DIONEX

Application Update 143

Determination of Chloride in Acid Copper Plating Bath

INTRODUCTION

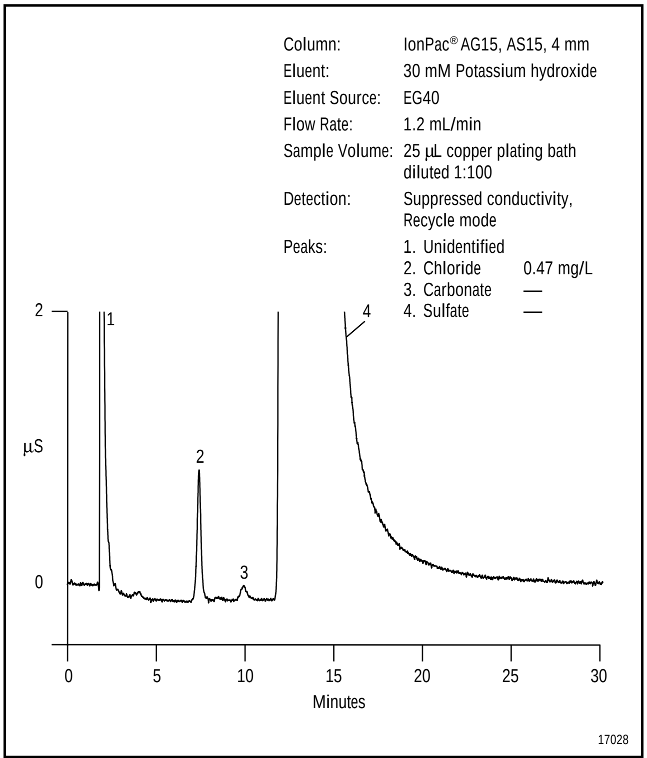
Ion chromatography (IC) provides a convenient method for the determination of chloride in acid copper plating baths. These baths are used for deposition of copper on semiconductor wafers. Monitoring chloride concentration is of interest because it plays an important role in the quality of copper deposition. Compared to standard wet chemical techniques, IC offers improved speed and accuracy for this analysis. An acid copper bath typically contains copper sulfate, sulfuric acid, hydrochloric acid, and a variety of proprietary additives. Figure 1 shows an analysis of a 25-µL sample of copper plating bath diluted 1:100. Chloride is detected by suppressed conductivity and the EG40 eluent generator is used to prepare the 30 mM potassium hydroxide eluent on-line. Chloride is separated from the excess of sulfate present in the copper plating bath. This Application Update describes the setup and procedure to determine chloride in a copper plating bath using the IonPac® AS15 column.

EQUIPMENT

Dionex DX-600 ion chromatography system consisting of:

- GP50 Gradient Pump
- CD25 Conductivity Detector
- EG40 Eluent Generator System with EluGen® EGC-KOH cartridge (P/N 053921)
- LC20 Chromatography Enclosure equipped with Rheodyne Model 9126
- Injector, PEEK, rear loading (P/N 052291)

Columns: IonPac AS15 analytical, 4 x 250 mm (P/N 053940)
IonPac AG15 guard, 4 x 50 mm (P/N 053942)
Trap Column: ATC-1 Trap, 9 x 24 mm (P/N 037151)
Suppressor: ASRS®-ULTRA, 4 mm (P/N 053947)
25-µL PEEK sample loop (P/N 042857)
PeakNet® Chromatography Workstation



Column: IonPac® AG15, AS15, 4 mm
Eluent: 30 mM Potassium hydroxide
Eluent Source: EG40
Flow Rate: 1.2 mL/min
Sample Volume: 25 µL copper plating bath diluted 1:100
Detection: Suppressed conductivity, Recycle mode
Peaks: 1. Unidentified
2. Chloride 0.47 mg/L
3. Carbonate —
4. Sulfate —

Figure 1. Determination of chloride in acid copper plating bath.

REAGENTS AND STANDARDS

Deionized water (DI H_2O), Type I reagent grade, 17.8 MΩ-cm resistance or better

Sodium hydroxide 50% w/w aqueous solution (Fisher Scientific)

Potassium hydroxide 45% w/w aqueous solution (Fisher Scientific; optional instead of sodium hydroxide)

Chloride standard 1000 mg/L, 100 mL (Dionex P/N 037159)

SAMPLE PREPARATION

Dilute the copper plating bath 1:100 with deionized water.

STANDARD

Dilute the 1000 mg/L chloride standard to bracket the expected chloride concentration.

CONDITIONS

Column:	IonPac AG15, AS15, 4 mm
Eluent:	30 mM Potassium hydroxide
Eluent Source:	EG40
Flow Rate:	1.2 mL/min
Sample Volume:	25 µL of copper plating bath diluted 1:100
Detection:	Suppressed conductivity, Recycle mode
EG40 Offset Volume:	0 µL

Pump Program:

Time (min)	Flow (mL/min)	%A	Valve	EG40 Conc. (mM)	Comments
Initial	1.2	100	Load	30	Load sample loop
0.00	1.2	100	Inject	30	Inject
30.00	1.2	100	Load	30	End acquisition

ASRS Current Setting:	100 mA
Expected Background Conductivity:	1 µS
Expected System Backpressure:	16.5 MPa (2400 psi)

ATC Regeneration Solution: 2 M Sodium Hydroxide

Dilute 160 g of 50% (w/w) sodium hydroxide with degassed, deionized water (with a specific resistance of 17.8 MΩ-cm or greater) to a final weight of 1080 g in an eluent bottle. Avoid the introduction of carbon dioxide from air. (2 M potassium hydroxide can be used instead of 2 M sodium hydroxide. Preparation is the same as above except that 249 g of 45% potassium hydroxide is used for a final weight of 1090 g.)

SYSTEM PREPARATION AND SETUP

Prepare the ASRS according to the *Quickstart Instructions for the ASRS-ULTRA* (Document No. 031368). Prepare the ATC for use by rinsing it with 200 mL of 2 M KOH or 2 M NaOH at 2.0 mL/min. This can be done off-line (without the GP50) by pressurizing an eluent bottle with helium using 0.030-in. (0.75-mm) i.d. PEEK tubing. Rinse the ATC with deionized water at 2.0 mL/min for 20 minutes. Install the EGC-OH EluGen cartridge according to the instructions in the Operator's Manual for the EG40 Eluent Generator System (Document No. 031373). Place the 4-mm ATC between the GP50 outlet and the KOH cartridge inlet.

PERFORMANCE CHARACTERISTICS

The nominal concentration of chloride in the copper plating bath is 45 mg/L (ppm). The method detection limit (MDL) for this procedure is 6 mg/L chloride. (This is based on an MDL of 0.06 mg/L for a 25-µL injection of a sample diluted 1:100.) The MDL was calculated using three times the noise. Noise was measured to be 17.5 ± 5.8 nS for an average of ten 1-minute sections of a representative baseline signal.

To verify proper quantification of chloride in the copper plating bath matrix, increasing concentrations of chloride were spiked in the deionized water used to dilute the copper bath 1:100. This fresh copper plating bath sample contained three proprietary additives. A coefficient of determination (r^2) value of 0.9983 was calculated for a three-level calibration curve with three replicates at each level. The three concentration levels were: 1) unspiked bath sample, 2) spike at 0.5 mg/L chloride, and 3) spike at 1.0 mg/L chloride. An average measured concentration of chloride in this sample was 47.2 ± 1.2 mg/L (based on the undiluted bath) for 21 replicate injections.

This method has been demonstrated to give reliable quantification of chloride for over 500 injections. Retention time for chloride can gradually decrease over time because of a loss of column capacity, probably due to bath components concentrating on the column. Depending on the nature of the contaminants it might be possible to clean the column. See the *Installation Instructions and Troubleshooting Guide for the IonPac AS15* (Document No. 031362) for more information about column cleanup protocols.

SUPPLIER

Fisher Scientific, 711 Forbes Avenue, Pittsburgh, PA 15219-4785, USA. Tel: 1-800-766-7000

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Dionex Corporation
1228 Titan Way
P.O. Box 3603
Sunnyvale, CA
94088-3603
(408) 737-0700

Dionex Corporation
Salt Lake City Technical Center
1515 West 2200 South, Suite A
Salt Lake City, UT
84119-1484
(801) 972-9292

Dionex U.S. Regional Offices
Sunnyvale, CA (408) 737-8522
Westmont, IL (630) 789-3660
Houston, TX (281) 847-5652
Atlanta, GA (770) 432-8100
Marlton, NJ (856) 596-0600

Dionex International Subsidiaries
Austria (01) 616 51 25 *Belgium* (015) 203800 *Canada* (905) 844-9650 *China* (852) 2428 3282 *Denmark* (45) 36 36 90 90
France 01 39 30 01 10 *Germany* (06126) 991-0 *Italy* (06) 66 51 50 52 *Japan* (06) 6885-1213 *The Netherlands* (0161) 43 43 03
Switzerland (062) 205 99 66 *United Kingdom* (01276) 691722

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