

AT&S Leoben, Austria – analytical process control using CVS

Determining organic additives in acidic copper baths



AT&S is an Austrian high-tech company. Apart from the company's logo, the picture shows the Austrian flag and the coat of arms of Styria Province.

Introduction

The Austrian company AT&S (Austria Technologie & Systemtechnik AG) with its headquarters in Vienna is one of the most advanced producers of printed circuit boards (PCBs) in the world. AT&S is perfectly positioned in the high-tech segment of HDI Microvia technology, which is primarily used in hand-held applications (e.g. in cell phones, PDAs, etc.). Further important areas of activity are PCBs for automobiles and for industrial and medical uses.

One of the most important process steps in the production of PCBs is the galvanic deposition of very thin copper coatings. In order to achieve a copper coating (deposit) of uniformly high quality, strict analytical control of the copper bath constituents is essential.

A company guaranteeing the highest product quality, innovative solutions, absolute customer loyalty and the best service has the right to demand the same from its suppliers. This is why the quality management of the Austrian company has relied on Metrohm instruments since 1988. They manage a large part of the workload and perform about 30 000 individual analyses per month.



One of the three Austrian production sites of AT&S is located in Leoben (Styria Province). Analytical instruments manufactured by Metrohm are used for analyzing the electroplating baths.

Problem

When present within very narrow concentration limits and at a defined ratio to each other, organic additives used in copper baths, for example suppressors and brighteners, ensure optimal copper deposition. Suppressors slow down the metal deposition rate; brighteners accelerate it. Using the same electrode reaction that occurs during the deposition process, Cyclic Voltammetric Stripping (CVS) provides the only possibility of directly measuring the activity of the additives and thus their effectiveness in the plating process. CVS has been used for this application since the end of the eighties.

In 2004, AT&S decided to replace their old CVS instruments by new ones. AT&S had been using a Metrohm 746 VA Trace Analyzer for trace metal analysis, which meant that neither Metrohm nor voltammetry were unknown to them. It seemed thus only logical to contact Metrohm to discuss possible uses of Metrohm instruments for CVS. Metrohm's 797 VA Computrace is a versatile analytical instrument for CVS determinations.

In order to be considered by AT&S, the Metrohm CVS system had to satisfy the following requirements:

- Suppressor determination by dilution titration (DT)
- Brightener determination by «Modified Linear Approximation Technique» (MLAT) in CVS mode and CPVS mode
- Analytical results comparable to those obtained previously
- Reproducible results
- Robust methods
- Transparent and flexible software
- Service at reasonable conditions
- After-sales support
- Lower running costs

The analytical system from Metrohm at a glance

The 797 VA Computrace is particularly suitable for the analysis of copper baths. In order to achieve even more precise results at less cost, the MVA-12 System with Dosing Interface for automatic solution addition was used.



The MVA-12 System with Dosing Interface for the comfortable analysis of copper baths.

Components of the MVA-12 System (Metrohm VA System 12) + Dosing Interface:

- 1 x 797 VA Computrace
- 1 x 846 Dosing Interface
- 7 x 800 Dosinos



The measuring head of the 797 VA Computrace equipped with (left to right) Pt auxiliary electrode, working electrode (rotating Pt-disk electrode) and reference electrode (silver/silver chloride electrode).

Method description

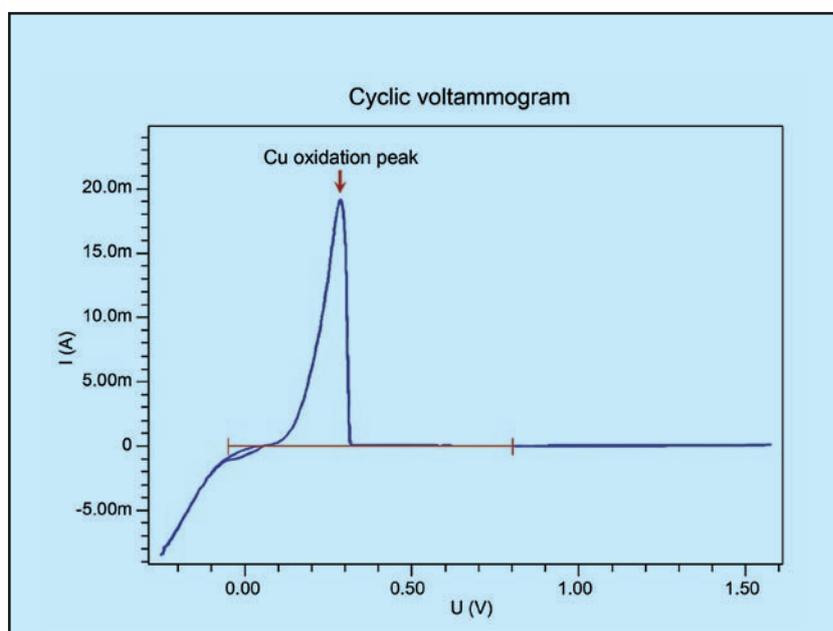
The copper bath to be analyzed is used for manufacturing PCBs for cell phones and consists of a mixture of various components. Specific analytical techniques are used for determining the content of these components in the copper bath (see table below).

Analyte	Method
CuSO ₄	Titration
H ₂ SO ₄	Titration
Chloride	Titration
Iron(II)	Titration
Iron(III)	Spectroscopy
Suppressors	CVS
Brighteners	CVS

Determining the concentration of suppressors using DT / CVS

Dilution titration in combination with the CVS measuring technique is used for determining the concentration of suppressors in an acidic copper bath. In order to carry out a CVS determination, a defined amount of the virgin makeup solution (VMS) – copper bath without organic additives – is pipetted into the measuring vessel. By applying a cyclic potential sweep (triangular sweep) to first reductively deposit the copper onto the rotating Pt-disk electrode and then oxidatively dissolve it in a second step, a cyclic voltammogram is recorded. The area obtained under the dissolution peak (oxidation peak) is evaluated and used as the start area Q_0 in the subsequent calculation. The addition of suppressor reduces this area. The area of the oxidation peak is given as an electric charge in coulombs. In order to record a calibration curve, aliquots of suppressor standard are added to the VMS (dilution titration) and the area under the oxidation peak is determined each time. The measured charge becomes continually smaller until it reaches a particular percentage of the original value Q_0 and the addition of the standard solution is stopped. In the determination step the same procedure is repeated with new VMS and the addition of bath sample instead of suppressor standard solution.

By using the results of the two dilution titrations the suppressor concentration in the copper bath can be calculated.



Example of a cyclic voltammogram with the oxidation peak, whose area is used to determine the suppressor concentration in a copper bath.

Determining the concentration of brighteners using MLAT / CPVS



Andreas Siberl analyzing a bath sample with the 797 VA Computrace. In the foreground the Dosinos used for automatic solution addition are clearly visible.

Brighteners increase the area under the dissolution peak. Based on this characteristic property, the concentration of a brightener in an acidic copper bath is determined using the MLAT calibration technique in combination with the CPVS measuring technique.

To carry out a determination, an aliquot of copper bath without organic additives (VMS) is pipetted into the measuring vessel and saturated with suppressor concentrate. This mixture is known as the «intercept solution». A chronoamperogram is then recorded with the CPVS measuring technique. The area obtained under the oxidation peak is evaluated and then used as the intercept value.

A defined amount of bath sample is pipetted into the intercept solution and a chronoamperogram is again recorded. The brightener contained in the bath sample increases the area under the oxidation peak. This is followed by the addition of two portions of pure standard brightener solution. From the data obtained by the use of the standard addition method and a linear regression (MLAT calibration technique) the brightener concentration in the bath sample can be calculated.

Conclusions

In 2004 the first system based on the 797 VA Computrace was commissioned in the AT&S chemistry laboratory; the second system followed one year later. The use of the two measuring systems, which work around the clock in 4-shift operation, permits continuous monitoring of the organic additives contained in the copper process electrolyte. The easy-to-use software, which documents each individual measuring point of a determination, allows for the first time to keep track of all analytical procedures. With the 800 Dosino, handling solutions containing sulfuric acid has become simple, flexible and safe.

Last but not least, the prompt service by the competent team from Metrohm (Inula) has been greatly valued for many years. In addition to titration, KF titration and voltammetry, it is now also possible to carry out CVS analysis with a Metrohm instrument to both the operators' and the laboratory management's satisfaction.

Information about the author

We would like to thank Dipl. Ing. Gerhard Haiden, the manager of the AT&S works laboratory in Leoben, for allowing us to describe this application in Metrohm Information.

*What really matters is
what you do
with what you have.*

Shirley Lord