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APPLICATION UPDATE 143

Determination of chloride in acid copper plating bath

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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 Thermo Scientific™ Dionex™ 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 Thermo Scientific™ Dionex™ IonPac™ AS15 column.

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

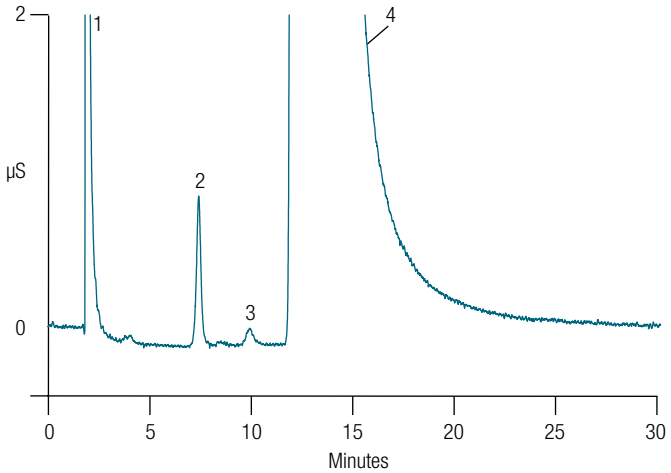

Figure 1. Determination of chloride in acid copper plating bath.

Experimental

Equipment*

- Thermo Scientific™ Dionex™ DX-600 ion chromatography system consisting of:
  - GP50 Gradient Pump
  - CD25 Conductivity Detector
  - EG40 Eluent Generator System with Thermo Scientific™ Dionex™ EluGen™ EGC-KOH cartridge
  - LC20 Chromatography Enclosure equipped with Rheodyne® Model 9126

* Equivalent or improved results can be achieved using the Thermo Scientific™ Dionex™ ICS-5000⁺ HPIC™ system or the Thermo Scientific™ Dionex™ Integrion™ HPIC™ system.

- Columns:
  - Dionex IonPac AS15 analytical, 4 × 250 mm (P/N 053940)
  - Dionex IonPac AG15 guard, 4 × 50 mm (P/N 053942)
  - Thermo Scientific™ Dionex™ IonPac™ ATC-3 trap column, 9 × 24 mm (P/N 059660)
- Suppressor: Thermo Scientific™ Dionex™ ASRS™ ULTRA, 4 mm
- 25 µL PEEK sample loop (P/N 042857)
- Thermo Scientific™ Dionex™ PeakNet™ Chromatography Workstation

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 1,000 mg/L, 100 mL (Dionex P/N 037159)

Sample preparation

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

Standard

Dilute the 1,000 mg/L chloride standard to bracket the expected chloride concentration.

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 1,080 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 1,090 g.)

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

Dionex ASRS Current Setting:	100 mA
Expected Background Conductivity:	1 µS
Expected System Backpressure:	16.5 MPa (2,400 psi)

System preparation and setup

Prepare the Dionex 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 Dionex EGC-OH EluGen cartridge according to the instructions in the Operator's Manual for the Dionex 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.

Find out more at **thermofisher.com/IC**

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