

Pulsed Electrodeposition of the Eutectic Au/Sn Solder for Optoelectronic Packaging

B. DJURFORS^{1,2} and D.G. IVEY¹

1.—University of Alberta, Department of Chemical and Materials Engineering, 536 Chemical & Materials Engineering Building, Edmonton, AB, T6G 2G6 Canada. 2.—djurfors@ualberta.ca

As an alternative to the time-consuming solder pastes and preforms currently being used, a method of electroplating the eutectic Au/Sn alloy has been developed. Using a pulsed co-deposition process, it is possible to plate the solder directly onto a wafer at or near the eutectic composition from a single solution. It has been shown that two distinct phases, Au₅Sn and AuSn, can be deposited separately over a range of current densities at compositions of 15 at.%Sn and 50 at.%Sn, respectively. By adjusting the deposition current pulse, it is possible to plate both phases in a layered composite thereby achieving any desired composition between 15 and 50 at.%Sn, including the commercially important eutectic composition.

Key words: Electroplating, eutectic, solder, optoelectronic packaging, pulse deposition, Au/Sn

INTRODUCTION

One of the lead-free solders currently being used in optoelectronic packaging applications is the eutectic Au/Sn alloy (30 at.%Sn). In addition to the obvious environmental advantages of not containing lead, it also has excellent thermal and mechanical properties making this hard solder well suited for packaging applications in which long-term device reliability is important.¹ In addition, its comparatively low melting temperature of 280°C makes it ideally suited for applications in which the materials are temperature sensitive.²

Presently, most eutectic Au/Sn alloys are prepared as solder preforms. The major drawback of this technique is that it requires expensive robots to place the preforms or it must be done manually, which is very labor intensive. Thin film deposition by evaporation or sputtering of the solder is an attractive alternative, since the oxide content is reduced relative to preforms and process control is better in terms of thickness uniformity and solder alignment.³ However, standard thin-film equipment is costly from a production viewpoint.

An alternate thin-film deposition technique is electrodeposition. The benefits include reduced oxide formation, thickness uniformity, improved solder

alignment (relative to preforms) and significantly reduced capital costs, suggesting a strong commercial viability for this technique. Electrodeposition of an alloy solder can be either done sequentially or simultaneously. With sequential deposition, a pure Sn layer is deposited on top of a pure Au layer. The disadvantage of this technique is that a post-deposition anneal is required to homogenize the composition through interdiffusion.² In addition to being a time-consuming, multi-step process, such treatments often lead to segregation of the tin to the surface of the alloy layer, resulting in the formation of an oxide layer that interferes with bonding.²

Unfortunately, direct alloy co-electroplating can be a difficult process to control, but the application of pulse plating can vastly improve the properties of the deposit.⁴ Most importantly, it is a one-step deposition procedure that requires no further heat treatment or diffusion during bonding.

The purpose of this work is to develop a method of depositing eutectic and near eutectic Au/Sn alloys from a single plating bath using the principles of alloy co-deposition. In this way, deposition can occur directly on the wafer substrate without the need for any further homogenization treatments. The goal is to tailor the process to produce any composition near the eutectic composition without having to adjust the solution composition. Ultimately, a completely interspersed structure can be produced with the same

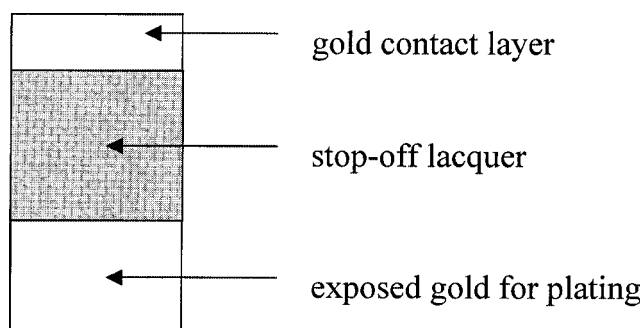


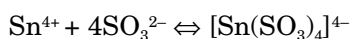
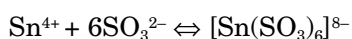
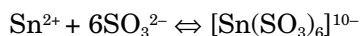
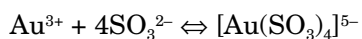
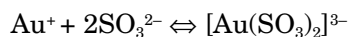
Fig. 1. Schematic representation of wafer preparation.

physical properties of the eutectic structure.

EXPERIMENTAL PROCEDURE

A single plating solution was utilized for the deposition of the Au/Sn alloys. As with all alloy co-deposition baths, there is an intrinsic voltage that exists in the solution between the two metal ions since the tin will tend to reduce the gold ions. As a result, other chemicals were added to the solution to prevent this spontaneous reaction between the two metal ions. These complexing agents served two purposes. The first was to increase the stability of the solution and prevent the spontaneous reaction between the two metal ions, and the second was to bring the dynamic potentials of the two metals close enough together that they will deposit simultaneously without the application of a significant overvoltage.

The plating solution had five major constituents; the solution development details have been published elsewhere.^{5,6} The KAuCl_4 and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ salts were the sources of the initial Au (III) and Sn(II) ions, some of which immediately form the other possible valence states: Au (I) and Sn(IV). Tri-ammonium citrate was added as a buffer to maintain a nearly neutral solution pH. Sodium sulfite acted as a complexing agent for the gold, and, to some degree,⁷ the tin. The following reactions are the most likely complexing reactions according to the specific stereochemistry of the Au(I), Au(III), Sn(II), and Sn(IV) ions.⁷ The plating solution likely contains a mixture of all possible ions.



The l-ascorbic acid was used to prevent the hydrolysis of the tin in water. It acts as a chelating agent for the tin, thereby preventing its reaction with water. Although no specific reaction mechanism has been reported in the literature, the following reactions are suggested as possible complexing reactions between the tin and the l-ascorbic acid.

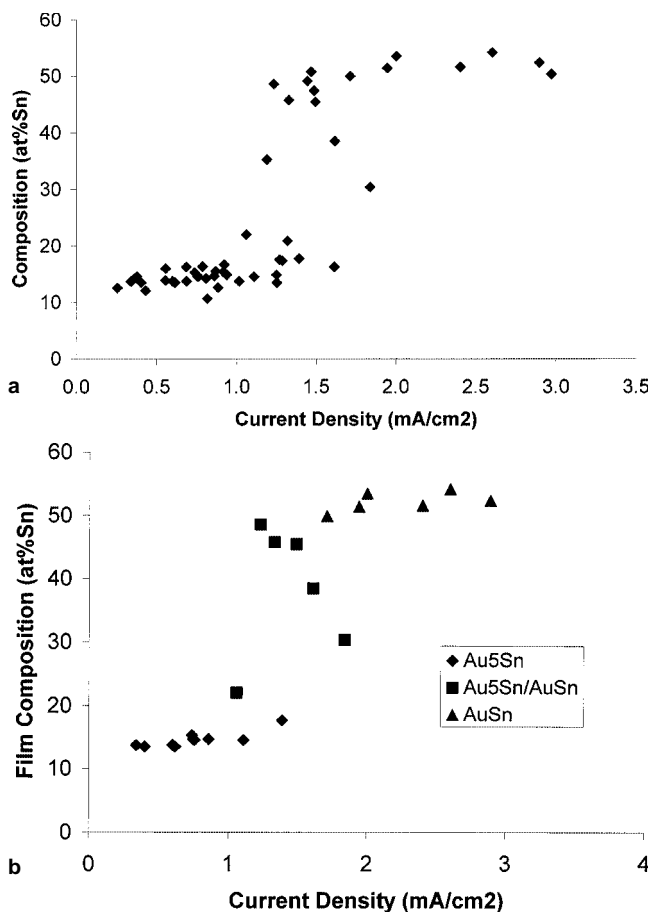
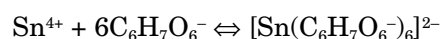
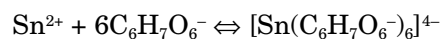


Fig. 2 (a) Plot of deposit composition vs. current density, (b) plot of current density vs. composition showing phase analysis.



All electroplating was done on metallized Si or InP wafers with evaporated Ti and Au layers, 25 nm and 250 nm thick, respectively. The gold provided a seed layer for electroplating, while the Ti acted as an adhesion layer between the gold and the substrate. Prior to deposition, the backs of the wafers were covered completely with stop-off lacquer to prevent deposition on the rear of the wafer surface. In addition, stop-off lacquer was applied to the front of the wafer over top of the gold seed layer to isolate a portion of the wafer of known area on which the deposition could occur (Fig. 1). Generally, these areas were not in excess of 1 cm^2 . In this way, the current density of deposition could be calculated prior to plating.

A Dynatronix DuPR 10-0.1-0.3 pulse plating power supply was used for deposition with a maximum current rating of 100 mA average current and 300 mA peak current. Based on previous work^{5,6} the forward direction was set at 10 ms, with a forward on-time of 2 ms, and a forward off-time of 8 ms. This resulted in a 20% forward duty cycle for plating. Typical deposition currents for this particular solution were between 5 and 10 mA of peak current. Plating times were usually 1.5 h to 2 h to ensure a sufficiently thick

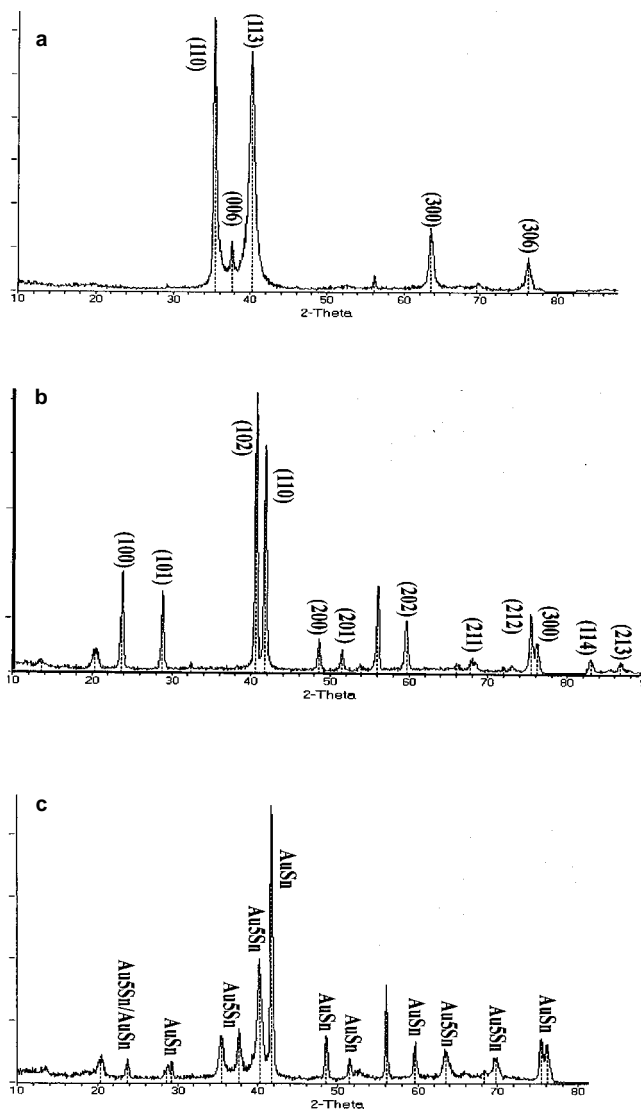


Fig. 3. XRD pattern from (a) Au₅Sn phase, (b) AuSn phases, and (c) mixed phase (AuSn/Au₅Sn) sample.

deposit (>1.5 μm) for composition analysis.

For multi-layer plating, two specific current densities were selected for deposition. The rationale for this is discussed in the next section. The two current densities were then cycled to produce the separate phase layers; thickness and composition control was achieved by adjusting the plating time used for each phase.

Imaging of the solder layers was done using a Hitachi Scanning Electron Microscope (SEM) with an energy dispersive x-ray (EDX) analysis system. Compositional analysis of all layers was done at 20 kV from a working distance of 17 cm and a count rate of 3500 counts/second. Pure Au and Sn standards were applied in order to obtain quantitative results accurate to within 2 at.%Sn.

X-ray diffraction (XRD) phase analysis was carried out using a Rigaku Rotaflex rotating anode diffractometer with a thin film camera attachment. The filament voltage and current were set at 40 kV and 110 mA, respectively. The sample was scanned between

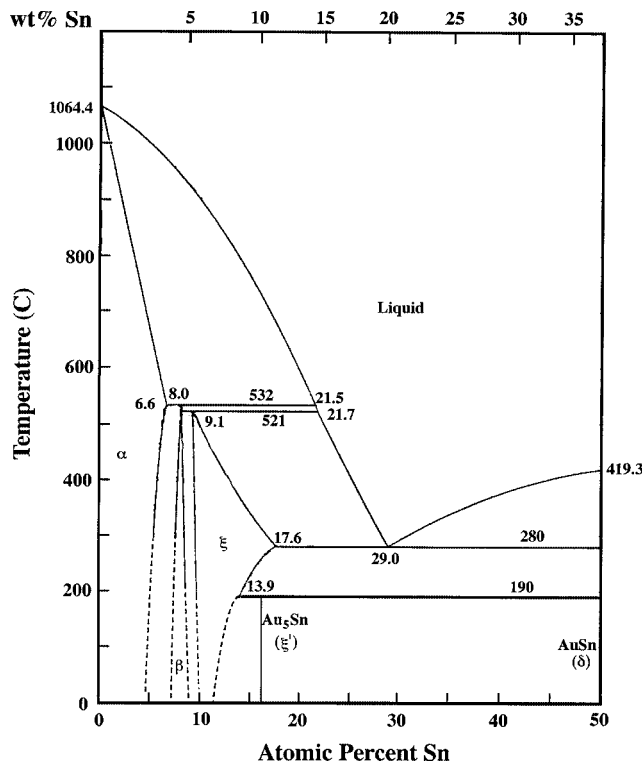


Fig. 4. Au/Sn phase diagram.²

10° and 90° at a rate of 1°/min using an incidence angle of 3° to ensure no substrate was sampled. A blank wafer was run for background signal comparison and elimination. Ti/Pt metallized wafers instead of Ti/Au metallized wafers were used for deposition so that it could be determined whether or not atomic gold was being plated in addition to the gold/tin compounds.

RESULTS AND DISCUSSION

Current Density/Composition/Phase Relationship

A range of current densities was sampled in order to determine the effect of current density on the composition of the alloy, since it is the easiest and most effective method of adjusting the composition of the alloy. In addition, it is important to have a firm grasp on the types of alloys that can be produced using this method: solid solutions with impurity levels of Sn, or actual alloy compounds with significant Sn content.

Previous work had already established the existence of a compositional plateau at 50 at.% Sn in the current density range from 2.5 to 3.5 mA/cm².⁵ Building on this work, the compositional plateau at 50 at.% Sn has been extended back from 2.5 to 2 mA/cm². A lower compositional plateau was also found at an average Sn composition of 15 at.% Sn extending up to 1 mA/cm². Between 1 mA/cm² and 2 mA/cm² there is a transition region where the composition of the film is variable with the current density. These trends are illustrated in Fig. 2a.

Since two plateaus exist, it is realistic to assume that within these plateaus, a single phase is being deposited in each accounting for the constant Sn composition. XRD analysis was performed in order to

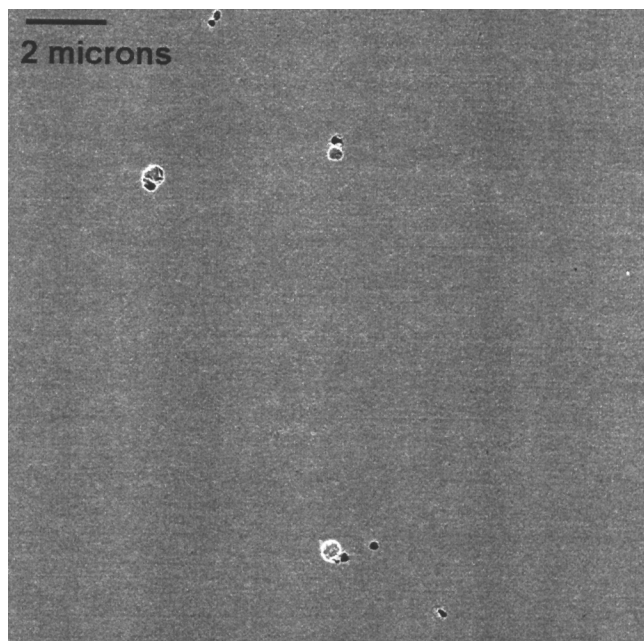


Fig. 5. SEM secondary electron (SE) image of Au_5Sn film with a composition of 16 at.%Sn.

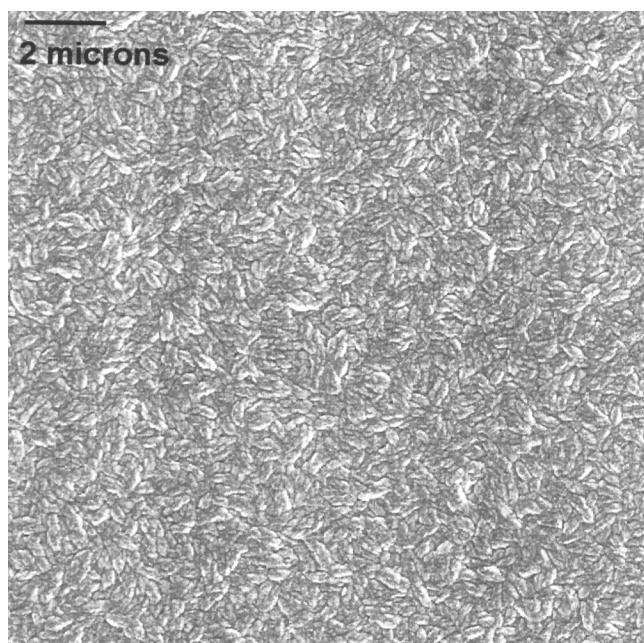


Fig. 6. SEM SE image of an AuSn film with a composition of 50 at.%Sn.

identify the phases present and also to validate the EDX analysis. Figure 2b shows the results of the XRD analysis. The XRD testing verified the existence of the AuSn phase within the 50 at.%Sn compositional plateau and the existence of the Au_5Sn phase within the lower plateau at 15 at.%Sn. Unfortunately, it was not possible to determine which phase, ordered Au_5Sn or disordered Au_5Sn , was present since their d-spacings are too close to be separated and no distinctive x-ray lines were present to suggest one phase over the other. Within the transition region, both phases Au_5Sn and AuSn are deposited.

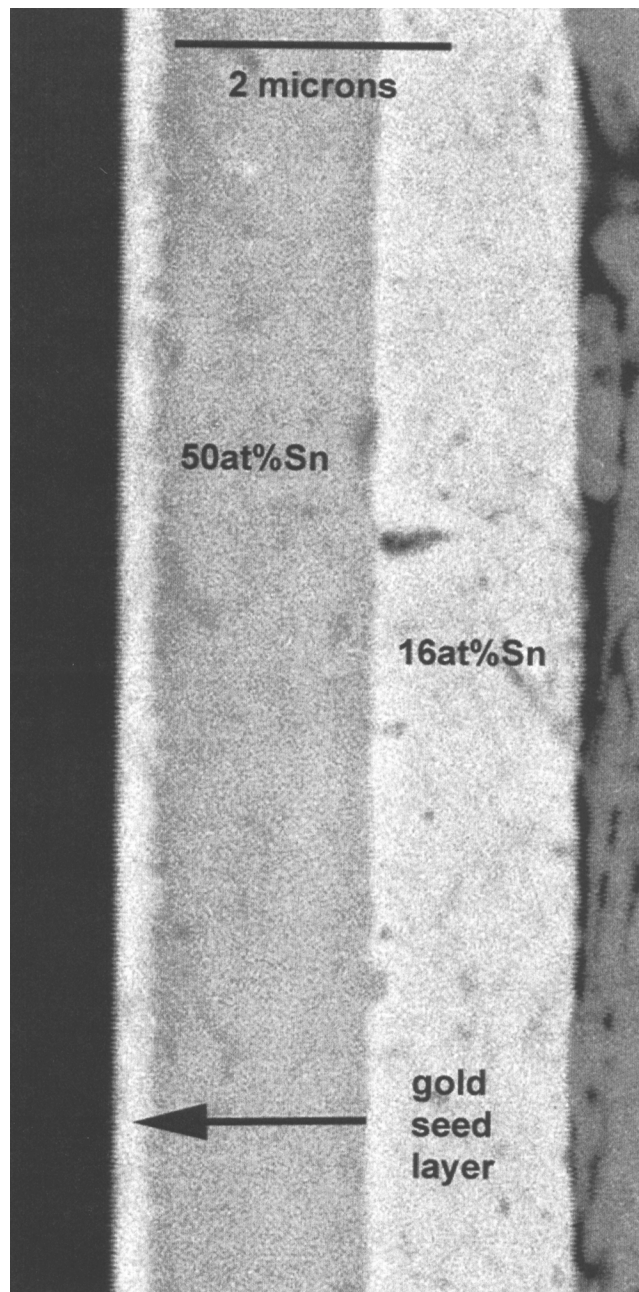


Fig. 7. SEM backscattered (BSE) image of a cross-section from a multi-layer deposit.

Figure 3a–c shows examples of the diffraction patterns obtained from each of the three regions. Figure 3a is a spectrum for Au_5Sn from a deposit done at 0.8 mA/cm^2 with an average composition of 15 at.%Sn. Figure 3b is a spectrum for the AuSn phase from a deposit done at 1.94 mA/cm^2 with an average composition of 52 at.%Sn and Fig. 3c is a spectrum showing the two phases from a deposit done at 1.33 mA/cm^2 and a composition of 46 at.%Sn.

Using the Au/Sn phase diagram shown in Fig. 4 as a guide, it is reasonable that the compositional plateau at 50 at.%Sn would correspond to the AuSn or δ intermetallic phase. In addition, it is probable that the lower plateau at 15 at.%Sn would correspond to

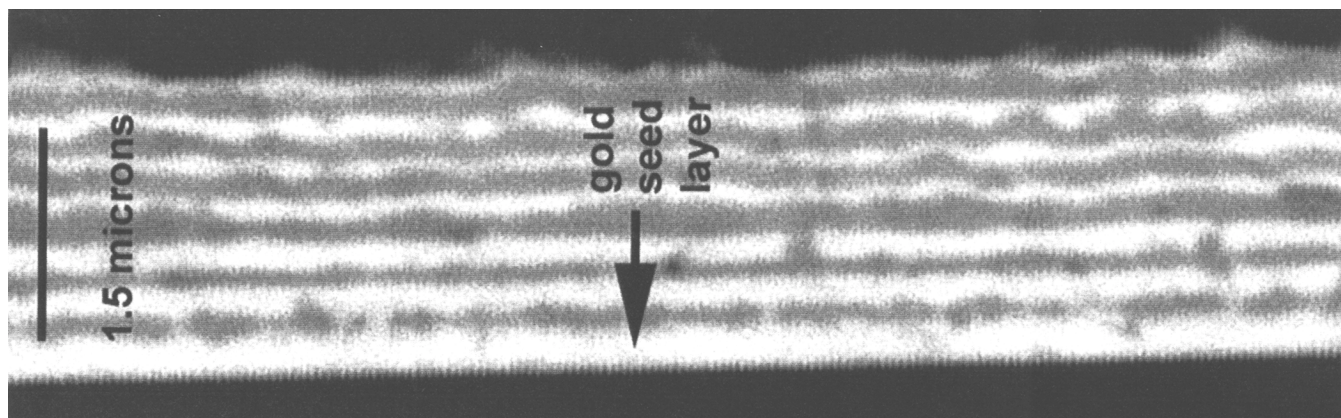


Fig. 8. SEM BSE cross-section image from a multi-layer deposit. The lighter layers are Au_5Sn and the darker layers are AuSn.

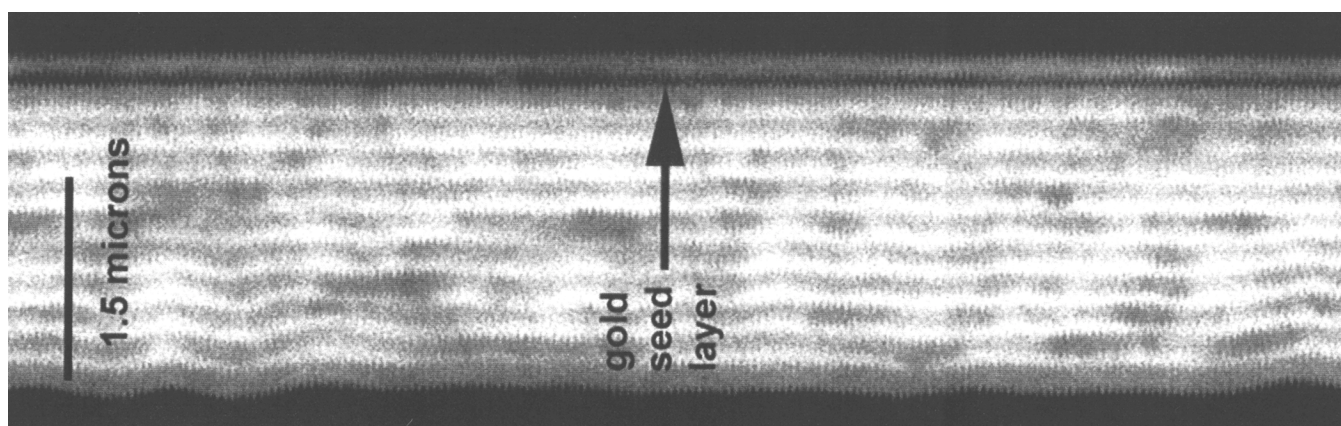


Fig. 9. SEM BSE image of a cross-section from a multi-layer deposit. The lighter layers are Au_5Sn and the darker layers are AuSn.

the Au_5Sn phase. As seen in Fig. 4, there are two Au_5Sn phases, the ordered ζ' and the disordered ζ . The ordered phase is an intermetallic compound with a composition of 16.7 at.% Sn and a homogeneity range of less than 1 at.% Sn. It has a close-packed-hexagonal structure with the unit cell of the superstructure containing 15 Au and 3 Sn atoms.² The lattice parameters a and c are 0.5092 nm and 1.4333 nm, respectively. The disordered phase, however, extends between 9.1 at.% Sn and 17.6 at.% Sn at 280°C² but is not considered to be stable at room temperature. It is a Mg-type close-packed hexagonal lattice structure with variable lattice constants depending upon composition. For compositions varying from 11.07 to 16.31 at.% Sn, the lattice constant, a , changes from 0.29084 nm to 0.29386 nm and c changes from 0.47864 nm to 0.47694 nm.⁸

Since it is possible to electroplate non-equilibrium phases and the Au/Sn phase diagram is not well established in the gold-rich region, it is suspected that the disordered Au_5Sn phase is being deposited, which would account for both the off-stoichiometric average composition, 15 at.% Sn instead of 16.7 at.% Sn, and the significant scatter in the compositional data (Fig. 2a) with values ranging from 13 at.% Sn to 17 at.% Sn.

The XRD work verifies that there is both a compositional and phase plateau from 2 to 3 mA/cm² and a separate compositional and phase plateau up to 1 mA/

cm². As suspected, there is a mixture of the two phases (AuSn and Au_5Sn) deposited within the transition region accounting for the significant variability in composition.

Figure 2a and b can be most easily explained by examining the behavior of the individual metal ions in solution. In general, Au is a more noble metal than Sn. Even with the addition of the sulfite as a complexing agent to bring the potentials of the two metals closer together, the Au will remain more noble relative to the Sn although the new potential difference between the two metals as a result of complexing is unknown. As a result, the Au will still tend to deposit more readily than the Sn.

At the lower current densities, or lower applied overpotentials, the Au, tending to reduce more easily than the Sn, will be in greater concentration on the wafer surface. Since a greater concentration of Au is depositing compared with Sn, the formation of the Au-rich compound, Au_5Sn , occurs. As the current density increases, the overpotential of both the Sn and the Au increases as well. At higher current densities, 2–3 mA/cm², it is assumed that the reduction of Au ions has reached its limiting current density and is therefore reacting on the surface at a constant rate. The increase in overpotential, however, increases the deposition of Sn and since the Au deposition remains fixed, the Sn/Au ratio on the wafer

surface increases. As a result, Au₅Sn is no longer the preferred phase for deposition. The next possible phase for deposition, as seen from the Au/Sn phase diagram in Fig. 4, is AuSn. This results in the AuSn plateau seen in Fig. 2a and b.

The two-phase transition region represents an intermediate condition to the two cases discussed above. Local variations in current density may favor nucleation of one phase over the other, resulting in the formation of both phases. It is possible that local variations in microstructure, protrusions for example, may provide a sufficient local increase in overpotential⁹ causing AuSn to become the more favorable compound for deposition in those regions. However, in areas when the overpotential is not increased by the film morphology, the ratio of ions reacting at the wafer surface will remain more conducive for depositing Au₅Sn. As a result, it becomes possible to deposit both phases in this transition region.

The determination of the two composition plateaus, one at 50 at.%Sn and one at 15 at.%Sn means that the appropriate combination of these phases will result in the eutectic composition or, for that matter, any composition between 15 at.% and 50 at.%. In a sense, the current density/composition graph (Fig. 2a) mimics the structure of the phase diagram. Referring to Fig. 4, the 10 to 50 at.%Sn region is bordered by the two phases, Au₅Sn and AuSn, separated by a mixed phase region. This is mimicked in the current density/composition relationship where the two phases make up the boundaries of the plating curve separated by a two-phase transition region that includes the eutectic composition.

Layer Structure and Morphology

Within each compositional plateau, there are two distinctly different film structures. In the lower plateau, the Au₅Sn films produced are smooth and shiny with a mirror-like reflective quality. Very little structure is apparent, even on examination in the SEM (Fig. 5). At 50 at.%Sn, the surface appears gray, dull, and rougher (upon visual examination), typical of AuSn,² since the grain structure appears coarser than that of the Au₅Sn (Fig. 6).

Multi-Layer Plating

Once the two separate plateaus at 50 at.% Sn and 15 at.% Sn had been established, multi-layer plating of the two different compositions was attempted to achieve the desired eutectic composition of 30 at.% Sn overall or any composition desired between 15 and 50 at.%Sn.

Having already established that two phases can be deposited individually, it is a simple matter to combine the two phases in a single deposit to achieve the overall eutectic composition. The first attempt in the mixed phase plating was to plate one phase layer on top of the other to establish compatibility. The first layer deposited was the 50 at.%Sn, with the 15 at.%Sn layer on top. 0.8 mA/cm² was chosen for the Au₅Sn deposition, since it was near the upper end of the

lower plateau and gave a higher plating rate. 2.4 mA/cm² was chosen for the AuSn phase deposition, since this current density has been shown previously to provide a fairly rapid deposition rate coupled with a relatively fine-grained structure.^{5,6} The as-deposited structure is shown in Fig. 7—backscattered electron (BSE) imaging was used to enhance atomic number contrast. The figure clearly shows that both layers are extremely uniform with good adhesion to one another. Of particular importance is the apparent lack of voids along the interface between the phases suggesting excellent integration of the two layers.

The next attempt was to plate a sequence of much finer phase layers in order to produce a final product of completely intermixed phases. Figure 8 shows a cross-section of a deposit made by plating at 2.4 mA/cm² for 5 min., followed by 0.8 mA/cm² for 20 min. and then repeating the cycle to build up the deposit. The same pulse cycle of 2 ms on-time and 8 ms off-time was maintained. The overall composition of the deposit is 30%. Figure 9 shows another attempt using much shorter plating times: 2.5 min. for the higher current density, and 10 min. for the lower current density. The result is a deposit made up of finer layers than in Fig. 8, with an overall composition of 26 at.%Sn. In the three cases cited above, the current pulse was changed manually. In the future, the process will be automated to allow for much shorter pulses to deposit very thin multiple layers (<10 nm) of Au₅Sn and AuSn to produce a completely interspersed structure of eutectic or near-eutectic composition.

SUMMARY

Using a single solution, it has been shown that by altering the deposition current density, it is possible to plate two different phases, the AuSn intermetallic, and the Au₅Sn intermetallic. In addition, by controlling the pulse length and number, a multilayer composite can be successfully produced consisting of both phases with an overall composition between 15 and 50 at.%Sn. Although there is strong evidence to suggest that Au₅Sn is the disordered compound, further work is required for verification.

REFERENCES

1. W. Plumbridge, *J. Mater. Sci.* 31, 2501 (1996).
2. G. Matijasevic, *Thin Solid Films*, 223, 276 (1993).
3. D.G. Ivey, *Micron*, 29, 281 (1998).
4. A.J. Avila, *Theory and Practice of Pulse Plating*, ed. Puipe and Leaman (Orlando, FL: Amer Electroplaters and Surface Finishers Soc., 1989), pp. 189–202.
5. J. Doesburg and D.G. Ivey, *Plating and Surface Finishing* 88, 78 (2001).
6. W. Sun and D.G. Ivey, *Mater. Sci. and Eng. B* 65, 111 (1999).
7. D.D. Perrin, *Organic Complexing Reagents: Structure, Behavior, and Application to Inorganic Analysis* (New York: John Wiley & Sons, 1964), p. 35.
8. T.B. Massalski and H.W. King, *Acta Metall.* 8, 677 (1960).
9. O. Dossenback, *Theory and Practice of Pulse Plating*, ed. Puipe and Leaman (Orlando, FL: Amer Electroplaters and Surface Finishers Soc., 1989), pp. 73–92.