



Application Note AN-PAN-1067

Online analysis of organic additives in copper plating process

Demand for printed circuit boards (PCBs) manufacturing is on the rise. This requires exploration into techniques to optimize the PCB manufacturing process for maximum efficiency and superior product quality.

The deposition of copper from galvanic plating baths is an important stage during the production of PCBs, and monitoring the organic additive content is critical for ensuring a high-quality product. This is frequently achieved by using analytical techniques such as cyclic voltammetric stripping (CVS).

CVS allows the precise measurement and control of additive levels (e.g., brighteners, suppressors, and levelers), hence maintaining optimal plating conditions and improving the overall efficiency and reliability of the manufacturing process.

This Process Application Note presents a technique to optimize the electroplating copper process for PCBs online with a 2060 CVS Process Analyzer. This process analyzer ensures consistent quality and precise control over copper deposition.

As electronic devices like mobile phones and miniature computers continue to shrink in size and gain more features, PCBs need to utilize the most of their available space.

To pack in more connections, new PCB layouts feature more, smaller vias that connect components with shorter paths. However, achieving this level of complexity requires highly precise manufacturing techniques.

Galvanic copper plating of drill holes and board surfaces is a critical production step in PCB manufacturing [1]. The plating solution requires constant monitoring of several key components such as copper, sulfuric acid, chloride, and organic additives. These additives include suppressors, levelers, and brighteners, each playing a crucial role in achieving the desired physical properties and finish. Maintaining the concentration of these additives within a narrow range is critical. This is why accurate copper plating bath monitoring is essential for the plating process to function correctly.

While copper, sulfuric acid, and chloride

concentrations can be measured using titration, CVS is the industry standard approach for analyzing the organic additives. This technique analyzes how the additives affect the copper plating process to determine their concentration. This is because the amount of additives in the solution impacts how quickly the copper plating reaction happens.

Each organic additive in the copper plating bath plays a specific role in shaping the final copper layer. For example, suppressors directly reduce the rate of copper deposition in order to achieve a more well-ordered deposit with tighter grain structure (Figure 1, left).

In contrast, brighteners, when added to a solution saturated with suppressor, slightly counteract this effect and increase copper deposition (Figure 1, right). The purpose of the brightener is to encourage the growth of equiaxed (non-directional) grains.

Levelers, while less potent than suppressors, also influence the final copper layer by smoothing out its surface [2].

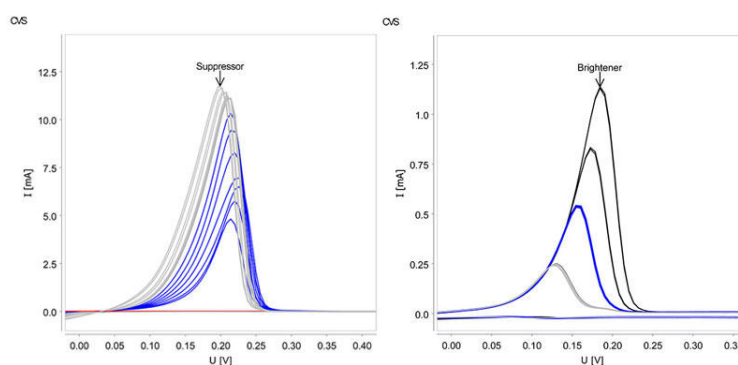


Figure 1. Influence of organic additives on copper plating of PCBs. Left: Suppressor effect. Right: brightener effect. All example determinations are derived from Metrohm viva software.

INTRODUCTION

Traditionally, CVS has been performed in a laboratory setting, where samples are manually extracted from the plating bath for analysis. While this approach offers high accuracy and sensitivity, it represents only a snapshot of the process conditions.

Changes that occur between sampling events can be entirely missed due to this limited representation. Additionally, manual sample handling can introduce variability in the results due to factors like incomplete extraction or contamination.

Online process analyzers overcome these limitations by performing CVS directly within the process stream. The 2060 CVS Process Analyzer, for example, provides real-time monitoring, allowing continuous observation of the baths and detection of even rapid changes in the parameters being measured.

Automation of sample preconditioning and analysis steps minimizes human error and improves consistency. This process analyzer eliminates the need for manual handling of harsh chemicals, improving safety in the plant. Finally, customizable alarm and intervention settings based on the obtained results enable proactive process control. By incorporating the 2060 CVS Process Analyzer, a more comprehensive understanding can be achieved about the PCB manufacturing process and consistent product quality can be ensured.



Figure 2. 2060 CVS Process Analyzer from Metrohm Process Analytics.

APPLICATION

The 2060 CVS Process Analyzer is an excellent choice for analyzing organic additives (e.g., brightener, suppressor, and leveler) online in electroplating baths for copper plating bath monitoring purposes.

The CVS analysis involves the utilization of an electrochemical cell (**Figure 3**), which is equipped with a three-electrode system and located within the wet part cabinet. Among these electrodes, there is a **rotating platinum (Pt) disk** electrode precisely managed by the process analyzer. The CVS technique involves applying a specific voltage waveform to the Pt disk (working electrode). This waveform simulates copper deposition and subsequent stripping of the deposited copper. Throughout this process, the current flowing through the electrode is continuously monitored. By observing changes that occur to the copper stripping peak it is possible to extrapolate information about the organic additives that are present, including their effective concentration in the bath.

REMARKS

Additionally, copper, sulfuric acid, and chloride concentrations can be measured by titration and photometry using a 2060 TI Process Analyzer from

In conclusion, achieving high-quality PCBs requires precise copper plating with meticulous monitoring of the plating solution. Traditional laboratory-based CVS analysis, while accurate, offers limited snapshots of the process.

The 2060 CVS Process Analyzer ensures optimal



Figure 3. Close-up of the electrochemical cell in the 2060 CVS Process Analyzer.

Metrohm Process Analytics to get a complete overview of the health of the plating bath.

performance in the electrolytic plating process by precisely monitoring and controlling organic additives (e.g., brighteners, suppressors, and levelers) which are crucial for high-quality copper deposition in PCB manufacturing.

REFERENCES

1. The Influence of Copper Distribution on PCB Quality. *Eurocircuits*, 2022.
2. Yen, M.-Y.; Chiang, M.-H.; Tai, H.-H.; et al. Next Generation Electroplating Technology for High Planarity, Minimum Surface Deposition Microvia Filling. In *2012 7th International Microsystems, Packaging, Assembly and Circuits Technology Conference (IMPACT)*; 2012; pp 259–262.
<https://doi.org/10.1109/IMPACT.2012.6420290>.

RELATED DOCUMENTS

WP-051 Automated CVS method development and optimization of multicomponent plating baths

BENEFITS FOR ONLINE PROCESS ANALYSIS

- **Cost savings** – minimizing waste and maximizing the efficiency of additive usage.
- **Mitigate the risk of defects** – consistent monitoring of organic additives.
- **Optimal plating performance** – online precise analysis and quantification of organic additives' concentrations to maintain within the narrow range required.
- **Frees up laboratory personnel** – reduces the need for skilled laboratory personnel to perform the CVS analysis.



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CONFIGURATION



2060 VA/CVS Process Analyzer

The 2060 VA Process Analyzer is an online process analyzer that implements voltammetric analyses to deliver accurate process monitoring. Thanks to its customizable wet part modules, dosing units, pumps, and level sensors can be integrated to target any challenge.

The 2060 CVS Process Analyzer is an online process analyzer designed for online analysis of organic additives in electroplating baths within PCB and semiconductor industries. By using an electrode reaction that mimics the production process, it makes it possible to quantify additives in authentic conditions. Additionally, the modularity of the analyzer supports titration, photometry, sample preconditioning, and interfacing with multiple sample streams.