
6.12 g 2,2,3,4,4,4-hexafluoro-1-butanol (HFB)
0.164 g triarylsulfonium hexafluoroantimonate, mixed salts
5.236 g Fluorolink-D epoxy

Scheme 1 Epoxidation of perfluoropolyether alcohol using epichlorohydrin.

An example of this formulation has an 80 : 20 ratio (w : w) of 1,4-bis(trifluoromethylbenzene): 2,2,3,4,4,4-hexafluoro-1-butanol, 15% solids, and 3% photoacid. The substrate for coating was a Si wafer with an SU-8 underlayer processed through the post expose bake processing step (95°C, 2 min is recommended by Microchem for SU8-5). A layer containing the Fluorolink D epoxy formulation was spin-coated using the following process: 100 rpm/3 s dispense, 10 s ramp to 1000 rpm/60 s coating spin. After coating the wet film, the substrate was softbaked at 90°C for 10 min. Exposure through a glass photomask was done on an OAI Hybralign Series 200 aligner (total exposure = 600 mJ/cm², measured at 365 nm). After exposure, a postexpose bake was done (90°C/2 min) and the wafer was cooled for 10 min at room temperature. The unexposed areas of the Fluorolink D film were then developed off with 1,4-bis(trifluoromethylbenzene) (30 s spray) followed by an ethyl lactate rinse (90 s). Final crosslinking of the film was done with a 170°C/30 min hardbake.

Characterization

Fourier transform infrared (FTIR) samples of the various batches were analyzed in transmission on

silicon coupons. To more closely examine the weak peaks in the C—H and O—H region of the IR spectra, spectra were collected that intentionally over-absorbed the C—F region. Additional spectra were collected in transmission on a Spectra-Tech IRus FTIR microscope using a Cassegrain objective with a mercury cadmium telluride (MCT-A) detector. Infrared spectra at a spectral resolution of 4 cm⁻¹ were obtained from Fourier transforms of 256 coadded interferograms. Other transmission methods such as diamond cell or salt plate could be used instead.

The NMR samples were analyzed using a 400 MHz Bruker NMR. For sample preparation, 0.8 mL of the perfluoropolyether sample was added to 0.1 mL Freon 113 and 0.1 mL of CDCl₃ then transferred to a 5 mm NMR tube. The ¹H-NMR spectrum was run at a 400 MHz resonance frequency, the ¹³C-NMR spectrum was run at 100 MHz resonance frequency and the ¹⁹F NMR spectrum was run at 282 MHz resonance frequency.

The hydrophobic photoresist develop experiments were done by liquid injection gas chromatography-mass spectrometry (GC/MS) using an Agilent 6890N/5973 Inert GC/MS.

Time of flight secondary ion mass spectrometry (TOF-SIMS) analysis used a Physical Electronics
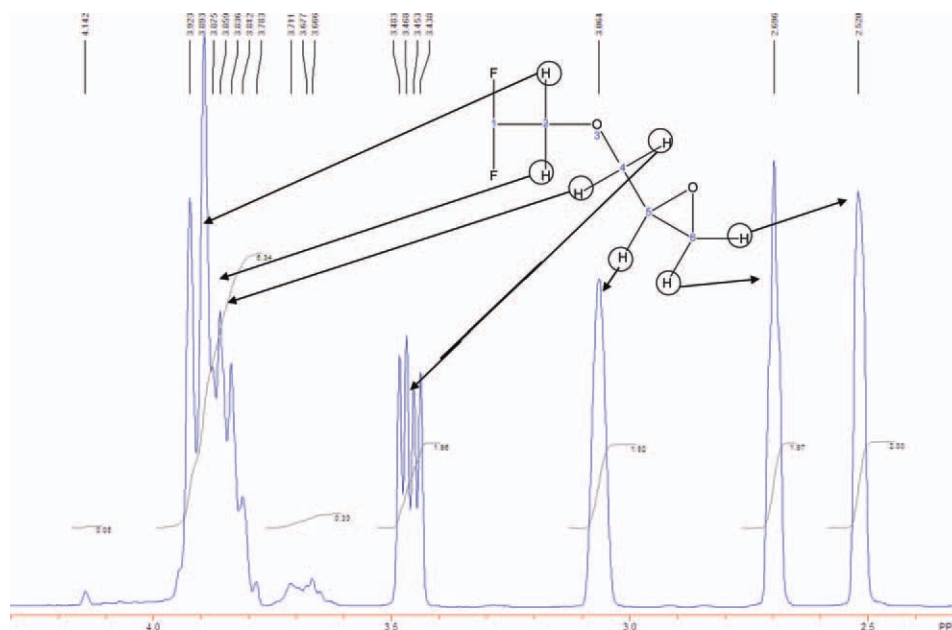

Figure 1 ¹H-NMR assignments on eFLKD product from Batch C-1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
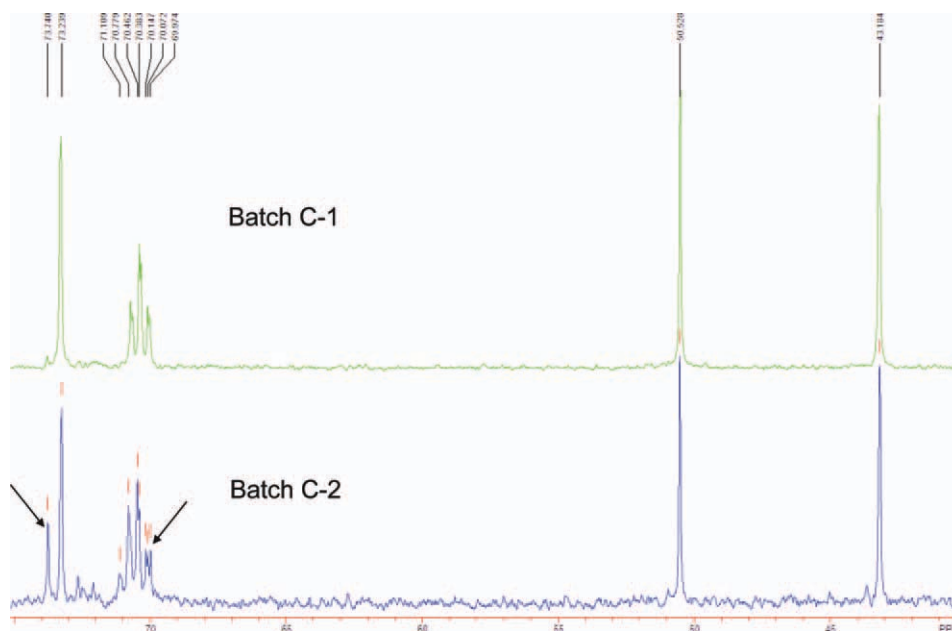
Figure 2 ^{13}C-NMR of batches C-1 (top) and C-2 (bottom). Batch C-2 has a larger than expected integration in the ^{1}H-NMR at 3.9 and 3.7 ppm which is accompanied by an intensity increase of ^{13}C-NMR resonances at 73.6 and 69.9 ppm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TRIFT II time of flight-secondary ion mass spectrometry instrument with the following analysis parameters: primary ions = Ga; beam voltage = 15 keV, beam current = 0.6 nA; bunched = yes; gun aperture = 3; contrast diaphragm = 0; and mass range = 2–2000 amu.

RESULTS AND DISCUSSION

Chemical structure

Slight modification to an existing synthetic pathway was used in the preparation of an epoxidized perfluoropolyether (eFLKD, Scheme 1).[24] Starting from commercially available Fluorolink D, epoxidation of terminal alcohols is used to create an epoxy perfluoropolyether. This general approach is suitable to other commercially available perfluoropolyethers with varying molecular weights and end group chemistry.

Chemical structure of the synthesized eFLKD product was first characterized using NMR. In particular, epoxide conversion was characterized since this attribute should have a significant effect on photoresolution and chemical resistance. The presence of the epoxide ring is clearly evident from the three resonances at 2.6, 2.7, and 3.1 ppm (Fig. 1). The resonance centered at 3.4 ppm is one of the two nonequivalent protons on the CH_2 resonance between the epoxy and ether link (labeled as C4 in the model shown in Fig. 1). The other proton on this carbon is found near 3.9 ppm. The two protons on the C2 carbon, as labeled in Figure 1, are also found near 3.9 ppm. Integration of the peaks in the proton spectrum was done using one of the epoxide protons as a reference and setting that value to two which assumes that both ends of the Fluorolink D are completely epoxidized. These assignments are in agreement with the literature.[24]

Batch C produced two products (C-1 and C-2) which varied structurally and were fairly simple to separate during workup as described in the Experimental section. The resonance at 3.9 ppm would be expected to represent six proton resonances but integrates to 6.34 in batch C-1. Additionally, there is a resonance centered near 3.7 ppm that integrates to 0.33 protons. It is observed in C-1 that integrate at 3.9 ppm is consistently closely equal to 6 + the integral of the peak at 3.7 ppm.

It is also observed in the ^{13}C-NMR spectra for batches C-1 and C-2 that as the integration value increases at 3.9 and 3.7 ppm there is an increase in peak intensity at 73.6 and 69.9 ppm. These are the
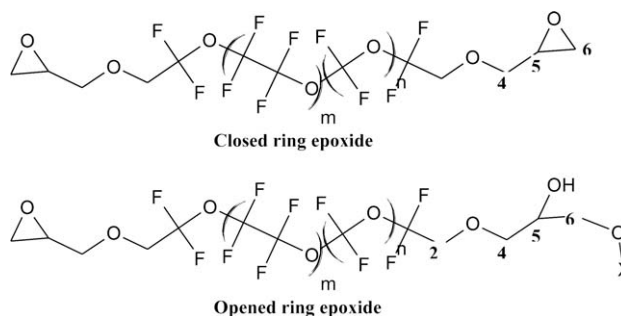

Figure 3 Chemical structure of closed ring epoxide (top) and open ring epoxide (bottom).

TABLE I
Analytical Dashboard for Characterizing Chemical Structure and Lithographic Performance

Batch	NMR (open epoxide)	FTIR (open epoxide)
A	27%	26%
B	20%	23%
C-1	7%	7%[a]
C-2	35%	39%

[a] The ratio for batch C-1 was normalized to 7%, whereas other batches were calculated.

only additional peaks consistently seen to change in the ^{13}C-NMR spectra (Fig. 2).

One interpretation of these results is that these peaks are evidence of the formation of the open-ring epoxide (Fig. 3). Based on this interpretation, the relative amount of the open ring form in these samples was calculated from the integration of the peak at 3.7 ppm and that for every one proton for C6 of the epoxide resonance at 2.49 ppm (since the two protons on this carbon are nonequivalent in the oxirane ring), there would be two protons of the C6 at 3.7 ppm. The data are shown in Table I with batch C-1 having $\sim$ 7.5% open epoxide, batch B has 20% open epoxide, batch A has 28% open epoxide, and batch C-2 has $\sim$ 35% open epoxide.

Of the two ^{13}C-NMR resonances associated with the open ring form, the resonance at 73.6 is readily observed whereas the resonance 69.9 ppm is overlapped by the C2 carbon resonances. Integration of the peak at 73.6 ppm for the open ring C6 relative to the closed ring C6 resonance at 43.2ppm was used to also get an idea of the relative abundance of these two forms. There was very good agreement ($\pm$ 1%) between the ^{13}C and ^{1}H-NMR integral values for the percent open-ring epoxide.

A semiquantitative analysis in FTIR was also used to correlate percent open epoxide as was done with NMR. The signal at 3063 cm^{-1} is related to the C—H stretch on the epoxy ring. By building a correlation between batch signals at 3063 cm^{-1}, epoxy content could be quantified using FTIR. By comparison to NMR results, FTIR correlation gives a good indication for open epoxide.

NMR and FTIR analysis shows that open epoxide ranged from 7 to 35%. A simple formulation was made to functionally test the sensitivity of eFLKD to open epoxide. The details of the formulation and processing are discussed in the Experimental and Formulation sections. As processed through hardbake, no significant photoresolution differences were found at the macroscale. Exposed squares of photoresist appear uniform across batches with the exception of coating defects. Under these processing and

formulation conditions, this material appears to tolerate a broad range of open epoxy.

Photoresist formulation

Creating a hydrophobic photoresist has significant formulation challenges, primarily hinging around the solubility of materials. Our initial challenge was to find a solvent or solvent mixture that would enable the solubility of eFLKD (hydrophobic) and the photoacid (hydrophilic). Spin coating processing constraints preclude the use of low boiling point solvents since they do not lead to good quality coatings (due to rapid solvent evaporation). As a result, we primarily screened solvents for component solubility with boiling points between $\sim$ 100 and 130°C.

eFLKD is readily soluble in fluorinated nonpolar solvents, but this is in direct contrast to the solubility of the photoacid generator, an onium salt. Onium salt photoacids are typically sold in propylene carbonate solutions, a polar aprotic solvent. Thus, it is important to select a solvent set that is just polar enough to solubilize $\sim$ 3% photoacid into the formulation. Finally, considering the density of the resin ($\sim$ 1.8 g/cm^3) and corresponding fluorinated solvents ($>$1 g/cm^3), simply selecting nonpolar aprotic solvents is not adequate.

In testing the solubility of triarylsulfonium hexafluoroantimonate salts, the solvents which solubilized the photoacid were indeed incompatible with eFLKD. For eFLKD, 20% (w/w) mixtures in the designated solvent were made and visually inspected for solubility. For the photoacid, 10% (w/w) mixtures in the designated solvent were made. Table II shows a list of solvents tested and whether the

TABLE II
Solubility of Photoacid (Triarylsulfonium Hexafluoroantimonate (SbF$_6^-$) Salts) and eFLKD in Various Flourinated Solvents

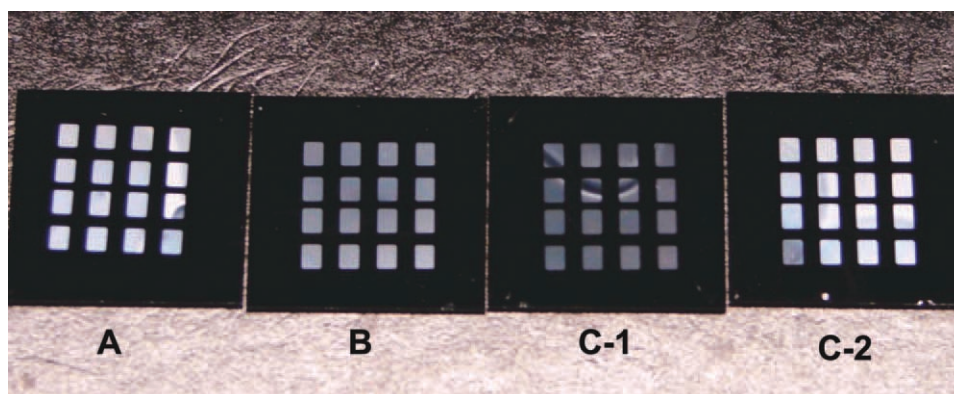| Solvent	eFLKD soluble (Y/N)	SbF6 soluble (Y/N)
3-(Trifluoromethyl) acetophenone	N	Y
a,a,a-Trifluoro-m-tolunitrile	N	Y
1,3,5-Tris(trifluoromethyl)benzene	Y	N
2-Chlorobenzotrifluoride	N	N
4-Methylbenzotrifluoride	N	N
2,5-Bis(trifluoromethyl)bromobenzene	Y/N	N
2-Fluorobenzotrifluoride	N	Y
3-Methylbenzotrifluoride	N	N
1,4-Bis(trifluoromethyl)benzene	Y	N
Trifluorotoluene	N	Y
H-Galden ZV60	Y	N
1-Hexanol	N	N
1-Pentanol	N	N
1-Butanol	N	N
2,2,3,4,4,4-Hexafluorobutanol	Y/N	Y

Figure 4 Images of processed eFLKD photoresist batches on one inch silicon coupons. Each batch had varying open epoxy, yet qualitative observation shows little difference in photoresolution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

photoacid (SbF_6^-) or photoresist (eFLKD) are readily soluble.

A simple formulation described for processing utilized a solvent mixture of 1,4-bis(trifluoromethylbenzene) and hexafluorobutanol at a ratio of 4 : 1 (w/w). The primary role of the hexafluorobutanol was to ensure adequate photoacid solubility. Then, at 15% total "solids" (w/w), using 3 :97 ratio of photoacid to eFLKD, a functional photolithographic formulation was realized.

Photoresist processing

Good photoresolution was demonstrated at the coupon level and is pictured in Figure 4. In scaling up to processing at the wafer level, good photoresolution was also demonstrated as shown in Figure 5. Optical defects include rounded edges and bubbles within the photoresist film. We suspect bubble defects are caused by phase separation during post expose bake when hydrophilic acid mediates the polymerization of hydrophobic photoresist. We speculate this could be reduced by using suitable cosolvents or surfactants to allow these otherwise incompatible phases to become miscible. Improving edge crispness could be done by optimizing the expose and postexpose bake processes, and perhaps by adjusting the eFLKD formulation.

In typical microfabrication processing environments, automated tooling transfer wafers from one process to another by touching the underside and edge of the wafer. It is imperative that contamination from one wafer is not passed to subsequent wafers. In the event of contamination by a hydrophobic material, inadequate adhesion of films on subsequent wafers could result. Therefore, creating a clean removal process for processing steps is critical to enable use in a microfabrication manufacturing environment.

The photolithography application process requires the removal of uncured resist by solvent washing. A 1 in. silicon coupon was first coated with the eFLKD resist, then washed with the develop solvent (1,4-bis(trifluoromethylbenzene)). Five washings of
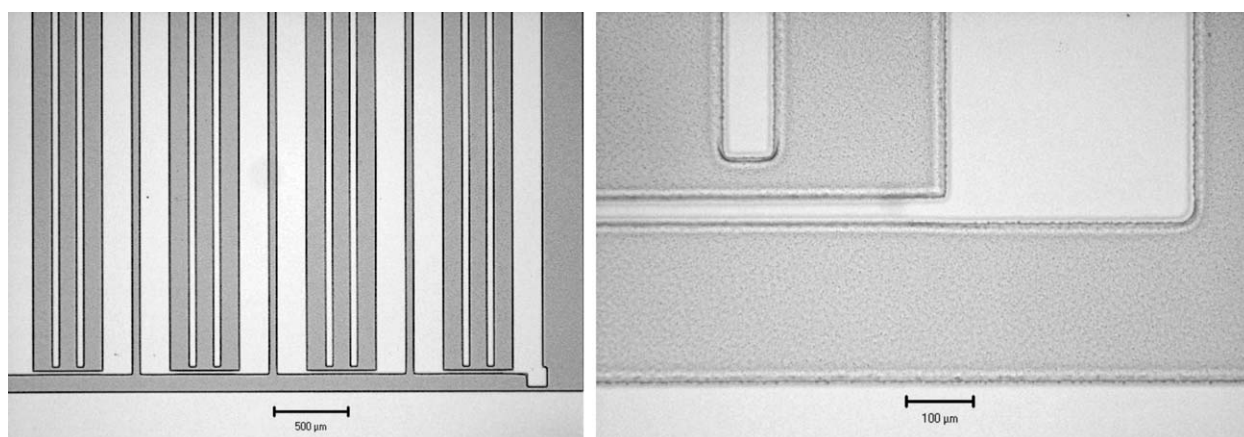

Figure 5 Optical microscope images of eFLKD photoresist formulation at 2.5× magnification (left) and 10× magnification (right).

Sample Legend
Sample 2: 2mL Rinse
Sample 4: Additional 2mL rinse (4mL rinse equivalent)
Sample 6: Additional 2mL rinse (6mL rinse equivalent)
Each sample consists of 2mL of 1,4-bis(trifluoromethylbenzene) collected from the rinse
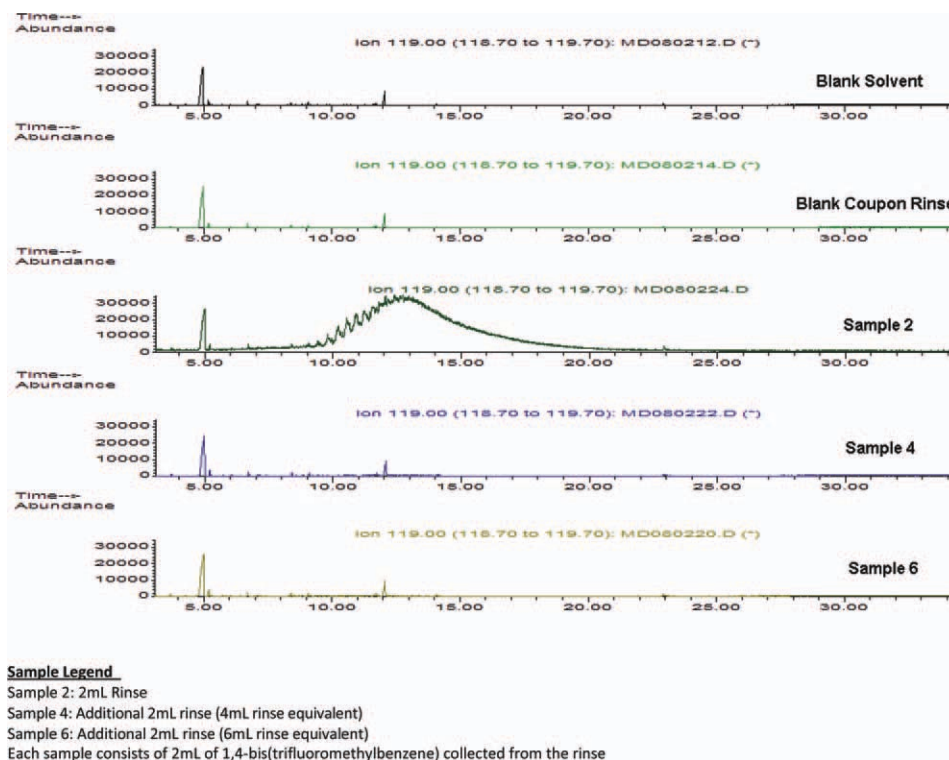
Figure 6 GCMS of collected solvent rinses using 1,4-bis (trifluoromethylbenzene). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

2 mL were collected and analyzed for eFLKD materials by GC-MS. The data show the majority of eFLKD removal occurring in the first washing (Fig. 6). Other peaks observed are due to solvent contamination.

Examination of the developed surface was done to understand whether residual eFLKD material existed after solvent washing. The surface was then analyzed by TOF-SIMS for residual eFLKD that was not removed from the coupon (TOF-SIMS is not quantitative, but normalized values for species can be compared between samples of similar composition). These are unitless values normalized to total spectrum counts and multiplied by an arbitrary factor to bring the values into a convenient range. The epoxidized perfluoropolyether in negative polarity has a few very distinctive fragments with the one at 113 amu ($C_2F_3O_2$) being the most intense. In positive polarity the fragments for the aliphatic fluorocarbon component (similar to poly(tetrafluoroethylene)) are most intense. The ratio of 113/119 in negative polarity gives an indication of which component dominates (C_2F_5 at 119 amu being primarily an aliphatic fragment). Table III has relative values for the amounts of eFLKD detected on the washed coupons by TOF-SIMS analysis. As compared with 1,4-bis(trifluoromethylbenzene) (BTFB), three other solvents performed better at removing resist residue (ZV60 and ZT130 are perfluoropolyether solvents from Solvay-Solexis). It is found that hexafluoroisopropyl alcohol (HFiPA) is the best solvent tested to enable a clean removal of eFLKD during processing.

Chemical resistance

The chemical resistance of a photoresist determines its utility to assist in patterning underlying material or serving as a functional structure in a device. In the case of a resist, dry or wet etch chemistries are used to remove underlying metals, ceramics, or plastics. The resist must be more tolerant than the material being etched to provide the protection needed to pattern underlying layers. As a functional structure in a device, the material should provide resistance against attack of other device components. For example, as a microfluidic structural element, the

TABLE III
TOF-SIMS Results (113/119 Ratio) from Developed eFLKD Coupon

Sample	Solvent	Volume	Normalized counts
eFLKD	ZT130	10 mL	1.47
	ZV60	10 mL	5.97
	HFiPA	10 mL	0.14
	BTFB	10 mL	117
Si control	None	N/A	2

TABLE IV
Contact Angle on Blanket-Coated eFLKD as a Result of Wafer Processing

Wafer #	Process	Contact angle (degrees, $x=6$)	Std. dev.
1	SB, expose, PEB	107.7	1.6
2	SB, expose, PEB, BTFB	109.5	0.6
3	SB, expose, PEB, BTFB, EL (bath)	109.0	1.7
4	SB, expose, PEB, BTFB, EL (bath), HB	100.2	5.4
5	SB, expose, PEB, BTFB, EL (bath), HB, Ash	109.8	1.9
6	SB, expose, PEB, BTFB, EL (bath), HB, Ash, TMAH	109.9	3.2
7	Crosslinked SU-8 (control)	74.4	0.0

SB, softbake; PEB, post expose bake; BTFB, BTFB develop; EL, ethyl lactate rinse; HB, hardbake; ash, O2 plasma ash; TMAH, TMAH wet etch.

resist will come in contact with fluids that may attack the resist interface or swell the structural element. It has been shown that while PDMS-like microfluidics are not very chemically resistant,[25] perfluoropolyether-based microfluidics are more resistant.[23]

Chemical resistance was tested by measuring contact angle after representative chemical treatments commonly used in photolithography (Table IV). Blanket coated wafers of eFLKD were prepared and exposed to common photolithographic process steps. In particular, ash (oxygen plasma) and tetramethylammonium hydroxide (TMAH, basic wet etch) steps dramatically decrease the contact angle of most polymeric materials. For eFLKD, however, surface properties were retained as evidenced by static contact angles in deionized water near 110° throughout processing.

Resist stripping

Many photoresists are used for the purpose of providing chemical protection to regions during an etch process. Following an etch process step, the photoresist is removed and is not a permanent part of the final device. Removal of the photoresist is typically done using solvent, strong acid, or specific dry etch conditions. We did not explore a stripping process since we were more interested in the photoresist as a permanent feature. The class of permanent photoresists is commonly used to create the fluidic paths in microfluidic devices.

CONCLUSIONS

This report details our work in developing a highly fluorinated photoresist based on an epoxidized perfluoropolyether. Characterization of epoxidized product showed batch variation of open epoxide.

Within the space of our simple photoresist formulation, however, there were no observed differences in photoresolution of large patterns. Formulation and processing challenges were discussed and excellent chemical resistance throughout a typical processing protocol was demonstrated. Thus, we have provided a basic set of conditions necessary to synthesize, formulate, and process a hydrophobic photoresist.

We would like to offer two specific areas in which material and formulation improvements could be made in order for this photoresist to become a drop-in solution for traditional photolithography. First, the glass transition temperatures of perfluoropolyethers are typically below room temperature. Ideally, a photoresist would have a glass transition temperature (T_g) above room temperature so the coating would be solid from the coat step to the softbake or expose step. We believe this could be accomplished through chemical modification (see Fluorolink A10 from Solvay-Solexis) or polymer blending. Also, the photoacid generator we chose was adequate for broadband exposure. Improving photospeed or sensitivity to a specific wavelength could be done by modifying the photoacid and/or by adding sensitizers.

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