Technical Article

Effect of Processing Parameters On the Electroplating of Au-Sn Solders

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Gold-tin eutectic solders have been widely used in the optoelectronics/microelectronics industry. The prominent characteristics of this solder include high thermal fatigue resistance in addition to excellent thermal properties. An electroplating process was used in this study to deposit Au-30 Sn (at%) solder from a single, non-cyanide, slightly acidic bath onto metallized semiconductor substrates. The electroplating solution stability along with the effect of agitation and temperature on the electroplating process was studied. The useful lifetime of the solution is about three days. In addition, deposit uniformity could be improved through solution agitation, although too much agitation reduced the tin content and increased the surface roughness in the deposit. Moreover, it was observed that increasing the solution temperature to above 35°C (95°F) was not beneficial, due primarily to an increase in the oxidation rate of tin in solution, which, in turn, reduced the amount of tin available for



*Fig. 1—Deposit tin content versus current density. Electroplating was performed at room temperature with no agitation.*¹¹

Nuts & Bolts: What This Paper Means to You

Gold-tin eutectic solders are commonly used in opto- and micro-electronics for integrated chip or die bonding. It can be applied in a number of ways, *i.e.*, as a preform, solder paste, by sequential evaporation or plating. Evaporated solder is cleaner and provides more precise control, but it involves expensive vacuum equipment. Sequential plating involves reflow of alternating layers of gold-tin-gold-tin, etc. ... not cheap either. Until now, any single-step alloy bath has involved cyanide chemistry. Finally, this work opens the door to a single, non-cyanide, slightly acidic gold-tin solder plating process.

plating. Both agitation and increased bath temperatures proved to be beneficial in terms of increasing plating rates.

Gold-tin eutectic solders are commonly used in the optoelectronic and microelectronic industries for integrated chip or die bonding. Au-Sn solder is classified as a "hard solder" with superior mechanical and thermal properties relative to "soft solders", such as the Pb-Sn system. Au-Sn solder can be applied in a number of ways, *i.e.*, as a preform, solder paste, by sequential evaporation or sequential electrodeposition. Compared with solder preforms and pastes, evaporated solder is cleaner and provides more precise thickness and positional control. Thin film deposition technology, however, involves expensive vacuum systems and skilled operators.¹⁻³

Electroplating of Au-Sn eutectic solder is an attractive alternative in that it is a low cost process, offering the thickness and positional control of vacuum deposition techniques. Commercially available gold and tin baths are available for sequential electrodeposition onto gold seed layers.⁴⁻⁶ As an alternative, co-electrodeposition of gold and tin from a single solution offers the same economic advantage of sequential plating relative to vacuum deposition techniques, as well as the prospect of depositing the solder in a single step without oxidation of an outer tin layer or the formation of unwanted Au-Sn compounds during reflow (*e.g.*, AuSn₄). The deposited material from solution goes only onto the desired area, as delineated by a photoresist mask, and is therefore more efficient with regard to material consumption.

Co-electrodeposition of Au-Sn alloys generally involves cyanide-based solutions,^{7,8} which are desirable from a solution stability standpoint. They are however, incompatible with many photoresists employed in microelectronics and optoelectronics processing and present environmental issues. A non-cyanide electroplating solution has been developed for depositing Au-Sn alloys, over a range of compositions (15 to 50 at% Sn, including the 30 at% Sn eutectic composition) and thicknesses up to several microns, from a single solution.⁹⁻¹³ The deposit composition can be altered by varying the plating current density (Fig. 1).¹¹ The plating solution contains gold and tin chlo-

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Fig. 2—Solution lifetime tests under various storage conditions. Electroplating was performed for 90 min at $25^{\circ}C$ (77°F) at a current density of 0.24 A/dm² (2.23 A/ft²) with a pulsed current of 2 ms on and 8 ms off and no agitation.

ride salts (KAuCl₄ and SnCl₂ • H₂O), tri-ammonium citrate, ascorbic acid and sodium sulphite.^{9,10,12} Ammonium citrate is added as a buffer to maintain a slightly acidic solution pH. An acidic plating solution is more compatible with photoresist developers, although if the acidity is too high hydrogen evolution becomes a problem. Sodium sulfite acts as a complexing agent for the gold, and to some degree the tin, while ascorbic acid is used to prevent the hydrolysis of the tin in water. In the present work, the solution lifetime and the effect of processing parameters, such as agitation and temperature, on electroplating are studied. The overall goal is to develop a AuSn plating process suitable for commercial exploitation.

Experimental Procedure

The solution used for electroplating of Au-Sn solders was a weakly acidic, chloride-based solution, described above, composed of gold and tin salts, as well as a buffering agent and appropriate stabilizers.

The cathodes were silicon wafers, coated with Ti (25 nm)/Au (250 nm) blanket metallizations. Wafers were cleaved into small pieces, each exposing an opening $\sim 1 \text{ cm}^2$ ($\sim 0.16 \text{ in.}^2$) in area defined by stop-off lacquer. Platinum foil was used as the anode. The electroplating cells were set up with the cathodes facing the anodes spaced 20 mm (0.79 in.) apart. An overhead mechanical stirrer with a controllable speed was used to supply the agitation in the electroplating solution. The temperature of solution was controlled through a hot bath surrounding the electroplating tank, while a thermometer placed inside the electroplating solution continuously monitored the temperature.

Electroplating experiments were carried out under pulsed current (PC) conditions. The current density was varied from 0.20 to 0.24 A/dm² (1.86 to 2.23 A/ft²). This range of current densities should produce a deposit composition close to 50 at% Sn for plating done at room temperature with no agitation (Fig. 1).^{12,13} In the pulsed current mode, the on-time was set at 2 ms and the off-time at 8 ms, based on previous work.^{10,13} The current density was measured and frequently monitored using an oscilloscope and a 50- Ω resistor that was connected in series with the electroplating circuit.

The microstructural features of all the electrodeposited materials were examined in a scanning electron microscope (SEM),** equipped with an energy dispersive x-ray (EDX) spectroscopy system.*** An accelerating voltage of 20 kV was used for both imaging and composition analysis.



Fig. 3—The effect of solution agitation on deposit composition. Electroplating was conducted for 90 minutes at a current density of $0.22 \text{ A/dm}^2 (2.04 \text{ A/ft}^2)$ with a pulsed current of 2 ms on and 8 ms off, at 25°C (77°F).

Results & discussion Solution stability

Preliminary work carried out on the stability of the electroplating solution had shown that the lifetime was relatively long. However, the criterion used for stability was solution appearance, *i.e.*, color and clarity. It was shown that the plating solution remained clear and did not change color for up to 15 days.¹² In the present work, the decisive factor for stability was changed and the lifetime was defined based on useful plating lifetime. A series of solutions was produced and tested after storage. The results, plotted as deposit composition vs. storage time, are shown in Fig. 2. All plating was done at 0.24 A/dm² (2.23 A/ft²), which should have produced deposits containing approximately 50 at% Sn.12,13 The solutions were stable for up to three days, *i.e.*, deposit compositions were at or near 50 at% Sn. After three days the tin content in the deposits decreased steadily with storage time. Attempts were made to improve the stability by changing the storage conditions. Solutions were stored in the dark under both atmospheric and partial vacuum conditions. No improvement in stability was achieved (Fig. 2).

Effect of agitation

Agitation in the plating solution can be produced either by agitating the electrolyte or by moving the cathode.^{14,15} The former was chosen for this work in the form of an overhead stirrer. As is shown in Fig. 3, agitation had very little effect on deposit composition at low agitation rates. However, at high agitation rates the tin content in deposit decreased with increasing agitation rate. Furthermore, agitation increased the deposit roughness of the surface, although not markedly (Fig. 4).

The results in Fig. 3 can be easily explained. Agitation of the solution provided a fresh supply of metal salts or ions to the cathode and reduced the thickness of the diffusion layer. This facilitated replacement of the metal ions or complexes at the cathode surface, which in turn favored plating of the more noble metal (gold in this case).¹⁶ In the absence of agitation, the diffusion layer was wider and, as the noble metal deposited, the solution at the cathode surface became depleted in gold, because the gold was not quickly replenished. This paved the way for the incorporation of tin, which was present in the solution and accumulating near the cathode surface, into the deposit.

Agitation had the beneficial effect of increasing the plating rate. Depositions done at 25° C (77° F) show an increase in the plating rate by almost 70% for an agitation rate of 215 rpm compared with

^{**} Hitachi S-2700 SEM, Hitachi, Ltd., Japan.

^{***} Link eXL EDX system, Oxford Instruments, UK.



Fig. 4—SEM secondary electron (SE) images showing the effect of agitation on surface roughness. (a) No agitation and (b) agitation at 200 rpm. Electroplating was performed in both instances for 90 min in a pulsed current mode (2 ms on and 8 ms off) at a current density of 0.22 A/dm² (2.04 A/f^2).

a non-agitated solution. Higher agitation rates were not investigated, because of the corresponding decrease in deposit tin levels. Increased deposition rates have obvious practical implications. Faster deposition rates were again related to reductions in diffusion layer thickness, which enabled metal ions to be rapidly replenished at the cathode surface.

Other benefits of agitation include the sweeping away of bubbles, which may otherwise cause pits or porosity, and improved mixing of the solution, preventing settling of the heavier components towards the bottom of the tank. The net result is that agitation permits the use of higher current densities, because of higher limiting current densities.^{15,16}

Effect of temperature

The effect of temperature on deposit composition is shown in Fig. 5. The deposit composition remained approximately constant and then decreased with increasing temperature after about 35°C (95°F). Increasing the temperature also increased the surface roughness (Fig. 6).

The decrease in tin content with increasing temperature can be attributed to an increase in the oxidation rate of stannous tin (Sn^{+2}) to stannic tin (Sn^{+4}) , so that tin was not as readily incorporated into the deposit.^{14,15}

The electroplating rate can be improved by increasing the temperature. There is an approximately linear increase from 25 to 50° C (77 to 122° F) (2.3 times in this temperature range), which is



Fig. 5—The effect of solution temperature on deposit composition. Electroplating was conducted for 90 min at a current density of 0.24 A/dm^2 (2.23 A/ft^2) with a pulsed current of 2 ms on and 8 ms off. No agitation was employed.

interesting given that the tin content in the deposits drops significantly above 35° C (95°F). Even at 35°C there was a 32% increase in the plating rate.

In general, an increase in bath temperature caused an increase in the crystal size. The solubility of the metal salts increased, which in turn led to an increase in the conductivity of the solution. The mobility of the metal ions increased and the solution viscosity decreased, so that the diffusion layer was more rapidly replenished. This reduced the tendency toward treeing and also increased the current density obtained with a given voltage.¹⁴ These effects led to roughening of the surface of the deposit. The more rapid replenishment of the diffusion layer also increased the limiting current density, which contributed to the lower tin levels as the temperature was increased. There is an advantage to elevated temperatures, which is usually less adsorption of hydrogen in the deposits and less stress, reducing the tendency towards cracking.

The above findings show that the optimum conditions for electroplating of Au-Sn alloys are agitation of the electroplating solution in the 100 to 150 rpm range at slightly elevated temperatures (up to 35° C; 95° F). These moderate agitation and increased temperature conditions provide uniform deposits with increased deposition rates relative to deposits obtained at room temperature with no agitation.

Conclusions

The technical aspects of the electroplating process for deposition of Au-Sn solders were studied in the present work. The lifetime of the previously developed electroplating bath was found to be relatively short, *i.e.*, about three days. In addition, the effect of agitation on the electroplating deposit was investigated. Introducing agitation to the electroplating process is beneficial to some extent, *i.e.*, up to ~150 rpm. Beyond this amount the tin content in the deposit decreased steadily with increasing agitation. Increasing the solution temperature above 35°C (95°F) decreased the tin content in deposit. This finding was attributed to the oxidation of tin ions in the electroplating bath.

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Fig. 6—SEM SE images showing the effect of temperature on surface roughness. (a) $25^{\circ}C(77^{\circ}F)$ with no agitation and (b) $40^{\circ}C(104^{\circ}F)$ with no agitation. Electroplating was conducted in both instances for 90 min in a pulsed current mode (2 ms on and 8 ms off) at a current density of 0.24 A/dm² (2.23 A/ft²).

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