# **On-line Monitoring of Copper Interconnect Deposition Processes**

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The precision required for copper damascene deposition necessitates a fast and reliable on-line monitoring tool. Although all components of the copper bath must be monitored, major attention is usually focused on the organic additives. Typical acid copper plating bath additive systems contain at least two organic compounds – suppressor and accelerator. The actual concentration ratio of these two compounds determines the performance of the plating baths. This paper describes the results of on-line analyses by the Real Time Analyzer using AC and DC voltammetry to determine both inorganic and organic components of a copper bath.

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## Introduction

Electroplating is an important step in the manufacturing of electronic components. Precise chemical concentration monitoring and control of electroplating baths are needed to minimize costs and to satisfy process specifications. A typical electroplating bath is a multi-component mixture. The constituents have generally a very different chemical character, and usually are present at very different concentration levels. Therefore, it is virtually impossible, that all of them can be analyzed by a single technique or a single analytical device.

There is a definite need for an in-situ, online chemical instrument that would provide results in real time and as often as it is necessary (1-5). Process monitors should be easy to operate, reliable, highly accurate, precise, contamination free, have a small footprint, and be capable of being integrated into automated dosing systems. The Real Time Analyzer (RTA Figure 1) is a complete monitoring system that allows for a full chemical analysis of different chemical solutions. The fully computerized instrumentation requires no chemical operators, and practically eliminates the need for a chemical analytical laboratory

The methods of analysis employed by the RTA involve electroanalytical techniques such as direct current (DC) and alternating current (AC) voltammetry. In general, voltammetry is an electrochemical technique in which the currentpotential behavior at a sensing electrode is measured. The potential (voltage) is varied in such a manner, that the electroactive species is forced to be reduced (plated) or oxidized (stripped off) at the electrode. The resultant current is proportional to the concentration of the chemical species in solution. The range of



potential applications of voltammetry is very wide. Electroanalytical techniques are among the very few techniques that are equally suitable inorganic, for analyzing organic and organometallic compounds over a very broad range of concentration levels. By optimization of the DC potential range and sweep rate, the frequency and amplitude of the superimposed AC signal, and the proper selection of phase angle, specific regions in the voltammogram can be related to the concentration of particular plating bath components (6-9).

This paper describes some laboratory and on-line monitoring results for a copper damascene process.

## Experimental

All experiments were performed by means of the RTA (Figure 1). The RTA hardware is a fully digital electroanalytical system. The perturbation waveforms (step, triangle and sinewave) are generated digitally. The response current is recorded by a 16-bit data acquisition board, and analyzed using the fast Fourier transformation algorithm (FFT).

The measurements were performed inside an electrochemical cell, which is submersed in the plating. The cell consists of a relatively small compartment (volume ca 20 ml) filled with the solution to be analyzed. There are three electrodes submersed into the analyzed solution: the working (sensing), the counter (auxiliary) and the reference (constant voltage). These electrodes were connected to the signal source (voltage or current) and a meter (current or voltage).

A typical, sulfuric acid based copper plating bath with proprietary additives was used. Typical concentration ranges for copper sulfate, sulfuric acid and chloride ion were covered (target values: 17g/l, 180 g/l and 55 ppm for copper metal, acid and chloride, respectively). Two organic additives, suppressor and activator were studied.

### **Results and Discussion**

#### **Reproducibility and repeatability**

The demands of the semiconductor industry impose very tight requirements for monitoring techniques. Table 1 summarizes the laboratory results of experiments on precision and accuracy performed on standard plating solutions. Precision was expressed as a relative standard deviation,

$$Precision (\%) = 100*StdDev/Average (1)$$

and accuracy as an absolute value of the difference between expected and average values normalized for average.

The last column shows the Process Capability values (PC) calculated as:

$$PC = 6* StdDev / Process Range$$
 (3).

The results are far better than commonly accepted 5-7 % precision/accuracy requirements. It should be noted that these experiments were performed under very well controlled laboratory conditions. In particular, a precise control of bath temperature is known to have an extremely big impact on the final performance.

TABLE 1.

Laboratory results (N=16; total volume 11iter; temperature control  $25^{\circ} \pm 0.2^{\circ}$ C).

Component	Precision	Accuracy	РС
Copper	0.81 %	0.52 %	0.114
Acid	1.17 %	0.50 %	0.206
Chloride	1.88 %	0.71 %	0.162
Suppressor	0.86 %	1.25 %	0.066
Accelerator	3.87 %	3.13 %	0.225

A similar experiment was performed in a Copper Damascene plating tool. The RTA probe was placed directly in the sump tank filled with the copper plating solution. There was no plating during this experiment to avoid any dynamic changes to the solution. The solution was used for plating of copper on silicon wafers for several thousand amp hours prior to this reproducibility experiment. The results are summarized in Table 2. As with the laboratory results reported above, the precision achieved meets the requirements of the semiconductor industry. It should be noted that due to the chemical instability of the Accelerator, the standard deviation was expressed as a square root of the variance of residuals from the apparent decay line.

#### TABLE 2.

On-line results (N=53; in-tank; total volume 150 liters; no plating; no circulation)

Component	Precision	РС
Copper	0.97 %	0.145
Acid	1.58 %	0.298
Chloride	2.08 %	0.199
Suppressor	2.46 %	0.199
Accelerator	4.64 %	0.258

Figure 2 shows the results of the routine on-line analyses performed in a Damascene copper metallization tool for about 3 months. Each of the plots displays over 1500 single measurement points. The measurement schedule was set to perform a full 5-component analysis in duplicates every two hours. (One set of 5component analyses takes about 15 minutes). All dilutions and additions were recorded. The frequency of measurements allows tracing of chemical changes in virtually real time. As a result, the corrective action may be taken much faster than with CVS or titration. The fast and frequent measurements also allow for a finetuning of the plating process and for establishing target concentration levels with a very tight tolerance.

The RTA results were checked against the standard off-line methods. For the most part, the agreement was excellent. Unfortunately, there is no simple and reliable standard method for measuring organic additives in copper plating baths. The CVS technique was recently reported as inaccurate (5) and can not be considered as a standard. Figure 3 shows the results of measurements of suppressor in a copper damascene plating tool for a period of 24 hours. The triangles and squares correspond to the CVS and RTA measurements, respectively. The replenishment system was dosing the suppressor based on its own schedule, and the physical additions (assuming no consumption) are represented by circles. The plating was carried out with the average current of 20 A, during this experiment. It can be easily estimated that without any active consumption, the suppressor concentration will be about 5 ml/l higher than the initial one. Based on the RTA measurements, the consumption of the suppressor was about 0.7 ml/A hr. Based on the CVS measurements, the suppressor consumption would be over 2.2 ml/A hr, much too high according to the supplier specification. It is highly possible that CVS underestimates suppressor concentration which would be in line with the inability to detect a "dynamic suppression" by CVS, reported previously (5). The reliability of suppressor analysis is under thorough investigation,



FIGURE 2. The results of on-line analyses of 5 components of acid copper plating bath.



Figure3. The RTA and CVS measurement of suppressor concentration.



FIGURE 4. Curve 1,2 – typical voltammograms; curve 3 – contaminated solution.



FIGURE 5. Linear voltammograms of copper reduction with different combinations of additives. Suppressor to accelerator ratio: curve 1 - 1:1; curve 2 - 1:10; curve 3 - 10:1.

currently. The final results of this study will be published soon.

The on-line electrochemical analyzer is capable of performing functions far more complex than a straightforward measurement of concentration level. Figure 4 shows a set of voltammmograms recorded during a routine online analysis. Curves 1 and 2 represent typically shaped voltammograms, characteristic for this particular set of experimental conditions. The voltammogram 3 displays an unusual shape, with some features drastically different from the standard curves. The bath problem was readily detected by the RTA and reported as out of range concentration values. It is worth to noting that there was no indication of any problem from other standard analytical methods. All titration and CVS results were close to the expected values without any evidence of a bath problem. It appeared that the bath was contaminated (possibly with peroxide from the initial clean) during the initial make-up. The contaminated bath was disposed, the tanks carefully rinsed and a new bath installed, which did not display any abnormalities.

These kinds of shape recognition capabilities of the RTA open a quite new direction in process monitoring. The instant detection of contaminants and/or breakdown products can avoid serious plating defects. Moreover, the plating process can be electrochemically characterized, and qualified as being "in the operating range". Figure 5 shows voltammetric curves for copper reduction in the presence of organic additives at different concentration ratios. A quite drastic difference in additive concentration is clearly illustrated with a distinct change in the shape of the electrodreduction curves. Having such a difference in shape we may expect a different plating output as well. The simple Hull cell experiment confirms these differences. The variation will be even more noticeable when the more demanding process of plating into the small features is performed. The capabilities of RTA for the quantitative the shape characterization of the electrochemical process allow narrowing process limits. Using the RTA, possible problems may be readily identified and corrective action may be quickly performed to regain proper function.

### Conclusions

The RTA is a reliable on-line monitoring tool for the Copper Damascene electroplating process. It meets typical precision and accuracy requirements. The RTA provides unique capabilities of contamination and/or breakdown product detection. The quantitative electrochemical characterization capability may also allow for the early detection of plating problem.

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