Electrodeposition of Sn-0.7 wt% Cu Eutectic Alloys from Chloride-Citrate Solutions

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A simple and "green" Sn-Cu chloride-citrate solution was developed to electrodeposit Sn-Cu alloys. Copper remains more noble than tin in solutions with tri-ammonium citrate as the complexing agent, and co-deposited Sn-Cu films have similar morphology and structure for both pulsed current (PC) and direct current (DC) plating. Copper was evenly distributed through most of the deposit thickness (~0.7 wt% Cu), with higher copper levels (5.5 wt% Cu) at the interface. Plating rates of 20 to 27.5 µm/hr were attainable at average current densities of 10 to 12.5 mA/cm², producing deposits with near eutectic compositions. Two phases, tin and Cu_cSn_s, were detected for both PC and DC plating, with tin being the majority phase. Solutions were stable for more than 36 days and aged solutions had similar plating rates as fresh solutions. With solution aging, copper ions became easier to plate from the Cu-citrate complexes, which caused a slight increase in copper content in the deposits.

Keywords: Pb-free solders; Sn-Cu eutectic alloys; electrodeposition; complexing agent

Introduction

Solders are the most important joining materials in electronic assemblies.¹ During the past 60 years, eutectic and near-eutectic Sn-Pb alloys have been used as the principal joining materials because of their unique low melting point (183°C), outstanding solderability, formation of stable joints that are capable of operating in a wide variety of service environments and low cost.² However, increasing health and environmental concerns worldwide regarding the toxicity of lead have prompted countries such as Japan and those from the European Union to pass legislation prohibiting or restricting the use of Sn-Pb solders.³ These restrictions have stimulated the development of a large number of lead-free alternative solders.^{2,3,4}

The lead-free solders developed so far are tin-rich with a range of alloying elements such as Ag, Bi, Cu, In, Sb and Zn. Examples include Sn-0.7 wt% Cu, Sn-3.5 wt% Ag, Sn-3.8 wt% Ag-0.7 wt% Cu and Sn-3.5 wt% Ag-4.8 wt% Bi,⁴ with melting temperatures between 210°C and 227°C. Among these alloys, the Sn-0.7 wt% Cu eutectic alloy solder is particularly advantageous.^{2,5,6} With the

replacement of lead by copper, the Sn-0.7 wt% Cu alloy solder is non-toxic. Although the eutectic melting point (227°C) is relatively high, Sn-Cu solders are only about 1.3 times more expensive than Sn-Pb solders, whereas other lead-free solders typically cost 2 to 3 times more. The relatively low cost makes the Sn-Cu alloy a good candidate for wave-soldering processes in the mass production of commercial electronics. Although copper is not an abundant element in the Earth's crust, the extraction technology for copper is relatively straightforward so that its supply is secure. Furthermore, copper has been widely used in electronic devices and can be recycled from scrap electronic equipment. Therefore, the use of Sn-0.7 wt% Cu alloy solders will not introduce a new element into these recycling processes.

Electrodeposition is a useful technique to deposit different metals and alloys. A number of baths and additives have been developed to electrodeposit tin and tin-based alloys.⁷⁻¹¹ The standard electrode potential for Cu⁺²/Cu is 0.34 V_{SHE}, which is much higher than that of Sn⁺²/Sn (-0.14 V_{SHE}). Complexing reagents are often used to bring the standard reduction potentials of the two pairs closer.

Typical Sn-Cu plating solutions are strongly alkaline with alkali cyanide or alkali pyrophosphate as a complexing agent.¹² These solutions are not compatible with photoresists when plating on patterned substrates in printed circuit boards. Some solutions such as pyrophosphate baths and fluoborate baths are also used to co-deposit both the tin and copper. The purpose of these baths, however, is not to obtain a Sn-Cu eutectic alloy but rather to obtain an alloy with a much higher copper content. Other Sn-Cu plating solutions are based on sulfuric acid or methanesulfonic acid (MSA) with additives such as polyoxyethylene laurylether, sodium alkyl sulfate ester, thiourea, dimethylthiourea, polyoxy-

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Table 1

Volume of precipitates formed in different Sn-citrate solutions

	1	2	3	4	5	6
SnCl ₂ ·2H ₂ O (mol/L)	0.22	0.22	0.22	0.22	0.22	0.22
Tri-ammonium citrate (mol/L)	0.22	0.28	0.29	0.30	0.31	0.33
Volume of precipitates (%)	25	17	2	0	0	0

ethylene β -naphthol ether, 1-naphthaldehyde and tri-ammonium citrate, among others.^{12,13,14} These additives are believed to be helpful in forming smooth and homogeneous deposits, minimizing hydrogen gas evolution, improving solution stability and refining grain structures. In spite of these benefits, the application of many of these additives is undesirable from a safety and environmental perspective. The additives also create difficulty in the treatment of the wastewater streams. It is, therefore, desirable to develop new Sn-Cu solder plating processes where the deposition potential is controlled without using too many additives.¹⁵

Tri-ammonium citrate is an ammonium salt of citric acid and can be used as an emulsifier in dairy products, such as processed cheeses, and as an acidity regulator. Tin-citrate complexes have been reported to form in solutions containing both stannous chloride and ammonium citrate.¹⁶ The formation of the Sn-citrate complexes was deduced from the observation that the addition of sodium carbonate to the solution did not result in the precipitation of tin carbonate.¹⁶ Ammonium citrate has been used as complexing agent in both acidic and alkaline solutions for Sn-Co, Sn-Au, Co-Mo, Co-W and copper electrodeposition.^{15,17,19} Yanada, *et al.*¹² have used tri-ammonium citrate and Sn/Cu methanesulfonate to electrodeposit Sn-Cu alloys. Their electroplating baths also contain many other additives.¹² No report has been found focusing on the electrodeposition of Sn-Cu alloys from simple chloride-citrate solutions.

The objective of this study was to develop simple plating baths to electrodeposit Sn-Cu eutectic and near-eutectic solder films. A key target is to minimize the number of additives, thereby making the plating bath as "green" as possible. Both pulsed current (PC) and direct current (DC) plating have been utilized during electrodeposition for comparison purposes. This paper reports results on the tin and copper co-deposition behavior from the chloride-citrate baths, optimization of the electrodeposition conditions to obtain eutectic and near-eutectic Sn-Cu solder films by both PC and DC plating, the effect of current densities on the plating rate and copper content in the deposit and solution stability.

Experimental materials and procedure

The chemicals used were tri-ammonium citrate, $(NH_4)_3C_6H_5O_7$ (Alfa Aesar, 98%], SnCl₂·2H₂O (Fisher Scientific) and CuCl₂·2H₂O (Fisher Scientific). The chloride-citrate solutions were prepared by dissolving tri-ammonium citrate in deionized water and then dissolving SnCl₂·2H₂O and CuCl₂·2H₂O in the citrate solution. The chlorides were added as the source of Sn⁺² and Cu⁺² ions and the citrate was added as a stabilizer (complexing agent).

The prepared solutions were characterized using a Gamry electrochemical system with platinum as both the working and the counter electrodes, and a saturated calomel electrode (SCE) as the reference electrode. Before testing, the platinum electrodes were

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cleaned ultrasonically for 2.0 min in ethanol and then rinsed with deionized water. Polarization measurements were carried out at a scanning rate of 1.0 mV/sec. Cyclic voltammetric (CV) measurements were carried out from 0.9 V_{SCE} to -1.1 V_{SCE} at a scanning rate of 50 mV/sec.

Two types of substrates were used for electrodeposition. Silicon wafer pieces, metallized with a 25-nm titanium adhesion layer and a 200-nm gold seed layer, were used for electrodeposition on gold. Sectioned copper sheets with a nickel layer (~12 μ m thick) electroplated on one side were utilized for electrodeposition on nickel. A standard Watts nickel plating solution was used for nickel electrodeposition on copper. Before plating, the copper pieces were cleaned and any surface oxide layers removed by treating in a CuCl₂ + H₂SO₄ solution for about 20 sec, followed by rinsing with deionized water. A Dynatronix DuPR 10-0.1-0.3 pulse plating power supply was used for both PC and DC electrodeposition, with a 2 msec forward on-time and 8 msec forward off-time during PC plating. For both PC and DC plating, current densities were varied from 2.5 to 15 mA/cm² and all electrodeposition was done for 30 min at room temperature.

The microstructure and composition of the Sn-Cu films were characterized using a Hitachi H2700 scanning electron microscope (SEM) equipped with an ultrathin window energy dispersive x-ray (EDX) spectrometer. Deposit compositions were found by averaging measurements taken from at least three regions, each 400 \times 400 μ m in size. Phase analysis was performed using thin film x-ray diffraction (XRD) with a Rigaku rotating cobalt anode system, operating in continuous scanning mode at a voltage of 40 kV and a current of 160 mA. The thickness of the Sn-Cu films was measured using an Alpha-step 200 profilometer. The thickness was taken as the average of at least three measurements.

Results and discussion

Sn-citrate solution composition

Previous work by He, *et al.*²⁰ showed that solutions containing 0.31 to 0.41 mol/L (75 to 100 g/L) tri-ammonium citrate and 0.22 mol/L (50 g/L) SnCl₂·2H₂O can be used to electrodeposit in films. To determine the optimum ratio of tri-ammonium citrate to tin salt, both in terms of solution stability and electrodeposition of tin and Sn-Cu films, initial work focused on solutions containing 0.22 mol/L (50 g/L) SnCl₂·2H₂O and different amounts of tri-ammonium citrate. The concentrations of tri-ammonium citrate were varied from 0.22 mol/L (54 g/L) to 0.66 mol/L (160 g/L), *i.e.*, the molar ratio of Sn⁺²-to-citrate varied from 1:1 to 1:3. At a molar ratio of 1:1 (Solution 1 in Table 1), a white precipitate was formed after mixing SnCl₂·2H₂O with the tri-ammonium citrate solution. The precipitate occupied about 25% of the solution volume. The minimum concentration of tri-ammonium citrate required to com-

pletely dissolve $0.22 \text{ mol/L SnCl}_2 \cdot 2H_2O$, without forming precipitates, was found to be 0.30 mol/L (Table 1). The work that follows is, therefore, focused on solutions with tri-ammonium citrate concentrations ranging from 0.30 to 0.66 mol/L, which are identified as S1, S2, S3 and S4 in Table 2.

Polarization measurements for the four solutions are shown in Fig. 1. All four solutions showed similar polarization behavior. As the amount of tri-ammonium citrate in the solution was increased from 0.30 to 0.66 mol/L, the onset potential for the reduction of Sn(II)-citrate complexes decreased from about -0.64 V_{sce} to about -0.72 V_{sce}. One possible reason for the lower onset potential was the change of the distribution of different Sn(II)-citrate or citrate species with different amounts of tri-ammonium citrate.^{21,22}

The Sn-citrate solutions remained transparent and colorless for more than three months. After adding CuCl₂·2H₂O, however, the color changed upon aging, and electroplating from the aged solution gave rough and discontinuous films. The higher the triammonium citrate concentration, the sooner the color changed. Therefore, in all subsequent work, only the lowest tri-ammonium citrate concentration needed to completely dissolve the tin salt, *i.e.*, 0.30 mol/L, was utilized, while the SnCl₂·2H₂O concentration was maintained at 0.22 mol/L.

Sn-Cu electrodeposition from the chloride-citrate solution

Small amounts of CuCl₂·2H₂O were added to the Sn-citrate solution (S1) to co-deposit Sn-Cu alloys. Approximately 0.003 mol/L (0.53 g/L) of CuCl₂·2H₂O was needed to achieve the eutectic composition (0.7 wt% Cu) at a current density of 10 mA/cm². This Sn-Cu solution was stable for at least 36 days, with the pH stabilizing at around 4.

Cyclic voltammetric studies were carried out to separate the contributions to the cathodic current due to metal ion reduction from that due to hydrogen gas evolution, and to understand the stages of the reduction and oxidation reactions for different metal ions in the tri-ammonium citrate solutions. Figure 2 shows the voltammograms for a Sn-citrate solution, a Cu-citrate solution

Table 2Composition of Sn-citrate solutions studied by
polarization measurements

	S1	S2	S3	S4
SnCl ₂ ·2H ₂ O (mol/L)	0.22	0.22	0.22	0.22
Tri-ammonium citrate (mol/L)	0.30	0.33	0.44	0.66

and a combined Sn-Cu-citrate solution. The concentration of the tri-ammonium citrate was kept the same (0.30 mol/L) for all three solutions. For the Cu-citrate solution, a concentration of 0.22 mol/L was chosen for the copper salt to be consistent with the Sncitrate solution. All the tests were conducted without stirring. The two peaks at -0.26 $\rm V_{_{SCE}}$ and -0.6 $\rm V_{_{SCE}}$ for the Cu-citrate solution seem to indicate the two copper reduction reactions, Cu(I)-citrate \rightarrow Cu and Cu(II)-citrate \rightarrow Cu. The peak at about -0.98 V_{SCE} for the Sn-citrate solution indicates the Sn(II)-citrate \rightarrow Sn reaction. There are two steps for copper oxidation and three steps for tin oxidation in citrate solutions. Under these conditions, the onset of the voltammetric reduction current for the Sn-Cu-citrate solution appeared at an intermediate potential value between those corresponding to tin and copper reduction, but very close to that of tin. The same behavior was observed during oxidation. Both the reduction and oxidation potentials of copper were higher than those for tin in the tri-ammonium citrate solution, which indicates that copper remained more noble than tin with tri-ammonium citrate as a complexing agent. Therefore, by adding copper to the Sn-citrate solution, both the main reduction and oxidation peaks shifted to more positive potentials. Since the concentration of copper salt in the Sn-Cu-citrate solution was very low, i.e., almost two orders of magnitude lower than that of the tin salt, the addition of the copper salt only caused a slight shift of the Sn-citrate curve towards that



Figure 1—Polarization curves for Sn-citrate solutions. In all four solutions, the concentration of $SnCl_2 \cdot 2H_2O$ was kept at 0.22 mol/L, while the concentration of tri-ammonium citrate was varied as follows: a) 0.30 mol/L; b) 0.33 mol/L; c) 0.44 mol/L; d) 0.66 mol/L.



Figure 2-Cyclic voltammetry measurements for various solutions: (a) 0.30 mol/L tri-ammonium citrate + 0.22 mol/L CuCl₂·2H₂O; (b) 0.30 mol/L tri-ammonium citrate + 0.22 mol/L SnCl₂·2H₂O; (c) 0.30 mol/L tri-ammonium citrate + 0.22 mol/L SnCl₂·2H₂O + 0.003 mol/L CuCl₂·2H₂O.



Figure 3—Deposit copper content as a function of average current density. The solution concentration was 0.30 mol/L tri-ammonium citrate + 0.22 mol/LSnCl, $2H_2O$ + 0.003 mol/L CuCl, $2H_2O$.

of the Cu-citrate curve. It is envisaged that copper electrodeposition from the Sn-Cu-citrate solution would dominate initially, but copper ions would be depleted quickly at the cathode surface, so that Sn electrodeposition would become dominant afterwards.

Smooth and dense Sn-0.7 wt% Cu films were obtained by both PC and DC plating from the above Sn-Cu-citrate solution with an average current density of 10 mA/cm². Plan view and cross section images of the plated films are shown in Figs. 5b and 5e and Figs. 6b and 6e. Both deposits were uniform with very similar surface morphologies, except that the DC deposit was slightly rougher. XRD analysis showed that for both deposits, two phases were detected. The major phase was tetragonal tin, with a small amount of the Cu₆Sn₅ intermetallic.

Effect of current density on Sn-Cu plating

Current density is an important parameter in electrodeposition. The effect of average current density on the copper content in PC and DC deposits was studied and the results are shown in Fig. 3. Copper content decreased with increasing current density, which was as expected since the limiting current density for copper electrodeposition would be significantly lower than that for tin, given the disparity in solution concentration. PC plating produced deposits with higher copper content, although at higher current densities, the differences were small, or even insignificant, particularly given the magnitude of the error bars. For both PC and DC plating, current densities higher than 10 mA/cm² gave near eutectic Sn-Cu deposits. Dendrites formed on the wafer edges when the average current density exceeded 15 mA/cm².

The effect of average current density on plating rate at a fixed plating time of 30 min is shown in Fig. 4. As expected, the plating rate increased with increasing current density but leveled off when the current density reached 13 to 15 mA/cm². An average current density of 10 to 12.5 mA/cm² was considered optimal, as the deposit copper concentration was near the eutectic composition (without dendrites) and plating rates were 20 to 27.5 μ m/hr. PC plating gave lower plating rates than DC plating. One possible reason is that the peak current density for PC plating was five times



Figure 4—Plating rate as a function of average current density for both PC and DC plating. The solution concentration was 0.30 mol/L tri-ammonium citrate + 0.22 mol/L SnCl; 2H,O + 0.003 mol/L CuCl; 2H,O.

the value for DC plating for the duty cycle utilized, *i.e.*, 2 msec on and 8 msec off and hydrogen evolution was more significant under these high current densities. Chang, *et al.*²³ studied both PC and DC chromium electrodeposition and reported that during PC plating, the applied cathodic current charged the interface between the electrode and the electrolyte before any reduction happened. This charging current only had a capacitance effect for the electrical double layer and was not involved in any reduction reaction. This interfacial charging current was required for each PC cycle, thereby reducing the current efficiency for PC plating relative to DC plating for the same average current density.

It is generally believed that the surface roughness of plated films changes with current density.24 Figures 5a thru f show SEM plan view images of Sn-Cu films plated at average current densities of 5, 10 and 15 mA/cm², respectively, by both PC and DC plating, from a solution with 0.22 mol/L of SnCl₂·2H₂O, 0.003 mol/L of CuCl₂·2H₂O and 0.30 mol/L of tri-ammonium citrate. The corresponding cross section images are shown in Figs. 6a thru f. The plan view images show that for both PC and DC plating, Sn-Cu films plated at low current densities had a rougher surface morphology than the ones plated at higher current densities. The difference in surface morphology between PC deposits and DC deposits becomes more significant at the highest current densities, because the difference in peak current densities between PC plating and DC plating is larger. Cross section images in Fig. 9 show that the Sn-Cu films became less dense as the current density was increased. Pores appear at average current densities of 15 mA/cm², and can be attributed to hydrogen evolution.

X-ray diffraction patterns for PC plated Sn-Cu deposits on gold seed layers at different current densities are shown in Fig. 7. In this figure, the vertical axis is plotted on a log scale in order to better show the intensity of the minority Cu_6Sn_5 phase. The structures of the three films are similar. As the current density was increased from 5 to 10 mA/cm², the Cu_6Sn_5 peak at 25° disappeared and the ones at 50.7° and 63.1° became weaker. As the current density was further increased to 15 mA/cm², additional Cu_6Sn_5 peaks at 63.1° disappeared and the ones at 35.0° and 50.7° became even weaker. This is because at higher current densities, the deposits contained less copper, so less Cu_6Sn_5 formed.



Figure 5-SEM SE plan view images of Sn-Cu films electrodeposited onto gold seed layers from Sn-Cu-citrate solutions (0.22 mol/L SnCl₂:2H₂O + 0.003 mol/L CuCl₂:2H₂O + 0.30 mol/L tri-ammonium citrate).



Figure 6-SEM SE cross section images of Sn-Cu films electrodeposited onto gold seed layers from a Sn-Cu-citrate solution (0.22 mol/L $SnCl_2:2H_2O + 0.003$ mol/L $CuCl_2:2H_2O + 0.30$ mol/L tri-ammonium citrate).



Figure 7–XRD patterns from PC plated Sn-Cu films onto gold seed layers from a Sn-Cu-citrate solution (0.30 mol/L tri-ammonium citrate + $0.22 \text{ mol/L SnCl}_{2}$: (a) 5 mA/cm²; (b) 10 mA/cm²; (c) 5 mA/cm².

To determine the through-thickness copper distribution in Sn-Cu deposits, EDX analysis at 2 μ m intervals across the thickness was carried out and the results are shown in Fig. 8 for both PC and DC plating. To avoid the effects of Sn-Au interdiffusion at room temperature, as well as the effect of copper from a copper substrate on any composition measurements, nickel-coated copper substrates were used. As can be seen from Fig. 8, for both PC and DC plating, the copper concentration was uniform across the thickness, except at the Sn-Cu solder/Ni interface where the copper content was much higher. As discussed previously, Cu⁺² ions are more noble than Sn⁺² ions in citrate solutions, so Cu⁺² reduction would dominate initially, giving a higher copper composition in the initial deposits. This initial enrichment disappears quickly, due to the low levels of copper in the electrolytes.

Solution stability tests

Solution stability is another key consideration when developing new plating solutions. Two series of aging tests were conducted, one in which the solution was repeatedly used for electrodeposition over a given length of time (Test 1), and the other in which the solution was aged for a given length of time and then used for electrodeposition (Test 2). All the solutions were stored in sealed bottles when not used for electrodeposition. To ensure that there would be sufficient copper in the deposit to be detected by EDX analysis, a current density of 5 mA/cm² was applied in all the tests. Deposit copper content remained approximately constant throughout the aging tests for both Test 1 (Fig. 9) and Test 2 (Fig. 10). In Test 1, the copper content was in the 1.5 to 3.5 wt% range for PC plating and in the 1.5 to 2.5 wt% range for DC plating. In Test 2, the copper contents for both PC and DC plating were close to each other, and were in the range of 1.5 to 3.0 wt%. SEM images for the PC deposits from a 36-day old solution from Test 1 and Test 2 are shown in Fig. 11. Both surfaces were smooth and the plating rate was about 11 μ m/hr at a current density of 5 mA/cm², which was almost the same as that for a fresh solution. A simple, approximate calculation can be done to determine whether the metal ion consumption over time would have any effect on the electrodeposition process. The tin deposits are assumed to have densities corresponding to the bulk value for tin (7.3 g/cm³). The plating rates are

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assumed to be the same for aged and fresh solutions and the plated area is taken to be the maximum sample area utilized (0.8 cm^2). The amount of tin consumed during each electrodeposition process is about 3.2 mg or 0.03% of the tin in solution. For Test 1, where the same solution is used for each deposition after aging, the total amount of tin consumed after 12 electroplating cycles was about 38.5 mg or about 0.37% of the tin in solution. Both of these values are essentially negligible, so that the tin concentration in solution remains approximately constant and should have no effect on electrodeposition. Copper is assumed to be evenly distributed inside the deposits and copper content in the deposit is taken to be 3.4 wt%, which is the highest amount among all the EDX results for both Tests 1 and 2. The amount of copper consumed during each electrodeposition process was about 0.1 mg or 1.4% of the copper



Figure 8–Deposit copper content as a function of the distance from the solder/ substrate interface for both PC and DC Sn-Cu films electrodeposited from a Sn-Cu-citrate solution (0.30 mol/L tri-ammonium citrate + 0.22 mol/L SnCl₂·2H₂O) + 0.003 mol/L CuCl₂·2H₂O). Plating was done at 10 mA/cm² on Ni-coated copper substrates.

in solution. For Test 1, after 12 electrodeposition cycles, the total amount of copper consumed was about 1.35 mg or about 17% of the copper in solution. As such, the deposit copper content might be expected to drop, particularly after the longer aging times (*e.g.*, 21 and 28 days), as shown in Fig. 9. However, copper consumption from the electrolyte does not account for the initial increase in deposit copper content for both Tests 1 and 2 when the aging times were less than 15 days (Figs. 9 and 10).

To determine whether any changes occurred to Cu(II)-citrate and Sn(II)-citrate solutions during aging, polarization tests were done for Cu(II)-citrate solutions containing 0.22 mol/L CuCl₂·2H₂O and 0.30 mol/L tri-ammonium citrate and Sn(II)-citrate solutions containing 0.22 mol/L SnCl₂·2H₂O and 0.30 mol/L tri-ammonium citrate after different aging times. The results are shown in Figs. 12 and 13, respectively. After the Cu(II)-citrate solutions were aged for one day, three days and as long as 28 days, the onset reduction potential moved from -0.33V_{SCE} to less negative values, *i.e.*, -0.26V_{SCE} after aging for one day, -0.05V_{SCE} after aging for three days and as long as 28 days (Fig. 12). The Cu-citrate complexes became easier to reduce upon aging. One possible reason is that some of the Cu⁺² ions were reduced to Cu⁺ in the citrate solution and formed Cu(I)-citrate complexes. It also can be noticed that after the solution was aged for three days, an additional small plateau appeared right after the onset of reduction reactions and became larger with longer aging times. This plateau may have been due to the reduction of Cu(I)-citrate ions. For the Sn(II)citrate solution, the onset reduction potential remained essentially constant even after aging for 28 days, which is an indication that the Sn(II)-citrate solution is quite stable. Since Cu-citrate became easier to reduce and the Sn-citrate did not change, the deposit copper content would be expected to increase upon aging, as evident in Figs. 9 and 10. After 14 days, the reaction between Cu⁺² ions and Cu+ ions probably reached equilibrium, while the solution became increasingly depleted of the copper ions with each plating cycle, leading to decreasing deposit copper contents, as shown in Fig. 9. Copper was not consumed during Test 2 prior to plating, so that the deposit copper content stayed almost the same after aging for more than 14 days.



Figure 9–Deposit copper content as a function of solution aging time for both PC and DC plating (Test 1). The solution concentration was 0.30 mol/L triammonium citrate + $0.22 \text{ mol/L } \text{SnCl}_2 \cdot 2H_2 O + 0.003 \text{ mol/L } \text{CuCl}_2 \cdot 2H_2 O$ and the average current density was 5 mA/cm².

Conclusions

The Sn-Cu chloride-citrate solutions developed for electrodepositing eutectic and near-eutectic Sn-Cu films are simple with only one additive (tri-ammonium citrate) other than the chloride salts of the metal ions. The pH of the solutions is around 4.0. Copper remains more noble than tin in the tri-ammonium citrate solution so that copper reduction initially dominates. But since the copper concentration in the solution is almost two orders of magnitude lower than that of tin, it is rapidly depleted and tin reduction soon becomes dominant. This causes copper enrichment at the Sn-Cu solder/substrate interface. For both PC and DC plating, the average deposit copper content decreases and plating rate increases as the current density increases. PC plating gives slightly higher copper contents in the deposits but lower plating rates than DC plating. A current density between 10 and 12.5 mA/cm² gives near-eutectic Sn-Cu compositions with a plating rate between 20 and 27.5 μ m/hr.

The co-deposition of tin and copper from the Sn-Cu chloridecitrate solutions leads to the formation of two phases, *i.e.*, tin as the major phase with small amounts of Cu_6Sn_5 . The developed Sn-Cu chloride-citrate solutions are stable for at least 36 days, with similar plating rates as for fresh solutions. The copper ions in the Cu-citrate complexes become easier to reduce with aging while Sn-citrate is stable, therefore the copper content in the deposited Sn-Cu films increases slightly when the solutions, aged for up to 14 days, were used to plate these films.

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Figure 10—Deposit copper content as a function of solution ageing time for both PC and DC plating (Test 2). The solution concentration was 0.30 mol/L tri-ammonium citrate $+ 0.22 \text{ mol/L} \text{ SnCl}_2 \cdot 2H \cdot O + 0.003 \text{ mol/L} \text{ CuCl}_2 \cdot 2H_2O$ and the average current density was 5 mA/cm^2 .



Figure 11—SEM SE images (plan view and cross section) for Sn-Cu films PC plated in a solution aged for 36 days: (a) Test 1; (b) Test 2. The solution composition was 0.30 mol/L tri-ammonium citrate + 0.22 mol/L SnCl₂·2H₂O + 0.003 mol/L CuCl₂·2H₂O. Plating was done at 5 mA/cm2.







Figure 13–Polarization curves for a Sn-citrate solution containing 0.22 mol/L SnCl, 2H₂O and 0.30 mol/L tri-ammonium citrate after different aging times.

References

- J.W. Evans, D. Kwon & J.Y. Evans, A Guide to Lead-free Solders: Physical Metallurgy and Reliability, Springer-Verlag London Ltd., London, UK, 2007.
- K. Suganuma, Current Opinion in Solid State and Materials Science, 5 (1), 55 (2001).
- 3. M. Abtewa & C. Selvaduray, *Materials Science and Engineering: R: Reports*, **27** (5-6), 95 (2000).
- S.K. Kang, et al., *IBM Journal of Research and Development*, 49 (4-5), 607 (2005).
- K.N. Tu, A.M. Gusak & M. Li, J. Appl. Phys., 93 (3), 1335 (2003).
- K.J. Puttlitz & K.A. Stalter, Handbook of Lead-free Solder Technology for Microelectronic Assemblies, Marcel Dekker, New York, NY, 2004.
- 7. J.H. Commander & V. Paneccasio, U.S. Patent 5,061,351 (1991).
- S. Igarashi, Y. Fujisawa & T. Igarashi, U.S. Patent 4,163,700 (1979).
- 9. T. Makino & A. Maeda, U.S. Patent 5,118,394 (1992).
- 10. V.C. Opaskar & L.D. Capper, U.S. Patent 6,436,269 (2002).
- 11. M.P. Toben, et al., U.S. Patent 6,210,556 (2001).
- 12. I. Yanada, et al., U.S. Patent 6,508,927 (2003).
- 13. M. Fukuda, K. Imayoshi & Y. Matsumoto, *Surface and Coatings Technology*, **169-170**, 128 (2003).
- N.M. Martyak & R. Seefeldt, *Electrochim. Acta*, 49 (25), 4303 (2004).
- 15. A. Survila, et al., J. Appl. Electrochem., 31 (10), 1109 (2001).
- R.H. Hess & R. Taft, Transactions of the Kansas Academy of Science, 41, 171 (1938).
- S.J. Kimz & D.J. Duquette, J. Electrochem. Soc., 153 (6), C417 (2006).
- A. Subramania, A.R. Sathiya Priya & V.S. Muralidharan, Int. J. Hydrogen Energy, 32 (14), 2843 (2007).
- C.L. Aravinda, V.S. Muralidharan & S.M. Mayanna, J. Appl. Electrochem., 30 (5), 601 (2000).
- 20. A. He, Q. Liu & D.G. Ivey, J. Materials Science: Materials in Electronics, 19 (6), 553 (2008).
- A.S. Tikhonov & N. S. Kurolap, *Trudy Voronezh University*, 42, 61 (1956).
- 22. A. Survila, Z. Mockus & S. Kanapeckaite, *Electrochim. Acta*, **46** (4), 571 (2000).
- 23. J.H. Chang, et al., Applied Surface Science, **253** (16), 6829 (2007).
- 24. T. Watanabe, *Nano-plating: Microstructure Control Theory* of *Plated Film and Data Base of Plated Film Microstructure*, Elsevier, Oxford, UK, 2004.

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