The Effect of Additives on the Electroless Deposition of Gold from a Thiosulfate – Ascorbic Acid Bath

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Conventional electroless gold plating utilises gold(I) cyanide as the gold source. However several factors, including safety and environmental issues, have driven efforts to develop alternative electroless baths. The performance of alternative thiosulfate baths, however, is still inferior to that of conventional gold electroless plating from cyanide. Possible methods of improving the performance have been investigated, including the addition of thallium and thiourea. It will be shown that although bath decomposition is a major problem when using ascorbic acid as the reducing agent, this can be largely overcome with the addition of thiosulfate. This has lead to the development of baths containing either thiourea or thallium which offer better plating rates and longer bath lifetime.

Introduction

Electroless plating is one of the most important processes for the production of gold patterns on semiconductor surfaces in the electronics industry. Although several methods of plating such as conventional electroplating, sputtering, and etching have long been used, interest in electroless gold plating has been growing due to the process simplicity and its ability to coat a wide variety of non-metallic substrates. Currently, typical electroless gold plating is carried out using a bath containing dicyanoaurate(I) ions. However there are a number of issues associated with the use of cyanide baths:

- safety and environmental issues with the use of cyanide
- free cyanide ions are known to be incompatible with positive photoresists, which are commonly used to delineate circuit patterns (9).
- high alkalinity is required as the electroless reduction of gold cyanide occurs at high pH.

As a result of these issues, several alternative complexing agents have been investigated such as sulfite, thiosulfate, thiomalate, chloride, and phosphate (6). Among these complexing agents, thiosulfate has been investigated most extensively. Sullivan and Kohl (13) have formulated an electroless gold plating bath which utilised gold(I) thiosulfate as the gold source with ascorbic acid as the reducing agent. The reduction of gold thiosulfate proceeds according to the following equation:

\[
\text{Au(S}_2\text{O}_3\text{)}_2^{3-} + e^{-} \rightarrow \text{Au} + 2\text{S}_2\text{O}_3^{2-}
\]

Ascorbic acid, a heterocyclic compound with an enediol group, is oxidised to produce dehydroascorbic acid, which is represented by:
\[ C_6H_8O_6 \rightarrow C_6H_6O_6 + 2e^- + 2H^+ \]  

The pKa values of ascorbic acid are 4.03 and 11.34 at 25 °C (12).

Despite the feasibility of electroless plating from gold thiosulfate, the plating rate is lower than that of the conventional cyanide bath, and it also has shorter bath lifetime. Therefore a comprehensive study was undertaken to improve the plating rate and bath stability.

**Experimental**

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. The basic composition and operating conditions of the electroless gold plating bath used in this study are listed in Table I, which were taken from the original paper published by Sullivan and Kohl (13).

<table>
<thead>
<tr>
<th>TABLE I. Composition and operating conditions of the thiosulfate – ascorbic acid electroless gold plating bath.</th>
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<tbody>
<tr>
<td><strong>Experimental Variable</strong></td>
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<tr>
<td>Na(_3)Au(S(_2)O(_3))(_2)</td>
</tr>
<tr>
<td>Citric Acid</td>
</tr>
<tr>
<td>Ascorbic Acid</td>
</tr>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>pH (adjusted using KOH)</td>
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All solutions were prepared using analytical grade reagents and Milipore Elix water. Mass changes were recorded in ‘real time’ using the REQCM. The changes in thickness were then calculated from the recorded mass change. A conventional three-electrode system was used to perform all electrochemical experiments. The counter electrode was a platinum wire, and all potentials were recorded with respect to a saturated calomel reference electrode (SCE, +242 mV versus SHE) but are reported relative to the SHE. All cyclic voltammetry experiments were performed at a scan rate of 1 mV s\(^{-1}\) using an EG&G Princeton Applied Research Potentiostat / Galvanostat Model 273. Data acquisition was accomplished using an IBM PC and a DATATAKER DT100 data logger. The electrode rotation rate was at 300 rpm.

Prior to each experiment, electrolytic gold with a thickness of 2.5 µm was plated onto the quartz crystal using a plating solution containing: 0.02 M potassium dicyanoaurate, 0.23 M potassium cyanide, and 0.086 M potassium carbonate. The reaction cell was cleaned using aqua regia after each experiment to ensure complete removal of gold from the surface of the cell wall.
Results and Discussion

Figure 1 shows the kinetics and mixed potential of electroless gold plating from thiosulfate with ascorbic acid as a reducing agent. Noticeably, there is an induction period, where little plating is observed during the first 200 s, before the plating rate increases rapidly. This is indicative of autocatalytic baths where initially they have a low plating rate until a sufficient amount of electroless gold has plated. From the slope, the average plating rate was calculated to be ca. 0.85 \( \mu \text{m h}^{-1} \). Several repetitive experiments were carried out which gave a plating rate in the range of 0.85 – 0.95 \( \mu \text{m h}^{-1} \). However the bath plating rate is still significantly lower than that obtained for gold cyanide electroless baths, 3.27 \( \mu \text{m h}^{-1} \) (1).

![Figure 1. Electroless plating of gold from the thiosulfate - ascorbic bath on gold. Experimental conditions as in Table I.](image)

Effect of Cations

Potassium dihydrogen orthophosphate is one of the commonly used buffers in the pH range of 4 to 8. In phosphate solutions, the pH is primarily controlled by the dissociation reaction shown in Equation 3.

\[
\text{H}_2\text{PO}_4^- \leftrightarrow \text{HPO}_4^{2-} + \text{H}^+ \quad [3]
\]

The use of phosphate buffer in the thiosulfate – ascorbic bath has been investigated, and it was found that the plating rate and lifetime of the bath at pH 6.0 was unchanged, indicating that changing from citrate buffer to a phosphate buffer had no effect on the bath performance.

Another experiment was carried out using disodium hydrogen orthophosphate, with the pH adjusted to 6.0 with the addition of NaOH. The plating rate was found to be lower at 0.63 \( \mu \text{m h}^{-1} \), 75% of that obtained from the original bath, as shown in Figure 2. This result is surprising given that the use of potassium dihydrogen orthophosphate in place of citric acid does not give rise to any significant change in plating rate. Therefore the effect
of cations on the plating rate was investigated further. Experiments using ammonium phosphate buffer were carried out using equal amounts of ammonium dihydrogen orthophosphate and di-ammonium hydrogen orthophosphate, and the pH was adjusted with the addition of H2SO4. The plating rate in this case, 1.85 µm h⁻¹, was found to be more than double that for the original bath. It has been previously shown that gold deposition from thiosulfate solutions is dramatically affected by the cation used in the electrolyte, and changing from Na⁺ to K⁺ resulted in gold reduction at more positive potentials (3;15). This is consistent with the high electroless deposition rates in solutions containing K⁺ presented here.

It was found that the effect of the cation was not limited to the phosphate buffer. The original citrate bath contains significant amount of K⁺ as a result of using KOH to adjust the pH. Experiments were also carried out using ammonium citrate where pH regulation was achieved by the addition of NaOH. The use of ammonium citrate resulted in a significantly higher plating rate, 1.56 µm h⁻¹. This is comparable to the plating rate obtained for the ammonium phosphate buffer, 1.85 µm h⁻¹. However, in this case the gold deposition was found to be uncontrollable, with plating also occurring on the quartz crystal, the PVC holder, and the cell wall.

Figure 2. Effect of different cations on the electroless plating of gold. Experimental Conditions: 0.4 M buffer, pH = 5.9 – 6.1, 5 mM gold thiosulfate, 50 mM ascorbic acid, 30 °C.

Linear sweep voltammograms have been obtained for gold deposition from baths containing the three cations studied, and these are shown in Figure 3. It is clear that although the overpotential required to initiate gold deposition was unchanged, the maximum current density was highest in the presence of ammonium ions and lowest in the presence of sodium ions. This result is consistent with previous electrochemical studies of gold thiosulfate deposition (3;15). However the mechanism by which the cation affects gold deposition is still unclear. It has been suggested that the water molecules in the solvation sheath around a larger and heavier cations are not held as strongly, which leads to a greater tendency for the formation of an ion-pair between the gold complex and the cations (11). The ion-pair is less negatively charged and hence easier to reduce at a negatively charged electrode.
Figure 3. Linear sweep voltammograms for the thiosulfate - ascorbic bath showing the effect of cations when using either phosphate or citrate buffer.

Further characterisation of the ammonium phosphate containing bath was carried out by obtaining the polarisation curves for both the anodic and cathodic half reactions. As can be seen in Figure 4, the use of ammonium phosphate buffer not only enhances gold deposition, but also the oxidation of ascorbic acid on the gold substrate. Both of these factors lead to a significant increase in gold deposition rate. The mixed potential predicted from Figure 4, 200 mV, compares well to that measured during the electroless plating, 195 mV.

Figure 4. An Evans'-type diagram showing the effect of buffer on gold thiosulfate reduction and ascorbic acid oxidation.
Ammonium Phosphate Buffer – Thiosulfate Concentration. It has been shown that the addition of free thiosulfate to the thiosulfate – ascorbic acid bath containing citric acid prolongs the bath life, although it also results in a decrease in the gold deposition rate (1). The effect of free thiosulfate addition on the ammonium phosphate containing bath is shown in Figure 5. The initial gold deposition rates for 5 mM and 10 mM thiosulfate were 1.40 \( \mu \text{m h}^{-1} \) and 0.44 \( \mu \text{m h}^{-1} \) respectively. The addition of free thiosulfate was found to stabilise the bath to some extent by increasing the stability of the \( \text{Au(S}_2\text{O}_3)_2^{3-} \) complex. However, with an addition of 10 mM thiosulfate, the bath was found to decompose after one hour, as indicated by the lack of plating after this time, shown in Figure 5. With 5 mM thiosulfate, no plating was observed after 36 mins.

Ammonium Phosphate Buffer – Ascorbic Acid Concentrations. The thiosulfate – ascorbic acid bath can also be stabilised by decreasing the ascorbic acid concentration. Therefore electroless plating was carried out for the bath containing ammonium phosphate at various ascorbic acid concentrations, and the results are shown in Figure 6. It is interesting to note that there was not a significant decrease in the initial plating rate as the ascorbic acid was decreased. However the decrease in ascorbic acid concentration did result in a prolonged bath lifetime, as shown in Table II. With 25 mM ascorbic acid, plating was still observed after 1 hour, although the plating rate does steadily decrease. For 10 mM ascorbic acid, plating was still observed after 1.5 hours. Another experiment was carried out using 70 mM ascorbic acid, and it was found that the maximum plating rate was 1.76 \( \mu \text{m h}^{-1} \), which is comparable to the values obtained in the presence of 50 mM and 25 mM ascorbic acid of 1.85 \( \mu \text{m h}^{-1} \). As seen in Figure 7, in the presence of 70 mM ascorbic acid, the bath decomposed rapidly, as shown by the rapid decrease in plating rate and mixed potential.
TABLE II. Effect of ascorbic acid concentration on plating rate (µm h⁻¹).

<table>
<thead>
<tr>
<th>Time / h</th>
<th>Ascorbic Acid Concentration / mM</th>
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<tbody>
<tr>
<td></td>
<td>50</td>
</tr>
<tr>
<td>0</td>
<td>1.85</td>
</tr>
<tr>
<td>1</td>
<td>none</td>
</tr>
<tr>
<td>1.5</td>
<td>none</td>
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Figure 7. Plating rate and mixed potential in the presence of 70 mM ascorbic acid.

Experiments were also carried out with 5 mM thiosulfate added to the solutions containing a lower concentration of ascorbic acid. The initial plating rates obtained with 5 mM free thiosulfate were 1.40 µm h⁻¹ and 1.38 µm h⁻¹ for 50 mM and 25 mM ascorbic acid respectively. In the bath with 25 mM ascorbic acid and 5 mM thiosulfate, the bath was found to be quite stable, although some decrease in plating rate with time was still observed, as shown in Table III.

TABLE III. Bath plating rate for ammonium phosphate buffer with 5 mM thiosulfate and 25 mM ascorbic acid.

<table>
<thead>
<tr>
<th>Time after preparation</th>
<th>Plating rate / µm h⁻¹</th>
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<tbody>
<tr>
<td>0 hour</td>
<td>1.38</td>
</tr>
<tr>
<td>1 hour</td>
<td>0.86</td>
</tr>
<tr>
<td>2 hour</td>
<td>0.86</td>
</tr>
<tr>
<td>3 hour</td>
<td>0.61</td>
</tr>
<tr>
<td>4 hour</td>
<td>0.45</td>
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Thallium as an Additive

Thallium has been used to enhance deposition in both gold cyanide electrodeposition and electroless gold deposition. However, the addition of thallium has not been trialled in the thiosulfate based baths. Therefore, kinetic studies were carried using the phosphate bath with thallium nitrate added, and the results are shown in Figure 8. It can be seen that initially when thallium was present, the plating rate was more than double that without thallium addition. However, the addition of thallium also influences the bath stability, as it can be seen that the plating rate decreased rapidly with time. Figure 8 also shows that the initial gold deposition rate for thallium concentrations of 7.5 and 3.75 ppm are significantly different. However, at the lower thallium concentration, the bath appears to be more stable, as the decrease in plating rate is less rapid.

The effect of thallium concentration on the initial gold deposition rate is shown in Figure 9. As can be seen, increasing the thallium concentration up to 3.75 ppm results in an increase in the initial gold deposition rate. However, at thallium concentrations higher than 3.75 ppm, the addition of extra thallium does not increase the deposition rate. These results are not surprising as it has been suggested that thallium adsorption onto the gold surface only forms a monolayer coverage (7), and therefore once the monolayer coverage is formed, the addition of extra thallium will not change the surface coverage. A similar investigation of the addition of thallium to the ammonium phosphate found that the bath spontaneously decomposed due to rapid homogenous gold reduction.

Electrochemical studies were also carried out to investigate the effect of thallium on the gold deposition reaction. The gold reduction curves have been obtained for 3.75 and 7.5 ppm thallium. As can be seen in Figure 10, the addition of thallium results in a dramatic shift in the cathodic curve of ca. 200 mV in the positive direction. This indicates...
that, in a similar manner to cyanide baths (8;14), the deposition of gold occurs much more readily in the presence of thallium.

Effect of Thiosulfate Addition. Addition of free thiosulfate enhances the stability of the bath. Therefore experiments were carried out with the addition of 5 mM and 10 mM thiosulfate to the bath containing 3.75 ppm thallium. As seen in Figure 11, the gold plating rates obtained when thiosulfate was added are lower than those shown in Figure 8 in the absence of added free thiosulfate. However, the bath stability was dramatically improved by the addition of free thiosulfate. When 5 mM thiosulfate was added, the plating rate remains high for 6 hours, but some bath decomposition was observed thereafter, as indicated by the formation of a fine gold precipitate. With 10 mM thiosulfate, the plating rate is lower, but the bath remains stable for more than 11 hours. The plating rate for the original bath is also shown in Figure 11, and it should be clear that the performance of the bath with thallium and free thiosulfate is vastly superior.

Figure 10. Gold reduction polarisation curves with different thallium concentration. 5 mM gold thiosulfate, 0.4 M KH₂PO₄, pH 6, 30 °C.

The morphology of the gold deposits obtained was analysed to ascertain the viability of the bath with 3.75 ppm thallium and 5 mM free thiosulfate. It was found that the gold surface obtained was more porous than that obtained in the absence of thallium. Such a result is not surprising, as a higher plating rate leads to more dendritic growth (10).

Effect of ascorbic acid concentration. An alternative to adding free thiosulfate to stabilise the bath is to decrease the reducing agent concentration. As shown in Figure 12, a decrease in ascorbic acid concentration leads to a decrease in bath plating rate, which is as expected. The bath lifetime, however, was not improved by the reduction in ascorbic acid concentration at all the ascorbic acid concentrations investigated in the presence of 3.75 ppm Tl⁺.
Figure 12. Effect of ascorbic acid concentration on plating rate. 0.4 M KH$_2$PO$_4$, pH 6, 3.75 ppm Tl$^+$, 5 mM gold thiosulfate, 30 °C.

Lead as an Additive

The addition of lead to the cyanide bath has the same effect as the addition of thallium, in that it acts as a depolariser. 10 ppm lead was added as Pb(NO$_3$)$_2$, and it was found that lead did not change either the plating rate or have any effect on the bath lifetime. This result is consistent with those reported by Kato et al. (5) who showed that lead did not affect the plating in the sulfite – thiosulfate electroless gold plating bath. Electrochemical studies carried out on the thiosulfate – ascorbic bath with lead addition confirmed that the addition of lead did not have any significant effect on either the reduction of gold or oxidation of ascorbic acid.

MBT as Additive

Heterocyclic mercapto compounds such as 2-Mercaptobenzothiazole (MBT) have been used in the thiosulfate-sulfite gold electroless plating bath as stabilisers, and it was found that MBT improves the bath lifetime without decreasing the plating rate significantly (6). Therefore, the addition of MBT to the thiosulfate – ascorbic bath was investigated. Due to its low solubility, the solution was saturated with MBT, and no significant differences in either the gold deposition rate or bath lifetime were observed.

EDTA and N-methylamine HCl

EDTA and n-methylamine groups have been used in several different cyanide electroless gold plating baths as a chelating agent for impurities. These stabilisers form complexes with metallic contaminants, making them less susceptible in catalysing the homogeneous decomposition. Experiments showed that the use of EDTA or n-methylamine hydrochloride as additives to the thiosulfate – ascorbic bath do not have a significant effect on either the bath plating rate or bath lifetime in the absence of impurity metals.
Thiourea as an Additive

Chandra and Jeffrey (2) have shown that the presence of thiourea greatly improves the oxidation of gold in thiosulfate solutions. Thus, the use of thiourea as an additive for the thiosulfate electroless bath was investigated. An initial concentration of 10 mM thiourea was used and it was found that a high plating rate of 3.9 µm h⁻¹ was obtained, which is approximately 4 times than that obtained from the original bath. However, the bath lifetime in the presence of thiourea decreased substantially. Decreasing the thiourea concentration to 5mM results in a decrease in the initial plating rate to 3.2 µm h⁻¹, and the bath lifetime was slightly improved.

Shown in Figure 13 is the Evans’-type diagram for the thiosulfate – ascorbic bath in the presence of 5 mM thiourea, and the original polarisation curves are shown for comparison. As can be seen the presence of thiourea significantly enhances both the anodic and cathodic reactions, which leads to substantial improvement in the bath plating rate. It is believed that this is a result of thiourea adsorption onto the gold surface.

Effect of ascorbic acid concentration. The effect of ascorbic acid on the initial plating rate for the bath with 5mM thiourea is shown in Table IV. It should be clear that a decrease in ascorbic acid concentration leads to a decrease in the bath plating rate. It was also observed that decreasing the ascorbic acid concentration increased the bath lifetime. In the presence of 50 and 25 mM ascorbic acid, no gold deposition was observed after 1 hour of solution preparation, whereas in the presence of 10 mM ascorbic acid, a gold plating at a rate of 0.5 µm h⁻¹ was observed.

<table>
<thead>
<tr>
<th>Ascorbic acid (mM)</th>
<th>Plating rate (µm h⁻¹)</th>
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<tbody>
<tr>
<td>50</td>
<td>3.2</td>
</tr>
<tr>
<td>25</td>
<td>2.68</td>
</tr>
<tr>
<td>10</td>
<td>2.30</td>
</tr>
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</table>

Effect of free thiosulfate. The bath stability can also be improved by the addition of free thiosulfate, and the effect of 5 mM thiosulfate addition on the bath containing 5 mM thiourea is shown in Figure 14. As can be seen, the bath lifetime is improved considerably by the addition of thiosulfate, although the plating rate is much lower in the presence of free thiosulfate. However, the initial plating rate in solutions containing 5 mM thiosulfate, 0.5 µm h⁻¹, is comparable to the original bath plating rate of 0.85 µm h⁻¹, and the gold deposition rate was essentially constant over 8 hours. This indicates that no bath decomposition occurs under these experimental conditions.
Conclusions

Ascorbic acid was found to be a suitable reducing agent for use with gold thiosulfate, although the gold deposition rate obtained was less than that obtained from the cyanide electroless gold plating bath. The gold deposit obtained from the bath has a smooth and compact surface.

Cations were found to have a considerable effect on the bath performance. The use of heavier cations leads to an increase in plating rates, but also a shorter bath lifetime. However, by using ammonium phosphate buffer, the ascorbic acid concentration can be lowered without significantly affecting the plating rate.

Several commonly used additives for cyanide electroless gold plating baths have been investigated. Of those trialled, thallium and thiourea were found to significantly improve the bath plating rate, although at the expense of bath lifetime. The addition of free thiosulfate and/or decreasing ascorbic acid concentration was found to give significantly higher bath stability with minimal impact on the gold deposition rate.
References