

Development of Simple Electrolytes for the Electrodeposition and Electrophoretic Deposition of Pb-free, Sn-based Alloy Solder Films

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Abstract

A large number of Pb-free solders have been developed due to restrictions on the use of Pb in conventional Pb-Sn solders. The most promising examples of these solders are Sn-based; e.g., the Sn-0.7wt%Cu alloy and eutectic and near-eutectic SAC (Sn-Ag-Cu) alloys. Alloy solder films can be deposited from electrolytes containing several additives which are used to improve solution stability and deposit morphology. However, these additives make the electrodeposition process difficult to control. Two approaches have been studied in our laboratory to simplify the process and to make the electrolytes environmentally friendly. In the first approach, Sn-based, slightly acidic electrolytes have been developed, which contain only one additive (tri-ammonium citrate) other than the metal salts. The optimum citrate concentration was 0.30 mol/L for a solution containing 0.22 mol/L of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. The addition of 0.003 mol/L of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ to this solution can give near eutectic Sn-Cu deposits at current densities of 10-12.5 mA/cm² with dense and uniform Sn-Cu deposits and a plating rate of 20-27.5 $\mu\text{m/hr}$ at room temperature. The solution is stable for more than 36 days. In the second approach, nano-size Cu powders are suspended in the simple Sn solution with the aid of a dispersant. Near eutectic Sn-Cu films can be obtained with the addition of 0.004 mol/L (0.25 g/L) of Cu particles.

INTRODUCTION

The health hazards posed by Pb in conventional Pb-Sn solders have prompted countries, such as Japan and those from the European Union, to pass legislation prohibiting or restricting the use of these types of solders. One result of this legislation has been the development of a large number of Pb-free alternative solders. The most promising examples of these solders are Sn-based; e.g., the Sn-0.7wt%Cu eutectic alloy and eutectic and near-eutectic SAC (Sn-Ag-Cu) alloys. The Sn-0.7wt%Cu alloy solder is particularly advantageous^[1, 2]. With the replacement of Pb by Cu, the Sn-0.7wt%Cu alloy solder is non-toxic. It is only about 1.3 times more expensive than the Sn-Pb solders, whereas other Pb-free solders typically cost 2 to 3 times more. Although Cu is not an abundant element in Earth's crust, the extraction technology for copper is relatively straightforward so that its supply is secure. Furthermore, Cu has been widely used in electronic devices and can be recycled from scrap electronic equipment. The use of Sn-0.7wt%Cu alloy solders will not introduce a new element in these recycling processes.

Although the Sn-Cu eutectic alloy solder has many advantages as outlined above, the electroplating solutions that are used to obtain the Sn-Cu eutectic alloy films are extremely complex. Conventional Sn-Cu alloy plating solutions are either strongly alkaline with alkali cyanide or alkali pyrophosphate as a complexing agent^[3] or are acidic and based on sulfuric acid^[4], pyrophosphate-iodide^[5] or methanesulfonic acid (MSA)^[6]. In the acidic solutions, many other chemicals, such as polyoxyethylene laurylether, triethanolamine, sorbitol, sodium gluconate, 1,4-hydroxybenzene, Trion X100 or polypropylene glycol, may be added as complexing agents. In fact, some Sn-based alloy electroplating solutions have been reported to contain as many as 13 additives. The additives are necessary to improve solution stability and deposit morphology. However, they also make the electrodeposition process difficult to control. The composition of the alkaline solutions may be simpler, however, they are not compatible with photoresists when plating on patterned substrates.

In this paper, work that has been conducted to develop a simple, cyanide-free, slightly acidic chloride-based solution for the electrodeposition of Sn-0.7wt%Cu solder films is reported. Two types of solutions have been studied: one that contains soluble salts of Sn and Cu and a complexing agent (for electrodeposition), and one that contains a soluble salt of Sn, a complexing agent, Cu particles and a dispersing agent (for electrophoretic deposition). Both solutions are based on a simple, stable Sn solution developed in our laboratory, containing $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and $(\text{NH}_4)_3\text{C}_6\text{H}_5\text{O}_7$. The pH of the two solutions is between 4 and 5.

EXPERIMENTAL PROCEDURE

The plating solutions used for electrodeposition contained only $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and tri-ammonium citrate $(\text{NH}_4)_3\text{C}_6\text{H}_5\text{O}_7$. The base solution contained 0.30 mol/L (73g/L) of tri-ammonium citrate and 0.22 mol/L (50g/L) of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. The chlorides were added as the sources of the Sn and Cu ions, and the citrate was added as a stabilizer. The plating solution used for electrophoretic deposition consisted of copper particles (200-300 nm in size) suspended in a $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and tri-ammonium citrate solution. The solutions were characterized using a Gamry electrochemical system. Platinum was used as both the working and the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. Before testing, wafers were cleaned ultrasonically for 2 minutes in ethanol and then

rinsed in deionized water. The cathodic potential scanning rate was set at 1 mV/s.

All electrodeposition was done on Si wafer pieces, metallized with a 25 nm Ti adhesion layer and a 200 nm Au seed layer, at room temperature for 30 minutes. A Dynatronix DuPR 10-0.1-0.3 pulse plating power supply was used, with a 2 ms forward on-time and 8 ms forward off-time. Current densities were varied from 2.5 mA/cm² to 20 mA/cm². Solutions were agitated during deposition. 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 obtained by average measurements taken from at least three regions, 400 × 400 μm² in size. Phase analysis was done using thin film X-ray diffraction (XRD) in continuous scanning mode with a Rigaku rotating Co anode system, at an operating voltage of 40kV and a current of 160mA.

RESULTS AND DISCUSSION

Sn-Cu salt solution

Small amounts of CuCl₂•2H₂O were added to the base Sn-citrate solution. Approximately 0.003 mol/L (0.53g/L) of CuCl₂•2H₂O was needed to achieve the eutectic composition (0.7 wt% Cu) at a current density of 10mA/cm².

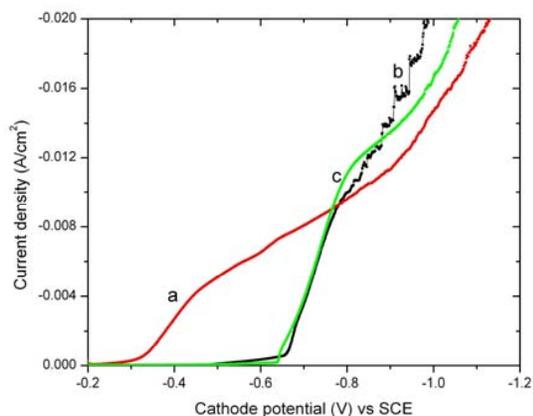


Figure I: Polarization curves for solutions: a) 0.30 mol/L (NH₄)₃C₆H₅O₇ + 0.22 mol/L CuCl₂•2H₂O; b) 0.30 mol/L (NH₄)₃C₆H₅O₇ + 0.22 mol/L SnCl₂•2H₂O; c) 0.30 mol/L (NH₄)₃C₆H₅O₇ + 0.22 mol/L SnCl₂•2H₂O + 0.003 mol/L CuCl₂•2H₂O.

Polarization curves for the stable Sn-citrate solution, a Cu-citrate solution and the combined Sn-Cu-citrate solution are shown in Figure I. The concentration of tri-ammonium citrate was kept the same for all three solutions. For the Cu-citrate solution, a concentration of 0.22mol/L was chosen for the Cu salt to be consistent with the Sn-citrate solution. The reduction of Cu²⁺ ions began at about -0.3 V, which was significantly higher than the reduction potential for Sn²⁺ ions (-0.64 V). Copper is nobler than Sn in the absence of a

complexing agent in aqueous solutions. The polarization curves indicate that in the presence of tri-ammonium citrate as a complexing agent, Cu was still nobler than Sn. The polarization curve for the Sn-Cu-citrate solution was very similar in appearance to the Sn-citrate curve. This is not surprising, as the concentration of Cu salt in the Sn-Cu-citrate solution was almost two orders of magnitude lower than that of the Sn salt. It is envisaged that Cu electrodeposition from the Sn-Cu-citrate solution would dominate initially, but Cu would be depleted quickly at the cathode surface, so that Sn electrodeposition would become dominant.

Sn-Cu electrodeposition

Both pulsed current (PC) and direct current (DC) were used to plate Sn-Cu alloys. Figure II shows plan view and cross section images of deposits obtained with an average current density of 10mA/cm². Both deposits were uniform with very similar surface morphology.

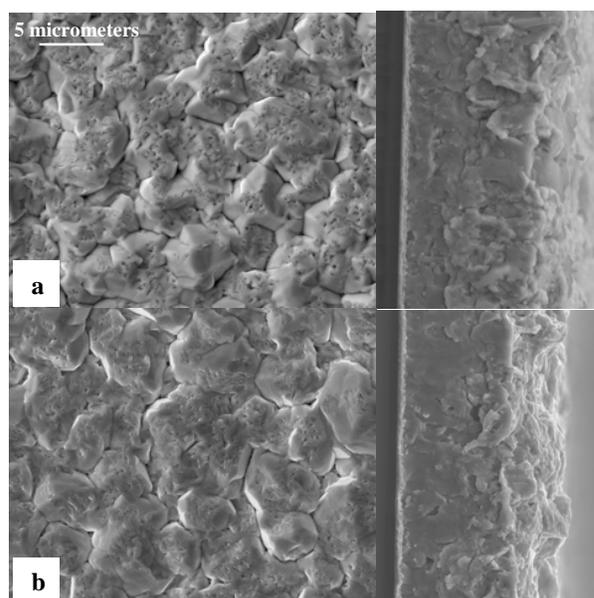


Figure II: SEM SE images (plan view and cross section) of Sn-Cu films electrodeposited from a Sn-Cu-citrate solution (0.22 mol/L SnCl₂•2H₂O + 0.003 mol/L CuCl₂•2H₂O + 0.30 mol/L (NH₄)₃C₆H₅O₇) with (a) PC plating and (b) DC plating.

The effect of average current density on deposit Cu content was studied and the results are shown in Figure IV. Copper content decreased with increasing current density, which would be expected since the limiting current density for Cu electrodeposition would be significantly lower than that for Sn given the disparity in solution concentration. PC plating produced deposits with higher Cu 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 10mA/cm² gave near eutectic Sn-Cu deposits, but dendrites formed on the wafer edges when the average current density exceeded 15mA/cm².

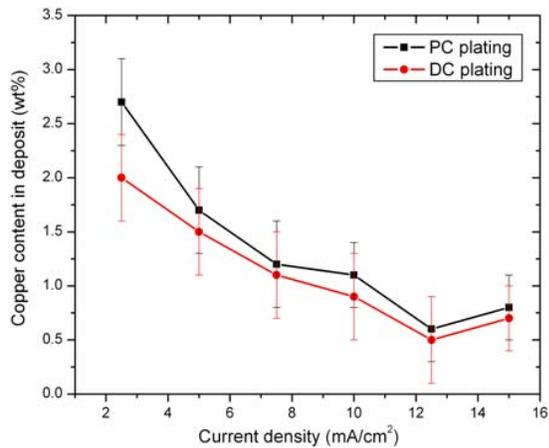


Figure III: Deposit Cu content as a function of current density. The solution concentration was 0.30 mol/L $(\text{NH}_4)_3\text{C}_6\text{H}_5\text{O}_7$ + 0.22 mol/L $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ + 0.003 mol/L $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$.

The effect of average current density on plating rate at a fixed plating time of 30 minutes is shown in Figure IV. As expected, the plating rate increases with increasing current density but levels off at ~13-15 mA/cm². An average current density of 10-12.5 mA/cm² was considered optimal, as the deposit Cu concentration was near the eutectic composition (without dendrites) and plating rates were 20-27.5 μm/hr. PC plating has lower plating rates than DC plating.

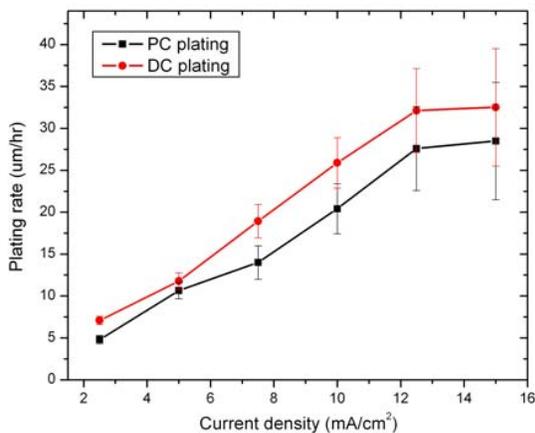


Figure IV: Plating rate as a function of current density. The solution concentration was 0.30 mol/L $(\text{NH}_4)_3\text{C}_6\text{H}_5\text{O}_7$ + 0.22 mol/L $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ + 0.003 mol/L $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$.

The X-ray diffraction spectra (Figure V) for PC and DC plated deposits were similar, with two phases detected. The major phase was Sn, with small amounts of the Cu_6Sn_5 intermetallic. In this figure the vertical axis is plotted on a log scale in order to show the intensity of the minority Cu_6Sn_5 phase. The major difference between the PC and DC plated deposits was a stronger (200) preferred orientation for the PC plated deposit.

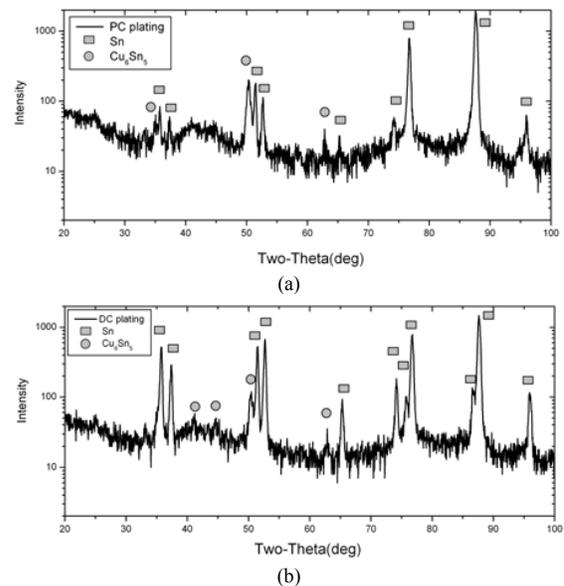


Figure V: XRD spectra from deposits plated using (a) PC and (b) DC conditions. The solution composition was 0.30 mol/L $(\text{NH}_4)_3\text{C}_6\text{H}_5\text{O}_7$ + 0.22 mol/L $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ + 0.003 mol/L $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $j = 10 \text{ mA/cm}^2$.

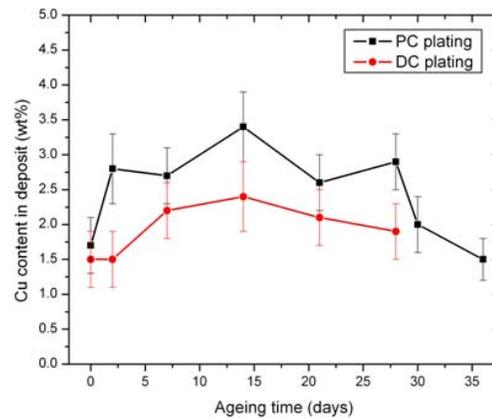


Figure VI: Deposit Cu content as a function of solution ageing time with both PC and DC plating. The solution composition was 0.30 mol/L $(\text{NH}_4)_3\text{C}_6\text{H}_5\text{O}_7$ + 0.22 mol/L $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ + 0.003 mol/L $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $j = 5 \text{ mA/cm}^2$.

Solution stability is another key consideration when developing new plating solutions. Ageing tests using the same solution were conducted. To ensure that there would be sufficient Cu in the deposit to be detected by EDX analysis, a current density of 5 mA/cm² was applied in all tests. Deposit Cu content remained approximately constant throughout the ageing tests. For PC plating, the Cu composition was in the 1.5-3.5 wt% range, while for DC plating, the Cu content was in the 1.5-2.5 wt% range. SEM images for a deposit, by PC plating, from a 36 day old solution are shown in Figure VII. The surface was smooth and the plating rate was about 10 μm/hr at a current density of 5 mA/cm², which was almost the same as that for a fresh solution.

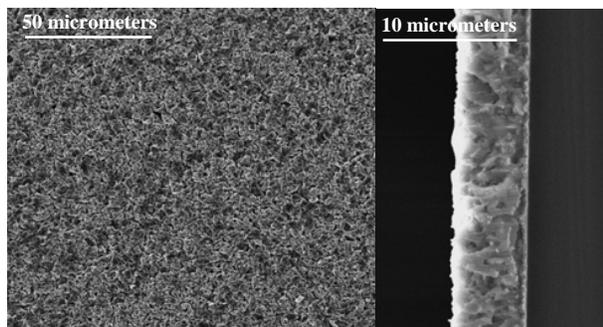


Figure VII: SEM SE images (plan view and cross section) of a Sn-Cu film PC plated from a solution after ageing for 36 days. The solution composition was 0.30 mol/L $(\text{NH}_4)_3\text{C}_6\text{H}_5\text{O}_7$ + 0.22 mol/L $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ + 0.003 mol/L $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and $j = 5 \text{ mA/cm}^2$.

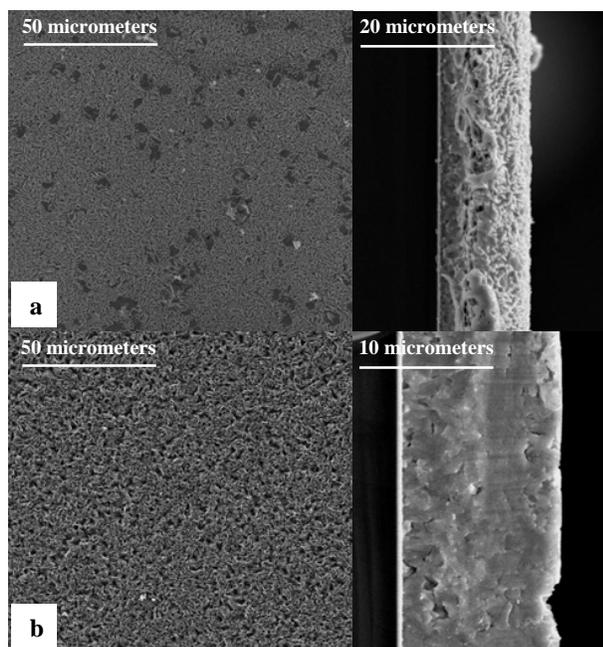


Figure VIII: SEM SE images of Sn-Cu films PC deposited from a Sn-citrate solution with 0.008 mol/L (0.5 g/L) suspended Cu particles, (a) without and (b) with a dispersant, and $j = 10 \text{ mA/cm}^2$.

Sn solution with Cu particles in suspension

Copper particles, 200 nm to 300 nm in diameter, were suspended in the Sn-citrate base solution. A dispersant was added to prevent particle agglomeration. The suspension was stirred at a rate of 80 rpm during electrophoretic deposition. A particle concentration of 0.004 mol/L (0.25 g/L) was required to give a deposit composition of $1.1 \pm 0.3 \text{ wt}\%$ Cu at a plating current density of 10 mA/cm^2 . Figure VIII shows secondary electron images of Sn-Cu films plated from these suspensions with and without a dispersant. The deposit obtained from the suspension without the dispersant was plated for 1 hour, while the deposit obtained from the suspension with the dispersant was plated for 30 minutes. Both were plated at 10 mA/cm^2 . Without the dispersant, the plating rate was about $13 \text{ }\mu\text{m/hr}$, and the copper content in the

deposit was about $11.3 \pm 0.4 \text{ wt}\%$. After adding the dispersant, the plating rate increased to about $23.5 \text{ }\mu\text{m/hr}$ and the copper content in the deposit decreased to about $2.3 \pm 0.4 \text{ wt}\%$. The deposit from the suspension containing the dispersant had a higher plating rate, improved surface morphology and more uniform Cu distribution.

CONCLUSIONS

Two different types of simple Sn-Cu electrodeposition solutions were developed. One solution contained simple Sn and Cu salts, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and tri-ammonium citrate as a complexing agent and stabilizer. The solution composition was optimized with respect to the stability of the solution and the properties of the deposits. Plating rates of 20-27.5 $\mu\text{m/hr}$ were attainable at average current densities of 10-12.5 mA/cm^2 , producing deposits with near eutectic compositions. The solution was stable for at least 36 days. The other solution was made up of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and tri-ammonium citrate with suspended Cu particles, along with a dispersant which prevented the copper particles from agglomerating. With 0.008 mol/L copper particles suspended in solution, the presence of a dispersant increased the plating rate from about $13 \text{ }\mu\text{m/hr}$ to about $23.5 \text{ }\mu\text{m/hr}$, with a corresponding decrease in deposit Cu content from $11.3 \pm 0.4 \text{ wt}\%$ to $2.3 \pm 0.4 \text{ wt}\%$, and improved the deposit surface morphology and uniformity. A near eutectic deposit composition was attainable for a Cu particle concentration of 0.004 mol/L and a plating current density of 10 mA/cm^2 .

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ACRONYMS

SEM: Scanning Electron Microscope
 EDX: Energy Dispersive X-ray XRD: X-Ray Diffraction
 PC: Pulsed Current DC: Direct Current