

# A Novel Analytical Method of Thallium Determination in Gold Electrodeposition

Patrick Saitta, Jingjing Wang, and Eugene Shalyt  
KLA-Tencor  
60 Gordon Drive  
Totowa, New Jersey 07512 USA  
Ph: (973) 890-1114 Ext. 411; Fax: 973-890-1118  
Email: Patrick.Saitta@kla.com

## Abstract

Thallium is used in both cyanide and sulfite-based gold plating bath solutions as an additive that modulates how gold deposits on the target substrate. The level of Tl in the plating solutions has a large effect on the properties of the gold being deposited, including its microstructure and hardness. Thus, especially in commercial process applications, it is critical to be able to measure the Tl content of plating solutions accurately, quickly, and facily in order to ensure proper quality of the products being manufactured. The cyclic voltametric behavior of Tl-containing gold plating bath solutions has been investigated, but quantification of its Tl content is unsatisfactory, either expensive and time consuming, or not accurate in complexed matrices. Here, we present a proprietary, electroanalytical method of Tl measurement that is fast and gives excellent accuracy and sensitivity, even in the presence of common bath breakdown products.

## Key words

Cyclic voltammetry, Electrochemical deposition, Gold plating solution, Thallium, Sulfite bath solution.

## I. Introduction

Gold electroplating is a critical element in electronics manufacturing and functional coating applications and is sought after for its excellent corrosion characteristics and conductivity. Gold baths used for gold plating typically consist of a high level (in g/L range) of gold salts, complexing agent (e.g., sulfite), buffering agents, surfactants, and additives to help modulate the microstructure of the gold being deposited. Commonly used metal ion additives include  $Pb^{2+}$ ,  $As^{3+}$ ,  $Tl^+$ , and  $Bi^{3+}$  in the ppm range that act as depolarizers to accelerate Au deposition and to achieve a desired microstructure (e.g., a particular grain size). This is also important when filling in recessed features, which are prone to defects like voids and seams when filling (i.e., gold deposition) is subconformal. Thallium salts have been widely employed in recent commercial formulations to modulate these properties. Its level must be controlled within tight process limits to achieve good process performance.

Analysis of Tl at ppm level is quite difficult especially in presence of a thousand-fold more gold in solution. Several methods have evolved over years to measure Tl: Spectrophotometric methods targeting a  $Tl^+$  – organic dye complex are not selective and require onerous pre-

preparation or harsh reaction conditions [1]–[3]; polarographic methods focusing the reduction of  $Tl^+$  to metallic Tl employ liquid mercury electrodes which are banned in industrial laboratories due to their toxicity [4], [5]; element analysis methods such as inductively coupled plasma optical emission/mass spectrometry (ICP-OES/MS) and atomic adsorption spectrometry (AAS) are impractical in both cost and bulkiness for fab use, and are difficult to maintain [6], [7]. There is a need for a simple/low-cost metrology for Tl (and similar elements). This work describes a novel method for Tl analysis based on its catalytic effect on gold electroplating. It is sensitive, selective, inexpensive, rapid, and free from various interfering ions, making it a desirable online technique for gold plating process.

## II. Method

Samples (numbered) were prepared from known standard solutions of their components. Aged and Fresh samples were plating samples obtained from a commercial process bath, right after preparation and after some time, respectively. Cyclic voltametric behavior of gold bath containing different

levels of thallium was investigated using a platinum rotating disk electrode and Ag/AgCl reference electrode. A proprietary electrochemical etching method is applied to remove plated gold during the analysis leading to fresh Pt surface for new analysis. Upon the increase of the  $\text{Tl}^+$  concentration, the gold deposition potential shifts to less negative direction and plating current increases which is in agreement with previous work [8], [9], accelerating the initial deposition of gold. The hysteretic behavior observed

in the cyclic voltammetry (Fig. 1) also supports the acceleration mechanism as being modulated by the adsorption of thallium on the surface of the electrode. Gold electrodeposition is constrained by forming inhibiting species (such as  $\text{SO}_3^{2-}$  in gold sulfite bath) and the  $\text{Tl}^+$  adsorption on the surface can lift the inhibition and destabilize the gold complexes.

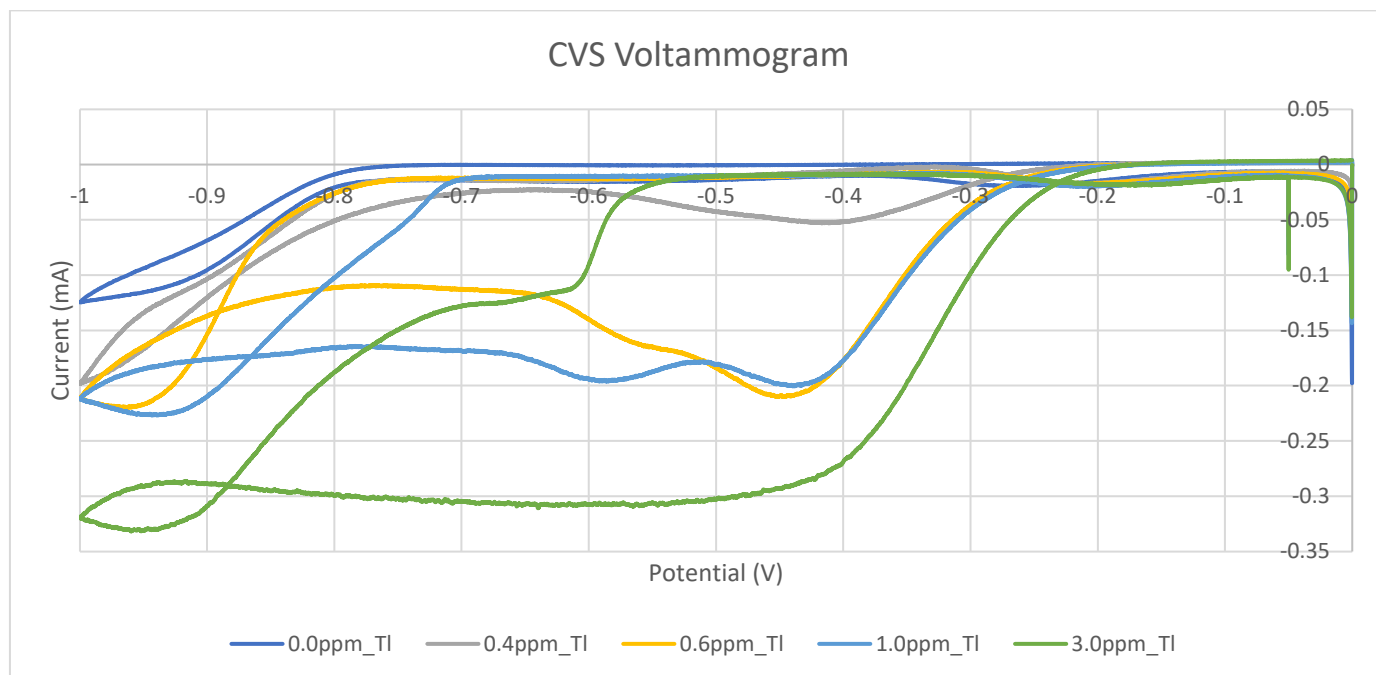


Fig. 1: CVS Voltammogram of Au plating with different  $\text{Tl}^+$  concentrations sweeping from 0V to -1V and back.

A linear correlation can be established between the  $\text{Tl}^+$  concentration and the plating current after normalizing the signal, which is of great importance for the success of the method. It stabilizes the signal and minimizes the noise coming from the electrodes that otherwise would interfere with the signal. The method is validated with full matrix standards, demonstrating the ability to achieve 5% accuracy. However, it is not as satisfactory in terms of sensitivity and analysis time – 66.7% variation of Tl in the sample results in 14.8% variation in analytical signal, with a typical analysis time of 20 minutes. Thus, a better method of analysis that overcomes these limitations is desired.

### III. Results

To overcome these issues, an improved proprietary method was developed, also based on electrochemical techniques (Fig. 2). The method exhibits excellent linearity between the electrochemical signal and

concentration of thallium in the sample, as shown in Fig 3. Samples were made from standard solutions of their components, in proportions in line with commercial plating bath formulations. The method has been tested with two different commercial gold electroplating formulations that have different ranges of gold and thallium prescribed. These methods are validated for these formulations with 5% accuracy and 3% repeatability (i.e., relative standard deviation (RSD)), without interference from the matrix including gold, sulfite, and unknown proprietary ingredients in the formulation (Table 1 and 3). In another test, sulfate, the main by-product of the commercial plating process due to the oxidation of sulfite, was spiked into samples of plating solution and tested to see if this common breakdown product affected the analysis. The sulfate spikes demonstrated no impact on the Tl measurement result. Thus, this method is well suited for use in the measurement of Tl in plating solutions containing breakdown products, such as an aged bath. Additionally, the analysis works well across a wide range of gold and thallium levels, making this a robust electroanalytical method.

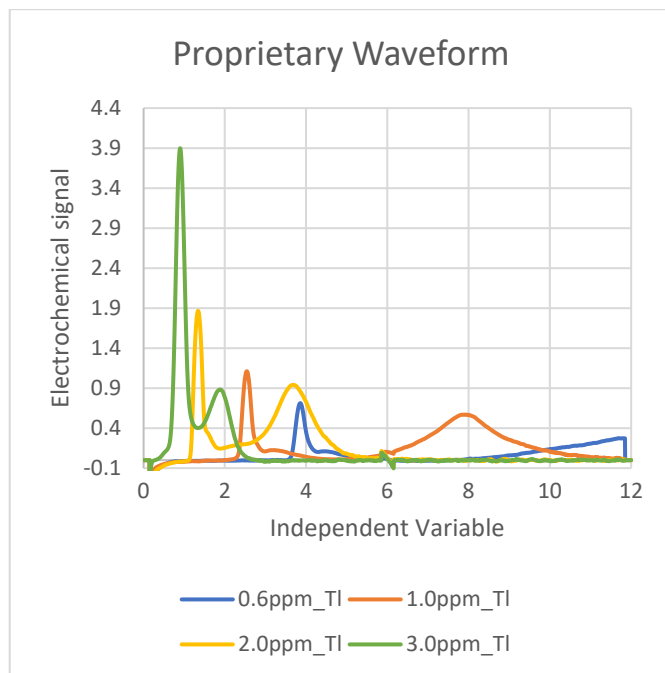


Fig. 2: Voltammogram of Au plating with different level of  $Tl^+$  using ECI proprietary waveform.

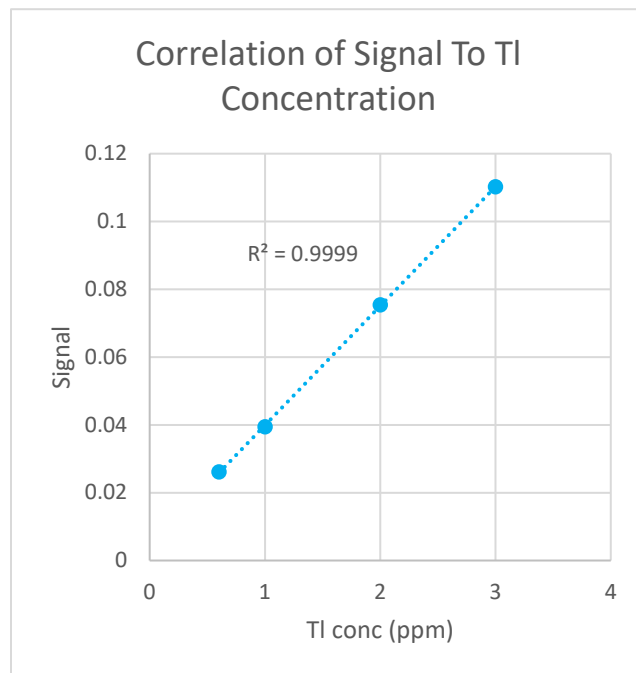


Fig. 3: Calibration curve using the first peak in the voltammogram

Table 1: Analysis results of Tl in full matrix standards of commercial Au plating formulation 1 (Au range 13-17 g/L, Sulfite range 20-90 g/L).

	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #2 spiked with 80g/L $SO_4$
Au in sample, g/L	13	15	17	17	13	15
Sulfite in sample, g/L	20	40	90	90	20	40
Expected Tl, ppm	20	30	40	20	40	30
Measured Tl #1, ppm	19.43	30.50	38.80	19.18	38.77	30.04
Measured Tl #2, ppm	19.85	30.66	40.46	N/A	N/A	N/A
Measured Tl Average, ppm	19.64	30.58	39.63	19.18	38.77	30.04
Accuracy	-1.79%	1.93%	-0.92%	-4.08%	-3.08%	0.13%
RSD	1.49%	0.38%	2.96%	N/A	N/A	N/A

Actual process bath samples (Fresh and Aged) at different bath lifetime were also tested and showed excellent recovery in spiked and diluted samples (Table 2). Spiked samples were spiked with commercial standardized solutions. Good sensitivity is demonstrated, with 66.7% variation of Tl in the sample results in 53.9% variation in analytical signal and a detection limit down to 0.1ppm. Additionally, the typical analysis time is 5 minutes, with both measurement and etching times reduced. All of these advantages make this method superior for online monitoring of Tl in gold electrodeposition process.

Table 2: Analysis of Tl in Fresh and Aged samples.

	Fresh	Aged	Aged spiked with 10 ppm Tl	Aged, 75% diluted
Expected, ppm	30.0	N/A	42.5	24.4
Measured, ppm	29.6	32.5	42.9	24.3
Accuracy	1.3%	N/A	0.9%	-0.4%
RSD	< 5%			

Table 3: Analysis results of Tl in full matrix standards of commercial Au plating formulation 2 (Au range 10-22 g/L, Sulfite range 10-100 g/L)

	Sample #6	Sample #7	Sample #8	Sample #9	Sample #10
Au in sample, g/L	10	16	22	22	10
Sulfite in sample, g/L	10	30	100	100	10
Expected Tl, ppm	5	12	20	5	20
Measured Tl #1, ppm	5.0	12.4	19.9	4.8	19.8
Measured Tl #2, ppm	5.2	12.3	20.2	4.8	19.7
Measured average, ppm	5.1	12.4	20.1	4.8	19.7
Accuracy	1.6%	3.1%	0.4%	-4.0%	-1.3%
RSD	2.1%	0.5%	1.00%	0.7%	0.6%

## IV. Conclusion

A novel method of measuring Tl levels in gold plating baths solution has been presented. Compared to the state-of-the-art methods that involve cumbersome pre-preparation, onerous equipment, or larger expense, the method given here is facile, accessible, and fast, all while affording excellent accuracy and repeatability. What's more, this method is undisturbed by common process bath solutions by-products, including sulfate and other potential proprietary commercial ingredients. The work outlined in this paper is focused on measuring the thallium content of gold plating bath solutions, however future work examining the generalizability of this electroanalytical method to different metal ion additives in these solutions or in other plating bath would be a natural extension of this work.

## References

- [1] D. S. Younger, "Pollutants and industrial hazards," in *Merritt's Textbook of Neurology*, 9th ed., L.P. Rowland, Ed. Baltimore, MD: Williams and Wilkins, 1995, pp. 992.
- [2] Z. Gregorowicz, J. Ciba, B. Kowalczyk, "Studies on spectrophotometric methods of thallium determination," *Talanta*, vol. 28, 1981, pp. 858.
- [3] N. Agarwal and K. S. Patel, "Extraction-spectrophotometric determination of thallium with amidine and Brilliant Green in sequence," *Analisis*, vol. 19(4), 1991, pp. 134-135.
- [4] B. Griepink, M. Sager and G. Tolg. "Determination of traces of thallium in various matrices," *Pure & Appl. Chem.*, vol. 60(9), 1988, pp. 1425-1436.
- [5] E. Shams and M. Yekehtaz "Determination of trace amounts of thallium by adsorptive cathodic stripping voltammetry with Xylenol Orange," *Anal. Sci.*, vol. 18(9), 2002, pp. 993-996.
- [6] I. Chamberlain, K. Adams, and S. Le, "ICP-MS determination of trace elements in fish," *Atom. Spectrosc.*, vol. 21(4), 2000, pp. 118-122.
- [7] S. Dadfarnia, T. Assadollahi, and A. M. Haji Shabani, "Speciation and determination of thallium by on-line microcolumn separation/preconcentration by flow injection-flame atomic absorption spectrometry using immobilized oxine as sorbent," *J. Hazard Mater.*, vol. 148, 2007, pp. 446-452.
- [8] P. L. Cavallotti, P. Cojocar, and L. Magagnin, "Soft gold coatings: influence of additives and pulse plating," *Transactions of the IMF*, vol. 90(5), 2012, pp. 246-251.
- [9] D. Josell and T. P. Moffat. "Additives for superconformal gold feature filling". *J. Electrochem. Soc.*, vol. 168(5), 2011, 052502