Advances in Gold Metallization at Motorola's Compound Semiconductor Fab (CS1)

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Abstract

The use of Au(I)-sulfite complex bath for gold metallization in the compound semiconductor industry is gradually increasing. However, manufacturing costs have limited its widespread application since such baths decompose rapidly and have to be replaced frequently at a high cost. This work centers on the setting up of a cost effective pilot laboratory for routine bath analysis, the development of analytical tools used in the evaluation of the bath variables, and effects on statistical process metrics such as gold reflectivity and film stress. Atomic absorption spectroscopy determines concentration of Au and Tl, titrimetric methods are used to evaluate EDTA and free sulfite concentrations in the bath, while Au conductivity and bath pH are determined using a combination meter. Results from routine analysis and consequent bath adjustments have led to a fourfold retention in bath-life, while improving process integrity. Annual maintenance hours have been reduced by more than 400 hours at an annual savings of $90,000.

This article will begin by introducing the reasons that prompted the origination of an in-house lab. It will discuss the current baths on the market and why the sodium-gold-sulfite bath is chosen over other alternatives. Plating thicknesses, mask types, and current density will be discussed along with a brief overview of the current process. The primary chemicals and their roles in the chemistry will be detailed as well as the pertinent physical data. Details will be discussed about what procedures are performed in the lab as well as what equipment and reagents are required to perform those analyses.

Several groundbreaking results have stemmed from the analysis lab. These results include better process control, improved plating step coverage in backside vias, longer bath life, less maintenance and a highly cost efficient process. All of these improvements will be detailed. The paper concludes with a discussion about the lab's future contributions to the plating process as well as photo and wet etch processes.

Introduction

Compound semiconductor electroplating using sodium gold(I) sulfite $(Na_3Au(SO3)_2)$ complex baths is steadily increasing. Its' widespread application in manufacturing has been limited due to high costs. Tool up-time, yield, and maintenance costs are among the essential metrics that need improvement before the bath becomes widespread in the semiconductor industry. Understanding and manipulating the chemistry of the bath is essential to the improvement of those metrics. Large cost savings and improved process control of plating baths are achieved with the implementation of full time chemical analysis on key reagents and physical characteristics. The common method to monitor the reagents has been to depend upon the vendor for bath analysis, often resulting in slow turn-around time. A better alternative to this outsourcing is the development of an in-house laboratory.

This work centers on the setting up of a cost effective laboratory for routine on-site bath analysis, the development of analytical tools used in the evaluation of the bath variables, and effects on process parameters such as gold reflectivity and film stress. With a cost savings of over $90,000 annually and tool uptime increased by over 40%, the pilot laboratory has been declared a success and serves as a model for other factories using electroplating processes.

Background

There are two main gold plating baths in industry today, cyanide based and non-cyanide baths containing either sulfite or thiosulfate as the primary electrolyte. The cyanide bath is by far the dominant of the two. Cyanide baths in manufacturing show a longer bath life, more consistent plating cosmetics, high stability and a wealth of published knowledge exists for research. Conversely, the non-cyanide baths in particular sodium gold(I) sulfite complexes have shown short and unstable bath life, inconsistent gold cosmetics and little technical literature available outside of the vendor. However, cyanide baths require multi-million dollar containment systems due to toxicity while sodium gold(I) sulfite baths require virtually none. This difference in safety costs is the main driving reason why the sodium gold(I) sulfite bath is chosen over cyanide baths [1]. This facility's plating applications use sodium gold(I) sulfite bath to plate thicknesses ranging from ~1.0μm to 18 μm, both patterned and unpatterned. Patterned plating uses masks of varying reticle density while blanket metal plating uses no pattern and covers the entire substrate surface. Keeping current density constant across the plating spectrum eliminates one source of variation from the plating process. Therefore, if the plating process fails in some way, the failure is limited to either a tool failure or the bath chemistry.

The Na$_3$Au(SO3)$_2$ bath contains seven key constituents, each of which play an integral role in the plating process. Sulfite (SO$_3^{2-}$) acts as the primary electrolyte. An electrolyte is defined as an ionic solution that conducts electricity better than pure water. Sulfate (SO$_4^{2-}$) is formed as a product of the oxidation of sulfite during the electrolytic process. The buildup of sulfate decreases the efficiency of the bath because it is difficult to oxidize, thus allowing electrons to transfer. Equations 1 and 2 show the oxidation mechanisms for the electrolytes. Sulfite to sulfate requires less activation energy than does sulfate to peroxydisulfate [2].

$$SO_3^{2-} \rightarrow SO_4^{2-} + 2e^- \quad [1]$$

$$SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^- \quad [2]$$
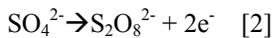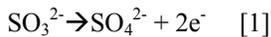
Gold (Au) is ionized in the solution at the +1 oxidation state. The gold is plated using the wafer as a cathode attracting the positively charged gold ions to the surface and reducing them to Au(s). The cathodic reaction can be written as shown in Eq. 3.

$$[Au(SO_3)_2]^{3-} + e^- \rightarrow Au(s) + 2SO_3^{2-} \quad [3]$$

The gold reduction takes place on exposed sputtered seed gold, which covers the wafer. Refer to Figure 1 for a graphical representation of the electroplating process.
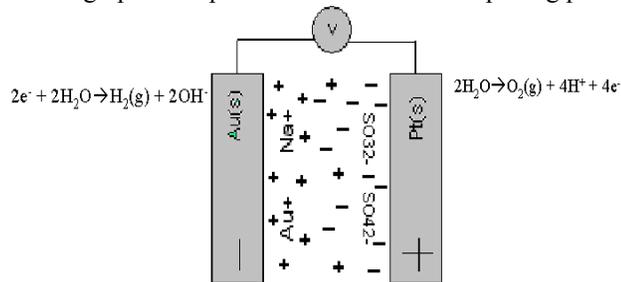

Figure 1- Electroplating Illustration

Ethylenediamine-tetraacetic acid (EDTA) plays a part in the bath by acting as a chelating agent. Chelating agents are large organic molecules that have multiple activation sights. These activation sights bind foreign, positively charged metal ions and hold them so they do not co-plate along with the gold or decompose the bath [3]. Thallium (Tl) is a metallic brightening agent that affects nucleation rate of the gold. Up to a point, the more thallium added, the brighter the gold. The ratio of gold to thallium is an important parameter to calculate and will be discussed in the process control section.

Monitoring and maintaining key physical variables of the bath contributes to the control of bath integrity and stability. These variables include pH, conductivity and specific gravity. pH is the measure of the free H$^+$ ions in a solution. In the case of the Na$_3$Au(SO3)$_2$ bath, it is a measure of the causticity of the bath. For example, the bath in use has an optimum pH of 9.5, an alkaline solution. pH is a vital physical characteristic because it controls the oxidation rate of the sulfite; hence it controls the stability of the gold in solution. Conductivity is the measurement of the amount of electricity that can be conducted through a solution. Conductivity measurements provide information on electrolyte concentration along with gold concentration. Specific gravity is a dimensionless measurement of the ratio of the mass of a substance to the mass of an equal volume of water. Since water has a density of exactly 1.00g/mL, specific gravity is interchangeable with the density of a solution. Specific gravity data gives indication about the amount of sulfate produced in the solution. It is also affected by gold concentration [3].

Laboratory Set-Up

Several factors led to the realization of the importance of an in-house laboratory. These factors included instability leading to spontaneous decomposition of the bath (i.e. gold out-plating on the chemical lines), random scrap occurrences due to poor or "rough" gold cosmetics, and a lack of troubleshooting options for bath problems, which often led to pouring new baths at high cost and lost tool time. Poor plating efficiency has proven itself most costly due to relative wafer loss. Through discussions with vendors and scientists it was determined that continuous analysis of the gold bath and resulting immediate corrections to the bath were essential for the bath to maintain integrity. With this information, a budget for the lab was established and factory space secured. The budgeted monies were based on projected cost savings of $60,000 annually, through the elimination of external laboratory support.

Extensive research on the equipment and techniques was conducted and in early 2001. All hardware, laboratory equipment, and necessary chemical reagents were ordered to operate the laboratory. The laboratory equipment ordered included a chemical hood, glassware, and a single lamp, flame Atomic Absorption spectrophotometer (AA). Other major pieces of equipment included a combination pH/conductivity meter, desiccating oven, UV-Vis spectrophotometer, repeater pipette, hot plate/stirrer, digital balance, burettes, glassware and lab computer. All the reagents required for the standard analysis, as well as chemicals for future techniques to be investigated, were ordered. Material Safety Data Sheets (MSDS) were organized in a folder in the lab as well as in the safety department. The total cost of the laboratory set-up, excluding installation costs, was less than $30,000 in year 2001.

Analysis Techniques

The standardization of the researched techniques began with the base lining of the AA. The AA is used to determine the concentration of gold and thallium in the bath. Au concentration in the electrolyte is run ideally at 1.75 Troy-oz/gallon. Since this is a high concentration bath, the sample is diluted, 1000 times, with water and the resulting dilution reads around 16ppm. Thallium concentration is targeted at an average of 5ppm. Since this concentration is within the detection limits of the AA, no dilution is required, and the concentration can be analyzed directly from the sample. Two titrimetric techniques are used to measure free sulfite and EDTA concentrations. A two-step iodometric titration is used to determine the concentration of the sulfite. A known concentration of iodine is added in excess to the sample reacting with the sulfite (Eq. 4). The surplus iodine is then titrated against sodium thiosulfate using starch as the indicator (Eq. 5). Knowing the initial iodine concentration, the sulfite concentration can be determined through back calculation [2].

$$H_2SO_3 + I_2 + H_2O \rightarrow H_2SO_4 + 2H^+ + 2I^- \qquad [4]$$

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-} \qquad [5]$$
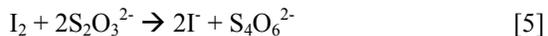
To determine the concentration of the chelating agent EDTA, a bath sample is titrated against zinc sulfate heptahydrate using the metallochromic indicator Eriochrome Black T. The indicator acts as a self-chelating agent. As a chelate, it has a color that is different than from the free solution, and it releases the metal ion at a pZn very close to the equivalence point [2].

The physical properties of the gold bath such as specific gravity, bath pH and conductivity, are measured using instrumentation techniques. Specific gravity is a key metric monitored to maintain a concentration range for sufficient fluidity and to safeguard against excessive sulfate buildup. It is determined from the mass of a 10-mL bath sample. Solution pH and conductivity are determined using a combination meter. The bath is operated at pH level between 9.0 and 10.0 and conductivity is maintained in the range from 55 to 120 mS. Table 1 shows a summary of the bath composition, operating conditions and corresponding analytical techniques.

Table 1 Bath composition averages and analytical techniques.

Gold	1.75 Troy-oz/Gal	Atomic Absorption
Thallium	5.0 ppm	Atomic Absorption
EDTA	7.5 g/L	Volumetric Titration
Sulfite	30 g/L	Volumetric Titration
PH	9.5	Meter
Specific Gravity	X	Hydrometer
Conductivity	80-120 mS	Meter

Before implementation a workable specification was developed and training followed. The specification includes a list of chemicals and analytic tools used in the lab, as well as step-by-step approach to performing bath analysis. Analysis is performed twice per week and data from the analysis is monitored using statistical process control methods.

Process Control

Operation of the gold electroplating bath involves constant monitoring of key process parameters, which include gold reflectivity, film stress, and film thickness. Reflectivity measurements are taken in-line from wafers using a bifurcated fiber system that uses an unfiltered white light source, with wavelength ranging from 410-nm to 800nm. Typical reflectivity plots are shown in Figure 4 for 2.6-μm gold films, as a function of bath life. Evident in this plot are regimes indicating new gold bath. The width of each regime is proportional to the duration of the gold bath. The gold reflectivity can be seen to range from 140-200%, and does not deviate from this range even with the extended use of the gold bath. One can conclude that prolonged use of the gold bath does not degrade surface appearance or brightness of the gold. To maintain the desired reflectance, gold-to-thallium ratio was kept nearly constant. Hence thallium, a gold grain refiner, was added to the gold bath as needed in small amounts ranging from 25-50ml.

Internal stress of the electrodeposited Au film is monitored regularly in order to achieve good adhesion of plated gold to the underlying material, to include the application of through wafer source-vias. The stress was measured using a blanket deposited 3μm gold film on a silicon substrate and is reported as a function of bath life in Figure 2. Individual stress measurements can be seen to fluctuate considerably with bath life. Cumulatively however, stress is maintained constant within a specified range over all the baths, A-B, B-C, and C-D. Continuous conditioning of bath electrolyte has led to almost four-fold increase in bath life with little effect on internal stress.
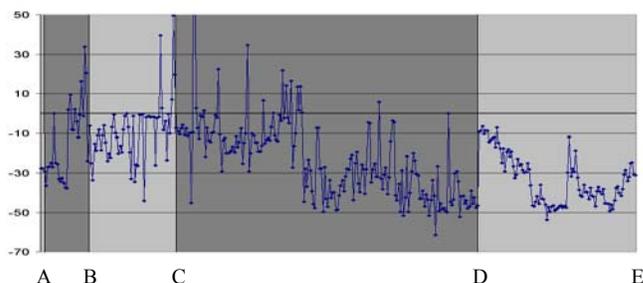

Figure 2: Plated Film Stress Over Time

It is important to note that process control improvements have been significant as a result of in-house bath monitoring. For example, electroplated Au reflectivity has become more stable with a tighter distribution over historical data (Figure 3). Average internal stress has become compressive, which is desirable in the local application, and not tensile as with baths prior to in-house analysis.

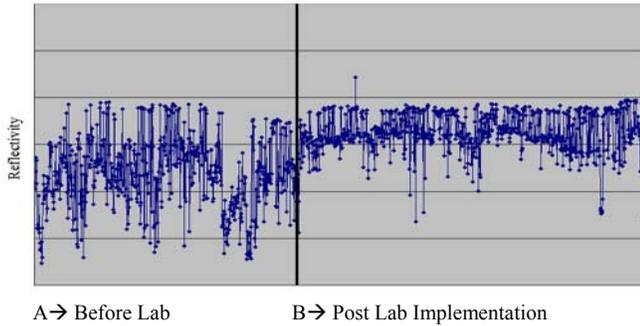A→ Before Lab   B→ Post Lab Implementation

Figure 3: Plated Gold Reflectivity Over Time

To maintain the integrity of the bath electrolyte, frequent adjustments are made to the bath through the addition of additives such as NaOH, thallium sulfate, sodium sulfite, and EDTA. Gold, in 2-TroyOz/L concentrations, is regularly added based on bath usage. Sulfite concentration is adjusted by adding sodium sulfite solution. Sodium hydroxide is added to maintain bath alkaline pH. It is important to note that all of these constituents interact together in the bath, producing secondary and tertiary effects. Thallium sulfate addition for example, increases thallium concentration in the bath, which then causes the plating rate to increase and consequent changes in Au reflectance and internal stress [4]. Specific gravity and conductivity tend to increase as the bath electrolyte ages, due to sulfate levels. The gold concentration is decreased in this case, by skipping regularly scheduled gold additions. Progressive increase in sulfate byproduct and its impact on both specific gravity and Au conductivity is key to defining the duration of a given bath; hence constant monitoring of the parameter is important.

Economic Considerations

Implementation of the analytical lab to monitor bath electrolyte has yielded many successful results. Currently, eight Au electroplating baths have been maintained at little additional cost. Bath life of the electrolyte has increased on the average, by more than four times over baths used prior to lab implementation as can be seen in Figure 2. Tool and bath maintenance hours have been reduced by more than 384 hours annually. The

resulting increases to bath life and lover maintenance costs equal annual savings of over $90,000. In addition, reliance on external laboratory results for sample testing was eliminated, cutting $60,000 in costs. Tool uptime has increased significantly. Losses due to poor gold cosmetics have been nearly eliminated, as well as the engineering time determining the various causes. Typical in-house analysis requires approximately 30 minutes per bath sample when conducted by a trained technician, whereas past turnaround time from external vendors averaged four days. Engineering decisions, which include necessary bath adjustments can now be made as the tool continues to run with results from in-house bath analysis.

Conclusions

$Na_3Au(SO3)_2$ plating applications ranging from 1 to 2 μm for patterned plating and up to 18 μm for blanket plating. Process issues responsible for past yield losses prompted the development of an in-house lab to monitor plating chemistries. Techniques were researched, cost analyses were performed and monies were acquired for the development of the lab. The lab was set up and training ensued. As a result of the pilot lab scrap has been reduced, maintenance hours have been reduced, product quality has improved, and control of the process has greatly increased. The pilot lab is considered a tremendous success and is now serving as a model for other factories in the development of their own in-house labs.

Acknowledgements

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