Investigation on the Stability of a Au-Sn Electroplating Solution

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Au-Sn alloys, with a range of compositions, can be successfully pulse plated onto blank wafers and patterned wafers using a slightly acidic, chloride based solution. However, the plating solutions have limited stability (about two to three days), after which deposit compositions are not controllable. The aim of this work was to employ a number of characterization techniques to study the degradation of the plating solution in an effort to develop an understanding of the causes and mechanisms associated with instability. The techniques employed include scanning and transmission electron microscopy (SEM/TEM), x-ray diffraction (XRD), ultraviolet/visible (UV/Vis) spectroscopy and turbidity measurements. Nano-sized Au particles (<10 nm), were present in freshly mixed solutions. These increased in number over time, peaking out after about two days, before agglomerating into visible particles. UV/Vis spectroscopic analysis showed that ascorbic acid (present in the electroplating solution) acted as a reducing agent for the ionic complexes of gold.

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Introduction

Au-Sn eutectic solder has excellent mechanical and thermal properties compared with traditional Pb-Sn solders. It is especially ideal for flip-chip and optoelectronic device packaging. Au-Sn alloys have been successfully pulse plated onto blank wafers and patterned wafers using a slightly acidic, chloride based solution.[1-3] Alloys with Sn concentrations of ~15 at% and ~50 at% can be reproducibly deposited at current densities less than 1.0 mA/cm^2 (0.93 A/ft^2) for 15 at% Sn, and at current densities greater than 2.0 mA/cm^2 (1.86 A/ft^2) for 50 at% Sn.[2,3] A composition of 15 at% Sn corresponds to the Au_5Sn intermetallic phase and 50 at% Sn to AuSn. By alternatively electroplating these two phases, an Au-Sn alloy with a Sn concentration between 15 and 50 at% (including the eutectic composition – 30 at% Sn) can be deposited by adjusting the electroplating time for both phases (Figure 1).

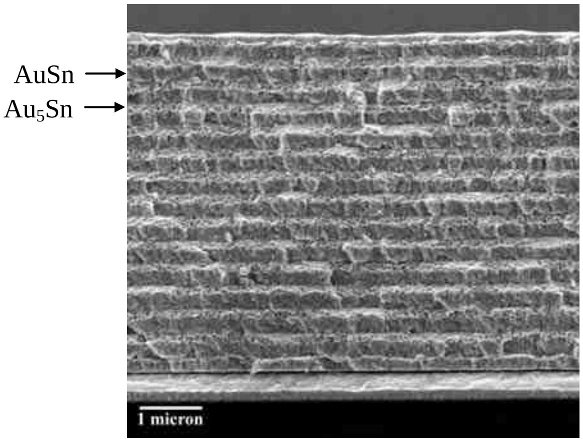


Figure 1 SEM secondary electron (SE) image showing an Au-Sn deposit with an overall composition of 30 at% Sn. The structure consists of alternating layers of Au_5Sn and AuSn, which were obtained by using alternate current pulses of 0.8 mA/cm^2 (0.74 A/ft^2) and 2.4 mA/cm^2 (2.23 A/ft^2) respectively.

The major limitation of the above electroplating solution is that it only has a useful lifetime of about two to three days. After this period, the deposit composition changes to Au-rich or Sn deficient. For example, deposits obtained from a solution approximately three days old and plated at a current density of 3.0 mA/cm^2 (2.79 A/ft^2) had an overall composition of about 25 at% Sn (which corresponds to a mixture of Au_5Sn and AuSn), compared with 50 at% Sn (AuSn) obtained at the same current density for films deposited from freshly prepared solutions.[4] In addition, the deposit morphology deteriorates as plating solutions age beyond two days (Figure 2). There is no apparent change in solution color or appearance after ageing for up to seven days; however, after this time, black or yellow particles begin to precipitate. Longer term ageing leads to precipitate formation on the polypropylene or glass container sides and bottom.

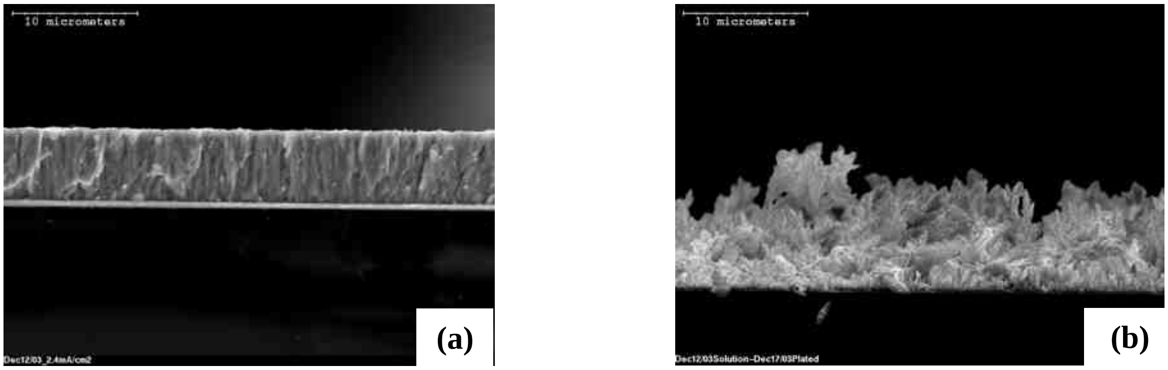


Figure 2 SEM SE images showing Au-Sn deposits obtained from an as prepared solution (a) and a solution that has been aged for 5 days (b). In both cases, pulse plating (2ms ON and 8ms OFF) at 2.4 mA/cm^2 (2.23 A/ft^2) was used.

The net result of this plating solution instability is that it will increase the cost and inconvenience of commercialization. As such, methods of improving useful plating bath lifetime are essential. The purpose of the work reported here is to investigate the mechanisms involved in solution degradation. Identifying these will provide a basis for improving solution stability to make the process more commercially viable. Several techniques are utilized to characterize the solution and any precipitates that form; these include UV/Vis spectroscopy, turbidity measurements, scanning and transmission electron microscopy (SEM/TEM) and x-ray diffraction (XRD).

Experimental Methods

The electroplating solution tested in this work was the same as that reported previously.[2,3] The solution consisted of chloride salts as the source for Au and Sn ($KAuCl_4$ and $SnCl_2.2H_2O$), as well as additives of sodium sulfite, ammonium citrate and L-ascorbic acid. The chemicals were all reagent grade and were completely dissolved in de-ionized water at room temperature. The prepared solution was partitioned into smaller volumes (~30 ml), with each portion stored in sealed bottles. Each bottle was filled to overflowing before sealing to prevent any air from being trapped in the bottles. The filled bottles were then stored for up to several weeks before characterization. Selected tests were also performed on prepared solutions not containing all five components (e.g., $KAuCl_4$ dissolved in de-ionized water).

Turbidity measurements were carried out on the electroplating solution, after various ageing time intervals, using a VWR Model 66120-200 Turbidity Meter. Turbidity is a measure of the degree at which light is scattered by a liquid sample and thus it reflects the sample's heterogeneity.[5] The higher the intensity of scattered light, the higher the turbidity. In theory, any material can scatter light to a certain degree, but a liquid sample with suspended solids, such as the aged electroplating solution, presents a highly heterogeneous system that would give rise to its turbidity. The VWR Model 66120-200 uses nephelometric method that measures the intensity of scattered light at 90° to the incident light path through the sample, and the units of the turbidity are expressed as nephelometric turbidity units (NTU).

UV/Vis spectroscopic measurements were also used to monitor the electroplating solutions over time, using a Jenway Model 6405 UV/Vis spectrophotometer. The wavelength of UV/Vis light varies from 190 to 800 nm. The energies associated with the photons at these wavelengths have the same magnitude as the energy differences between electronic states of many molecules. Therefore, when there is a match, the incident light will be absorbed which shows up in the UV/Vis spectrum as an absorption peak. Electronic transitions such as $\sigma\rightarrow\sigma^*$, $n\rightarrow\sigma^*$, $n\rightarrow\pi$, $\pi\rightarrow\pi^*$, and $n\rightarrow\pi^*$, etc., can be detected by UV/Vis spectroscopic measurements.[6] Therefore, UV/Vis spectroscopic measurements can be used to identify specific bonds (thus molecules) with characteristic electronic structures, and are often used for quantitative analysis. In our measurements, samples were initially scanned at wavelengths from 190 to 1100 nm with a resolution of 1.0 nm to find out which wavelengths were absorbed. The scans were then narrowed to those specific wavelength regions.

Precipitates that accumulated on the internal surfaces of the sample containers were removed, dried, and analyzed by scanning electron microscopy (Hitachi H2700 SEM) and x-ray diffraction (Rigaku Rotating Anode XRD System). The solutions were also periodically examined for precipitates not visible to the naked eye. This was done by extracting a drop of liquid from the solution and placing it on a 3 mm (0.12 in.) diameter copper grid coated with a thin holey carbon film. After evaporation of the liquid, the sample was examined by transmission electron microscopy (JEOL 2010 TEM). Both the TEM and SEM were equipped with ultra thin window (UTW) energy dispersive x-ray (EDX) spectrometers for composition analysis.

Results and Discussion

Precipitation from the electroplating solution

The as prepared Au-Sn electroplating solution was transparent with a faint yellow color. The solution retained its color and clarity for about two to three days, although in some cases for more than seven days. At this point, visible precipitates began to appear in the solution. Initially the precipitates were suspended in the solution; over time they aggregated together and settled to the bottom of the bottles and/or formed a film on the inside walls. Figure 3 shows SEM images of a precipitated film removed from a bottle containing solution that had been aged for twenty-one days. The low magnification image (Figure 3a) shows that the precipitated film is porous, while the higher magnification image (Figure 3b) indicates that the film consists of small particles, predominantly 500 nm or less in diameter. EDX analysis (Figure 3c) of the film shows that it contains only Au, with no Sn or other solution components. XRD analysis (Figure 4) confirms the SEM results, i.e., only peaks corresponding to Au were detected.

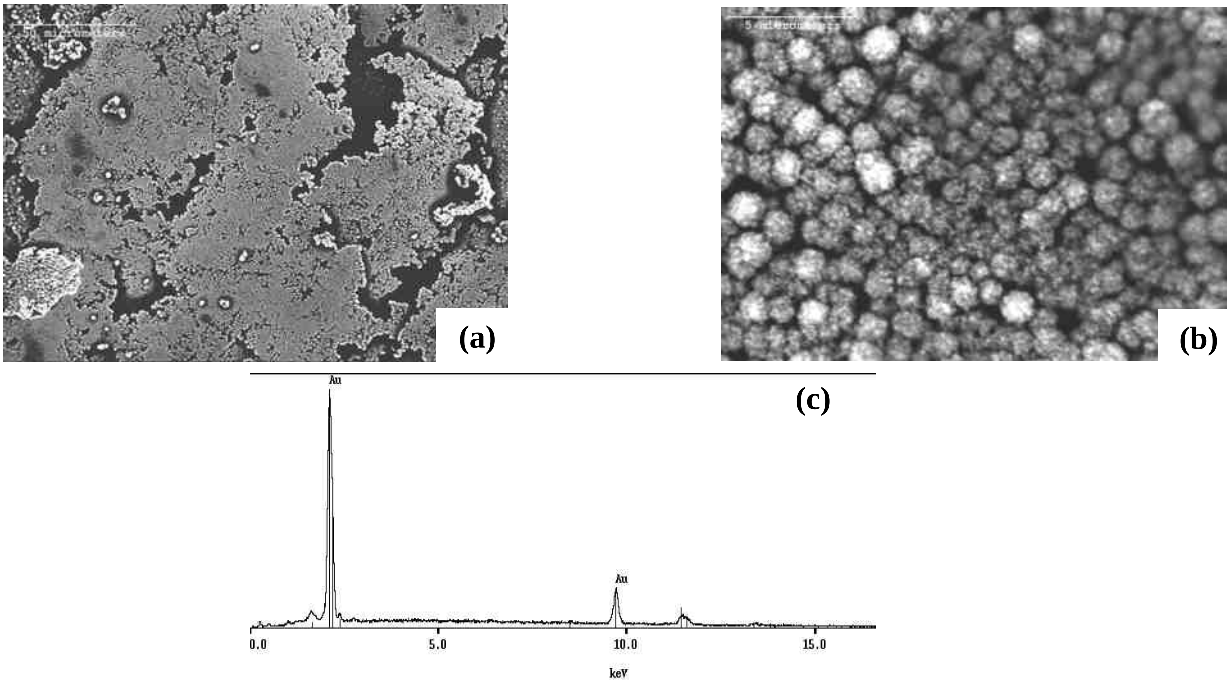


Figure 3 a) and b) SEM SE images of a precipitated film from a solution aged for 21 days. c) EDX spectrum from the region shown in (b).

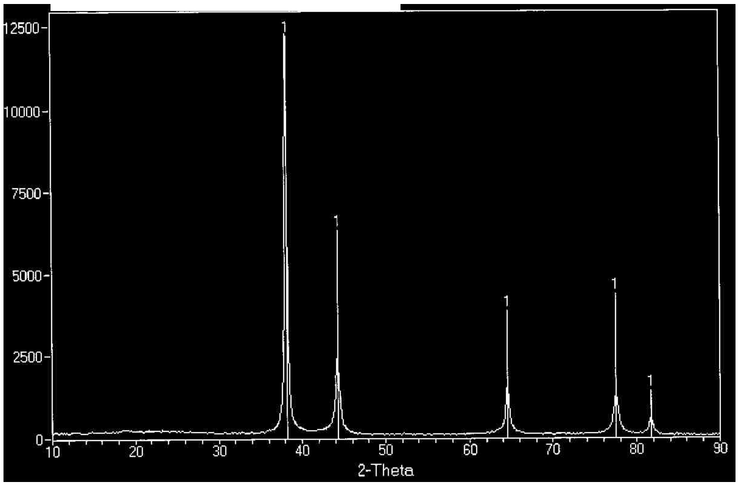


Figure 4   XRD spectrum from the precipitated film shown in Figure 3. All diffraction peaks can be indexed to metallic Au.

Turbidity measurements

Turbidity measurements were utilized to monitor precipitation from the electroplating solution over time. Figure 5 shows a typical plot of the turbidity of the electroplating solution as a function of ageing time. The plot can be divided into four major regions, representing different ageing stages of the solution. The first region shows that the turbidity of a freshly prepared solution decreases from ~4 NTU to ~2 NTU, over a period of about one day. This is followed by the second region in which a rapid increase in turbidity is observed, which peaks out after about two days (~12 NTU). The turbidity then decreases gradually in the third region over the next six days before leveling off at almost 0 NTU. The turbidity remains at close to 0 NTU for more than 2 weeks (fourth region). Similar plots were obtained for all solutions measured, and the only difference was the time periods it took to complete each stage. In some instances the first stage took only about ten hours and in others the maximum turbidity occurred after three days instead of two. During the first and second stages, the solution remained transparent with a faint yellow color. No visible precipitation occurred. However, soon after the peak turbidity was reached, small, suspended particles were visible in the solution; these particles agglomerated over time and gradually deposited on the bottom and sidewalls of the bottles

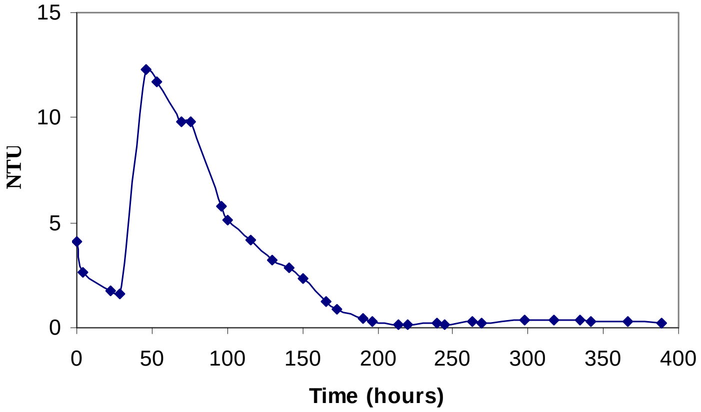


Figure 5 Typical turbidity plot as a function of ageing time for a Au-Sn electroplating solution.

Clearly, very small solid particles precipitated out from the electroplating solution long before they became visible to the naked eyes. In fact, it is likely that precipitation began as soon as the solutions were mixed. The proliferation of precipitates led to more light scattering centers, thus the observed increase in turbidity. The decrease in turbidity, after peaking out at about two days, was probably due to the agglomeration of the small particles, and possibly also due to exhaustion of the reducing agent that was available (see Discussion Section below). Both of these would reduce the number of scattering centers in the solution, resulting in a decrease in turbidity.

TEM analysis was used to confirm the presence of precipitates before they were visible in the solution. As described in the Experimental Section, a drop of solution was deposited onto a carbon coated grid. Once the liquid had evaporated, the grid with any remaining residue was imaged in the TEM. Samples were taken from the three regions in the turbidity plot, i.e., freshly prepared solution, solution with the highest turbidity and solution with almost zero turbidity.

TEM bright field images from two samples, i.e., the freshly prepared solution and the solution with the maximum turbidity (turbid solution), are shown in Figure 6. Isolated particles are clearly visible in both cases. The particles are less than 10 nm in size for the freshly prepared solution (Figure 6a) and between 10 and 20 nm for the turbid solution (Figure 6b). The particle concentration is higher in Figure 6b, which is consistent with a higher turbidity. Particle compositions were analyzed using EDX spectroscopy. In both cases, only Au was detected. Convergent beam electron diffraction (CBED) patterns were obtained from individual particles and confirmed them to be single crystal Au. The TEM sample taken from the fourth region of the turbidity plot (i.e., solution with almost zero turbidity) also contained Au particles (<5nm in diameter), but the number was less than that obtained from the freshly prepared solution. Note, that the large particles had already settled at this point.

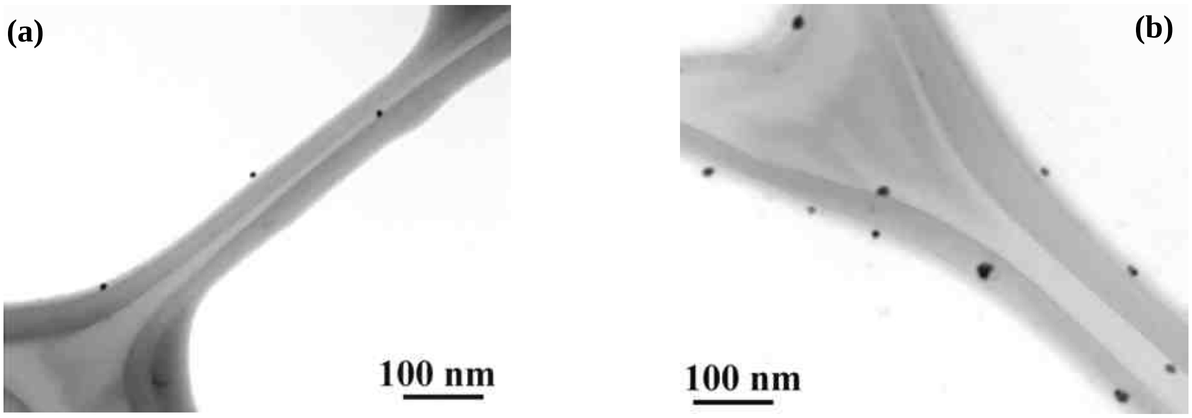


Figure 6 a) TEM BF image from a sample obtained from an as prepared Au-Sn solution. b) TEM BF image from a sample obtained from a Au-Sn solution aged for 2 days.

UV/Vis spectroscopy

In addition to the turbidity measurements, UV/Vis spectroscopy was utilized to monitor changes in the electroplating solution over time. In order to identify the contribution to a given spectrum from an individual chemical component, spectra were obtained for each component dissolved separately in water. Preliminary measurements indicated that there was significant overlap in the 190-200 nm range of absorption peaks from individual solutions of $KAuCl_4$, $SnCl_2.2H_2O$, sodium sulfite, ammonium citrate and L-ascorbic acid. An absorption peak at ~535 nm, claimed to be characteristic of Au nano-particles, has been reported in the literature.[7,8] All subsequent scans, therefore, were done at wavelengths from 200-700 nm; in some cases the range was extended to 900 nm.

Figure 7 shows the UV/Vis spectra as a function of ageing time for the electroplating solution. The solutions were diluted prior to analysis so that the absorbance did not go off scale. Several peaks are visible in the spectra. The peak at ~385 nm was present in all the spectra and corresponds to de-ionized water. The peak at ~265 nm was due to ascorbic acid.[9] The intensity of this peak was the highest for the freshly prepared solution (Figure 7a). It decreased with ageing time and reached zero after about two days (Figure 7e). The disappearance of the ascorbic acid peak indicated that it was completely consumed after about two days. The appearance of (reduced) gold particles and the disappearance of the ascorbic acid seem to indicate that the ascorbic acid acted as a reducing agent in the electroplating solution.

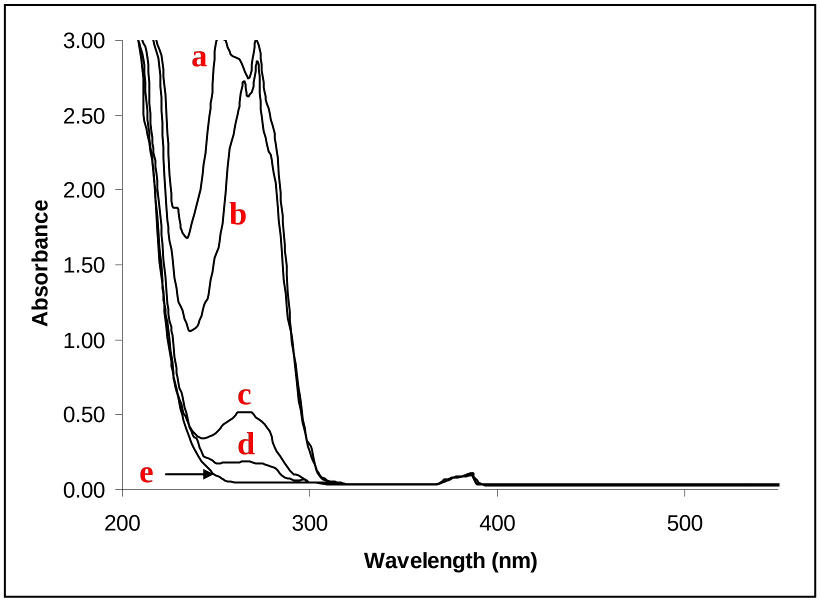


Figure 7 UV/Vis spectra obtained from a Au-Sn electroplating solution after ageing for: a) 0 hrs, b) 4.5 hrs, c) 22 hrs, d) 28 hrs and e) 46 hrs.

As mentioned above, it has been reported that nano-size (~10 nm) Au particles are detectable by UV/Vis spectroscopy, with an absorption peak appearing in the 500-600 nm range and centered at ~535 nm.[7,8] No such peak was detected in this work (see Figure 7), even though the precipitated Au particles were of similar size. Even non-diluted solution did not produce spectra with a peak at 535 nm. The reasons for the discrepancy between the literature results and the observed results are unclear at this time.

Discussion

First of all, it should be noted that the electroplating mechanism for Au and Sn from a bath containing $KAuCl_4$, $SnCl_2.2H_2O$, sodium sulfite, ammonium citrate and ascorbic acid is still not fully understood. Complex $AuCl_4^-$ anions may not be readily plated on a cathode due to their negative charge, and cations such as Au^{3+} and Au^+ would be much easier to plate. However, due to the large stability constants of the complex ions involving Au^{3+} or Au^+ and the available complexing ligands such as Cl^- and SO_3^{2-} in the solution[10,11] (see Eqs. 1-3), it is unlikely that uncomplexed gold cations such as Au^{3+} and Au^+ would exist in the solution.

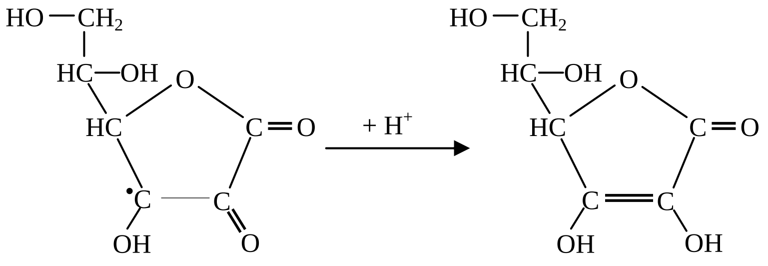
$$Au^{3+} + 4\,Cl^- \rightarrow AuCl_4^- \qquad \beta_4 = 1.75 \times 10^{25} \qquad (1)$$
$$Au^+ + 2\,Cl^- \rightarrow AuCl_2^- \qquad \beta_2 = 2.51 \times 10^{8} \qquad (2)$$
$$Au^+ + 2\,SO_3^{2-} \rightarrow [Au(SO_3)_2]^{3-} \qquad \beta_2 = 10^{10} \qquad (3)$$

Therefore, direct gold electroplating from $AuCl_4^-$, $AuCl_2^-$, or $[Au(SO_3)_2]^{3-}$ complex anions may be possible.

Some of the ingredients in the electroplating solution may act as reducing agents that can reduce the anionic complexes of gold before it is electroplated. For convenience of discussion, standard electrode potentials (vs. SHE) of some of the components in the electroplating solution are listed below:[11,12]

$$AuCl_4^- + 3\,e \rightarrow Au + 4\,Cl^- \qquad E^\circ = 1.0\ V \qquad (4)$$
$$AuCl_4^- + 2\,e \rightarrow AuCl_2^- + 2\,Cl^- \qquad E^\circ = 0.92\ V \qquad (5)$$
$$AuCl_2^- + e \rightarrow Au + 2\,Cl^- \qquad E^\circ = 1.15\ V \qquad (6)$$
$$Sn^{2+} + 2\,e \rightarrow Sn \qquad E^\circ = -0.1375\ V \qquad (7)$$
$$Sn^{4+} + 2\,e \rightarrow Sn^{2+} \qquad E^\circ = 0.151\ V \qquad (8)$$
$$SnO_2 + 4\,H^+ + 4\,e \rightarrow Sn^{2+} + 2H_2O \qquad E^\circ = -0.094\ V \qquad (9)$$
$$SO_4^{2-} + H_2O + 2\,e \rightarrow SO_3^{2-} + 2\,OH^- \qquad E^\circ = -0.93\ V \qquad (10)$$

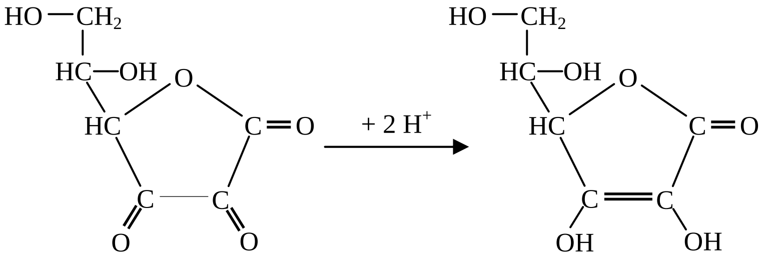
The reduction reaction for semi-dehydroascorbic acid (semi-DHA) to ascorbic acid is:[13]



Semi-DHA Ascorbic acid

$$E^\circ = +0.34\ V \qquad (11)$$

The final oxidation product of ascorbic acid is typically dehydroascorbic acid (DHA) as shown in the following; however, the corresponding redox potential for this reaction was not available in the literature.



DHA   Ascorbic acid   (12)

As can be seen, reduction potentials for Au-Cl^- complexes are clearly much higher than those of the other ingredients in the electroplating solution. In fact, the listed standard electrode potentials indicate that if $SnCl_2.2H_2O$ is mixed with $KAuCl_4$ solutions, the $AuCl_4^-$ ions will be reduced to Au and the Sn^{2+} ions will be oxidized to Sn^{4+}. This was confirmed in an experiment in which a separately prepared $KAuCl_4$ solution was mixed with a $SnCl_2.2H_2O$ solution (no additives in either case). Initially, the $KAuCl_4$ solution was transparent with a yellowish tinge (more yellow than the normal plating solution) while the $SnCl_2.2H_2O$ solution had a slight milky appearance. When the two solutions were mixed, the resultant solution became opaque with a burgundy color. After standing for a few days, the mixed solution became clear again with settled solid particles in the bottom.

A drop of the opaque burgundy solution was deposited on a carbon coated Cu grid for TEM analysis. A bright field image of the sample is shown in Figure 8a, along with a selected area diffraction (SAD) pattern and relevant EDX spectra. Two types of particles are visible on the Cu grid. The smaller particles (<5 nm in size) consist of only Sn and O (Figure 8b), while the larger particles (>10 nm in size) contain only Au (Figure 8c). The Cu and C peaks are artifacts arising from the grid itself. The SAD pattern in Figure 8d, which is taken from the area shown in Figure 8a, contains continuous rings as well as discontinuous rings with discrete spots. The continuous rings are from the smaller particles (containing Sn and O) and can be indexed to SnO_2, which has a tetragonal crystal structure (P42/mnm) with a = 0.4738 nm and b = 0.3187 nm. The discontinuous rings are from the larger particles and can be indexed to fcc Au. Therefore, when $KAuCl_4$ is mixed with $SnCl_2.2H_2O$ solutions, the $AuCl_4^-$ ions are reduced by the Sn^{2+} ions to form metallic Au (either in a single step or in two steps via $AuCl_2^-$). The Sn^{2+} ions are oxidized to Sn^{4+} ions, which hydrolyzes to form SnO_2. Electroplating from a solution containing only $KAuCl_4$ and $SnCl_2.2H_2O$ would not be desirable since only solid Au and SnO_2 particles are present in the solution.

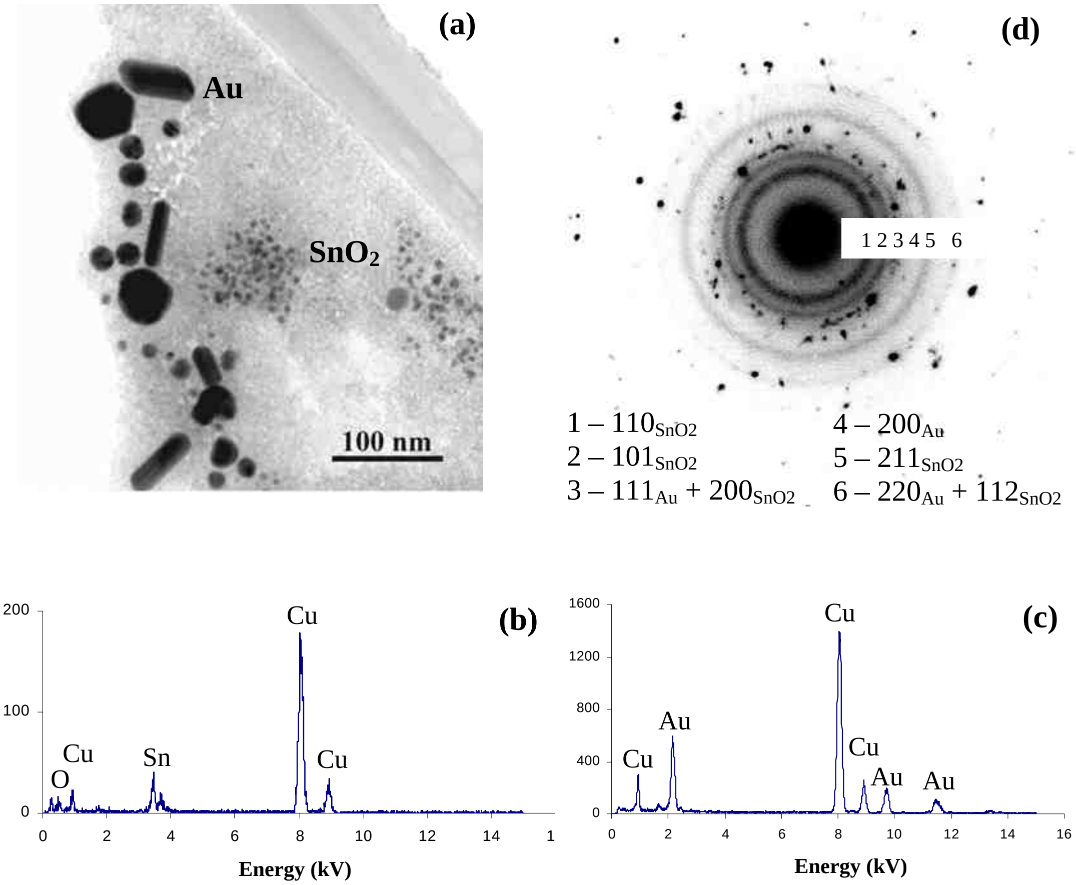


Figure 8 a) TEM BF image from a sample obtained from a suspension that developed on mixing individual Au and Sn solutions. b) EDX spectrum obtained from several of the smaller particles in (a). c) EDX spectrum from one of the larger particles in (a). d) SAD pattern from the region shown in (a). The continuous rings correspond to SnO_2 *and the discontinuous rings to Au.*

When sodium sulfite and ammonium citrate were present together with $KAuCl_4$ and $SnCl_2.2H_2O$ (i.e., the regular Au-Sn plating solution except for the absence of ascorbic acid), the solution was stable for months without visible precipitates and had a low turbidity of about 1.5 NTU. UV/Vis spectra indicated that the absorption peak at 222 nm in the $KAuCl_4$ solution, which was probably due to the interactions of the *d*-electrons of gold with Cl^-, disappeared upon mixing the $KAuCl_4$ with sodium sulfite. Exactly what happened in this solution mixture was unclear, but it was obvious that the presence of sodium sulfite and ammonium citrate stabilized the system so that the $AuCl_4^-$ was not reduced to metallic gold and the Sn^{2+} was not oxidized. Though stable, the solution mixture did not yield the desired Au-Sn deposits in an electroplating experiment and only a thin black colored film was observed on the wafer.

Only when ascorbic acid was added to this solution mixture was the desired Au-Sn plating behavior observed. The addition of ascorbic acid, unfortunately, also reduced the stability of the solution and, as mentioned, precipitation of nano-size gold particles began almost immediately. In addition, the overall Au-Sn ratio in the deposits became uncontrollable after two to three days.

Obviously, the ascorbic acid acted as a strong reducing agent, which destroyed the delicate balance established in the $KAuCl_4$-$SnCl_2.2H_2O$-sodium sulfite-ammonium citrate mixture. The ascorbic acid was probably oxidized to dehydroascorbic acid. This oxidation-reduction reaction was a slow process and was completed in about two to three days under the electroplating conditions. Accompanied by this oxidation-reduction reaction, Au-Sn electroplating was successful. When the ascorbic acid was completely oxidized (as indicated by the disappearance of the UV absorption peak at 265 nm), the solution turbidity also dropped sharply. The turbidity drop may have been caused by two reasons: 1) no more ultrafine gold particles were generated because the ascorbic acid was exhausted, and 2) the ultrafine gold particles agglomerated into large particles and settled out from the solution. The net result was a solution with few ultrafine metallic gold particles but some relatively large gold agglomerates. Under these conditions the electroplating of the Au-Sn alloy became erratic – deposit morphology was rougher and overall deposit compositions were Au-rich or Sn-deficient relative to fresh solutions.

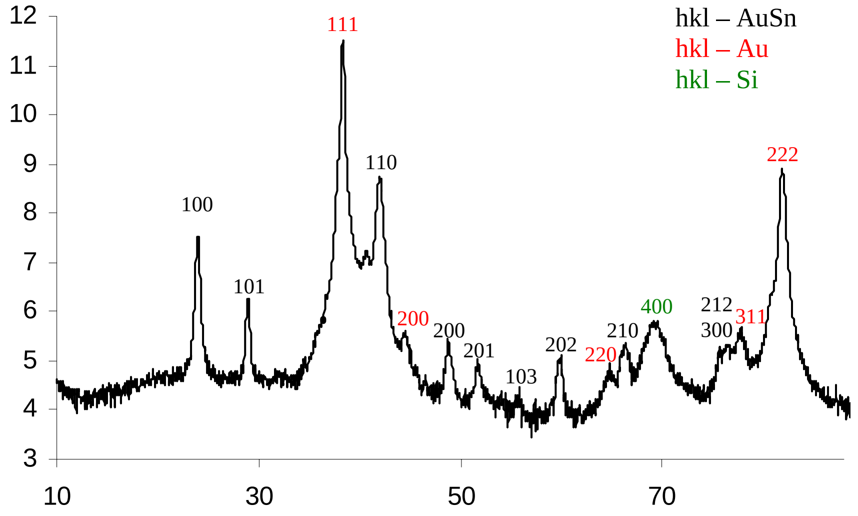


Figure 9 XRD spectrum from a Au-Sn deposit obtained from a plating solution aged for five days. The relative intensity is plotted on a log scale to accentuate the less intense peaks. The diffraction peaks can be indexed to AuSn and Au.

Gold reduction and precipitation can account for the poor long-term stability of the plating solution, but does not account for the increase in gold levels in Au-Sn deposits obtained from solutions aged for more than three days. In fact, precipitation of gold from the plating solution will decrease the amount of gold available for plating and should lead to Au-deficient deposits. Deposits were obtained from solutions that were aged for five days and analyzed by XRD and SEM. At the current density utilized ($2.4 mA/cm^2$ or $2.23 A/ft^2$) the deposits should be single phase, containing ~50 at% Sn (AuSn). EDX analysis showed that the overall composition of the deposit was about 37-40 at% Sn, which suggests a two phase mixture of AuSn and Au_5Sn (~16 at% Sn). Indexing of XRD spectra from the deposits (Figure 9) showed that two phases were present, but these were AuSn and Au (not Au_5Sn). It appears then that only AuSn was electroplated, as would be expected for the current density employed. However, the nano-size particles of Au, suspended in solution, may have been physically incorporated during plating giving an overall deposit content less than 50 at% Sn. Incorporation of the Au particles is also likely a contributing factor to the increased surface roughness exhibited by deposits obtained from aged solutions (e.g., Figure 2b).

In view of the fact that Au(I) and Au(III) complexes in the plating solutions are anions, and that a stable solution of such anions did not yield Au-Sn deposits unless ascorbic acid was added, which almost immediately caused the formation of nano-sized Au particles, it is possible that electrodeposition of Au is through the deposition of clusters of reduced Au (aggregates of several Au atoms). These clusters would then be incorporated, along with reduced Sn atoms, into a uniform Au-Sn deposit. As the clusters grow into larger particles, e.g., tens of nanometers in size, the electroplating process would become erratic, since it has changed to an electrophoretic process.

This paper has touched upon the stability of the Au-Sn plating solution as related to the electroplating behavior of the Au-Sn alloy. More research along this direction is required before the process can be completely understood.

Summary

The degradation of a chloride-based solution, used for simultaneous electrodeposition of Au-Sn alloys, has been studied using a combination of turbidity measurements, UV/Vis spectroscopy, XRD and SEM/TEM. Degradation begins virtually immediately after the solution is prepared, due to the gradual reduction of ionic complexes of gold by ascorbic acid. The resulting Au precipitates are initially less than 10 nm in size, but agglomerate after 2 to 3 days to form visible particles that settle and coat the container walls. To solve the bath stability problem, a thorough understanding of the mechanism of the Au-Sn plating process and the roles played by each ingredient are required.

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