Developing a non-cyanide gold bath free of heavy metals for via-fill applications

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Abstract
Electrochemically filling vias and trenches using gold solutions is increasingly important in developing electronic devices with strict reliability requirements in the compound semiconductor field. The difficulty in developing these solutions is sufficiently suppressing sidewall growth to provide a void-free, bottom-up fill (BUF). Thallium, lead, and bismuth have been used in gold baths to enable BUF. However, new chemistries that exclude these metals are being developed to avoid the high toxicity of thallium and lead, along with the possible effects of bismuth co-deposition. This report describes the preparation and characterization of novel non-cyanide gold baths that do not require additional metal ions to fill vias and trenches. These baths use organic additives to suppress sidewall growth and facilitate acceleration from within the features that enable BUF.

Baths were prepared using an accelerator and a variety of suppressors. These baths were tested using chronopotentiometry to predict the fill-type according to Dow's Model. The baths were then electroplated on coupons with vias, or trenches, and cross-section electron microscopy was used to analyze the fill-type and grain morphology within the plated features. Although typically applied to copper chemistry, Dow's Model was also found to hold true for gold electroplating baths. This work identified organic additives capable of driving low-impurity, void-free BUF of vias.

Key words
grain structure, heavy metal-free, non-cyanide gold, via fill

I. Introduction
Within the growing compound semiconductor market of wafer-level packaging (WLP), gold baths are used at the back end of the microchip assembly process to fill interconnect features [1], [2] electrochemically. Copper is more commonly used to fill interconnects than gold, partially due to the associated cost. However, gold provides higher thermal conductivity that is second only to silver, the third best electrical conductivity, and has excellent corrosion resistance [2]–[4]. These fundamental aspects of gold make it the metal of choice for WLP applications requiring high efficiency and reliability, including radio frequency (RF) and optoelectronic devices [5].

Gold electrochemical plating (ECP) baths for art applications traditionally used cyanide to stabilize gold in solution as far back as 1805 [6]. However, due to brittleness of deposits, incompatibility with photoresist on wafers, and detrimental health effects – particularly at low pH where HCN is generated – gold cyanide baths are being replaced with gold (thio)sulfite [3]–[5], [7]. Gold (thio)sulfite baths operate in the neutral to alkaline pH range while using organic and inorganic additives to modulate the electrochemical properties to achieve desired filling and physical properties of the deposited material [4], [5], [8]. The desired material properties include void-free fill, uniform thickness, high conductivity, specified hardness, bright appearance, and high purity [5].

Evaluating additives and conditions through electrochemical modeling would streamline the ECP process depending on wafers, additives, and analysis time. Electrochemical modeling through cyclic voltammetry (CV) or linear sweep voltammetry (LSV) and chronopotentiometry (CP) is used to predict the influence of additives and plating conditions on the electroplating

behavior of copper baths within defined features such as trenches, vias, or through silicon vias (TSVs) [9], [10]. The Dow model established the relationship between agitation-dependent polarization and filling performance for copper baths [9]. CV and chronoamperometry (CA) have recently been applied to gold electrodeposition; however, this area is still less well-understood than its copper counterpart [11], [12].

Many commercial gold solutions contain thallium, arsenic, or other heavy metals to achieve required plating performance. The work reported here aims to develop a gold bath capable of filling fully metallized features including vias and trenches while eliminating the health and environmental hazards of cyanide and heavy metals. Fully metalated features are difficult to fill in comparison to redistribution lines and pillars. This challenge is due to the seed layer that coats the features which results in sidewall growth leading to seam voids particularly with high aspect ratios features. Via fill-type (conformal versus BUF) is commonly characterized by the ratio of via fill to overburden growth. A low overburden and smooth surface is particularly important for filling vias when chemical mechanical polishing (CMP) is not applied [13]. Work was performed to reduce sidewall growth and promote a BUF type bath using organic additives informed by predictions from electrochemical techniques.

II. Materials and Methods

A. Chemical Solutions

The standard make-up solutions comprise 16 g/L Au(I), electrolyte, and deionized water. The plating baths additionally include an accelerator and suppressors.

B. Instrumentation

A Biologic VSP potentiostat and Pine Research RDE setup were used to perform electrochemical testing and coupon electroplating. A Zeiss CrossBeam 550 series was used for the electroplated material's SEM and FIB imaging. A NANOVEA PB1000 mechanical tester was used to collect hardness measurements by nanoindentation.

C. Electrochemical Methods

Agitation rate, current density, and chemical additives were investigated and correlations with surface morphology, filling type & performance and grain structure are discussed. Additives used in this work were categorized as accelerators, which depolarize the bath (toward more positive potentials), leading to faster deposition, or suppressors, which polarize the bath (toward more negative potentials), impeding deposition. Chronopotentiometry (CP) was used to evaluate electrochemical behavior and polarization strength through varied plating conditions and additive selection. At each current density, two agitation rates were used: 100 rpm and 1000 rpm. Electrochemical measurements used a three-electrode system with a 0.2 cm^2 glassy carbon rotating disk electrode (RDE) as the working electrode, a Hg/Hg_2SO_4 reference electrode, and a platinized titanium counter electrode. The glassy carbon RDE surface was cleaned with aqua regia and rinsed with deionized water between each electrochemical scan. Baths were adjusted to pH 8.0 using an aqueous sodium hydroxide or dilute sulfuric acid solution. Measurements were collected at 50 °C and 55 °C.

D. Electroplating Methods

Sections of wafer (coupons) were taped to a conductive disk, and insulating tape was used to control the plating area. The prepared coupons were degassed and attached to a rotating disk electrode setup tilted at an approximately 20-degree angle to allow any gases to escape. The coupon acted as the cathode while a platinized titanium counter electrode was used as the insoluble anode. Plating time was adjusted according to the current density applied (2 mA/cm^2 to 5 mA/cm^2) and the degree of desired fill. Coupons were plated at a 300 rpm agitation rate.

III. Results and Discussion

A. Fill-Type: Predictions and Performance

Dow's Model uses galvanostatic measurements based on convection-dependent adsorption (CDA) of additives. The constant current used in the Model is the current of interest for electroplating. One scan is collected at 100 rpm to simulate the bottom of the feature, and another scan is collected at 1000 rpm to represent the field. By comparing the two galvanostatic measurements of a bath, the type of fill, conformal versus BUF, can be predicted. More suppression at the higher agitation rate than the lower agitation rate suggests BUF. This Model was first established for copper baths [9], [14]. This work explores the merit of its application for studying gold baths.

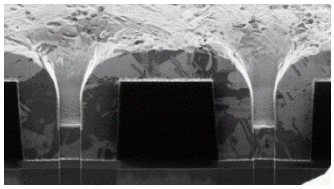


Fig. 1. Partial fill using accelerator-only bath 3 mA/cm^2 and 55 °C.

A bath containing only accelerator was tested as a control experiment (Fig. 1). This bath resulted in conformal fill as observed by the lack of suppression on the sidewalls and field [15], [16]. Suppressors were incorporated with the accelerator and these baths were tested using chronopotentiometry and partial fill electroplating. Partial

fill plating enables observation of initial growth patterns and characterizes the fill-type as conformal or BUF.

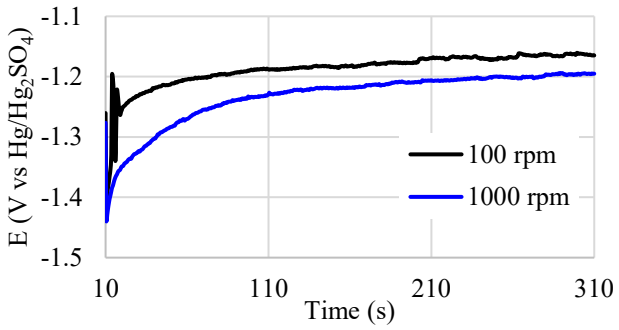


Fig. 2. CP of Bath 1 at 3 mA/cm^2 and 55 °C.

Bath 1, which contained the accelerator and suppressor, was predicted to give BUF based on the electrochemical response. CP showed the 1000 rpm scan being more negative (more suppressive) than the 100 rpm scan (Fig. 2). This bath was plated for 5, 8, and 13 minutes on coupons containing vias to evaluate the fill type at multiple time points. Images of cross sections revealed BUF supporting the use of Dow's Model for gold applications (Fig. 3). The overburden measured from Fig. 3c was found to be low at 0.432 µm.

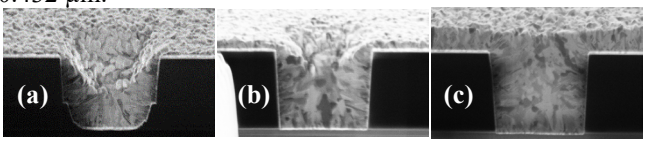


Fig. 3. Cross section images of coupons electroplated at 3 mA/cm^2 and 55 °C using Bath 1 for (a) 5 minutes, (b) 8 minutes, and (c) 13 minutes.

Bath 2 was prepared with an accelerator and an alternative suppressor. Fig. 4 shows the CP of Bath 2. The 1000 and 100 rpm scans are similar in voltage, then converge at 5 minutes, suggesting a conformal fill after the first 5 minutes (Fig. 4).

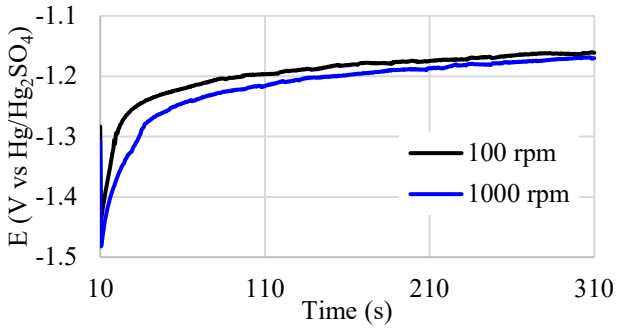


Fig. 4. CP of Bath 2 at 3 mA/cm^2 and 55 °C.

Bath 2 was plated on coupons with vias to assess the prediction accuracy from CP. The bath was plated for 8 and 13 minutes, and the cross-sections' images indicated conformal fill, which supports Dow's Model prediction. The overburden in Fig. 5b was measured to be 1.44 µm, more than three times as thick as that of Fig. 3c.

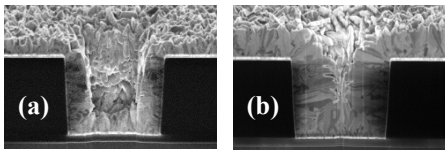


Fig. 5. Cross-section images of coupons electroplated at 3 mA/cm^2 and 55 °C using Bath 2 for (a) 8 minutes and (b) 13 minutes.

The difference in fill type and overburden between Bath 1 and Bath 2 shows that the additives used as suppressors influence the plating performance.

B. Influence of Organic Additives on Grain Structure

A Design of Experiment (DOE) was performed using a 3-additive bath to evaluate the interactions between the additives.

Table I. Relative additive concentrations for DOE.

ID	Accelerator Concentration	Suppressor 1 Concentration	Suppressor 2 Concentration
A	Low	Low	High
B	High	Low	Low
C	Intermediate	Intermediate	Intermediate
D	Low	High	Low
E	High	High	High

The five baths described in Table I were electroplated on coupons containing vias, and cross-sections of the features were imaged. The DOE was centered around bath C, which has intermediate concentrations of additives. Bath C was found to give large grains in the features and fine grains on the surface (Fig. 6C).

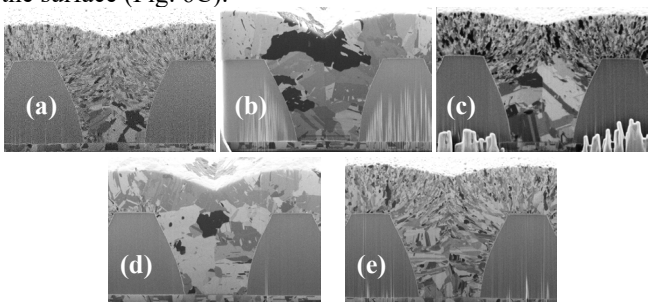


Fig. 6. Cross-section images of coupons electroplated at 2 mA/cm^2 and 50 °C with baths A-E described in Table I.

Samples A and E (Fig. 6A, E) have fine grains in the features and overburden, whereas samples B and D (Fig. 6B, D) have large grains throughout the plated material.

This result suggests that the interactions between the accelerator and suppressor 2 govern the grain size. This conclusion was supported by plating Bath 3, which contained the same accelerator-to-suppressor 2 ratio but with a lower concentration. Bath 3 gave the same fill and grain structure as Bath C. Within the feature, the grains are large, while the overburden has fine grains (Fig. 7).

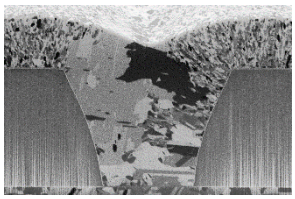
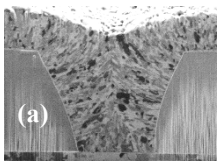
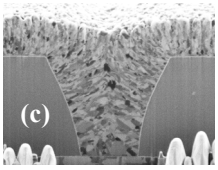
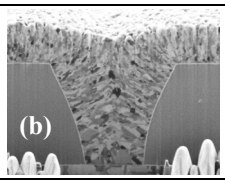
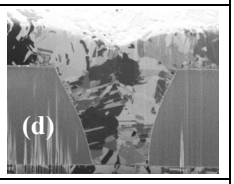


Fig. 7. Cross-section image of coupon electroplated at 2 mA/cm^2 and 50 °C with Bath 3.

Annealing samples at elevated temperature is often used to influence the grain structure of plated materials. A two-additive bath comprising accelerator and suppressor 2 was used for plating coupons that were imaged, annealed at 150 °C for 2 hours, then reimaged (Table II).

Table II. Additive concentrations and pre- and post-annealed images for Baths F and G.

	Bath F	**Bath G**
Accelerator (mL/L)	4	4
Suppressor (mL/L)	3	1.45
Pre-anneal		
Post-anneal		
The coupons were plated at 2 mA/cm^2 and 50 °C then annealed at 150 °C for 2 hours under N_2 atmosphere		

The high suppressor concentration (3 mL/L) in Bath F was observed to pin the grains so that no growth occurred during the 2 hour anneal at 150 °C (Table II a, b). The lower suppressor concentration (1.45 mL/L) in Bath G was found to provide enough sidewall and field suppression to facilitate BUF while allowing the grain size to grow during the annealing process (Table II c, d). Notably, both baths provided BUF that was void-free before and after annealing. These two baths highlight how the use of a single organic suppressor can control the grain size of electroplated gold films when annealed at elevated temperatures.

C. Materials Properties

The influence of material properties by grain structure modulation was investigated. Hardness is a key property for gold electroplated materials. The grain sizes and material properties can be adjusted by modulating the accelerator and suppressor 2 ratio. Electroplated gold has Vickers hardness (HV) values around 140 HV up to 180 HV, which can be influenced by grain size, grain orientation, and heavy metal doping [17]–[19].

Two blanket, featureless coupons were electroplated with the control bath comprising only accelerator (Fig. 1) and accelerator plus suppressor 2. These baths were plated at 50 °C, pH 8.0, and 2 mA/cm^2. Hardness of the coupon plated using the accelerator-only bath is 108.4 HV average with a 9.065 HV standard deviation. Upon incorporation of suppressor 2, the hardness increases to 160.2 HV with 11.89 HV standard deviation. These results demonstrate the ability to modulate the hardness of electroplated gold using only organic additives.

IV. Conclusion

A non-cyanide gold bath was developed for via and trench fill applications. Without the use of heavy metals such as thallium, the organic additives were able to sufficiently suppress sidewall growth, which makes filling fully metalated features challenging. Partial fill electroplating demonstrated the BUF capabilities of this chemistry. The interaction between accelerator and suppressor was observed to influence grain structure. Suppressor can also be used to control the grain size of annealed samples and increase hardness.

Acknowledgment

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