Improved Determination of Additives in Acid Copper Plating Baths

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High Performance Liquid Chromatography (HPLC) methods have been developed for the determination of organic components, chloride and byproducts in an acid copper-plating bath. HPLC has been demonstrated to be an effective means for monitoring the levels of these analytes of interest.[1-3] Monitoring and controlling the concentration of these species is important for ensuring the quality of the copper deposition in semiconductor devices.

A typical high performance liquid chromatograph (HPLC) would not be suitable for this analysis. These highly acidic plating bath samples (10 % sulfuric acid) would corrode the stainless steel fluid pathway in the instrument. For that reason, a liquid chromatography system that has a flow pathway made of PEEK (polyetherether ketone) was used for this work. This inert polymer is resistant to the corrosive effects of the sulfuric acid in the copper plating bath and the mobile phase.

In this study, organic additives and byproducts were separated on an IonPac NS1 polymeric reverse phase column and detected with a UV detector. A silica-based reverse phase column would normally be used for the separation of these neutral and polar organic analytes. However the silica column packing is not suitable for use with this acidic sample matrix. The packing material of the NS1 is well suited for this analysis because it is resistant to the acid content of the bath.[4] The mobile phase consisted of an acetonitrile gradient in dilute sulfuric acid. The following chromatographic conditions were optimized: sample injection volume, absorbance wavelength, and acetonitrile gradient profile.

The detection of the suppressor additive is challenging because it does not have conductive or chromaphoric properties. Evaporative light scattering detection (ELSD) was investigated as a means of detection for this additive. ELSD was shown to be an effective means of detection of the non-volatile suppressor additive in a volatile solvent stream.

An ion chromatographic (IC) method was developed for the determination of chloride in acid copper plating baths. Compared to standard wet chemical techniques IC offers improved speed and accuracy for this analysis. Chloride is detected by suppressed conductivity.[5] The EG40 eluent generator was used to prepare the potassium hydroxide eluent on-line.[6] Chloride was separated from the excess of sulfate present in the copper-plating bath.

References

1. Reid, J.D. *Plat. and Surf. Fin.*, **1988**, **75**, 108-112.
2. Heberling, S.; Campbell, D.; Carson, S. *PC Fab.*, **1989,** *12(8)***,** 72.
3. Taylor, T.; Ritzdorf, T.; Lindberg, F.; Carpenter, B. *Solid State Technol.,* **1989,** *41(11)*, 47-57.
4. Weiss, J. *J. Chromatogr*. **1986**, *353*, 303-307.
5. Small, H.; Stevens, T.S.; Bauman, W. C. *Anal Chem*., **1975**, *47* 1801
6. Liu, Y.; Avdalovic. N.; Pohl, C.; Matt, R.; Dhillon, H.; Kiser. R. *Am. Lab*., **1998** 30 (23) 48C-58C