A Comparison of Cyanide and Thiosulfate Baths for the Electroless Plating of Gold Thin Films

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Despite the high cost, gold is indispensable in the electronics industry. Gold-plated electrical contacts are important due to their unique properties such as good electrical conductivity, high ductility, high thermal conductivity and excellent corrosion resistance.

Electroless plating is one of the most important processes used in industry to produce gold patterns on semiconductor surfaces. Although electroplated gold has long been used, interest in electroless gold plating has been growing due to the process simplicity, as it does not require any external source of current and its ability to coat a wide variety of non metallic substrates. Conventional electroless gold plating baths utilize the gold (I) cyanide complex as a gold source. Due to safety and environmental concerns over the use of cyanide, there are great interests in developing a cyanide-free bath. Several alternative complexing agents have been investigated such as sulfite, thiosulfate, thiomalate, chloride and phosphate (1). Of these alternatives, the use of an Au (I)-thiosulfate complex shows a considerable prospect and has been extensively investigated in several journals and patents. Sullivan and Kohl (2)(3) have made an extensive study on the cathodic reduction of $[Au(S_2O_3)_2]^{3-}$ and anodic oxidation of various reducing agents at a gold electrode.

A Rotating Electrochemical Quartz Crystal Microbalance (REQCM), which is described elsewhere (4), was used to measure the electroless plating rates and to perform electrochemical studies of several electroless gold plating baths. A REQCM combines an electrochemical quartz crystal microbalance (EQCM) and a rotating disc electrode (RDE). The REQCM has several advantages, including:

- The capability of measuring mass changes in ‘real time’ under defined and reproducible hydrodynamic conditions;
- The rate at which reactants are transferred to the solid-solution interface, often called the flux, can be calculated using the Levich equation.

A classic cyanide bath containing borohydride (5) as the reducing agent was compared with a thiosulfate bath containing ascorbic acid as the reducing agent (2). The plots of gold thickness vs. time for the baths are shown in figure 1. As one can observe from the graph, the cyanide bath is superior in plating rate than the thiosulfate bath. The cyanide bath under consideration has a plating rate of 3.27 μm/hr, whereas the thiosulfate – ascorbic bath has a plating rate of 0.41 μm/hr. Another point that can be observed with the thiosulfate bath is that there is a period of approximately 3 – 4 minutes where no plating occurs. This period, however, is not observed with the cyanide bath. This phenomenon will be discussed further in the paper.

There is a frequent demand in plating electroless gold on nickel substrate. Nickel, however, is known to have a poisoning effect on the cyanide – borohydride bath. Ni concentrations as low as 10^{-3} M in the cyanide bath has been discovered to considerably decrease the plating rates. Shown in figure 2 is a comparison of cyanide and thiosulfate electroless plating on a Ni substrate. The plating rate on the Ni substrate for the cyanide bath is much lower than on the gold substrate (figure 1). For the thiosulfate, the gold plating rate is substantially higher. Experiments performed for the thiosulfate bath in the absence of a reducing agent also show a high plating rate. Thus it can be concluded that gold plating on the Ni substrate occurs via nickel cementation of gold(I) thiosulfate (galvanic displacement). This phenomenon will be discussed in more detail. Possible approaches to improve the thiosulfate bath are also investigated and compared with the cyanide – borohydride bath. The effect of temperature, component concentrations, pH, substrate and additives on the performance of a thiosulfate bath will be discussed in regards to the plating rates, and reduction and oxidation voltammograms.

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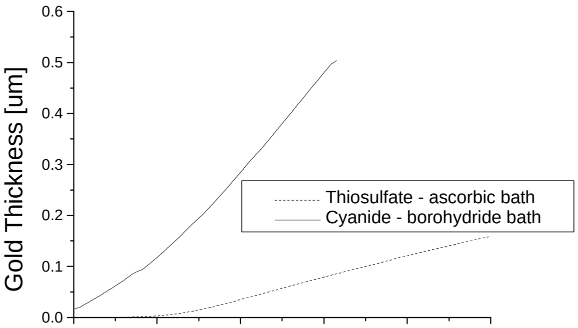

Fig. 1. Comparison of cyanide and thiosulfate bath on gold electrode.

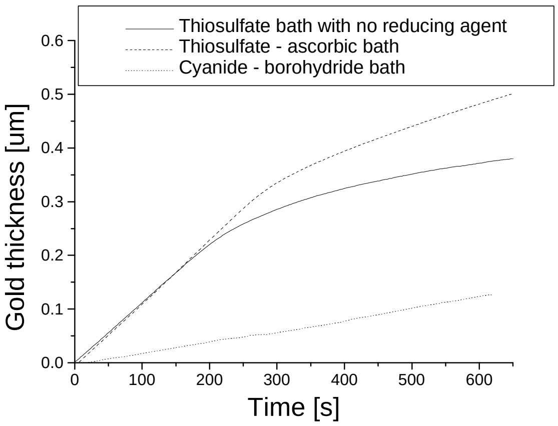

Fig. 2. Comparison of cyanide and thiosulfate bath on nickel electrode.