Control of Damascene Copper Processes By Cyclic Voltammetric Stripping

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Use of electroplated copper for on-chip metallization in ultra-large-scale integrated circuits (ULSI) devices is gaining momentum because of the low cost and high throughput of the process. Electroplated lines and trenches with submicron dimensions, however, are strongly affected by changes in the composition of the plating solution, thereby creating a high demand for control techniques. The most dynamic ingredients of electroplating solutions are organic additives. Even a small imbalance between components of the additive system can cause various defects in the filling of the trenches and properties of electroplated copper. On-line monitoring and control of these additive components is therefore desirable. Cyclic voltammetric stripping (CVS) analysis has long been used for just such a purpose in the manufacturing of printed circuits.

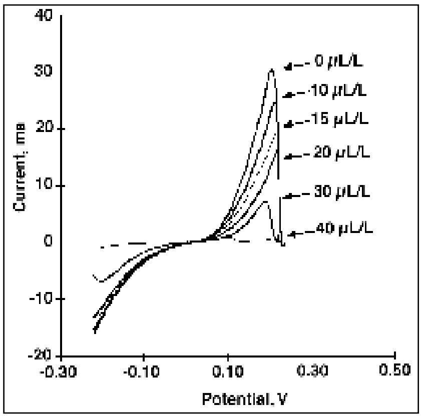

Fig 1—Effect of carrier on voltammogram

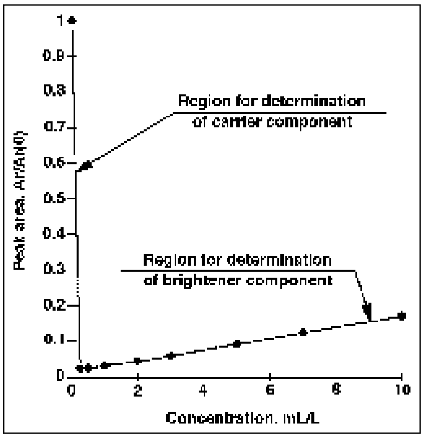

Fig. 2—Determination of premixed components

Numerous chemical and electrochemical processes (*i.e.* thermal decomposition, cathodic reduction, occlusion in the deposit, anodic oxidation, drag-out) contribute to additive consumption, as does time-dependent chemical decomposition in the bulk solution. Additive dosing is often done based on time or amp hours. Some companies have developed proprietary algorithms that predict additive consumption. However, even the best prediction algorithm requires an analytical tool to fine-tune the algorithm's coefficients, and it cannot predict changes due to equipment failure and human errors.

There is a variety of analytical equipment for monitoring the analytical concentration of plating additives. However, only CVS can monitor activity of individual components in a whole range of proprietary organic additives. Over the years, CVS has become a standard for monitoring these additives in copper plating solutions in the printed circuit industry, and is currently being tested by the majority of companies involved with Damascene processes.

With the CVS technique, the potential of the inert electrode is cycled at a constant rate in the electroplating bath, so that a small amount of copper is alternately deposited on the electrode surface and stripped off by anodic dissolution. The measured area under stripping peak is proportional to the plating rate, which strongly depends on active concentration of plating additives and their components (Fig. 1). A modification of the CVS technique, cyclic step voltammetric stripping (CSVS) employs a series of potential steps, instead of the linear sweep, to measure the effect of additives. CVS and CSVS scans, combined with proprietary analytical techniques, allow independent determination of up to three components (brightener, carrier and leveler) of the additives, even in cases of premixed additive system (Figs. 2-3). Additional applications of the CVS technique include monitoring of plating bath ageing.

Table 1
Analysis of Standard Solutions

Solution		Accuracy	Reproducibility
"Low" level of Additives	Brightener	8%	4%
	Carrier	6%	< 1%
"Middle" level of Additives	Brightener	4%	3%
	Carrier	<1 %	2 %
"High" level of Additives	Brightener	< 1%	4%
	Carrier	2%	2%

While most PWB manufacturers use bench-top analyzers, the requirements of the semiconductor industry are much more demanding. The small volume of plating solution creates very dynamic changes in chemical component activity that, when combined with a narrow operating window, generates demand for continuous on-line, closed-loop analytical systems. Other requirements adding to the value of on-line units are: (1) high frequency of analysis; (2) sample size limitation; (3) clean room requirements; and (4) automation concerns.

Demands Have Caused Changes

The demands of the semiconductor industry have led to the recent

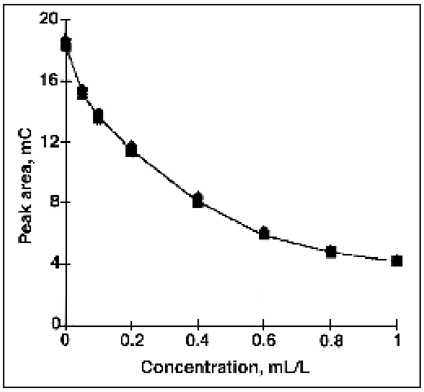

Fig. 3—Response of leveler component in presence of brightener and leveler.

redesign of the proprietary on-line acid copper bath controller* to meet the particular requirements of the semiconductor industry (Fig. 4). The unit, supported by all major additive suppliers, samples up to four plating tanks and standard solutions. It incorporates analysis for brightener, leveler, carrier and contamination level, and it replenishes the plating solutions as needed. The accuracy and reproducibility of on-line analysis are significantly better than lab instruments because the on-line unit includes temperature control, automatic calibration, reproducible conditioning and it eliminates human variations.

Table 1 summarizes results of on-line analysis of several Damascene

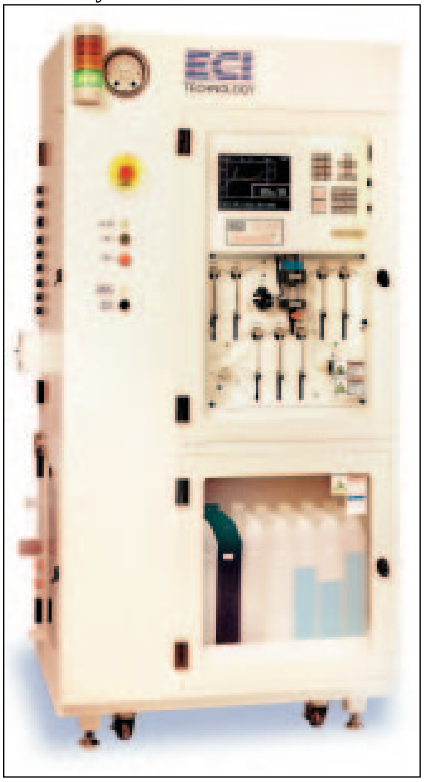

Fig. 4—Proprietary analyzer for semiconductor industsry.

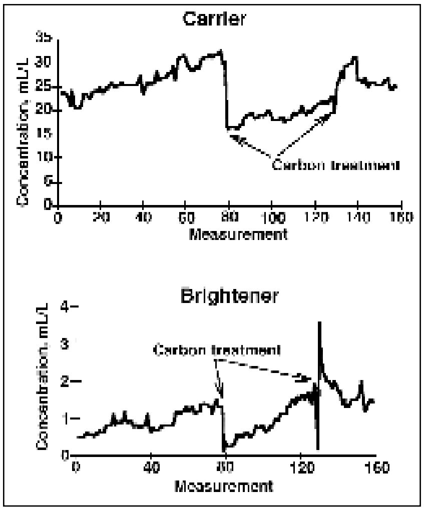

Fig. 5—History of plating solution.

plating solutions at high, middle and low levels of additive specifications. Results indicate very good accuracy and reproducibility of analysis for all components. Figure 5 illustrates the history of one plating solution followed for 160 measurements. Before measurements #79 and #130, the customer performed carbon treatment procedures.

In both cases, treatment effectively removed brightener, but left intact most parts of carrier the component.

Early Warning

Under ideal conditions, Damascene plating is performed at steady-state conditions, and readings in production solution are almost as stable as in standard solution. However, an on-line analyzer provides an early indication of process malfunctioning—*e.g.*, dosing pump failure (Fig. 6).

To test response of CVS to changes of additive levels, a series of additive spikes to a production solution was performed and measured. Figure 7 shows the results obtained for these spikes. Because of the extremely high

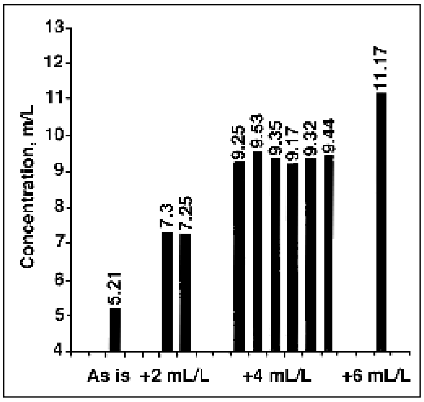

Fig. 7—Analysis of production solution as is and spiked with different concentrations of brightener.

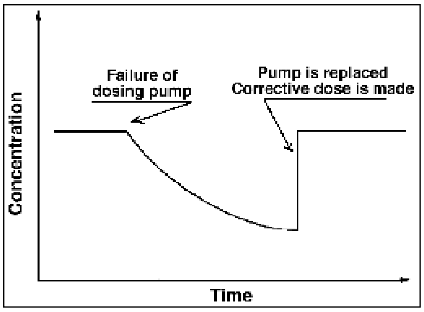

Fig. 6—Analyzer response fo dosing pump failure.

cost of wafers, a significant amount of work is being performed to correlate CVS results to the performance of the plating baths with different levels of additives and inorganic components.

Although organic additives present the main challenge in controlling plating solution, one needs to monitor inorganic components as well. Therefore, a new generation of CVS units is capable of monitoring both organic and inorganic components (copper, acid and chloride). All components are analyzed by potentiometric titration using proprietary procedures.

Table 2 summarizes the results of analysis for standard solution.

At the preparation time of this paper, the analyzer was tested at 10 facilities for an overall period of seven years, including four facilities performing Damascene plating for a 12-month period. Testing included several 5,000-wafer marathons. Use of the analyzer allowed manufactures to keep the process in a very tight window, resulting in a high yield of wafers. Results of the analyzer are in excellent correlation with results of bench-top analyzers. Results of long-term testing of the analyzer at customer facilities are now available. P&SF

Editor's note: This is an edited version of a presesentation given at SUR/FIN@ '99—Cincinnati.

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*The QUALI-LINE acid copper bath controller, ECI Technology, E. Rutherford, NJ.

Table 2a
Determination of Copper
In Standard Solutions

Solution	Accuracy	Reproducibility
0.15 M	0.1%	0.4 %
0.3 M	0.2%	0.7 %
0.6 M	0. 6 %	0.3 %

Table 2b
Determination of Sulfuric Acid
In Standard Solutions

Solution	Accuracy	Reproducibility
50 ml/l	0.1%	0.2 %
100 ml/l	0. 1%	0.1 %
200 ml/l	0.5 %	0.1 %

Table 2c
Determination of Chloride
In Standard Solutions

Solution	Accuracy	Reproducibility
10 ppm	0.5 ppm	0.25 ppm
30 ppm	0.5 ppm	0.35 ppm
50 ppm	0.25 ppm	0.15 ppm
70 ppm	0.35 ppm	0.5 ppm
100 ppm	0.6 ppm	0.35 ppm

development of electrochemical instrumentation for the electroplating industry.

He received his PhD in analytical chemistry from CUNY for work on polarographic instrumentation and did post-doctoral studies at Brooklyn College on photoelectrochemical solar cells.

As research chemist, project manager and vice president, Bratin has been involved for more than 15 years in developing electrochemical instrumentation for additive analysis, solderability, and surface area measurements. He is an author of numerous scientific papers.

He has served as chairman of the Analytical Topical Group of NY Section of ACS, chairman of the Analytical Methods Committee of the AESF, and currently serves on the Solderability Committee of the IPC.

Gene Chalyt is manager of the Chemical Department at ECI Technology. He is responsible for development of electroanalytical instrumentation and techniques for monitoring and control of process solutions.

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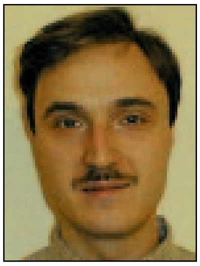
As research chemist and manager, he has been involved for more than eight years in the development of manual and automatic analyzers and controllers for electroplating solutions, cleaners, rinse waters and other process solutions. He has published more than 50 publications and patents.

Michael Pavlov is product manager at ECI Technology. He is responsible for the development of instrumentation and techniques for analysis of coatings used in the PCB industry.



He obtained a BS in metallurgy and MS in electrochemistry from the Moscow University of Steel and Alloys, Russia.

As a research chemist and project manager, he has been involved for more than 10 years in developing electrochemical instrumentation for analysis of electroplating solutions, metallic and organic coatings used in the printed circuit board industry. He has published approximately 40 scientific papers and obtained two patents.