Pulsed Electrodeposited Sn-Cu Alloys for Use as Pb-Free Component Finishes in Microelectronic Applications

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In recent years there has been a considerable push to develop replacements for Sn-Pb solders currently in use in microelectronic packaging. At this time, alloys based on the Sn-Ag-Cu (SAC) system seem to be favoured. The Pb-free push is in response to recent legislation in Japan and Europe banning its use in most electronics. Equally important is the replacement of Pb-bearing alloys that serve as a finish for solderable electronic component leads. This is a difficult task, since Pb additions benefit the performance of Sn. For example, Pb lowers the melting point, enhances solderability and reduces problems with whiskering. Finally, any Pb-free replacement finish must be compatible with SAC alloys. This paper considers pulsed electrodeposited Sn-Cu as a candidate.

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Introduction

The drive towards Pb-free electronics is gaining popularity, due mainly to the existence of legislation in Europe and Japan that will soon limit its range of use. Possibly the most visible product on the bandwagon is the solder that joins a wide variety of through-hole and surface mount devices onto printed wiring boards. Even in legislatively-slow North America, numerous companies are working to offer Pb-free versions of their existing products.[1]

Unfortunately, however, Pb is a difficult material to replace. To begin, Pb is inexpensive; both high-Pb and eutectic Pb-Sn solders enjoy widespread use, and the properties of these solder systems are well-known.[2] By the same reference, Pb-Sn alloys have lower melting points than pure Sn, and Pb reduces the tendency for Sn to form whiskers. During soldering, Pb acts to curb the reactive nature of liquid Sn, while improving solderability.[3]

The move to Pb-free presents difficulties from a plating perspective as well. Pb and Sn have similar reduction potentials, making electrolytic codeposition relatively easy.[3] In contrast are replacement candidates such as Cu or Ag, whose standard reduction potentials are 0.47 and 0.94V nobler than Sn, respectively. In addition, untreated ionic solutions of Cu and Ag present environmental concerns.

Through extensive research efforts, a number of Pb-free alternatives exist. Most are Sn-rich with additions of elements such as Ag, Cu, In and Bi.[3] While some properties of the Pb-free alternatives are superior, there are notable tradeoffs that prohibit the exclusive use of a single "drop-in" replacement.[4] According to iNEMI,[5] two Pb-free solutions exist for soldering. These are eutectic Sn-Cu for wave soldering and Sn-3.9wt%Ag-0.6wt%Cu ±0.2% for surface mounting. Sn-Cu itself is known to be a solderable alloy with good resistance to tarnish,[6,7] although there is a great deal of concern with the alloy's resistance to whisker growth.[5,8]

In addition to solders, solderable surfaces should also be Pb-free. This paper considers the development of a pulse-plating bath and process for depositing Sn-Cu films on Cu and Au-coated substrates. In this case, the solderable finish would have a composition that closely matches the solder.

Obviously, any finish with commercial potential will have to exhibit good resistance to whisker growth. While this may be possible through the judicious use of plating conditions,[6] such an approach is beyond the scope of this paper. Some of the more popular Pb-free finishes include Ni-Pd-Au and pure Sn over Ni on a Cu substrate.

For the purposes of this paper, an acceptable Sn-Cu film must exhibit a number of criteria.[9,10] These are listed below:

1. A smooth, bright surface: This criterion is mostly cosmetic, but reflects good surface coverage and efficient use of the electroplated material.

2. Resistance to edge effects: The electric field surrounding a cathode is much higher across a sharp corner than it is over a flat surface. Plated parts with such features must not exhibit dendritic or whisker-like growth here. It is expected that a system capable of plating smooth deposits over a wide range of average current densities will exhibit good resistance to edge effects

3. Complete, consistent surface coverage: This is required to protect the substrate from tarnish. Film coverage should also not be overly thick at the edges or too thin at its center.

4. Eutectic composition: For Sn-Cu, this occurs at 0.7%.[2] An eutectic film will have the lowest possible melting point, and will not exhibit separate liquidus and solidus temperatures. When these two values are different, a "mushy" temperature zone can be expected. Ideally, the composition should be constant and independent of current density.

5. Consistent composition: Small variations in the Cu content of a film can greatly increase the liquidus temperature of a Sn-Cu film. In general, consistency in composition is desirable,[6] and should give the film more predictable soldering performance in an industrial application.

6. Resistance to whisker growth: No comprehensive whiskering test exists.[5] However, one should expect that a low degree of compressive film stress is desirable.[11] Further, Zhang and Abys[3] report that the optimal grain size for a whisker-resistant, Sn-rich film is between 1 and 8μm. If the grain size is smaller, grains will deform to reduce the energy contained in grain boundaries. Because the 2D films are not restricted from movement above their surface, whiskers readily grow outwards.

While technology exists to produce such films, many such plating baths require the use of complexing agents that are highly toxic (such as CN^-)[9,10,12] or present difficulties with waste treatment.[13] The aim of this research effort was to employ a low-or-no additive plating bath with low environmental impact, and to attempt to meet as many of the above criterion as possible. While important, an investigation of whisker growth is beyond the scope of this paper.

Experimental Procedure

Au Substrate (Cathode) Preparation

Initial work focused on the deposition of Sn-Cu alloys on Au-coated Si wafers. Au was used for initial work, because it allowed for the determination of coverage via energy dispersive X-ray (EDX) analysis. The Au layer was sputter deposited to about 250nm (10μin) thickness. Between the Au and Si was a 25nm (1μin.) Ti adhesion layer. Because the Si wafers were polished, the Au layer was mirror smooth. Each wafer was rinsed with isopropyl alcohol, and then cleaved into pieces measuring about 1cm (0.39 in) by about 2cm (0.79 in).

The corners of a 3 x 3mm (0.12 x 0.12 in) square were marked on each wafer piece. The marks were used as a guide for the manual application of a lacquer mask. The purpose of the mask was to prevent electrodeposition and current transfer outside of the plating area, or on the edges of the Au-coated Si.

For each cathode, a new anode was used. Anodes were made from cleaved Si wafers that were coated on one side with Pt. The anode and cathode were placed in separate polypropylene holders inside a 250m*l* beaker. The anode to cathode area ratio was variable, but in all cases was at least 1:1. The distance between the electrodes was 2.4cm (0.94in.).

Cu Substrate (Cathode) Preparation

Electroplated surface finishes on Cu are seen as a possible commercial application for Sn-Cu films. In this study, the Cu substrates were prepared in two ways. The first type of Cu substrate was simply a sputtered Cu layer, about 250nm (10µin) thick on Si with a ~25nm (1µin.) Ti adhesion layer. As with Au, a mirror-smooth surface is obtained.

The second type of Cu substrate was made from rolled Cu sheet, approximately 1mm (0.040in.) thick. This Cu was sheared into pieces measuring 1cm (0.39in.) by about 2.5cm (1.0in.). These Cu pieces were placed in 2M H_2SO_4 for about 30s to remove surface oxides, then washed in a dilute solution of residue-free detergent. Next, they were washed three times in distilled water and finally rinsed in isopropyl alcohol.

Most of the other preparation steps were the same as for Au. This includes surface marking and masking. Pt-coated Si anodes were also used, and placed 2.0cm (0.8in.) apart. The anode to cathode ratios varied, but as before the anode area was equal to or greater than the cathode area. A number of samples with larger plating areas were used for a solderability study[14]. In this case, the areas were about 5 x 5mm (0.20 x 0.20 in).

Electrolyte Chemistry

A sulphate-based chemistry was chosen for this work, because it met a number of criteria. To start, it has a well-established record of use with both Sn and Cu[9,10,12]. Acid-based Sn-plating solutions use Sn^{2+} ions for cathodic reduction, and therefore consume less energy. By and large, a sulphate bath can be easy to control during electrodeposition, and the chemicals are not overly hazardous. Finally, sulphuric acid and metal sulphates are readily available at low cost.

The original goal of this research was to develop an additive-free sulphate solution for use with a pulsed square waveform. Such a technology would be attractive to an industrial user, especially since traditional additives are difficult to monitor in solution and need to be replenished.[9] The same reference also correlates the presence of additives with carbon content within the deposits, which inhibits solderability. In addition, no complexing agents were added.

In addition to this work, other research groups have developed DC plating baths whose compositions are publicly disclosed. For example, Fukada et al[15] use 2M H_2SO_4, 0.2M $SnSO_4$, 0.02M $CuSO_4 \cdot H_2O$ and polyoxyethylene lauryl ether (POELE) as an additive. The role of the POELE is reportedly as a grain refiner, although no data is given on roughness. POELE is quite expensive - over US$100 per gram. A more complex recipe is offered by Muramatsu et al,[13] who specify a list of acid media (including H_2SO_4), a $Sn^{2+}:Cu^{2+}$ ratio between 10 and 100:1, and thiourea or a thiourea compound to act as a stabilizer. In neither case is a pulsed current specified.

A series of preliminary experiments were carried out and it was found that promising deposits could be obtained at low H_2SO_4 concentrations. The rationale behind low levels of acid is cost and environmental impact. Table I outlines the standard bath chemistries used for this work. The amount of charge transferred to the cathode was fixed at 30mA*min. For Grid I, an unagitated standard solution was used. For Grid II, experimental conditions were similar, except that no $CuSO_4$ was added. For Grid III, the standard solution was agitated by stirring with a glass impellor at 200 RPM. All these samples were plated on Au seed layers.

Table I – Composition and conditions of electroplating baths for this work.

Grid	**Component**	**Concentration mol/*l***	**Concentration g/*l (oz/gal)***	**Agitation**
I "Standard"	H_2SO_4 $SnSO_4$ $CuSO_4 \cdot 5H_2O$	0.3 0.2 0.0016	29.4 (0.81) 43.00 (1.18) 0.40 (0.011)	0 RPM
II	Same as I, but no Cu			0 RPM
III	Same as I			200 RPM

Three main experimental grids were developed. Within the grid, the pulse duty (p) and average current density (j_{avg}) were varied. Pulse duty is defined as:

$$p(\%) = \frac{t_{on}}{t_{on} + t_{off}} * 100 \qquad (1)$$

Here t_{on} represents the time increment during which the deposition overpotential is applied. The time increment during which no deposition occurs is t_{off}. The sum of t_{on} and t_{off} is the total cycle time. In this work, the total cycle time was fixed at 10ms.

As the pulse duty decreases, the peak current density increases according to Equation 2.

$$j_{pk} = \frac{j_{avg}}{p} \qquad (2)$$

After electroplating, each Au-coated cathode was removed from the solution and rinsed with distilled water. It was then placed in acetone, in order to remove the plating mask.

Sample Analysis

Most of the analytical work was carried out using a scanning electron microscope. Films were examined in plan view at 50X and 200X. Films of particular interest were also examined at higher magnifications. All samples plated on Si wafers were cleaved through the center to obtain a cross-sectional views starting at 200X.

EDX analysis was carried out at 20 kV for 100 seconds on an area measuring about 450μm (0.018 in.) by 600μm (0.024 in.) or larger. Unless otherwise noted, all EDX measurements were taken at the center of the plating area.

In an attempt to quantify films plated on Au, the amount of Sn, Cu and Au was measured using EDX analysis. For coverage data, the total counts for each element were summed, and normalized percentages of Sn + Cu versus Au were taken as the degree of coverage. Later, the total Sn and Cu counts were normalized to obtain relative concentrations for deposit composition. All quantitative analyses were performed automatically by a commercial quantitative EDX software program using calibrated standards.

Results and Discussion

Pulse-Plated Morphology on Au-coated Substrates

In this work, 20 samples were plated using the unagitated, standardized plating solution (Grid I). These included samples plated at j_{avg}=5, 15, 30, 50 and 70mA/cm^2 (4.7, 14, 28, 46 and 65 ASF). For each constant pulse duty, a critical average current density ($j_{avg,c}$) was observed. Above this value, the deposit was highly dendritic. At 100% and 50% pulse duty, $j_{avg,c}$ is between 30 and 50mA/cm^2 (28 and 46 ASF); at 20% and 5% pulse duty, $j_{avg.c}$ is between 50 and 70mA/cm^2 (46 and 65 ASF).

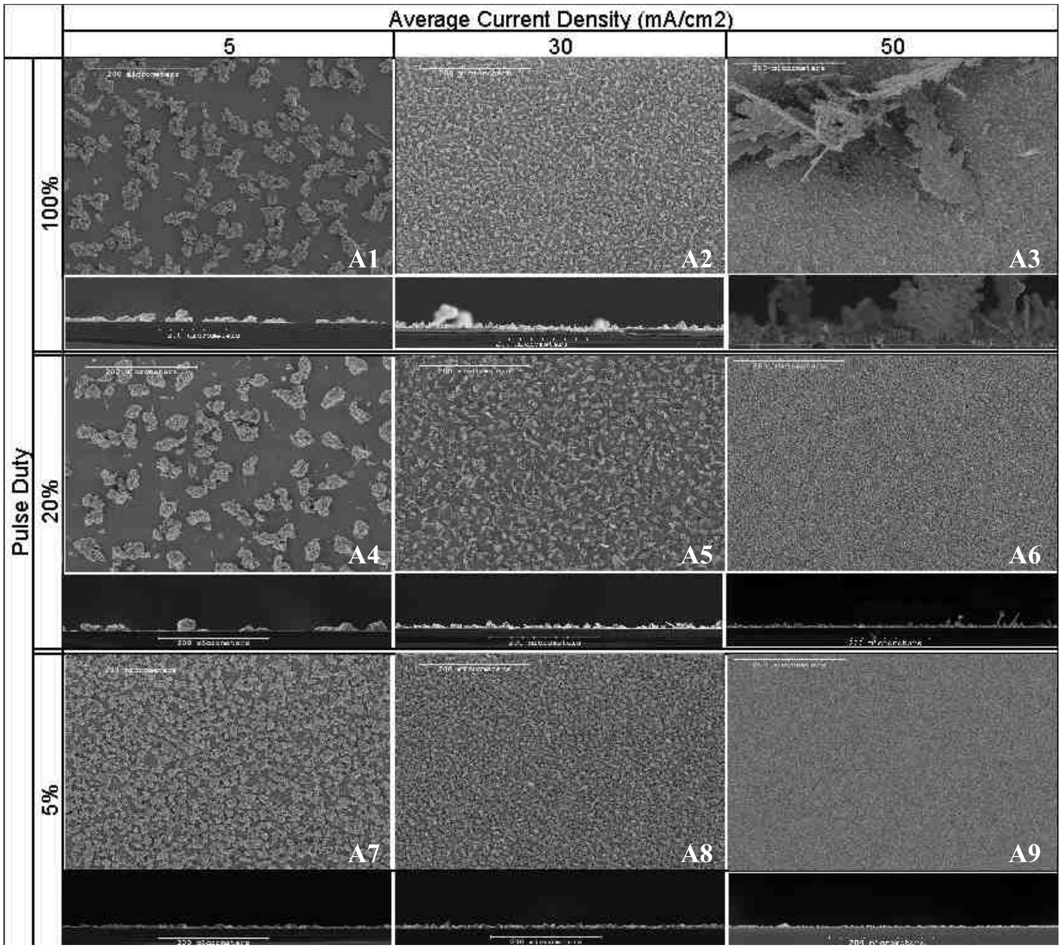

Figure 1 – Plan views and cross sectional views of Sn-Cu films electrodeposited onto Au-coated Si. The plating bath was not agitated. Surface coverage, feature size and film roughness are all functions of pulse duty and average current density. Scale bars are 200µm wide.

Figure 1 is a composite photo of nine samples. They are arranged in a grid to show the effects of average current density (left to right), and pulse duty (top to bottom). Each sample is labeled from A1 to A9, and both a plan and cross-sectional view are given. Note that a pulse duty of 100% is simply DC plating. For all samples, a fixed current of 30mA*min was deposited. Due to the manual masking procedure, the ratio of current per unit area varied. Average current density was controlled by measuring the area of each sample, and programming he power supply accordingly.

Clearly, there is a trend regarding the degree of coverage. The plan views give a good indication of how much of the Au substrate is covered, as well as the average feature size. Note that higher pulse duty and lower average current density yield films with poorer coverage and more agglomerated deposits. It is not known whether these agglomerates are composed of single Sn-Cu grains, however. From the cross-sections, it can be seen that the relief is greater for films made of larger agglomerates, such as A1.

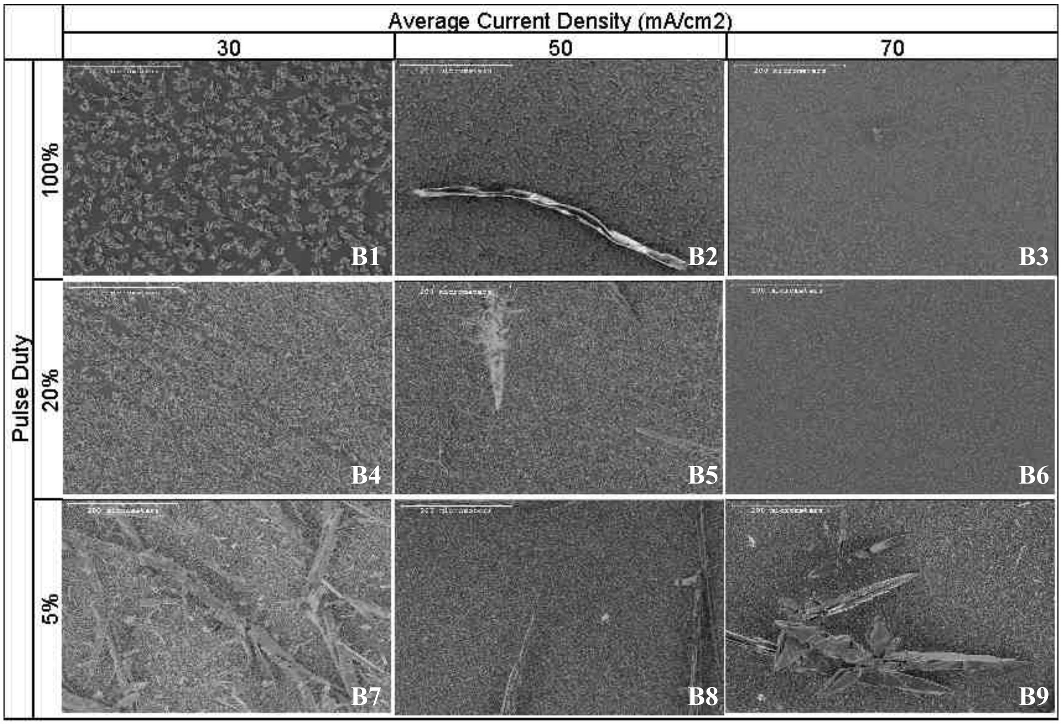

Figure 2 – Composite of pure Sn films at various pulse duty and j_{avg} *values.*

Figure 2 is a similar composite photo showing the effects of average current density and pulse duty using pure Sn (Grid II). Note that the j_{avg} values are much higher than in Figure 1, suggesting that Cu^{2+} limits the maximum plating current. This makes sense if one considers that the $Cu^{2+} \rightarrow Cu$ reduction is nobler than $Sn^{2+} \rightarrow Sn$ reduction. Trends similar to Figure 1 are observed regarding coverage, while the most noticeable difference is the existence of whisker-like dendrites. These structures have few, if any branches, and were observed in the SEM within hours of plating. They are most prevalent at low pulse duty. Some of the whisker-like dendrites were as long as 5mm.

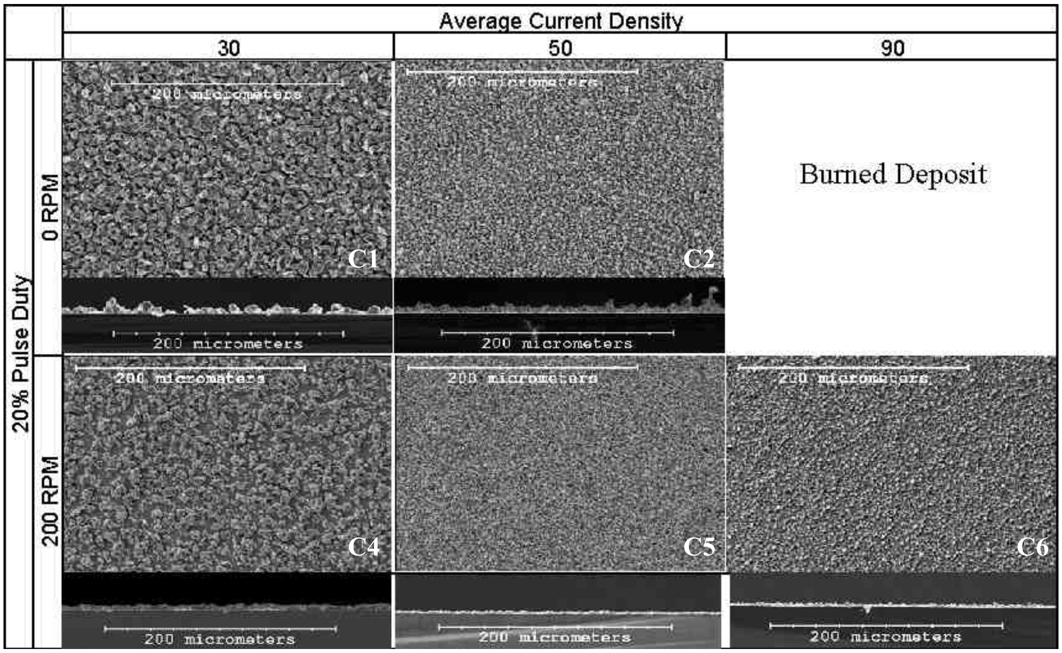

Figure 3 – Effects of agitation at 20% pulse duty. Better coverage, flatter films; higher $j_{avg,c}$ *allows faster plating and lower Cu content.*

Finally, the standard solution was stirred moderately using a small impellor rotating at 200 RPM. A comparison of agitated and non-agitated conditions is given in Figure 3, and shows that this level of agitation has both a refining and leveling effect. As one would expect, stirring enabled smooth films to be plated at higher average current densities.

Coverage was also observed to be a function of location, as shown in Figure 4. At lower average current density, the coverage decreases towards the center of the film. Edge definition is poorer with increasing average current density because of dendritic growth. This suggests that the range of current densities from which a smooth, well-covered, dendrite-free film can be deposited is narrow.

Using the EDX data, two separate plots were generated for coverage versus j_{avg} for 5% pulse duty and DC data. These plots are shown in Figures 5a and b. Note that the 5% pulse duty data points show high coverage for all values of j_{avg}. In contrast, the DC films seem to follow a trend of increasing coverage with increasing j_{avg}. For the 5% pulse data, the pure Sn films (hollow triangles) exhibit the highest coverage values. However, the Sn-Cu films deposited from the unstirred solution (hollow diamonds) are the most consistent. During experimental work, it was noted that at moderate current densities (i.e. around 30mA/cm^2 or 28 ASF for Grid I samples), increased plating times tend to improve coverage. At very high and very low current densities, increased plating times yielded granular or dendritic films whose features did not flatten out on the substrate. Therefore, coverage was poor to begin with and did not improve.

For the DC (100% pulse duty) plots, the Sn-Cu films deposited from unstirred solutions (solid diamonds) had the highest coverage values at moderate current densities. The most consistent trend belongs to pure Sn deposited from the unstirred solution (solid triangles).

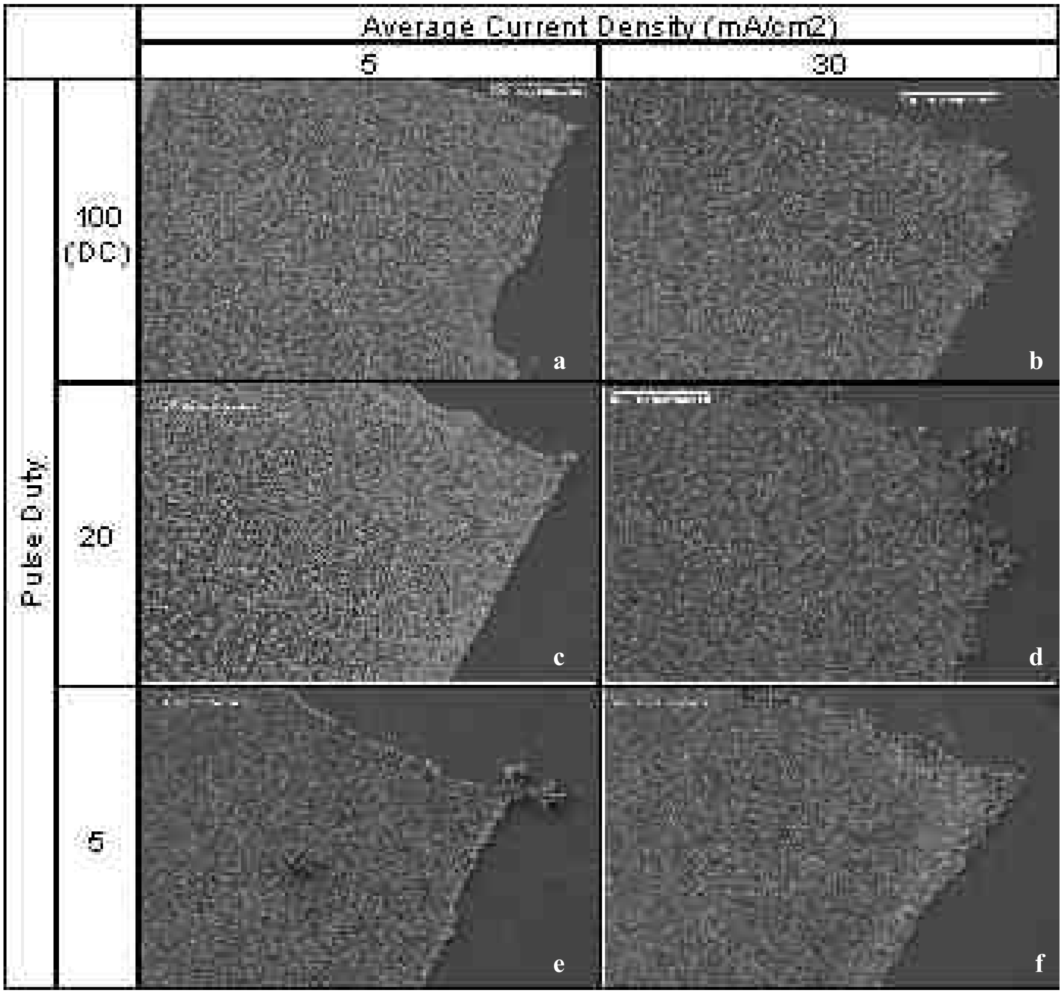

Figure 4 – Six low-magnification images of Sn-Cu samples plated on Au at variable pulse duty using an unagitated bath (Grid I).

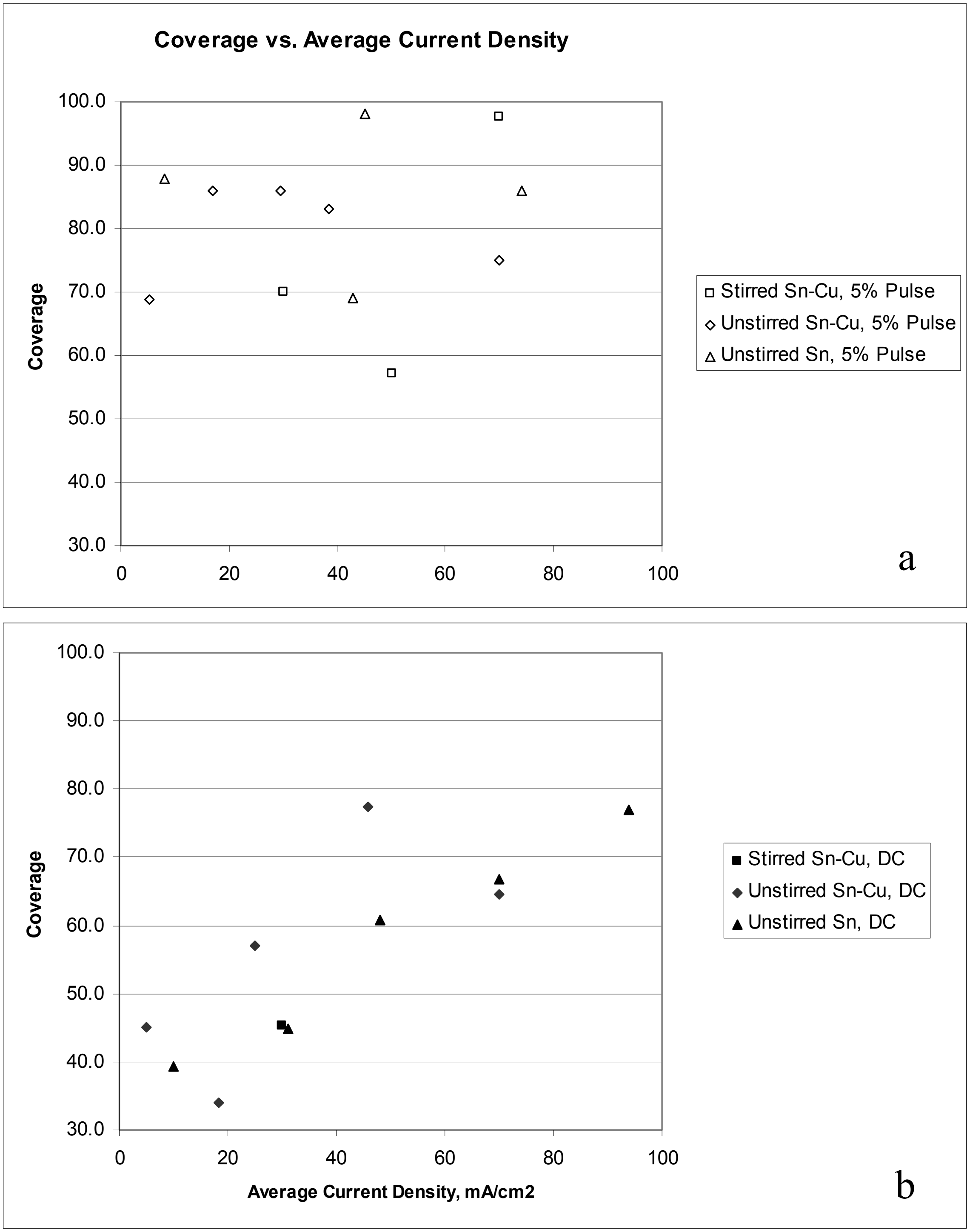

Figure 5 – Coverage plot, showing that 5% pulse duty films (a) tend to have better coverage than DC films (b). DC films show a linear trend for coverage vs. average current density. Measurement error limits are within the symbol size.

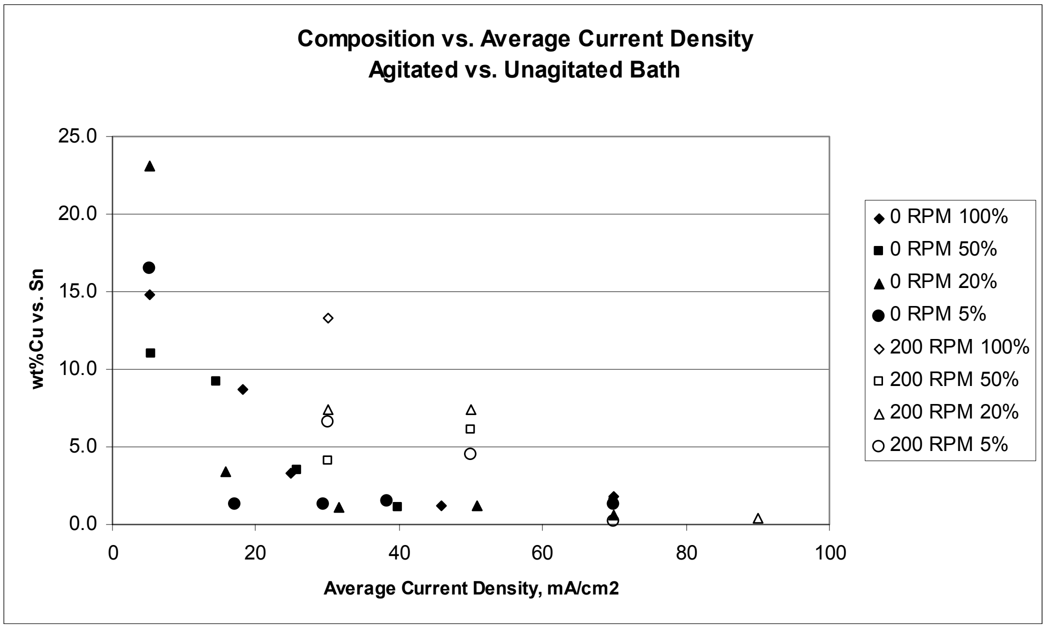

Figure 6 – Film composition as a function of j_{avg}.

Given the scatter, it is difficult to draw any conclusions. Therefore, one cannot say whether the presence of Cu or the use of agitation affects coverage. The clearest trend is a linear relationship between coverage and average current density for DC-plated films. Also, the 5% pulse duty films yield consistently better coverage.

Film Composition for Deposits on Au-coated Substrates

Figure 6 shows the relationship between deposit composition and average current density. Pulse duty seems to play a role at lower j_{avg} values, although the correlation is unclear. Above 50mA/cm^2 (46 ASF), only j_{avg} seems to have an influence. The data point at 90mA/cm^2 (84 ASF) was measured to be 0.4wt% Cu ± 0.2, which is very close to the 0.7% target.

The trend is somewhat deceiving, since the variance at 5mA/cm^2 (4.7 ASF) for an unagitated bath is between 11 and 23wt% Cu. Similarly, the largest variance for an agitated bath at 30mA/cm^2 (28 ASF) is between 4 and 13wt% Cu. Note that the EDX system uses flat standards for calibration, while the films plated at low j_{avg} tend to be rough. This may have an effect on the EDX composition values. Regardless, the percent Cu and level of variation seems to decrease with increasing j_{avg}. From a processing perspective, one may consider that plating at higher average current densities will yield less variation in film composition. Further, plating with unagitated baths yields near-eutectic films between 30 and 70 mA/cm^2 (28 and 65 ASF).

Near-Optimized Plating on Au Substrates

If a eutectic (0.7wt%Cu) film is desired, then this becomes a very restrictive parameter. This is due to the fact that composition is a function of j_{avg}, but not pulse duty. Further, the unagitated bath chemistry used in this work yields a deposit with a minimum Cu content of 1.1wt%Cu. Agitation of the plating bath allowed for higher j_{avg} values, and a smooth film with 0.4wt ±0.2%Cu was obtained.

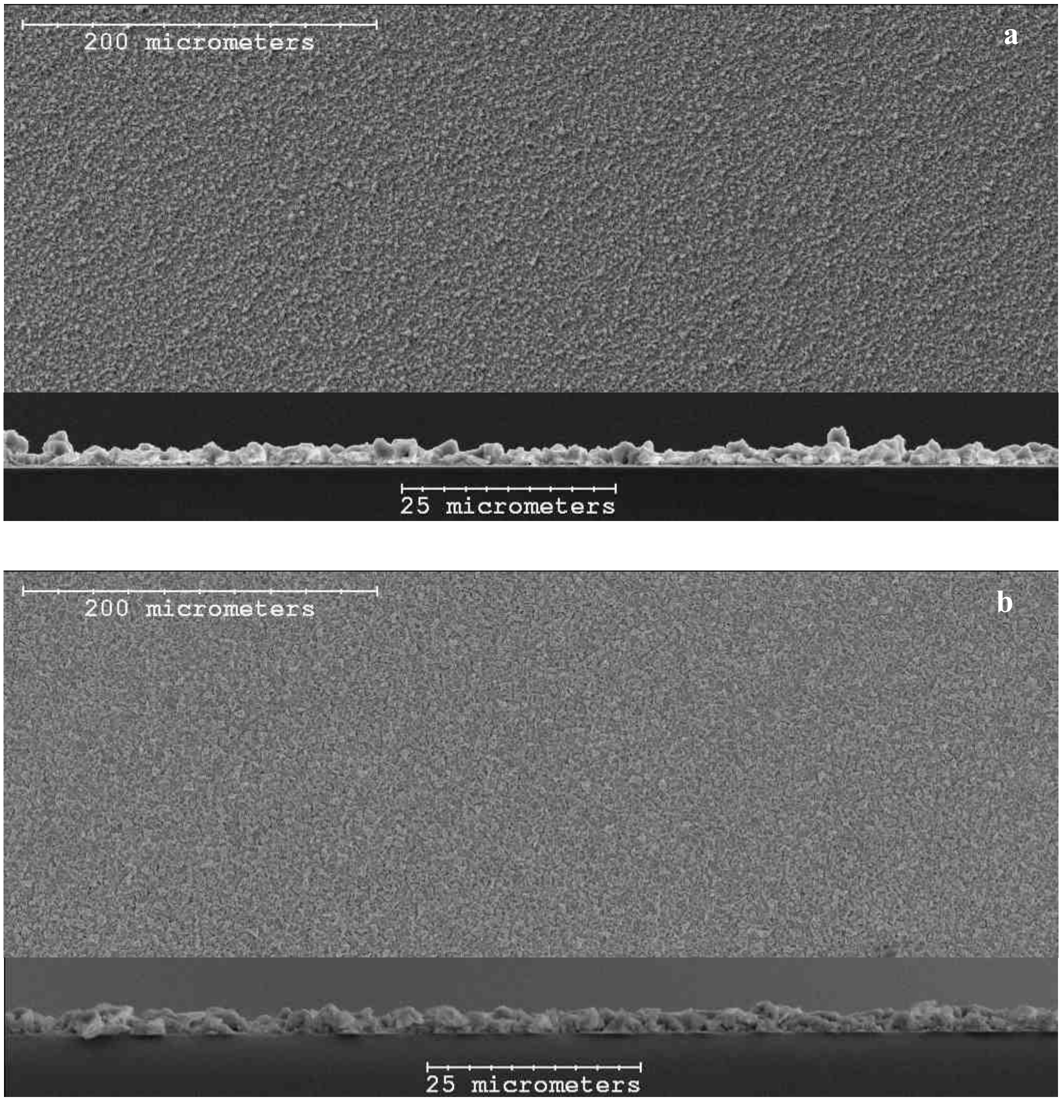

Figure 7 – a) Plan and edge views of a Sn-Cu film with sub-eutectic composition. Lighter shades on the plan view indicate higher regions on the film. b) Plan and edge views of a Sn-Cu film on Au with better morphology. Composition is 1.5wt%Cu ± 0.4. Plating conditions are 50mA/cm^2 (46 ASF), 5% pulse duty and unagitated bath.

For other film characteristics, there are similar restrictions. Good morphology is also confined to a narrow window of plating conditions; although the range of $_{javg}$ for a given pulse duty may be broader than that for composition. Coverage improves with decreasing pulse duty and increasing j_{avg}, so more flexibility is offered here. In the above cases, increasing j_{avg} seems to improve the deposit. Of course, there is an upper limit that has been observed as the critical current density or $j_{avg.c}$. Above this value, all deposits are highly dendritic. The $j_{avg,c}$ problem is also observed as edge dendrites, which form at lower j_{avg} value as a result of higher current densities at the edges of the plating mask.

Note that other variables such as different levels of stirring should affect composition. These are not considered in this paper. One might also expect Cu^{2+} concentration to be a factor. In an earlier investigation, however, solutions with a 20% larger Cu^{2+} concentration were used to deposit Sn-Cu films. The minimum attainable Cu content was similar to that for the current plating bath. This suggests that at such dilute Cu^{2+} concentrations, the reduction rate is no longer concentration-dependent.

Without any further optimization, the "best" film deposited on Au, whose composition was closest to 0.7%Cu appeared on Grid III as sample C6 in Figure 4 (ie, 90mA/cm^2 (84 ASF) with p=20% and 200 RPM stirring). A close-up is shown in Figure 7a. Unfortunately, low-Cu films such as C6 suffer from increased roughness. For comparison, a smoother film is shown in Figure 7b. This photo is a close-up of sample A9 from Grid I (Figure 2), plated at 50mA/cm^2 (46 ASF) with p=5% and no stirring. The Cu content is 1.5wt. For both films, however, edge dendrites are expected to be a problem.

Use of Citric Acid as a Stabilizer

Traditional acid-Sn plating baths use cresol sulphonic acid[12] to control oxidation of Sn^{2+} to Sn^{4+}. In this work, citric acid was investigated as a "green" substitute. In all, four different variations on the standard solution were considered. These were based on the standard solution (Table I), but included as much as 1.7M citric acid.

It was found that citric acid enhanced the solution shelf life in proportion to its concentration. In this simple study, shelf life is defined as the ability of a solution to remain clear and colourless while stored within a stopped flask. Citric acid extended the standard solution shelf life from about one day to several weeks. In addition, one solution contained 2.0M H_2SO_4 and no citric acid. It was found that the increased level of sulphuric acid enhanced shelf life, but not to the extent of citric acid.

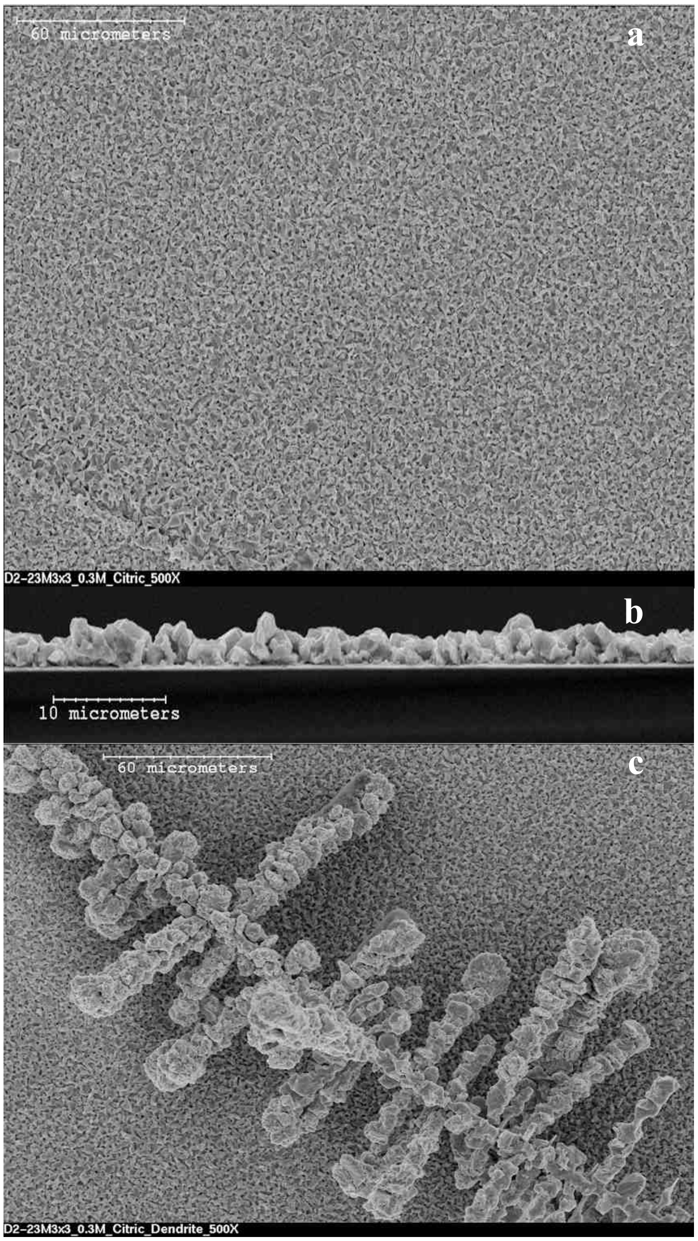

Figure 8 – Example of a near-eutectic (1.1wt%Cu) film plated on Au using citric acid.

a) Plan view showing good coverage (100%); 60µm bar.

b) The film is somewhat rough, with a 0.6µm/min (24 µin./min) plating rate that is typical of citric acid-free films plated at higher average current densities; 10µm bar.

c) Example of a dendritic defect that may be more common with citric acid additions; 60µm bar.

After a period of time, plating solutions containing H_2SO_4 turned yellow and became cloudy with yellow-white precipitates. With higher amounts of citric acid, the solution eventually yielded fine white precipitates that settled to the bottom of an otherwise clear solution. Afterwards, the solution would turn yellow and finally become cloudy. Citric acid additions were found to affect the plating process. One benefit was that the anode surface did not foul. In addition, plated films contained less Cu. Unfortunately, the limiting current density was severely reduced, and the appearance of dendrites on the surface of an otherwise smooth film was higher. No eutectic films were produced on Au using citric acid, although a 1.1wt%Cu film was produced on Au. The plating rate for this film was ~0.6µm per minute (24 µin./min), which is typical of some of the better films using the standard solution (Grids I and III). An example of a film plated with citric acid is shown in Figure 8.

Pulse Plating on Cu

One possible application for an eutectic Sn-Cu film is as a surface finish on Cu. While there are fears that the presence of Cu in an electroplated Sn finish will greatly accelerate whiskering,[5] it may be possible to use a combination of pulse parameters and additives to reduce some of the conditions that cause the whiskering problem. This section summarizes some of the initial work done in this area, while the results of a preliminary dip-and-look test are available elsewhere.[14]

Initially, conditions that yielded good films on Au were used to plate Sn-Cu on rolled Cu substrates. All attempts resulted in poor films, with the co-production of bubbles on the cathode. These bubbles are assumed to be hydrogen gas. A short study was carried out to determine if the problem was due to the change in material (i.e., Au to Cu) or the increased surface roughness of the rolled Cu. This was done by sputtering Cu onto polished Si (see Experimental Procedure) and plating at different conditions. In the end it was determined that both substrate composition and surface roughness played a role, although the material change had the greatest impact.

The problem was overcome by plating a Sn-Cu strike layer at low current density. In order to enhance the surface coverage, a low pulse duty was used. A Sn-Cu cap layer was then plated over the strike at much higher current density. The pulse duty was also increased in order to reduce the plating time. Note that the strike layer will contain a higher amount of Cu, while the cap layer contains less Cu. About 60mA*min of charge was transferred to plate the strike, while 140mA*min was transferred to plate the cap. EDX measurements yielded about 5wt%Cu, and this was the lowest obtainable value. Examples of the strike and cap layers are shown in Figures 9a and b, respectively. Note that the strike layer coverage is not 100%, and that dendrites typically grow around the edges of the film.

Edge dendrites are a problem that seems difficult to solve through the exclusive use of pulse plating. During deposition on Cu, a reverse pulse was added to each cycle. The duration was similar to the forward pulse, but the magnitude of the current density was set at 10% of the forward value. This seemed to have a small effect on edge dendrite growth, while increasing the time required for plating. It is understood that the formation of dendrites will increase the surface area of the

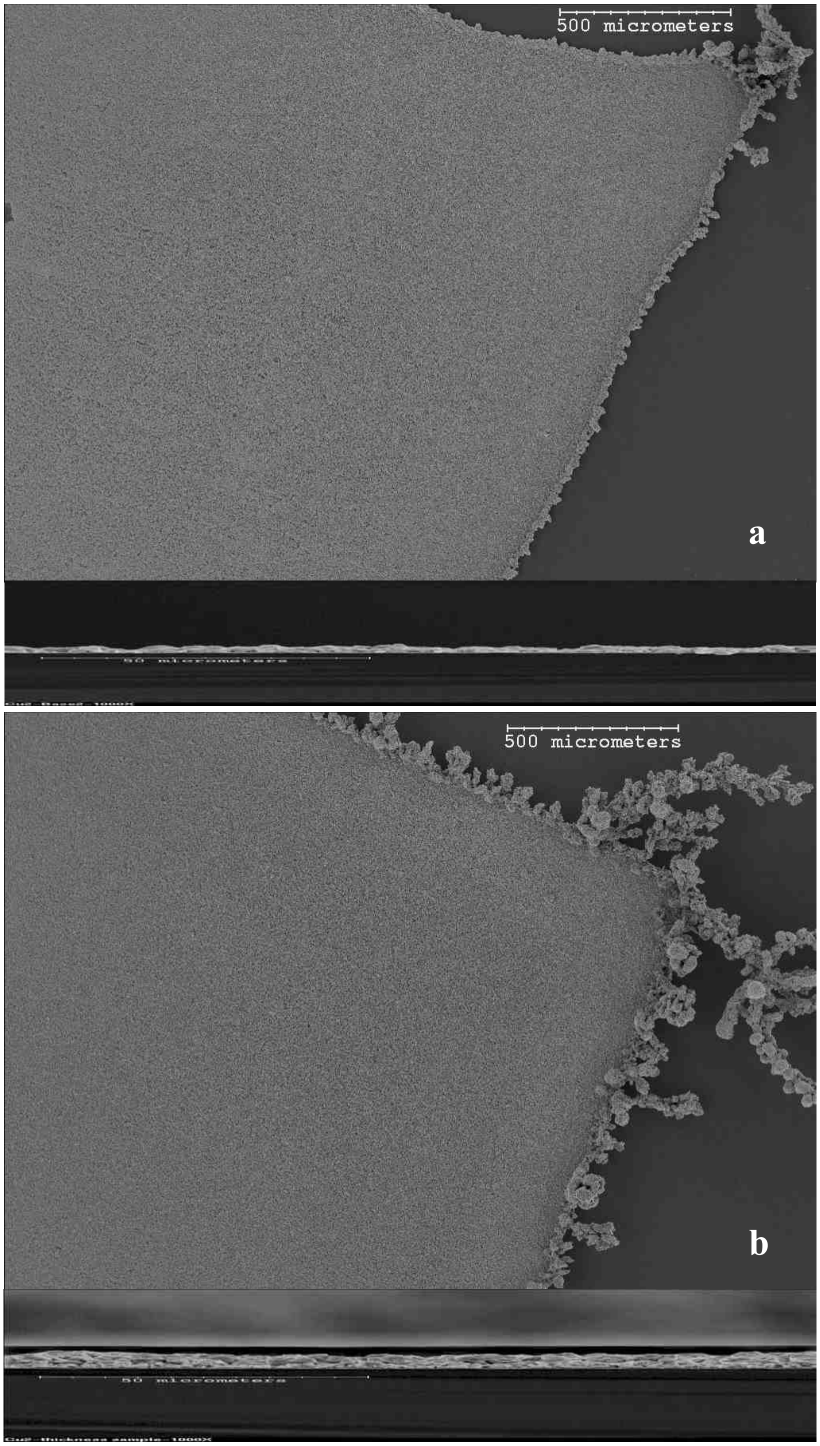

Figure 9 – Example of near-eutectic Sn-Cu film plated on Cu. a) Strike layer exhibiting incomplete coverage near the center (lower left) portion of the film. The strike layer allows for deposition of a Sn-Cu cap layer (b) at much higher average current density.

cathode, and therefore reduce the effective average current density. This should increase the Cu content of the film. Further work is required to reduce edge dendrite formation, and it is expected that such efforts will therefore reduce the Cu content as well.

Table II – Process Issues Related to Additive Free Pulse Plating of a Sn-Cu Sulphate Bath

Process	Problem	Description	Possible Solutions
Anodic	Oxygen formation at anode	▪ Presence of oxygen[12] accelerates the oxidation of $Sn^{2+} \rightarrow Sn^{4+}$.	▪ Use soluble (Sn) anode to eliminate oxygen formation. ▪ Change to methane-sulfonic acid.
	H^+ formation at anode	▪ H^+ formation leads to a localized pH drop and corresponding solubility drop of $SnSO_4$. The salt precipitates on the anode, causing passivation.[3]	
Cathodic	Pronounced edge effects	▪ Very large dendrites grow on the edges.	▪ Add organics to reduce deposition on high energy sites. ▪ Vary the reverse pulse parameters.
	Sulphur on deposits	▪ Sometimes small amounts of sulphur are detected on Sn-Cu films plated at high j_{avg}.	▪ Requires more investigation.

Table III – Performance Review of Sn-Cu films

Criterion	Film Performance
Smooth, bright surface	Promising as a matte finish.
Resistance to edge effects	Poor. Edge effects are worse at higher average current densities, where near-eutectic film compositions are obtained.
Complete, consistent surface coverage	Promising. Complete coverage can be obtained if enough Sn-Cu is deposited. A relatively wide range of average current densities and pulse duty values yield acceptable coverage.
Eutectic composition	Eutectic compositions can be met using Au substrates. Near-eutectic compositions are possible on Cu.
Consistent composition	Good consistency in composition observed at various locations on Cu substrate sample. Au substrate samples were only analyzed in the middle of the plated area, so no conclusions can be made.
Resistance to whisker growth	Unknown at this time. If the deposits are single-grains, then the grain size is fairly large. This may indicate lower film stress. Compressive stress was not measured, nor was a whisker test attempted.

Film Evaluation

While there are some perceived advantages of using an additive-free electroplating bath with pulsed deposition, the technique is not yet optimized. For issues like bath stability, the use of additives in a sulphate system is unavoidable. Finally, Cu immersion plating is a known issue that may also require the use of additives.[7] Table II illustrates the problems encountered from an experimental processing perspective. Also included are possible solutions. In a commercial process, Pt would need to be replaced with consumable Sn, Cu or Sn-Cu anodes.

Finally, the properties of as-plated films are summarized in Table III. Each criterion is based on the list given in the introduction.

Conclusions

The influence of pulse plating on an additive-free Sn-Cu sulphate bath was investigated. It was shown that film morphology is greatly dependent upon pulse plating parameters. Film composition is also affected by pulse parameters, but the difference is only seen at low average current densities. Some of the films show promise, although there are a number of processing issues with an additive-free sulphate bath that probably cannot be overcome by pulse plating alone.

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(Endnotes)

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