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Electrolytic Copper Bath Analysis for Printed Circuit Board Fabrication

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Maintaining electroplated copper deposit physical properties within specified ranges is critical to ensuring the reliability of Printed Circuit Boards. From thick panel, high aspect ratio backplanes to fine line HDI via fill applications, modern acid copper electroplating systems have been optimized to offer a variety of customized performance capabilities. Irrespective of the specific application, in order to allow consistent, predictable and reliable operation, the electroplating process parameters must be controlled within specifications. Perhaps the most critical aspect of copper electroplating bath control is the monitoring of organic additives. Failure to properly control the organic additives can quickly result in inconsistent performance and reduced deposit quality.

This paper provides an overview of methods used for copper electroplating bath control, including approaches to organic additive analysis, appropriate for use in PCB manufacturing.

The vast majority of copper electroplating baths used in the PCB industry today are based on electrolytes consisting of copper sulfate and sulfuric acid. Combining low cost and convenient operation, such acid sulfate based systems have now been used in the PCB industry for over 50 years. This article will therefore focus on methods used with this class of bath.

ANALYSIS OF INORGANIC COMPONENTS

A typical acid sulfate system contains copper sulfate (the primary source of cupric ions), sulfuric acid (for solution conductivity) and chloride ion (as a co-suppressor). Baths designed for high PCB through hole throwing power applications will typically have copper sulfate concentrations below 75 g/L and sulfuric acid concentrations above 160 g/L (to provide high solution conductivity to minimize the potential drop across holes). In contrast, baths designed for high current densities or for via filling will typically have much higher copper concentrations and lower acid concentrations. High copper concentrations favor via filling, due to the lower mass transport rate in blind microvias.

Analysis of inorganic components is typically done using the following techniques:

Table 1: Inorganic Component Analytical Methods

Parameter	Method	Comments
CuSO ₄	Iodometric titration Spectrophotometry	
H ₂ SO ₄	Acid base titration	
Cl ⁻	Potentiometric, using a Cl ion specific electrode Turbidimetric titration using Ag	Ag preferred to Hg which was more often used in the past
Trace Metals	Inductively coupled plasma atomic absorption (ICP-AA)	

ANALYSIS OF ORGANIC COMPONENTS

An acid copper sulfate system operated without organic additives yields deposits of poor physical properties. Proprietary organic additives are used to modify deposit characteristics, with the particular type(s) and concentration(s) of these components selected to enhance specific deposit attributes. Organic additives are employed to improve grain refinement and increase throwing power, leveling and brightening of the deposit. Generally, there are three basic types of additives used in acid copper plating: Carriers, Brighteners, and Levelers.

Carriers, also referred to as suppressors, are typically large molecular weight polyoxy-alkyl type compounds. Carriers adsorb at the surface of the cathode and, in concert with chloride ion, act to suppress the plating rate.

Brighteners, also referred to as accelerators, are typically organo-sulfur compounds that increase the plating reaction by displacing adsorbed carrier. Brightener compounds may exist in several forms in electrolytic working baths.

Levelers are typically nitrogen-bearing heterocyclic or non-heterocyclic aromatic compounds that act by displacing brightener species in high current density sites (for example, at protrusions). Adsorption of these additives at protrusions reduces the plating rate in those regions.

It is well known that brightener species generate byproducts during operation. This behavior is common to all organo-sulfur brightener species used in commercially available acid copper plating baths. These byproducts are formed both chemically, during idle time through interaction with Cu(0), and electrochemically, during deposition. Although a wide variety of different byproduct species can be formed, brightener reduction byproduct species are of particular concern, since these can greatly affect the performance of the bath. To offset byproduct accumulation in the plating bath over time, removal using carbon treatment, UV oxidation or polymer adsorbing materials is required to maintain consistent performance and deposit quality.

The detection, quantification and control of organic species is made more complex by the fact that they are used at very low concentrations, in some instances below 1 ppm.

Selection of analysis methods for trace components must take into consideration a number of factors:

- Measurement time
- Accuracy and repeatability
- Sensitivity
- Ability to separately detect all relevant bath components
 - Deliberately added components (Brightener, Carrier, Leveler)
 - Additive breakdown products (by-products)
 - Contaminants (from such sources as laminate materials, resists or drag-in)
 - Unexpected contamination
- Ease of use
- Safety and waste generation (environmental impact)
- Initial cost of test equipment
- Ongoing cost of ownership

Many analytical techniques have been used to monitor the organic components in a copper electroplating bath. The advantages and disadvantages of the more common methods are reviewed below.

DIRECT ANALYSIS METHODS - CHROMATOGRAPHY

Chromatographic separation of multi-component mixtures has been a standard technique for quantitative analysis for years and has been used in many applications. As practiced in electroplating, liquid chromatography has the capability to determine virtually all important bath additives and their breakdown products.

High Performance Liquid Chromatography (HPLC) and Ion Chromatography (IC) are the techniques most often used for electroplating component analysis, and share similar equipment architecture (1, 2). The chromatograph consists of an eluent delivery module, a sample port for analyte injection, a separation column and a detector. The eluent is a carrier solvent that transports small sample volumes through the separation and detection modules under high pressure. The separation column is packed with resin beads that may be coated with insoluble anionic or cationic films, or left uncoated. The various components present in a bath sample display differing affinities to the separation column; those adsorbed most weakly are eluted through the column more quickly, while those with increasing affinity have less mobility through the column, leading to separation into a series of discrete bands, before entering the detector module.

Detection can be accomplished in several ways, depending on the species characteristics. In Ion Chromatography, a common detection method for cationic or anionic species is based on the changing conductivity of the separated sample stream. Other detection methods include UV/VIS absorption or a form of amperometric detection. UV / VIS absorption is similar to other spectrophotometric methods, while the amperometric approach relies on measurements of current from oxidation or reduction reactions of the analyte species.

The output response of a chromatographic detector is plotted against time, with the resulting chromatogram displaying one or more separate response peaks. When compared against reference chromatograms of known composition samples, the identity and concentration of individual species can be established.

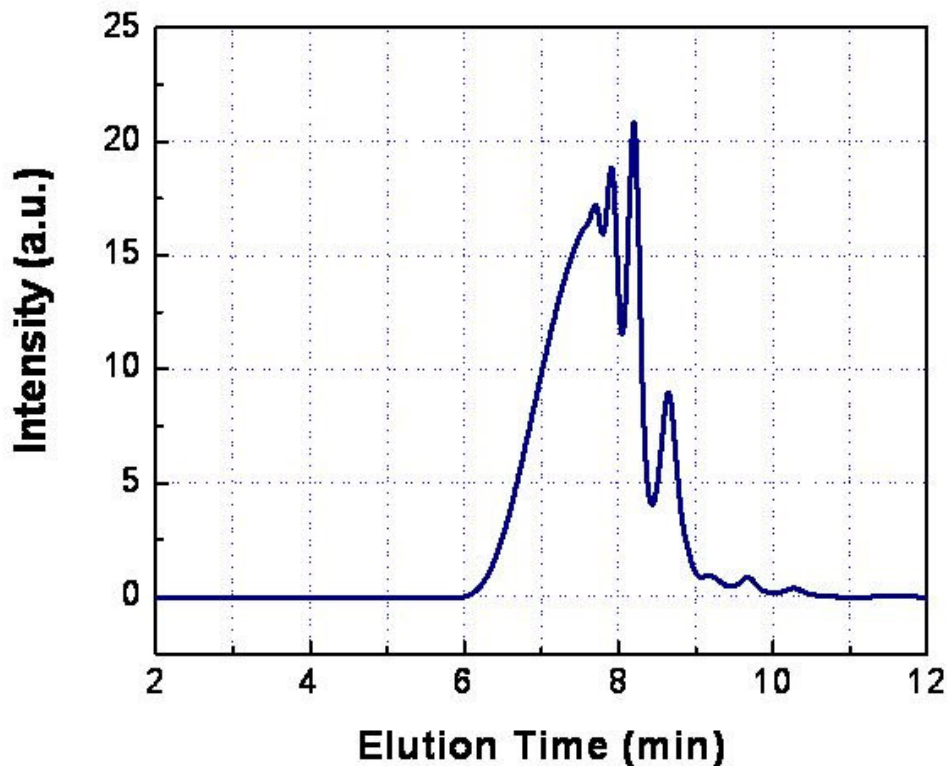


Figure 1: HPLC Chromatogram

Some of the shortcomings of chromatographic methods include waste generation, particularly the eluent liquid consumed during analyses. Since chromatography waste streams differ in makeup from the plating bath, they cannot be simply returned to the working plating bath. A second shortcoming is the relatively long times that may be required for analysis. Lastly, the end user may have to invest significant time to develop suitable methods for individual plating baths.

Chromatographic methods can also be vulnerable to introduction of unexpected contaminants, which may either not be detected, or may have an unexpected interaction with the species normally present.

TOTAL ORGANIC CARBON (TOC)

Total Organic Carbon is simply a measurement of the amount of organic carbon in a liquid sample. For electroplating baths, TOC is often used to both estimate the need for, and evaluate the effectiveness of bath purification treatments (i.e. carbon treatment). Since TOC does not differentiate between electrochemically active and inactive organic materials, the method cannot be used to control bath additives.

In addition, some electrochemically active byproducts, particularly brightener byproducts, may degrade plating performance or deposit quality at concentrations that are too low to affect TOC level, making the method inappropriate to be the sole means to determine need for carbon treatment.

SMALL SCALE PLATING TEST METHODS

Methods that directly measure the plating performance of a bath sample have the advantage that any significant changes in bath behavior are likely to be detected, even if associated with unexpected species. The challenge with direct evaluations of plating performance has always been to find ways to express the test response as a measurement that can be converted into a quantifiable expression of bath composition, so as to enable bath control.

HULL CELL

Until recent years, Hull cell tests were the industry standard for control of acid copper plating baths, and are still widely used today. A Hull cell (3) is a small volume plating cell, typically 267 ml, used to evaluate the deposition characteristics of an electroplating bath across a broad range of current densities. In a conventional electroplating cell, the cathode is oriented in parallel to the anode(s), to ensure uniform current distribution. In a Hull cell, the cathode, typically a brass panel or copper clad laminate, is deliberately placed at an angle to the anode, thus creating a regular and known current density distribution across the cathode. The plated deposit appearance will vary as a function of the local current density. For a given applied current, a “current density ruler” can be used to determine the current density at specific locations on the Hull cell panel, correlating to specific deposit characteristics, such as the range in which smooth, bright deposits are obtained.

Production bath Hull cell panels are compared to standard Hull cell panels, previously generated from a new acid copper bath at standard conditions, and also at additive levels outside the normal control ranges. By comparing the brightness, haze and burn regions of the production test panel with a standard test panel, a determination of what additive additions or dilutions might be necessary to correct the production bath can be made.

Dilution and depletion Hull cell tests can also provide more detailed information about the state of a plating bath. In a dilution Hull cell test, the working bath sample is tested after dilution with Virgin Makeup Solution (VMS), an electrolyte without organic additives. Results of these tests can aid detection of under or overdose situations. In a depletion Hull cell test, a series of panels are processed through the same Hull cell solution without replenishment, until a noticeable change in deposition is obtained. Depletion Hull cell testing can aid in detecting excessive brightener concentrations or brightener byproduct buildup.

While the exact component concentrations in a bath cannot be determined using this approach, the Hull cell can provide valuable qualitative information about the plating bath.

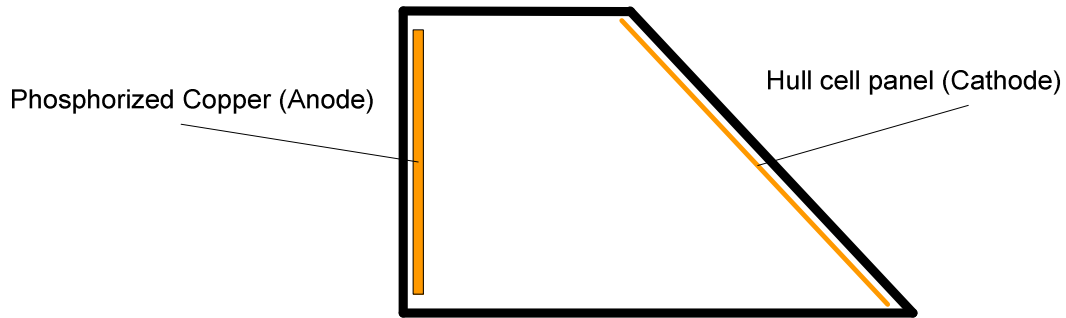


Figure 2: Schematic of Hull cell

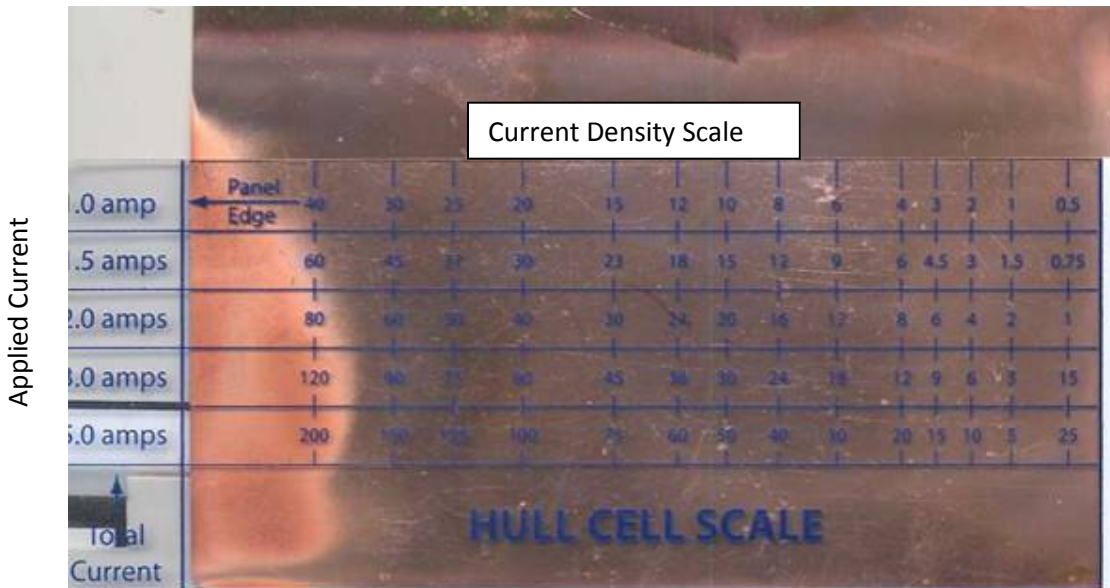


Figure 3: Hull cell panel from acid copper electroplating bath (with current density ruler overlay)

SLIT HULL CELL

A Slit Hull cell differs from a Hull cell in that the cathode is placed perpendicular and offset to one side relative to the anode, and a shield with a small opening at the end away from the anode is placed parallel to the cathode (Figure 4). This combination of anode and cathode placement, coupled with the slitted shield, imparts a predictable current density distribution across the cathode.

Slit Hull cells can be useful for monitoring organic bath components, particularly those that affect throwing power. The location of the burned area in the high current density region and the brightness of the low current density can be used to estimate the concentration of these specific components.

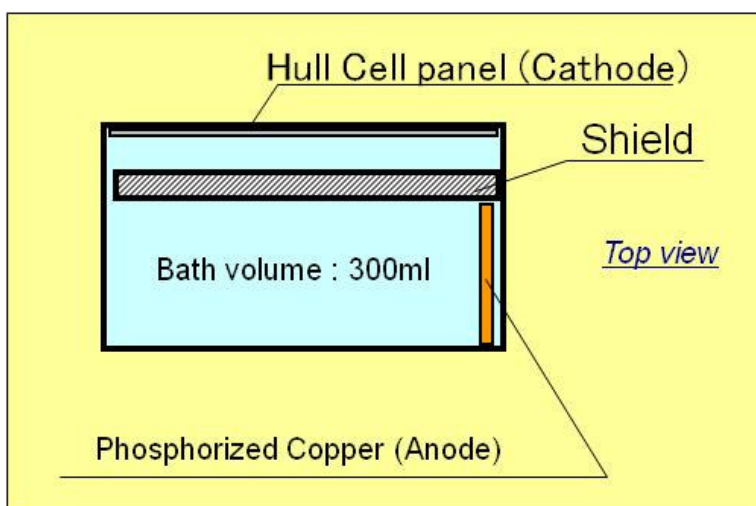


Figure 4: Schematic of Split Hull cell

OTHER CELL DESIGNS

While a number of other plating test cell designs are available (4), for example, Haring-Blum cell, Rotating Cylinder Hull cell and Gornall cell, such cells are more often used for formulation development than for production process control within a customer facility.

ELECTROANALYTICAL METHODS

Electroanalysis is an attractive approach to bath control as measurements of the electrochemical response of a bath sample to a specifically controlled electrical stimulus are strongly correlated to the balance in the bath behavior between suppression and acceleration. This correlation allows such methods to quantify species concentrations.

Voltammetry involves the measurement of current in an electrochemical cell flowing as a consequence of application of controlled potentials to a working electrode. The potential is expressed with respect to that of a reference electrode such as Ag/AgCl or Saturated Calomel Electrode (SCE). The most common type of working electrode used for analyzing electroplating additives is an inert Rotating Disk Electrode (RDE), with a Pt, Au, Pd, Ir or Rh surface.

A three electrode cell, with a working electrode, a secondary electrode (also referred to as a counter or auxiliary electrode) and a reference electrode is typically used. The potential at the working electrode is controlled using a potentiostat, which employs a feedback system to compare a fixed voltage with the voltage measured between the working and reference electrodes. The output of the feedback system controls the voltage between the working and secondary electrodes.

CYCLIC VOLTAMMETRIC STRIPPING (CVS)

The most common electroanalytical technique for PCB copper plating bath analysis is Cyclic Voltammetric Stripping (CVS). Since the method was first introduced in the 1980's, it has largely replaced Hull cell analysis as the primary control methodology for acid copper plating baths (5, 6).

The method is based on the formation of, and subsequent removal of, a plated deposit on the surface of the working electrode. The potential of the working electrode is swept at a constant rate between user defined limits. The voltage sweep typically starts at a potential at which metal deposition does not occur. The potential is then swept into the metal deposition range, and then back to anodic potentials at which the deposit is dissolved. This sequence may be repeated several times, with the working electrode alternating between film deposition (at cathodic potentials) and film stripping (at anodic potentials) until a repeatable current vs. voltage profile is obtained.

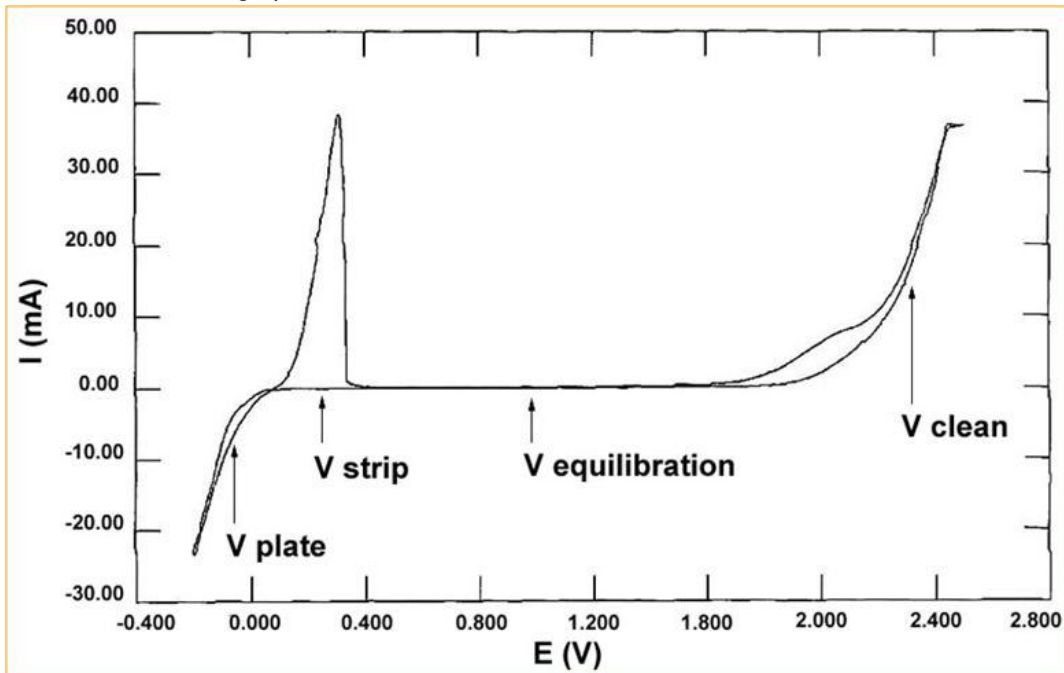


Figure 5: Typical CVS Voltammogram

Plating bath additive concentrations modify the metal deposition process, reflected by changes in the current vs. profile. For example, additions of carrier will tend to inhibit plating, corresponding to lower currents over a given voltage range, while additions of brightener will have the opposite effect.

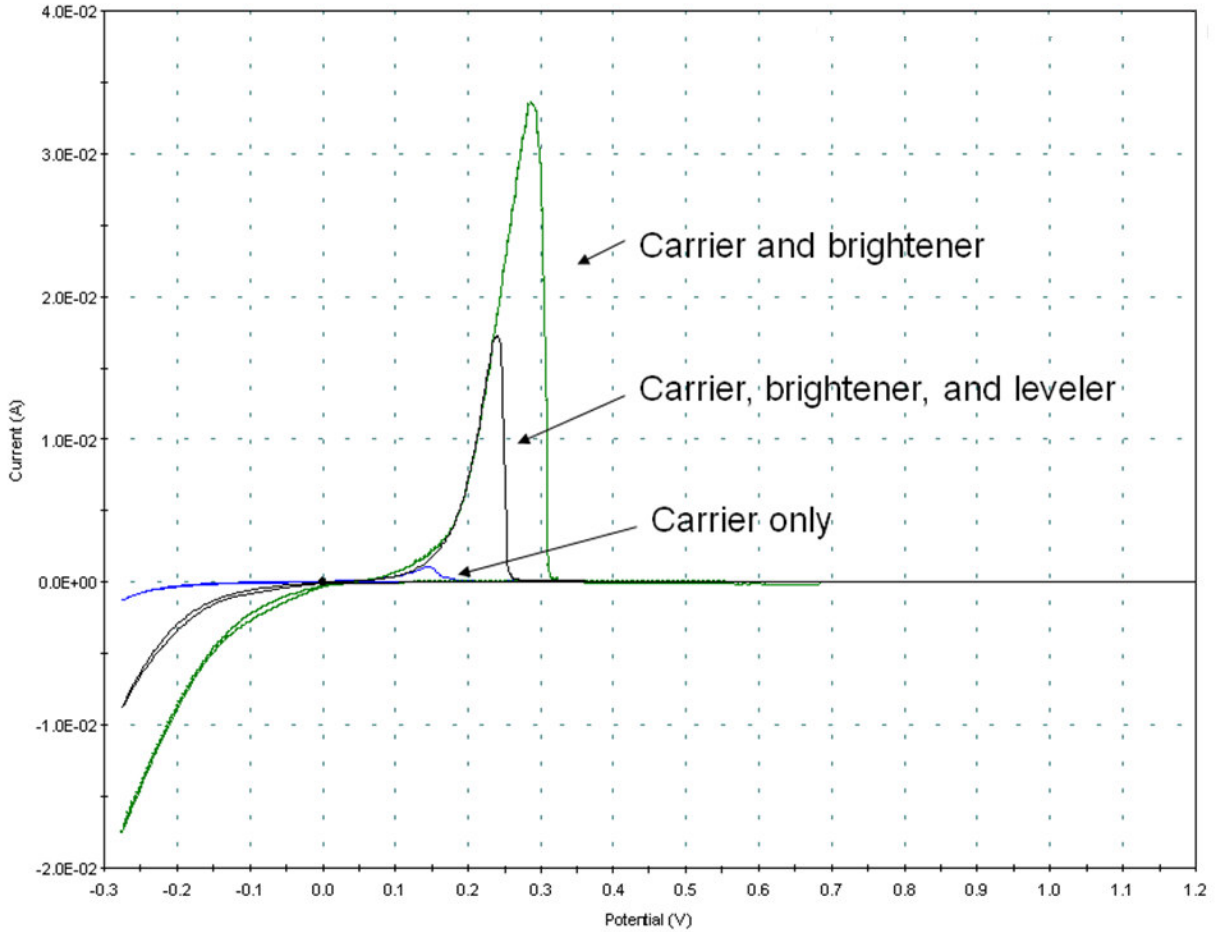


Figure 6: CVS voltammogram showing response to organic additives

During the CVS cycle, the charge (current x time) that flows during both the deposition and stripping portions of the scan are measured. By Faraday's law, charge is directly related to the quantity of an electrochemical process. While either the deposition or the stripping charge could be used, CVS measurements are typically based on the stripping charge, because the stripping charge has been found to be less affected by changes in the electrode surface condition.



Figure 7: CVS apparatus (image provided courtesy of ECI Technology, Inc., Totowa, NJ)

CYCLIC PULSED VOLTAMMETRIC STRIPPING (CPVS)

In CPVS analysis, the potential of a working electrode is pulsed between discrete values for fixed times, rather than being varied at a constant rate (7). The working electrode is first cleaned at a high anodic potential (V_{clean}) for a few seconds, followed by an equilibration step ($V_{\text{equilibration}}$). Metal is deposited on the working electrode during a cathodic pulse (V_{plate}), then held at an anodic potential (V_{strip}) until all the copper is dissolved. Again, the integration of either the charge during the plating or stripping cycle gives a measure of the deposition process.

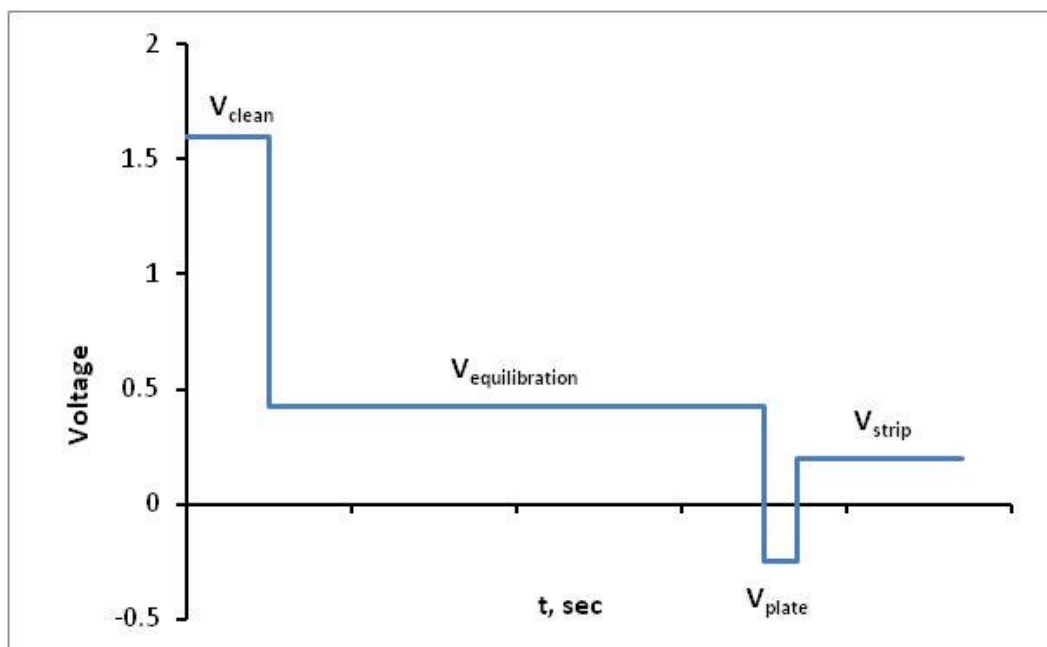


Figure 8: Typical CPVS waveform

Voltammetric stripping techniques are sensitive to working electrode surface condition and to electrolyte temperature, which can progressively degrade measurement precision and accuracy.

A technique that accounts for these variations is a form of voltammetric titration, in which aliquots of an electrochemically active organic additive are added to a baseline solution, and stripping charge measurements made for the baseline and for each successive add. The stripping charges are normalized against this baseline response and plotted against the cumulative added volume. This response is then compared to pre-existing calibration data for determination of analyte concentration. This charge ratio procedure tends to cancel out effects of changes in electrode surface or variations in electrolyte temperature, which might otherwise degrade measurement precision.

The volumes of plating solution required for these techniques is small (less than 100 ml) and do not require addition of any materials that are not used in the actual plating bath. In many cases, the analyte can be returned to the plating bath, completely eliminating waste. These methods are also very compatible with automatic sampling, and numeric measurement data can be easily acquired and converted to suitable formats for reporting and process control.

One of the shortcomings of electroanalytical methods is the inherent interaction within the bath additive chemistry. Plating bath components and their breakdown products can display confounding electrochemical interactions. Since such methods infer additive concentrations from the relative rate of the deposition process, the stripping charge responses (and attendant inferred component concentrations) can be ambiguous, if several bath constituents have undergone significant concentration changes simultaneously.

SUMMARY

As the capability of electroplating systems, both bath chemistry and electroplating equipment, has increased to match the increasingly stringent metallization requirements of advanced PCB designs, so too has the need for improved bath analysis and control. A range of analytical methods are available for the analysis and control of copper electroplating baths used in PCB metallization, with each method having its own specific advantages and disadvantages.

Chromatographic methods offer the ability to detect and quantify a wide variety of organic components, although requiring significant equipment cost, method development, measurement time and waste generation.

Small scale plating tests, such as Hull or Slit Hull cells, provide a qualitative "picture" of the overall bath condition. Supplemental techniques, such as dilution and sequential depletion Hull cell testing, can provide additional empirical information about the plating bath, even if exact component concentrations cannot be measured.

Electroanalytical methods, such as CVS and CPVS, provide a direct measure of the electrochemical activity of the plating bath. With commercially available systems providing prepackaged routines designed for production bath analysis, these methods are suitable for use in a typical PCB quality control laboratory. Rapid measurement of bath component concentration, facilitate the use of statistical process control methodologies.

Whether used separately or in combination, these methods provide customers with the capability to deliver consistent, predictable and reliable electroplated copper deposits.

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