

Phase Formation in Gold-Tin Alloys Electroplated from a Non-cyanide Bath

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Abstract

Au-Sn alloys are commonly used as solder materials in semiconductor industries. In this work, gold-tin alloys have been electroplated from a non-cyanide bath. The effects of bath composition and PC plating factors on compositions of Au-Sn deposits, intermetallic phase formation, and plating rates have been investigated. The transition current density for plating the two different gold-tin intermetallics, Au₅Sn and AuSn, was shifted to lower current densities at lower ammonium citrate dosage. In addition, deposits plated from solutions with lower ammonium citrate concentrations were denser. Thin film x-ray diffraction analysis showed that only Au₅Sn or/and AuSn phases are plated out in the deposits. The growth of either Au₅Sn or AuSn phases showed no preferred orientation.

INTRODUCTION

Au-Sn alloys, especially the eutectic composition (30at% Sn), are ideal solder materials for electronic and optoelectronic packaging. They are environmentally-friendly lead-free materials, and have mechanical and thermal properties superior to conventional Pb-Sn solders.

The electroplating of Au-Sn alloys has been studied extensively. In order to deposit Au-Sn alloys from a single bath, complexing agents are imperative to narrow the reduction potential gap between Au and Sn ions, and to stabilize the plating bath.

Because of the high stability of cyanide complexes of Au ions [1], cyanide-based plating baths have been employed by many researchers. Au-Sn alloys were plated out by Kubota et al with an acid cyanide system comprising KAu(CN)₂, and using pyrophosphate as a complexing agent for Sn²⁺ [2]. Holmbom and coworkers plated Au-Sn alloys from an alkaline cyanide bath containing Au(CN)₂⁻, CN⁻, SnO₃²⁻, and PO₄³⁻ [3].

Due to the negative effect of cyanides on the environment, efforts to develop non-cyanide baths have been made by several investigators. Matsumoto patented an Au-Sn alloy plating solution containing KAuCl₄, SnCl₂, ammonium citrate, and L-ascorbic acid with a pH of 3-7 [4]. Sun and Ivey developed a more stable bath based on Matsumoto's system by introducing sulfite as a complexing agent for gold [5]. Subsequent research to further improve

the bath stability and Au-Sn codeposition has been carried out in the group [6-8]. They have plated out Au-Sn intermetallic compounds separately, Au₅Sn at low current densities (<1mA/cm²) and AuSn at high current densities (>2mA/cm²). These two phases can be combined to produce the eutectic Au-Sn alloy for bonding applications, as well as any alloy with a composition from 15-50 at% Sn. Plating rates, however, are relatively low, particularly for the Au-rich phase (Au₅Sn) which plates out at low current densities.

There exist four main Au-Sn intermetallic compounds, Au₅Sn, AuSn, AuSn₂, and AuSn₄ [3]. In this work, the composition of Au-Sn deposits and intermetallic phases obtained from the plating baths similar to that proposed by Sun and Ivey have been studied [5]. Bath composition (i.e., ammonium citrate dosage and gold concentration) and plating process parameters (i.e., agitation) were varied in an effort to increase plating rates. Thin film XRD was employed to study the gold-tin phases plated and their growth orientation in the deposits. Compositions and microstructures of Au-Sn deposits were analyzed by means of SEM and EDX spectroscopy.

EXPERIMENTAL

The experimental procedures employed in this work were similar to those used in Sun and Ivey's work [5]. Si wafers coated with Ti/Au blanket metallizations were used as cathodes, with Au acting as a seed layer for plating. Platinum foil was used as the anode. The initial plating bath utilized was the one developed by Sun and Ivey [5], with the composition shown in Table 1. In subsequent experiments, the ammonium citrate dosage was reduced, from 200 g/L to 100 g/L, and the Au salt concentration was increased up to 12 g/L. All plating, unless otherwise indicated, was done using pulsed current with a duty cycle of 10ms - 2ms of on time and 8ms of off time. Agitation was introduced in some instances at a speed of 300 rpm. Plating times were set at 150-180 minutes for current densities less than 1.5 mA/cm² and 60-90 minutes for current densities greater than 1.5 mA/cm².

The compositions and microstructures of Au-Sn deposits were characterized using a Hitachi S-2700 SEM equipped with a UTW x-ray detector. A Rigaku rotating anode XRD system, with a thin film camera attachment, was employed to identify specific Au-Sn phases and any orientation relationships. A copper anode operating at 40kV and 100mA was used, with an incident angle of $2\theta = 2^\circ$.

Table 1
Composition of the initial gold-tin plating bath.

Chemical	Dosage
KAuCl_4	5 g/L
$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	5 g/L
Sodium sulfite	60 g/L
Ammonium citrate	100 g/L
L-ascorbic acid	15 g/L
pH	6.5

RESULTS AND DISCUSSION

Effect of ammonium citrate

In the plating solution employed by Sun and Ivey [5], the ammonium citrate dosage is the largest among all the reagents. Ammonium citrate mainly functions as a complexing agent, buffer and conducting salt in the plating bath. The large amount of ammonium citrate also increases markedly the viscosity of the plating solution, which can retard the diffusion of metal ions to the cathode surface during plating, and raise the ionic strength, which would decrease the activities of plating metal ions. In this investigation, the ammonium citrate dosage was decreased from 200g/L adopted by Sun [5] to 100g/L to probe its effects on the compositions, intermetallic phase formation, microstructures, and plating rates of deposited Au-Sn alloys.

The compositions of Au-Sn deposits, as a function of current density, with different ammonium citrate dosages, are illustrated in Figure 1. For an ammonium citrate dosage of 100g/L, the Au-Sn intermetallic Au_5Sn (containing 15-17at% Sn) was plated out at current densities $\leq 0.6 \text{ mA/cm}^2$, while AuSn (containing ~50% Sn) was plated out at densities $\geq 1.0 \text{ mA/cm}^2$. There exists a transition region between the two composition plateaus, at 0.6-1.0 mA/cm^2 .

The composition/current density plot is very similar to the results achieved previously with 200g/L ammonium citrate in the plating solution [7,8]. Those results are also plotted in Figure 1 for comparison. The major difference between the two curves is that the AuSn and Au_5Sn plateaus are shifted to lower current densities for solutions with 100 g/L ammonium citrate. It is believed that the lower ammonium citrate dosage results in Sn ions being less strongly complexed in the solution, leading to easier

deposition of tin and the shift of the composition plateaus to lower current densities.

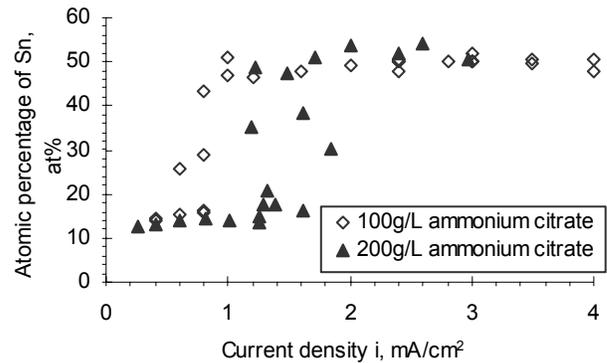
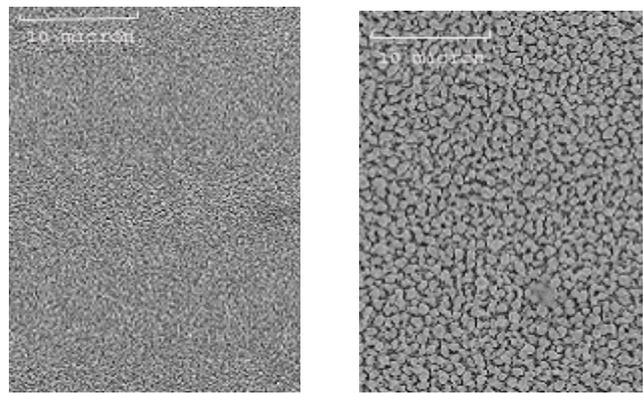


Figure 1 Composition of Au-Sn deposits obtained at various current densities with two ammonium citrate dosages (no agitation).

Plan view images of Au-Sn deposits plated at different ammonium citrate dosage are shown in Figure 2. In both cases, the current density was 2.4 mA/cm^2 , corresponding to ~50 at% Sn intermetallic AuSn. The AuSn deposit plated from a solution with 100g/L ammonium citrate is denser and smoother than the deposit from a solution with 200g/L ammonium citrate. This will lead to less voiding in the solder during the packaging process. Reducing the citrate concentration has the added benefit of reducing plating bath cost.



a. 100g/L ammonium citrate b. 200g/L ammonium citrate

Figure 2 SEM SE plan view images of AuSn deposits plated at 2.4 mA/cm^2 (no agitation). Both samples were plated for 90 minutes.

The plating rates for Au-Sn deposits at different current densities, for solutions containing 100g/L ammonium citrate, are shown in Figure 3. A good linear relation was obtained between plating rate and current density for current densities $\leq 0.8 \text{ mA/cm}^2$. The slope of the trend line is about $0.55 \text{ (}\mu\text{m/h)/(mA/cm}^2\text{)}$. At high current densities, the fit is not as good but still fairly linear with a slope of 1.19

($\mu\text{m/h}/(\text{mA}/\text{cm}^2)$). The different plating rate/current density dependence for low and high current densities corresponds to the different plating products, which consume different amounts of electrons and have different densities. When the current density is too high (e.g., $4.0 \text{ mA}/\text{cm}^2$), the plating rate drops off due to unwanted electron consuming reactions, such as the reduction of hydrogen. This point ($4.0 \text{ mA}/\text{cm}^2$) was not included in the slope calculations.

The plating rate at a current density of $0.8 \text{ mA}/\text{cm}^2$ was about $0.4 \mu\text{m/h}$, while at a current density of $2.4 \text{ mA}/\text{cm}^2$, the rate was approximately $2.4 \mu\text{m/h}$. Compared with the results obtained by He et al with 200g/L ammonium citrate [8], which had plating rates of about $0.8 \mu\text{m/h}$ and $2.1 \mu\text{m/h}$ at current densities $0.8 \text{ mA}/\text{cm}^2$ and $2.4 \text{ mA}/\text{cm}^2$, respectively, the plating rate was slower at low current densities and a little faster at high current densities with solutions containing 100g/L ammonium citrate.

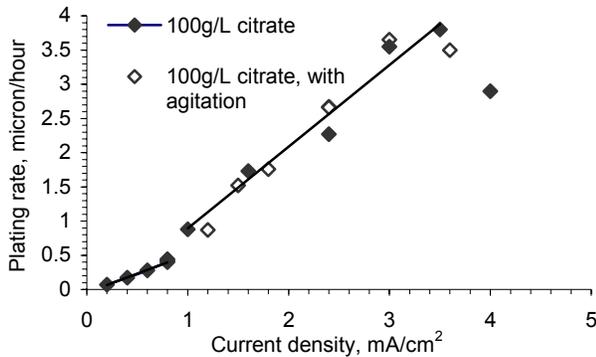


Figure 3 Plating rate of Au-Sn deposits at different current densities.

Effect of gold concentration

Increasing the Au content in the plating bath should increase the concentration of Au ions at the cathode surface, thereby increasing the likelihood of plating out Au_5Sn . The composition-current density dependence for Au-Sn deposits plated out from solutions with higher Au salt concentrations is illustrated in Figure 4. The gold concentrations were 10g/L and 12g/L of KAuCl_4 , corresponding to Au:Sn salt ratios of 2.0 and 2.4, respectively. For the Au-enriched solutions, compared with the bath containing 5g/L of KAuCl_4 (Figure 1), the plateau for Au_5Sn ($\sim 15\text{at}\% \text{ Sn}$) is shifted to higher current densities, i.e., $0.8 \text{ mA}/\text{cm}^2$ for 10 g/L Au salt and $1.2 \text{ mA}/\text{cm}^2$ for 12g/L Au salt. However, AuSn ($\sim 50\text{at}\% \text{ Sn}$) alone could not be deposited at higher current densities. The maximum Sn content in the deposits was less than $45\text{at}\%$. The Sn content, at higher current densities, increased initially with increasing current density, and then decreased steadily. Subsequent thin film XRD studies (reported in the following phase identification section) verified that both AuSn and Au_5Sn intermetallics were present in the higher current density deposits. The absence of a AuSn plateau is directly related to the high concentration of Au ions at the cathode surface, which

extends the possibility of depositing Au_5Sn to higher current densities.

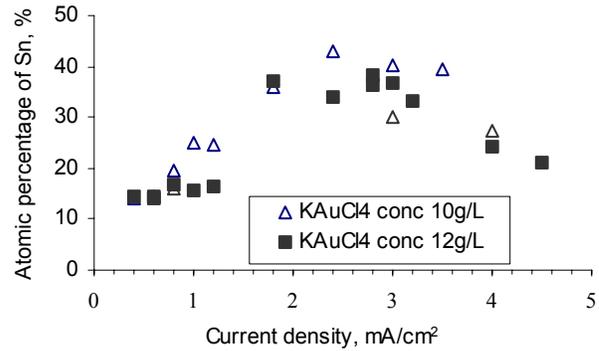


Figure 4 Composition of Au-Sn deposits obtained at various current densities from baths with higher Au concentrations (100g/L ammonium citrate without agitation).

Table 2
Thin film XRD analyses of electroplated Au-Sn deposits

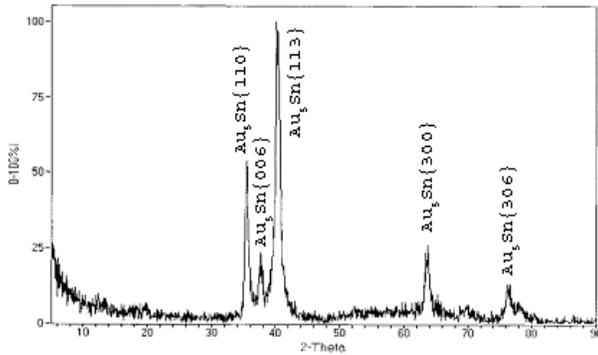
at% Sn	Plating conditions	Phase(s)
14.4	$i=0.4\text{mA}/\text{cm}^2$, KAuCl_4 conc. 5g/L	Au_5Sn
14.4	$i=0.4\text{mA}/\text{cm}^2$, KAuCl_4 conc. 12g/L	Au_5Sn
14.5	$i=0.6\text{mA}/\text{cm}^2$, KAuCl_4 conc. 12g/L	Au_5Sn
15.7	$i=0.8\text{mA}/\text{cm}^2$, KAuCl_4 conc. 5g/L	Au_5Sn
16.4	$i=1.2\text{mA}/\text{cm}^2$, KAuCl_4 conc. 12g/L	Au_5Sn
16.6	$i=0.8\text{mA}/\text{cm}^2$, KAuCl_4 conc. 12g/L	Au_5Sn
24	$i=4.0\text{mA}/\text{cm}^2$, KAuCl_4 conc. 12g/L	$\text{Au}_5\text{Sn} / \text{AuSn}$
25	$i=1.2\text{mA}/\text{cm}^2$, KAuCl_4 conc. 10g/L	$\text{Au}_5\text{Sn} / \text{AuSn}$
29	$i=0.8\text{mA}/\text{cm}^2$, KAuCl_4 conc. 5g/L	$\text{Au}_5\text{Sn} / \text{AuSn}$
30	$i=3.0\text{mA}/\text{cm}^2$, KAuCl_4 conc. 10g/L	$\text{Au}_5\text{Sn} / \text{AuSn}$
33	$i=3.2\text{mA}/\text{cm}^2$, KAuCl_4 conc. 12g/L	$\text{Au}_5\text{Sn} / \text{AuSn}$
36	$i=1.8\text{mA}/\text{cm}^2$, KAuCl_4 conc. 10g/L	$\text{Au}_5\text{Sn} / \text{AuSn}$
37	$i=3.0\text{mA}/\text{cm}^2$, KAuCl_4 conc. 12g/L	$\text{Au}_5\text{Sn} / \text{AuSn}$
38	$i=2.8\text{mA}/\text{cm}^2$, KAuCl_4 conc. 12g/L	$\text{Au}_5\text{Sn} / \text{AuSn}$
39	$i=3.5\text{mA}/\text{cm}^2$, KAuCl_4 conc. 10g/L	$\text{Au}_5\text{Sn} / \text{AuSn}$
40	$i=3.0\text{mA}/\text{cm}^2$, KAuCl_4 conc. 10g/L	AuSn
43	$i=2.4\text{mA}/\text{cm}^2$, KAuCl_4 conc. 10g/L	AuSn
43	$i=0.8\text{mA}/\text{cm}^2$, KAuCl_4 conc. 5g/L	$\text{Au}_5\text{Sn} / \text{AuSn}$
44	$i=1.2\text{mA}/\text{cm}^2$, agitation, KAuCl_4 conc. 5g/L	AuSn
45	$i=2.4\text{mA}/\text{cm}^2$, agitation, KAuCl_4 conc. 5g/L	AuSn
45	$i=3.0\text{mA}/\text{cm}^2$, agitation, KAuCl_4 conc. 5g/L	AuSn
45	$i=3.6\text{mA}/\text{cm}^2$, agitation, KAuCl_4 conc. 5g/L	AuSn
47	$i=2.4\text{mA}/\text{cm}^2$, agitation, KAuCl_4 conc. 5g/L	AuSn
50	$i=2.4\text{mA}/\text{cm}^2$, KAuCl_4 conc. 5g/L	AuSn

Phase identification and orientation determination by XRD

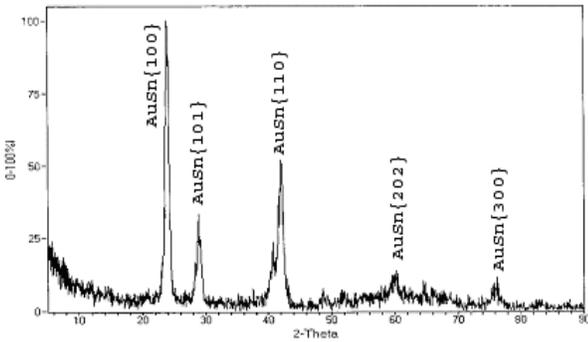
To identify the Au-Sn intermetallic phases plated out and any preferred orientation in the deposits, thin film XRD was employed. Standard XRD data (JCPDS powder diffraction

files) for all possible Au-Sn phases were obtained. The results are summarized in Table 2, with representative spectra shown in Figure 5.

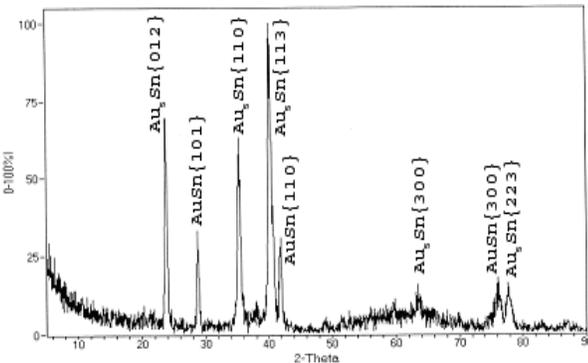
In the thin film XRD tests conducted, only two gold-tin intermetallic phases, Au₅Sn and AuSn, were detected. In deposits containing 40-45 at% Sn, no Au₅Sn was detected (with the exception of the sample containing 43 at% Sn and plated at 0.8 mA/cm² from a 5 g/L Au salt solution). It is likely that some Au₅Sn was present in these samples, but undetectable by XRD. For both Au₅Sn and AuSn, no signs of preferred orientation were evident.



a. 14.4at% Sn plated at 0.4mA/cm²; KAuCl₄ conc. 12g/L



b. 50at% Sn plated at 3.5mA/cm²; KAuCl₄ conc. 5g/L



c. 24at% Sn plated at 4.0mA/cm²; KAuCl₄ conc. 12g/L

Figure 5 Thin film XRD spectra of representative gold-tin deposits.

CONCLUSIONS

From the above, the following conclusions can be drawn:

The current density transition region for plating the two different gold-tin intermetallics, Au₅Sn and AuSn, was shifted from ~1.5 mA/cm² for solutions containing 200g/L ammonium citrate to ~0.8 mA/cm² for solutions with 100g/L ammonium citrate.

Smoother, denser deposits were obtained with plating solutions containing lower ammonium citrate concentrations. Reducing the citrate concentration has the added benefit of reducing plating bath cost.

Compared with results obtained previously for solutions with 200g/L ammonium citrate, plating rates were lower for Au₅Sn depositions and slightly higher for AuSn depositions for solutions containing 100 g/L ammonium citrate.

For solutions with higher Au concentrations, a separate AuSn plateau was not obtained, i.e., deposits contained both Au₅Sn and AuSn intermetallics when plated at higher current densities.

Thin film XRD analyses demonstrated that only two gold-tin intermetallic phases, Au₅Sn and AuSn, were present. No preferred growth of either phase was evident.

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REFERENCES

- [1] G. G. Stanley, Chapter 15, *The Extractive Metallurgy of Gold in South Africa*, Volume 2, The South African Institute of Mining and Metallurgy, (1987), p.842.
- [2] N. Kubota, T. Horikoshi and E. Sato, *J Met. Fin. Soc. Japan* **34**, (1983) 37.
- [3] G. Holmbom, J. A. Abys, H. K. Straschil and M. Svensson, *Plating & Surface Finishing* **85**, (1998) 66.
- [4] S. Matsumoto and Y. Inomata, *JP 61 15,992 [86 15,992]*, (Jan. 24, 1986).
- [5] W. Sun and D. G. Ivey, *Materials Science and Engineering*, **65B**, (1999) 111.
- [6] J. C. Doesburg, *MSc Thesis*, Department of Chemical and Materials Engineering, University of Alberta, (Feb. 2000).
- [7] B. Djurfors and D. Ivey, *GaAs Mantech Conference*, Las Vegas, USA, (May 2001), pp. 196-199.
- [8] A. He, B. Djurfors, S. Akhlaghi and D. G. Ivey, *AESF SUR/FIN 2002 Proceedings*, Chicago, USA, (June 2002), pp. 204-216.

ACRONYMS

PC: pulsed current XRD: x-ray diffraction
 UTW: ultra thin window SE: secondary electron
 SEM: scanning electron microscopy
 EDX: energy dispersive x-ray

