Analysis and Control of Plating Baths Chromatography Vs CVS

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Over the past few years, there has been a growing debate on the benefits of using chromatography versus CVS for plating bath analysis and control. Recent research by the semiconductor industry into copper plating bath technology has further fueled the debate due to the fact that plating technology for electronics and semiconductor applications requires rigid bath control and disciplined methodology. Establishing correlations between what is found in the plated film and bath control parameters is fundamental in producing platings that are consistent and reliable. This paper will compare and contrast the use of chromatography versus CVS for the analysis of a variety of constituents in plating baths.

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Introduction

Plating technology has been used in electronics manufacturing to plate through-holes and wiring on printed circuit boards since the early 1980's. Conductors, terminators, interconnections, ground planes and heat dissipaters are examples of multilayer board components which may be fabricated by electroplating operations. In addition to contributing important information for new plating bath research activities, HPLC and IC have played an important role in monitoring and controlling a diverse range of chemical species in on-site plating operations. An increased understanding of the plating operation through the use of IC/HPLC has resulted in reduced scrap rate, improved device quality and optimization of bath lifetime.

Most recently, the use of copper metallization on semiconductor devices has set the stage for increased requirements for the purity, plating effectiveness and plating speed of electroplating bath chemicals.¹ Increased requirements have also been set for monitoring and optimizing copper electroplating baths used in the manufacture of these devices. Although electrochemical deposition (ECD) is not a new technology, the requirements for precision and quality of the deposition in the semiconductor industry are, by far, more critical than that currently practiced in other industries. HPLC and IC provide the analytical capabilities to monitor plating bath additives and electrodeposition by-products to help optimize the process and improve yields.²

New copper plating bath products are being introduced to meet the emerging needs of this application. The new products are designed to provide a fast, efficient fill for even the most challenging wafer terrain. An example of these new products is the Enthone-OMI ViaForm[®].³ New analytical methodologies have also been developed using ion chromatography for evaluating these new electroplating products. Some typical applications for the analysis of the copper metallization plating bath are the determination of SPS additive concentrations and the analysis of SPS additive electrolysis by-products.

HPLC and IC Can Monitor a Variety of Plating Baths.

These baths are:

Acid Copper Sulfate Electroless Copper Gold Tin/Lead Nickel Sulfamate Electroless Nickel Watts Iron-Nickel Table 1 shows the various components of each of these baths which can be monitored using IC/HPLC.

Plating Bath	Constituents	Objective of Analysis
Acid Copper	Trace Chloride	Optimize throwing power
	Sulfate, Copper	Major constituents
	Brighteners/Additives	Improve deposition quality
	Trace Metals	Contaminants
Electroless Copper	Formate	Bath age evaluation
	Tartrate, Triethanolamine	Chelants
Gold	Arsenite	Stabilizer
	Sulfite, Sulfate	Major constituents
	Au (I), Au (III)	Determine total gold in addition
	Hydroquinone	to speciation
		Improve deposition quality
Tin/Lead	Sn(II) Pb (II)	Deposition efficiency
Nickel Sulfamate	Chloride	Anode corrosion
	Sulfamate	Major constituent
	Sulfate, Ammonia	Breakdown products
Electroless Nickel	Hypophosphite, Phosphite	Deposition efficiency
	Phosphate	
	Succinate, Citrate	Chelants
	Nickel, Cobalt	Major constituents
Watts Nickel	Chloride, Sulfate, Nickel, Iron	Major constituents
	Borate	Buffer
	Copper	Trace contaminant
	Saccharine	Deposition quality
	Lauryl Sulfate	Wetting agent

Table 1: Plating Baths Which Can Be Monitored By IC/HPLC

In the past, plating bath monitoring was mainly done by visual inspection of the plated product. Only when defects were found did the operator take action to either rejuvenate the bath or dump it. Clearly, as the features that are being plated become smaller or more complicated so that the plating quality is no longer a subjective visual evaluation does it become increasingly important to have ways to accurately monitor the plating bath.

Ion and High Performance Liquid Chromatography are analytical techniques that can provide critical information on the absolute concentration and proportional balances of components in plating solutions. These techniques can also provide information on contaminants and degradation products. A typical HPLC system is shown in figure 1. Figure 2 shows a typical Ion Chromatography system. Both systems consist of an eluent delivery mode, a separation mode and a detection mode. An eluent is pumped through the system and a liquid sample is introduced into the flowing eluent steam by means of an injection valve. The eluent flow carries the sample to the analytical column where it is separated into its individual components. These components are then swept into the detector. The detector signal provides information which helps identify and quantify the species. The separation and detection modes are dependent on the chemical nature of the species of interest.



Figure 1. Schematic of a High Performance Liquid Chromatograph



Figure 2. Schematic of an Ion Chromatograph



Figure 3. Analysis of chloride in an acid copper plating bath by IC.

The main difference between HPLC systems and IC systems is that IC has additional hardware which is used to suppress background conductivity and remove component interferences. An IC system also has an inert non-metal flow path. This is important because many plating bath applications involve corrosive samples and, unless passivated, metallic systems will corrode under these conditions. Analyses, which might be done using HPLC and IC for a typical acid copper sulfate bath, are:

1. The analysis of trace chloride. Chloride is used to improve the throwing power of the bath. However, it must be controlled within a narrow range for best results. See figure 3.

2. Analysis of part per million (ppm) levels of organic additives such as accelerators, brighteners, suppressors and levelers. These constituents are typically proprietary; however, a "fingerprint" analysis can be completed which can provide a multitude of information when correlated to deposit quality. See figure 4.

- 3. Analysis of levels of trace metals such as zinc and nickel. These metals can adversely affect the bath performance.
- 4. Analysis of electrolysis by-products. See figure 5.
- 5. On-line monitoring of bath composition.



Figure 4. Analysis of the accelerator additive in an acid copper plating bath.



Figure 5. Analysis of the accelerator additive electrolysis by-products in an acid copper plating bath.

Cyclic Stripping Voltammetry (CVS)⁴

Cyclic Voltammetric Stripping is an electrochemical technique used for the measurement of organic additives in plating baths. It is based on the effect that the additives have on the rate of electroplating. Regardless of the specific type of organic additive (brightener, leveler, grain refiner, etc.), its activity is reflected in a change in the plating rate.

The analysis is performed in an electrochemical cell using a three-electrode system, one of which is a platinum rotating disk electrode. During measurement, the potential of the platinum electrode is controlled by the instrument. The potential is scanned at a constant rate back and forth between negative and positive voltage limits. A small amount of metal from the plating bath is alternatively plated onto and stripped off the working electrode as the potential is changed. During the scan, the current at the working electrode is measured as a function of potential.

The activity of the additive will affect the plating rate of the metal onto the electrode. The plating rate is determined by calculating the charge required to strip the metal off the working electrode. The relationship between the stripping charge and the activity of the additives is used to quantitatively measure the additives and their components.

For a typical acid copper plating bath, CVS will monitor the same additives and electrolysis byproducts as can be monitored with HPLC and IC. 5

When To Use HPLC/Ion Chromatography versus CVS?

Due to the many innovations in both CVS and HPLC/IC over the past decade, there are fewer areas of distinction between the two techniques. Certainly for fast on-line production analysis of the "health" of an electrolytic plating bath, CVS is the method of choice. However, to get concentration values for specific ions such as sulfate in a gold bath, chromatography is still the preferred method of choice. Also, for electroless plating, chromatography is the only analytical method available to quantify low levels of ionic and organic additives (figure 6). New plating bath research is another area where chromatography can benefit the end-user. IC and HPLC Mass Spectrometry has been used successfully for plating bath research. In some cases end users, frustrated with lack of bath information from the proprietary suppliers, have selected chromatography and mass spectrometry to facilitate "reverse engineering" a plating bath so they can enhance the plating bath by adding additional additives for their needs.



Figure 6. Analysis of Organic Acids in an Electroless Copper Plating Bath

Conclusion:

CVS and HPLC/IC continue to be complimentary tools for the plating bath analyst. The techniques of ion chromatography and high performance liquid chromatography are ideally suited to the analysis of a variety of solutions used to electroplate printed wiring boards. These techniques can be used to monitor known key constituents and can also provide rapid "fingerprints" of proprietary additives. On-line systems can give trend information to monitor the decomposition of bath additives over time. IC and HPLC with mass spectrometry can be used to design new baths.

With the plating baths currently in use and as new plating bath products are introduced to this expanding marketplace, these analytical techniques will provide invaluable information for quality and cost control.

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