Pulse Plating of Gold-Tin Alloys for Microelectronic and Optoelectronic Applications

Anqiang He, Barbara Djurfors, Siamak Akhlaghi* and Douglas G. Ivey Dept. Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, Canada T6G 2G6 *Micralyne Inc., Edmonton, Alberta, Canada T6N 1E6

Gold-tin eutectic solders (30 at% Sn) are used for packaging microelectronic and optoelectronic devices, because of their excellent thermal and mechanical properties and relatively low melting or reflow temperature (280°C). Electroplating is a cost effective alternative to current commercial solder deposition processes, such as solder preforms and evaporation. A coelectroplating process for depositing Au/Sn alloys, from a slightly acidic, chloride-based solution using pulsed currents, onto metallized ceramic and semiconductor substrates has been developed. Two separate Au/Sn compositions, 15 at% Sn and 50 at% Sn, can be deposited under appropriate plating conditions, i.e., current density, and pulse on/off time and duration. These compositions, according to the Au-Sn phase diagram, correspond to Au₅Sn and AuSn, respectively. By using multiple current pulses and varying their duration, it is possible to deposit a composite solder structure with an overall composition ranging from 15-50 at% Sn, including the important eutectic composition.

Plating results for both unpatterned and patterned (with photoresist) substrates are presented. All substrates were metallized with Ti/Au or Ti/Mo/Au, to provide a gold seed layer for electroplating.

For more information, contact: Douglas G. Ivey Dept. of Chemical and Materials Engineering University of Alberta Edmonton, Alberta, Canada T6G 2G6 doug.ivey@ualberta.ca

Introduction

Gold-tin solder is used for bonding of opto/microelectronic devices to ceramic carriers as part of the packaging process. Au-Sn solder is classified as a "hard" solder and possesses excellent thermal and mechanical properties making it well suited to device packaging in which long-term device reliability is important¹. In addition, its comparatively low eutectic temperature of 280°C (Figure 1), relative to other hard solders such as Au-Ge and Au-Si, makes it ideally suited for temperature sensitive applications².



Fig. 1 Gold-rich portion of the Au-Sn phase diagram².

Currently, most eutectic Au/Sn alloys are deposited either as solder preforms or via vacuum deposition techniques, such as sputtering or evaporation. Bonding with solder preforms is relatively inexpensive and simple to implement; however, solder alignment and thickness control are sacrificed and the solder is easily oxidized which can compromise bond integrity. Vacuum deposition techniques provide much better process control and reduced oxidation, but are considerably more expensive to apply and can be time consuming³.

An alternative technique, which combines the process control of vacuum deposition techniques with the relatively low cost of preforms, is electrodeposition. 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 using two separate plating baths. The disadvantage of this technique is that a post-deposition anneal is required to homogenize the composition through interdiffusion². In addition to being a time consuming, multi-step process, such heat treatments often lead to Sn segregation to the surface of the deposit resulting in oxide formation². Coelectroplating from a single solution, although not without its own difficulties, circumvents these problems, since additional heat treatment is not needed to produce a homogeneous deposit.



Fig. 2 Plot of deposit Sn composition vs plating current density for electroplating of unpatterned substrates^{7,8}. All depositions were done with pulsed currents at an on-time of 2ms and an off-time of 8ms.

An electroplating solution has previously been developed, by the authors, for depositing Au-Sn alloys, over a range of compositions (15 to 50 at% Sn) with thicknesses up to several microns, from a single solution. The plating solution is chloride-based (non-cyanide) and made up of five major constituents; the solution development details have been published elsewhere⁴⁻⁶. KAuCl₄ and SnCb₂.2H₂O salts are 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 is added as a buffering agent to maintain a nearly neutral, slightly acidic solution pH. Sodium sulfite acts as a complexing agent for the gold, and to some degree the tin. Ascorbic acid is added to prevent hydrolysis of Sn in water; it acts as a chelating agent for the tin, thereby preventing its reaction with water. A range of compositions, from ~15at% Sn to ~50at% Sn, can be deposited from this solution by varying the plating current density (Figure 2)^{7,8}. Uniform deposits can be obtained on substrates with Au seed layers using either direct or pulsed currents; however, better overall surface morphology is attained with pulsed currents.

In this paper, the use of multi-pulse plating, from a single solution, to obtain Au-Sn alloy deposits with good compositional control and surface morphology is presented and discussed. Depositions are done on both unpatterned and patterned substrates with Au seed layers. Multi-layer deposits over a range of thicknesses can be obtained to generate compositions from 15-50at% Sn, including the important eutectic composition (30at% Sn).

Experimental

A single plating solution, briefly discussed above, was utilized for all depositions of Au/Sn alloys; the Au:Sn mass ratio in solution was ~1.0. All plating experiments were carried out on pieces sectioned from either metallized AlN (75mm x 75mm square) or Si (100mm diameter) substrates. AlN wafers were metallized with 25 nm of Ti, 75 nm of Mo and 1 μ m of Au, while Si wafers were metallized with 25 nm of Ti and 250 nm of Au. In both cases, Ti acted as an adhesion layer and the Au as a seed layer for plating. Wafers were either unpatterned or patterned, with one of two types of commercial photoresists: dry film laminate (negative resist) and wet photoresist (positive resist). Various pattern shapes were utilized, including circles, squares and crosses, with dimensions ranging from <10 μ m up to 1mm on the same

wafer. The dry photoresist was about 15μ m in thickness, light green in color and opaque; the wet photoresist was either 1.3μ m or 2.7μ m in thickness, yellowish in color and optically transparent. For electroplating experiments, substrates were sectioned into $1-2 \text{ cm}^2$ pieces.

A Dynatronix DuPR 10-0.1-0.3 pulse plating power supply was used for deposition with a maximum current rating of 100mA average current and 300mA peak current. Based on previous work^{7,9} the forward direction was set at 10ms, with a forward on-time of 2ms and a forward off-time of 8ms. This resulted in a 20% forward duty cycle for plating. No reverse pulse was used. For multi-layer plating, two specific current densities were selected to deposit individual phases. The rationale for this approach is discussed in the following section. The two current densities were then cycled to produce separate phase layers; thickness and composition control was achieved by adjusting the plating time used for each phase.

All deposits were characterized, in terms of morphology and composition, using optical microscopy or scanning electron microscopy (SEM). Either a Hitachi H2700 SEM equipped with a PGT IMIX ultra thin window (UTW) energy dispersive x-ray (EDX) detector or a Hitachi 4100 field emission gun (FEG) SEM was used for SEM analysis. Compositional analysis of all layers was done (through EDX analysis) at 20kV from a working distance of 17 mm and a count rate of 3500-4000 counts/second. Pure Au and Sn standards were applied in order to obtain quantitative results accurate to within 2at% Sn. A Rigaku Rotaflex rotating anode x-ray diffraction (XRD) system, equipped with a thin film camera attachment, was used for phase determination. The filament voltage and current were set at 40kV and 110mA respectively. Samples were scanned from10° to 90° at a rate of 1°/min using an incidence angle of 3° to ensure that the substrate was not sampled. A blank wafer was run for background signal comparison and elimination.

Results and Discussion

Depositions on Unpatterned Wafers

Examination of the Sn composition vs current density plot in Figure 2 reveals that there are 2 composition plateaus, one at current densities less than ~1.0 mA/cm² and one at current densities greater than ~2.0 mA/cm². The former corresponds to a specific Au-Sn intermediate phase, disordered Au₅Sn (ζ), while the latter corresponds to the intermediate phase AuSn (δ)⁷. Both phases are, in fact, the two eutectic phases which form during reflow of Au-30at% Sn solder (Figure 1). Phase identification was confirmed through XRD and electron diffraction. XRD spectra obtained during the early stages of Au₅Sn and AuSn formation are shown in Figure 3^{7,8}. In Figure 3a all peaks can be indexed to Au₅Sn, with the exception of the (111) and (220) Pt peaks from the Pt seed layer. All peaks in Figure 3b (again with the exception of the Pt peaks) can be indexed to AuSn. At intermediate current densities, from 1.0 mA/cm² to 2.0 mA/cm², a transition region exists where the composition of the film varies with the current density. Both intermediate phases, Au₅Sn and AuSn, form in varying amounts.



Fig. 3 XRD spectra for Au₅Sn (a) and AuSn (b) obtained during the early stages of electrodeposition of the individual phases ^{7,8}. Au₅Sn was plated at 0.8 mA/cm² and AuSn was plated at 2.4 mA/cm². The times indicated represent total deposition times.

The behavior exhibited in Figure 2 can be explained by considering the individual metal ions in solution. Gold is a more noble metal than Sn; the standard electrode potentials for Au^{3+} ions and the Sn^{2+} are 1.498 V and – 0.138 V (vs SHE) respectively¹⁰. As such, Sn^{2+} ions are not as easy to reduce as Au^{3+} ions. Even with the addition of sodium sulfite as a complexing agent to bring the potentials of the two metals closer together, Au will remain more noble relative to Sn and will tend to deposit more readily than Sn. At lower current densities (<1 mA/cm²) or lower applied overpotentials, Au, tending to reduce more easily than the Sn, will be in greater concentration on the wafer surface. Preferential Au reduction favors the formation of a Au-rich compound, such as Au₅Sn. As the current density is increased, the overpotential for both Sn and Au increases as well. At higher current densities, i.e., 2-3 mA/cm², the reduction of Au ions has likely reached its limiting current density and is therefore occurring on the surface at a constant rate. Any increase in overpotential, however, increases the deposition rate of Sn and since the Au deposition rate 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, apparent from the Au/Sn phase diagram in Figure 1, is AuSn.

The two-phase transition region represents an intermediate condition to the two cases discussed above. Local variations in current density lead to local surface compositional variations, which may favor nucleation of one phase over the other. It is possible that local variations in microstructure, protrusions for example, may provide a sufficient local increase in overpotential¹¹ causing AuSn to become the more

favorable compound for deposition in those regions. In areas where the overpotential is not increased by the film morphology; however, the ratio of ions reacting at the wafer surface will remain more conducive for depositing Au_5Sn . This model accounts for codeposition of Au_5Sn and AuSn as well as the large amount of composition scatter in the transition region.

Based on the above results and analysis, it follows that overall deposit compositions ranging from 15at% Sn to 50at% Sn can be reproducibly achieved through the appropriate integration of 2 current pulses corresponding to the respective plateaus in Figure 2. The utilization of 2 pulses, one at <1.0 mA/cm² and one at >2.0 mA/cm², is preferred over a single pulse corresponding to the desired deposit composition, because of improved process control, i.e., small current fluctuations will not alter the deposit composition. As an example, a slightly hypereutectic (~35at% Sn), 6 µm thick deposit was obtained by plating at current densities of 0.8 mA/cm² and 2.4 mA/cm² (Figures 4a and 4b).



Fig. 4 Cross section SEM secondary electron (SE) images of multilayer deposit at low (a) and higher magnification (b). Plan view SEM backscattered electron (BSE) image of deposit annealed at 300° C is shown in (c). The lighter phase is Au₅Sn and the darker phase is AuSn.

The duty cycle for each pulse was maintained at 20% (2ms on and 8 ms off) but the duration for plating of each phase was varied to yield the intended composition. The plating times for each layer in Figure 4a correspond to 20 min for 0.8 mA/cm² and 5 min for 2.4 mA/cm². The current densities utilized were chosen to provide reasonable plating rates, while ensuring good composition and morphology control. The deposit shown in Figure 4a was melted at 300°C in a furnace with a forming gas $(95\%N_2 + 5\%H_2)$ atmosphere to produce the eutectic microstructure shown in Figure 4c. Note, that the overall Sn content in the solder layer was reduced to the eutectic composition (from ~35at% Sn to ~30at% Sn) due to incorporation of Au from the seed layer.

Depositions on Patterned Wafers

Many packaging applications require solder to be deposited onto specific regions of the carrier or wafer, instead of the entire wafer. As such, the aim of the next portion of this work was to demonstrate the feasibility of multiple pulse plating of Au-Sn alloys on patterned structures. As mentioned in the Experimental Section, 2 types of photoresist were utilized for patterning, a dry, negative resist and a wet, positive resist.

Dry Photoresist

Initial electroplating on these wafers was done using a current density of 2.4 mA/cm², which should have produced deposits with ~50 at% Sn (Figure 2). Good coverage was obtained (Figure 5); however, Sn levels were unexpectedly markedly lower, i.e., in the 13-17 at% range (corresponds to Au₅Sn). The reasons for the reduced Sn levels were not obvious and required further investigation.



Fig. 5 Plan view SEM SE image showing uniform coverage of deposit within pattern openings (dry resist).

Examination of the photoresist surface using optical microscopy revealed the presence of pinholes, many of which had penetrated through to the underlying Au metallization (Figure 6a). The pinholes show up as gold-colored regions, several microns in diameter. Electrolyte can seep through the pinholes, lowering the effective electroplating current density. Electroplated regions were detected at the base of the pinholes (Figure 6b) and were identified, through EDX analysis in the SEM, as containing Au and Sn. Smaller scale porosity



Fig. 6a Optical microscopy image of dry photoresist surface. The gold-colored regions are pinholes that have penetrated through the resist layer.



Fig. 6b Plan view SEM SE image showing a Au-Sn particle which formed at the base of a pinhole in the photoresist. The photoresist has been removed after plating prior to imaging.

(not visible in the optical microscope) accounted for additional current loss through the photoresist. EDX analysis of the photoresist, which had been stripped from the wafer after electroplating, revealed the presence of low levels of Au and Sn as well as Cl and S (Figure 7). Both Au and Sn are added to the electroplating solution as chloride salts, so the presence of Cl is not surprising. The S comes from the sodium sulphite added as a complexing agent. The identification of Au and Sn in the photoresist is an indication that these species were diffusing through it. This phenomenon would also contribute to current loss, leading to lower effective plating current densities and correspondingly lower deposit Sn levels than expected.



Fig. 7 EDX spectrum taken from dry photoresist after electroplating.

Increasing the nominal current density to above 4.0 mA/cm² (as high as 30 mA/cm² in some cases), to compensate for current leakage through the photoresist, did produce 50 at% Sn deposits in some instances, but the results were not reproducible and deposits exhibited poor morphology, i.e., they were porous and gray-black in color. The porosity was likely due to a high rate of hydrogen formation on the cathodes, particularly at high current densities.

Wet Photoresist

Compared with the dry photoresist, the wet photoresist was much denser and was not expected to present the same current leakage problems. Optical microscopy observation revealed no pinholes, nor was any Au or Sn detected by EDX analysis in the photoresist after electroplating. Electroplating at current densities of 2.4 mA/cm² produced deposits with compositions close to 50 at% Sn in many cases. Figure 8 shows an example of one such deposit; the deposited film was smooth and uniform, with full coverage throughout the opening. Deposit thickness did, however, affect the deposit composition if the photoresist thickness was exceeded. This effect is illustrated in Figure 9, with a deposit on a substrate patterned with 2.7 μ m thick photoresist. Once the deposit thickness exceeded the resist thickness, the deposit began to grow laterally as well as vertically, which increased the area to be plated and reduced the effective plating current density. This effect can be compensated for by factoring in the additional plating area.



Fig. 8 Plan view SEM SE image showing a deposit in one of the wet photoresist openings. The plating current density was 2.4 mA/cm^2 .

As discussed previously and shown in Figure 2, for unpatterned, metallized wafers, deposits containing ~15 at% Sn (Au₅Sn) and ~50at% Sn (AuSn) can be obtained by plating at less than 1.0 mA/cm² and greater than 2.0 mA/cm², respectively. Even with the denser wet photoresist, only half the samples plated at 2.2 mA/cm² had deposits with compositions around 50 at% Sn. This may be attributable to "crowding" of the current lines in the openings near the photoresist, which could alter mass transport during plating^{12,13}. To minimize this effect, anodes were produced with the same type of pattern as the cathodes. Plating tests using the patterned anodes produced deposits containing 50 at% Sn at current densities \geq 2.2 mA/cm².



Fig. 9 Cross section SEM SE image of an electroplated sample (current density was 2.4 mA/cm^2). There is lateral growth of the deposit, over the wet photoresist.

Figure 10 summarizes the plating results in a plot of Sn concentration vs current density. The figure includes data from patterned (wet photoresist) wafers using either unpatterned or patterned anodes superimposed on the data from Figure 2 (unpatterned wafers). There is good correlation between the data for unpatterned wafers and the data for patterned wafers with patterned anodes. There appears, however, to be a shift in the plateaus to slightly higher current densities. The reason for this shift is unclear at this time.



Fig. 10 Plot of deposit composition vs current density for plating of Au-Sn alloys.

- ♦ unpatterned substrate
 - patterned substrate/unpatterned anode, deposit thickness greater than resist thickness
- Δ patterned substrate/unpatterned anode, deposit thickness greater than resist thickness (corrected)
- \times patterned substrate/patterned anode, deposit thickness less than resist thickness
- O patterned substrate/unpatterned anode, deposit thickness less than resist thickness

Multilayer eutectic deposits, similar to those shown in Figure 4 for unpatterned substrates, were obtained for substrates patterned with wet photoresist. Deposits, ~2.7 μ m in thickness, were electroplated uniformly within openings of varied shapes and sizes. One such deposit is shown in Figure 11 (low magnification optical microscopy images) and Figure 12 (higher magnification SEM cross section image), where 14 alternating layers of Au₅Sn and AuSn were deposited at current densities and durations of 2.5 mA/cm² and 5 min for AuSn and 1.0 mA/cm² and 21 min for Au₅Sn. Individual layers of Au₅Sn and AuSn are not visible in Figure 12, only 7 pairs of the Au₅Sn and AuSn layers. Reflow of the deposited material at 300°C produced a typical eutectic microstructure (Figure 13).



Fig. 11 Plan view optical microscopy images of multilayer Au-Sn deposits on patterned substrates (wet photoresist). Two current pulses of 1.0 mA/cm^2 and 2.5 mA/cm^2 , 21 min and 5 min respectively in duration, were utilized. The darker regions are the plated areas, while the lighter regions are covered with wet photoresist.



Fig. 12 Cross section SEM SE image through one of the openings in Figure 11.



Fig. 13 SEM BSE image of deposit in Figure 11 annealed at 300° C. The lighter phase corresponds to Au₅Sn. The darker phase is AuSn.

Summary

Co-electroplating of Au-Sn alloys from a slightly acidic, chloride-based solution onto metallized substrates was studied. Plating was done on both unpatterned and patterned wafers. The results can be summarized as follows:

- Au-Sn alloys can be plated from a single solution, with compositions ranging from $\sim 15at\%$ Sn to $\sim 50at\%$ Sn, by using multiple pulses and depositing alternating layers of Au₅Sn and AuSn.
- Dry photoresists tend to be porous, leading to current leakage effects which produce deposits with lower than expected Sn levels. Current leakage can be compensated for in part by increasing the nominal current density.
- Wet photoresists are more dense than their dry counterparts. As such, current leakage is not a problem and suitable deposits can be achieved using current densities similar to those employed for unpatterned wafers.
- Plating reproducibility can be enhanced by using patterned anodes when plating patterned cathodes.

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(4), 281 (1998).

- 4. W. Sun and D.G. Ivey, *Mater. Sci. and Eng. B*, **65**(2), 111 (1999).
- 5. J. Doesburg and D.G. Ivey, *Plating and Surface Finishing*, **88**, 78 (2001).
- 6. W. Sun and D.G. Ivey, U.S. Patent 6,245,208 (2001).
- 7. B. Djurfors and D.G. Ivey, J. Electron. Mater., 30, 1249 (2001).
- 8. B. Djurfors and D.G. Ivey, *Mater. Sci. and Eng. B*, in press, 29 manuscript pages.
- 9. W. Sun and D.G. Ivey, J. Mater. Sci., 36, 757 (2001).
- 10. S. Bradford, Corrosion Control, CASTI Publishing Inc., Edmonton, Canada, 2001; p. 18.
- 11. O. Dossenback, *Theory and Practice of Pulse Plating*, Ed., J-C. Puippe and F. Leaman, AESF, Orlando, Fla., 1989; p. 73.
- 12. S. Mehdizadeh, J. O. Dukovik, P.C. Andricacos, L. T. Romankiw and H. Y. Cheh, J. Electrochem. Soc., 139, 78 (1992).
- 13. S. Mehdizadeh, J. O. Dukovik, P.C. Andricacos and L. T. Romankiw, J. Electrochem. Soc., 140, 3497 (1993).

Acknowledgments

The authors wish to thank the Natural Sciences and Engineering Research Council (NSERC) of Canada, Micralyne Inc. and Nortel Networks for providing research funding and substrates for electroplating (Micralyne and Nortel).