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Short communication

Determination of fluorochemical surfactants in acid etch baths by ion chromatography with on-line matrix elimination

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Abstract

Fluorochemical surfactants are added to acid etching solutions to ensure good wetting of the wafer surface. Methods were developed to determine the fluorochemical surfactant FC-93 in an etch bath composed of HF–ammonium fluoride (1:6) and the fluorochemical surfactant FC-95 in an etch bath containing concentrated HF, HCl and HNO_3. On-line matrix elimination was accomplished on a polymeric reversed-phase column followed by separation on a multiphase HPLC column, and detection by suppressed conductivity. Using this method, we determined 5 mg/l of the surfactant FC-93 in 100 μl of the etch bath.

Keywords: Hydrofluoric acid; Perfluoroalkylsulfonates; Surfactants

1. Introduction

Perfluorinated surfactants are used as wetting agents in semi-conductor acid etching solutions. Poor wetting of the wafer (a 300-mm diameter silicon dioxide disk) surface by the acid etchant can result in air entrapment through the formation of small bubbles. These bubbles can lead to fine openings in the resistor surface and ultimately electrical shorts in the device. The addition of a small amount of surfactant greatly reduces air entrapment by improving the wetting properties of the solution. Because of their stability in acidic solutions, fluorochemical surfactants are the surfactant class of choice for acid etch baths. Solutions containing these surfactants have very low surface tensions which facilitates a uniform etch with sharp detail. The functional importance and high cost of fluorochemical surfactants necessitates their determination in the etchant.

Here we report the determination of the fluorochemical surfactants FC-93 and FC-95 in acid etch baths. FC-93 was determined in a hydrofluoric acid (HF)–ammonium fluoride (1:6) etch bath and FC-95 in an etch bath containing concentrated HF, HCl and HNO_3. FC-93 and FC-95 are perfluoralkylsulfonates that have minimal UV absorbance. These surfactants have the general formula of CF_3-$(CF_2)_n$-hydrocarbon group-SO_3 where n varies from six to 10 [1]. Analysis of low concentrations of these surfactants in acid baths requires elimination of the acid matrix and a sensitive detection scheme. To accomplish this we used on-line matrix elimination [2], separation on a multiphase high-performance liquid chromatography (HPLC) column [3], and detection by suppressed conductivity [4]. The surfactant is extracted from the acid matrix by passing the sample through a polymeric reversed-phase resin. After rinsing to remove

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the matrix, the concentrated surfactant is eluted from the polymeric reversed-phase resin onto a multiphase HPLC column where the surfactant is separated from residual strong acid anions and detected using suppressed conductivity detection. Eluent suppression reduces the conductivity of the eluent and enhances the conductivity of the analyte. We used this method to quantify the surfactant in the acid etch bath. Aliphatic anion surfactants (e.g., alkyl sulfates and alkyl sulfonates) have been separated using a polymeric reversed-phase column and detected by suppressed conductivity [5,6]. To our knowledge, there are no published methods for quantifying either FC-93 or FC-95 in an acid etch bath.

2. Experimental

2.1. Materials

Sodium hydroxide, 50% (w/w), was obtained from Fisher Scientific (Pittsburgh, PA, USA). High purity acetonitrile was purchased from EM Scientific (Gibbstown, NJ, USA). One acid etch bath (HF–ammonium fluoride, 1:6) and the surfactant FC-93 (3M Corp., Minneapolis, MN, USA) were kindly provided by Ashland Chemical (Dallas, TX, USA). FC-95 (3M Corp.) and a second acid etch bath containing concentrated HF, HCl and HNO_3 and 200 mg/l iron, chromium and nickel was kindly provided by Aerochem (Adelanto, CA, USA). Type I reagent grade deionized water (18 MΩ cm or better) was used for all sample and eluent preparations.

2.2. Standard preparation

A 1000 mg/l FC-93 primary standard was prepared by dissolving 4.15 g in either 1 l of water or etch bath. This standard was mixed with the appropriate volume of etch bath to produce surfactant concentrations of 5, 10 and 15 mg/l and each was analyzed twice to ascertain the linearity of the method. A 100 mg/l FC-95 primary standard was prepared by dissolving 0.67 g in 1 l of water. This standard was mixed with the appropriate volume of etch bath to produce surfactant concentrations of 10, 25 and 50 mg/l and each was analyzed twice to ascertain the linearity of the method. Standards were stored at room temperature.

2.3. Equipment

A DX-500 chromatography system (Dionex, Sunnyvale, CA, USA) consisting of a GP40 gradient pump, a CD20 conductivity detector, and a LC20 chromatography enclosure equipped with a rear-loading Rheodyne (Cotati, CA, USA) injection valve (valve 2) was used for all chromatography. A LC10 chromatography organizer containing a rear-loading injection valve (valve 1) was used for matrix elimination. Both valves contained Tefzel rotor seals. A single-piston pump (DQP, Dionex) was used to rinse the polymeric reversed-phase column prior to switching it in-line with the multiphase HPLC column set. An anion self-regenerating suppressor (ASRS-II, Dionex[1]) was used in the autosuppression external water mode at a power setting of 300 mA. A personal computer equipped with PeakNet chromatography software (Dionex) was used for data acquisition and instrument control.

2.4. Chromatography

The 20 m*M* NaOH eluent was prepared using 50% NaOH and vacuum-degassed water and installed as eluent A. Acetonitrile was vacuum-degassed for 5 min and installed as eluent B. Both eluents were pressurized with helium (8 p.s.i., 55.2 kPa). The chromatography system was configured as shown in Fig. 1 [7]. Fifty feet (1.52 m)×0.02 in. (0.051 cm) I.D. tubing was installed as the waste line to provide the necessary backpressure for the sample pump. The chromatography method is outlined in Table 1. In Fig. 1, valve 1 is in the load position and valve 2 is in the inject position. At 0 min valve 2 is switched to the load position and a 100-μl sample loop was loaded by pulling the sample into the loop using a syringe on the waste port of valve 1. The loop was overfilled with at least three-times the loop volume to ensure reproducible sampling. The sample was then injected onto the polymeric reversed-phase column (IonPac NG1, 5×0.4 cm, Dionex). For the

[1]Autosuppression, ASRS, IonPac and OmniPac, are registered trademarks of the Dionex Corporation.

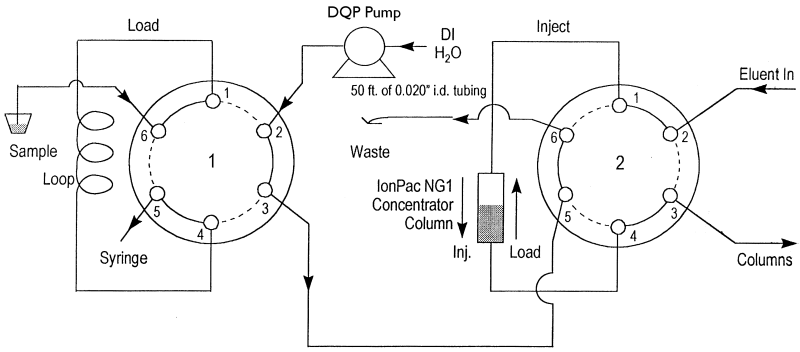

Fig. 1. Configuration of the chromatographic system for analyzing FC-93 in an acid etch bath. In this diagram, the system is at initial conditions with valve 1 in the load position and valve 2 in the inject position. Table 1 describes the state of both valves at each point in the analysis.

determination of FC-93 in the HF–ammonium fluoride bath, the column was rinsed with deionized water at a flow-rate of 2 ml/min using the DQP pump. When FC-95 was determined in the HF–HCl–HNO_3 bath, 20 m*M* NaOH was used as the rinsing solution. After a 20 min rinse, valve 2 was switched to the inject position. This placed the NG1 in line with the multiphase HPLC guard (5×0.4 cm) and separator (25×0.4 cm) columns (OmniPac PAX-500, Dionex). The surfactant was eluted from the NG1 column in the opposite direction of sample loading using 11 m*M* NaOH–45% acetonitrile at a flow-rate of 1 ml/min. This eluent was prepared by proportioning eluents A and B at the time of analysis because in NaOH, acetonitrile slowly degrades to ammonium and acetate. Therefore, when the system was not used for more than one day it was rinsed with deionized water to prevent a high background conductivity at start-up.

3. Results and discussion

To determine the FC-93 surfactant in a HF–ammonium fluoride etch bath, the acidic matrix must be eliminated. A direct analysis is precluded by the high concentration of fluoride ion relative to the low concentration of FC-93. Here we chose an acid-stable polymeric reversed-phase column (IonPac NG1) that binds FC-93 but not the other ionic

Table 1
Chromatography method for surfactant analysis

Time (min)	Eluent A (%) 20 m*M* NaOH	Eluent B (%) 100% MeCN	Valve 1 position and ports connected	Valve 2 position and ports connected	Remarks
Initial	55	45	Load 1-6, 2-3, 4-5	Inject 1-2, 3-4, 5-6	See Fig. 1
0.0	55	45	Load 1-6, 2-3, 4-5	Load 1-6, 2-3, 4-5	Fill sample loop
1.1	55	45	Inject 1-2, 3-4, 5-6	Load 1-6, 2-3, 4-5	Sample to NG1 and NG1 rinsing
20.5	55	45	Load 1-6, 2-3, 4-5	Inject 1-2, 3-4, 5-6	Begin sampling[a]
35.0	55	45	Load 1-6, 2-3, 4-5	Inject 1-2, 3-4, 5-6	Finish sampling

[a] Begin sampling refers to data collection (the NG1 concentrator column is switched in-line with the OmniPac PAX-500 analytical columns).

components in the etch bath. A rinse of 40 ml of deionized water (20 min at 2 ml/min) was used to deliver the contents of the sample loop to the concentrator column, as well as eliminate the matrix. Shorter rinse times do not eliminate enough of the matrix to reliably analyze the surfactant in 100 μl of the etch bath. FC-93 was then eluted from the NG1 column onto a multiphase HPLC column set (OmniPac PAX-500). The resin in the OmniPac PAX-500 column is a good match to the NG1 column because the OmniPac PAX-500 is prepared by agglomerating an anion-exchange latex onto the NG1 resin. The OmniPac PAX-500 is both acid and organic solvent compatible and can be used for reversed-phase, ion-pairing and anion-exchange separations. Here we use both the reversed-phase and anion-exchange modes of the column. Fig. 2 panel A shows the separation of 5 mg/l FC-93 in 100 μl of etch bath using an 11 m*M* NaOH–45% acetonitrile eluent. An eluent of 45% acetonitrile eluted FC-93 from the NG1 column and still allowed enough FC-93 retention on the PAX-500 column to separate FC-93 from residual fluoride. We chose NaOH as the ion-exchange eluent because the column's anion-exchange latex is selective for the hydroxide ion. Fig. 2 panel B shows the analysis of 100 μl of etch bath without added surfactant (matrix blank). This analysis was performed after the analysis of 5 mg/l FC-93 and shows that there is no measurable carry-over. The FC-93 surfactant elutes as a broad peak at approximately 6.3 min (peak 5). This peak has a signal-to-noise ratio of 7.4 (peak height/peak-to-peak noise from 8 to 9 min). The width of this peak is probably a result of heterogeneity in the fluorocarbon chain of the FC-93 surfactant. The width at half height is 0.7 min which compares favorably to published chromatography of anionic aliphatic surfactants using polymeric reversed-phase columns [5,6]. When 5 mg/l FC-93 was analyzed in water, the retention time and peak shape were the same as in the etch bath (chromatogram not shown). Peaks 1 and 2 are system peaks (observed when analyzing water) and peak 3 is fluoride. The identity of peak 4 is unknown, but it is not present in the analysis of FC-93 in water. Changes in either the NaOH or acetonitrile concentration can be used to change the retention time of the surfactant, but small (1%) changes in acetonitrile concentration have a greater effect on the retention time of the surfactant than small (1 m*M*) changes in NaOH concentration. For example, lowering the acetonitrile concentration 5% increases the FC-93 retention time by 5 min. The later that FC-93 elutes, the broader its peak. Using a stronger eluent, FC-93 elutes earlier in a sharper peak, but a longer rinse of the NG1 was required to reduce the fluoride peak size. The conditions presented here are a compromise between peak shape and maximizing separation of the surfactant from fluoride.

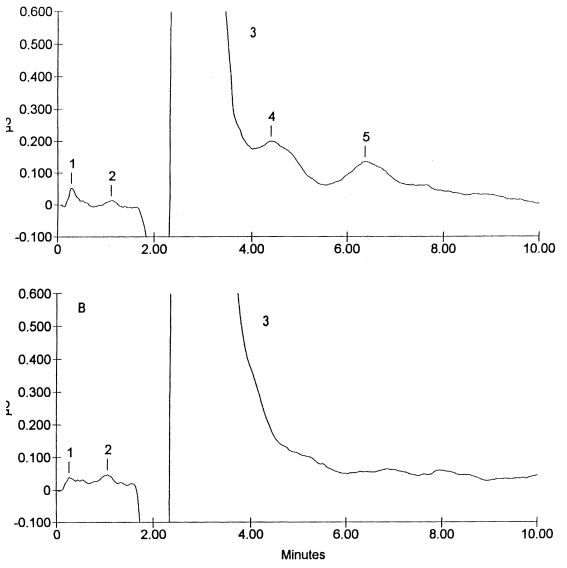

Fig. 2. Determination of FC-93 in the HF–ammonium fluoride etch bath. Panel A shows the determination of 5 mg/l FC-93 in 100 μl of etch bath. Panel B shows the determination of 100 μl of etch bath without FC-93. Peaks 1 and 2 are system peaks, peak 3 is fluoride, peak 4 is unknown, and peak 5 is FC-93. The chromatographic conditions are described in Section 2.4.

Because FC-93 has little UV absorbance, we detected it by suppressed conductivity. The external water mode of the ASRS-II was used due to the presence of acetonitrile in the eluent and to achieve maximum sensitivity. Using the method described here we could reproducibly analyze 5 mg/l FC-93 in the etch bath. For five replicate injections, the area relative standard deviation (R.S.D.) was 0.5% and the average retention time was 6.27 min with an R.S.D. of 2.2%. The average S/N ratio was 7.5. We determined that the analysis was linear between 5 and 15 mg/l ($r^2=0.9998$). This method could be used to determine lower concentrations of the surfac-

tant by injecting a larger volume of sample. However, larger sample volumes require longer NG1 rinse times. Higher concentrations of the surfactant were not investigated because they were outside of the range of the intended application for this surfactant.

We also analyzed the fluorochemical surfactant FC-95 in an acid etch bath containing concentrated HF, HCl and HNO_3 (Fig. 3). For this analysis we changed the rinse solution from water to 20 m*M* NaOH. This change was necessary to more efficiently remove nitrate which elutes after FC-95. Using the method described here we could reproducibly analyze 10 mg/l FC-95 in the etch bath. For seven replicate injections, the area R.S.D. was 0.6% and average retention time was 7.54 min with a R.S.D. of 0.7%. We determined that the analysis was linear between 10 and 50 mg/l (r^2=0.999). Higher concentrations of the surfactant were not investigated because they were outside of the range of the intended application for this surfactant.

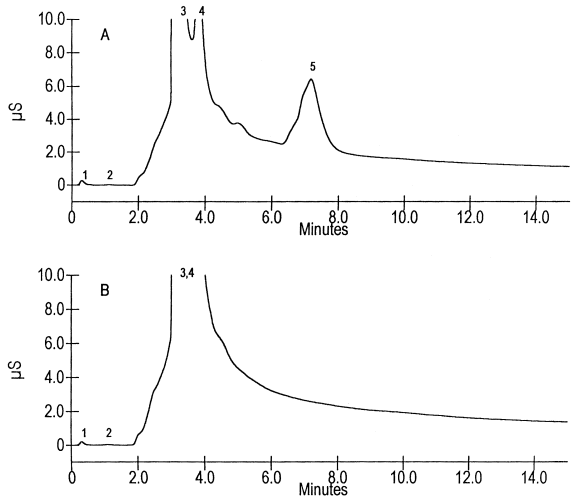

Fig. 3. Determination of FC-95 in the HF–HCl–HNO_3 etch bath. Panel A shows the determination of 25 mg/l FC-95 in 100 μl of etch bath. Panel B shows the determination of 100 μl of etch bath without FC-95. Peaks 1 and 2 are system peaks, peak 3 is bath components, peak 4 is unknown, and peak 5 is FC-95. The chromatographic conditions are described in Section 2.4.

We have demonstrated the analysis of two fluorochemical surfactants in two acid etch baths. If an anionic surfactant can bind to a polymeric reversed-phase column, we believe that the chromatographic system described here can be used to analyze that surfactant in HF or in another acidic or anionic matrix.

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