# Testing of Tin Plating
# By Use of a Rotating-cone Electrode

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**In this study of a tin electrolyte, the influence of additives, temperature variation and current density on the properties of the tin deposit were investigated by using a rotating-cone electrode (RCE). This type of electrode was used because of reproducible and controlled mass-transfer performance at fixed rotation speeds. The quality of the tin deposit depends on process parameters and electrolyte composition, and influences the reliability of the printed circuit board production process.**

In the process of etching surplus copper from printed circuit boards, electrochemically deposited tin is used as a protection layer on copper. For this purpose, a bright or semibright, ductile, nonporous tin layer with a thickness of 5-7 μm is used. The bright, nonporous tin layer prevents copper etching or partial copper etching in the hot etching ammoniacal copper(II) chloride solution. After the etching of surplus copper from a circuit board, tin is stripped away in hydrochloric acid solution with addition of copper(II) chloride and tin(II) chloride.

As a protection layer, electrochemically deposited bright tin is obtained from tin sulfate electrolyte with organic additives. Also, additives that include a brightening agent, a leveling agent (IRA) and a surface tension agent (AN 11)* are added to the tin electrolyte. The influence of additives on tin properties related to brightness, porosity and thickness distribution is considerable. During the operating time of the electrolyte, the additives are partly decomposed and partly incorporated into the tin deposit and must be renewed. The impurity level of the electrolyte with decomposed additives depends on electrochemical process conditions and the age of the electrolyte. The decomposed additives influence the quality and property of the tin layer. An analysis of tin and sulfuric acid is determined accurately by modern analytical techniques. An analysis of organic additives is very difficult, often polarography and cyclic voltammetry are used. The decomposed additives influence the accuracy of analysis and the usefulness of its performance. In practice, measurement with an angular cathode is used for testing the influence of additives on the quality of tin properties.

The disadvantage of an angular cathode is limited reproducibility because of uncontrolled hydrodynamic conditions and nonuniform current distribution on the cathode. The concentration of organic additives in the electrolyte throughout the elapsed A·hr and the square meters of boards produced must be calculated. In this study, the influence of additives, temperature and variation of current density on the properties of bright tin was investigated by using a rotating-cone electrode.

* Additives obtained from Dr. ing. M. Schlötter, Germany

## Electrolyte

The tin electrolyte is composed as follows: tin sulfate, sulfuric acid and additives (brightener, IRA agent and AN 11 agent). The amount of tin in the electrolyte influences the metal distribution on a circuit board. The amount of sulfuric acid must be optimized within a given range. An increase in sulfuric acid influences tin anode passivation, which must be avoided. The basic additive mixture is added for make-up of the electrolyte.

The amount of brightener is applicable to all current density areas. A gradual consumption of brightener is indicated by decreasing brightness in the low-current-density area. In larger surface areas, the lack of brightener causes dull deposits. Small overdoses of brightener cause dull, nonuniform and brown tin deposition and step plating in areas with good metal distribution. A large overdose of brightener might inhibit tin deposition completely. An overdose of brightener with larger surface areas causes burned deposits in high-current-density areas. On such surfaces, the tin deposit is dull and brown. Overdoses of brightener can be compensated with additions of the other additives.

The additives IRA and AN 11 have a supporting effect on the deposition of bright tin. Additive IRA is responsible for the bright throwing and leveling of the bath. Overdoses lead to decreasing brightness of the tin deposit. Additive AN 11 contains surface-active ingredients that stabilize operation of the electrolyte. Overdosage leads to decreasing brightness of the tin and a surplus of other additives.

## Experimental Procedure

Testing of the tin electrolyte was performed by using a rotating-cone electrode (RCE). Design of the electrode and the method of use are described in an earlier study.[1,2] The test arrangement for the RCE is shown in Fig. 1.

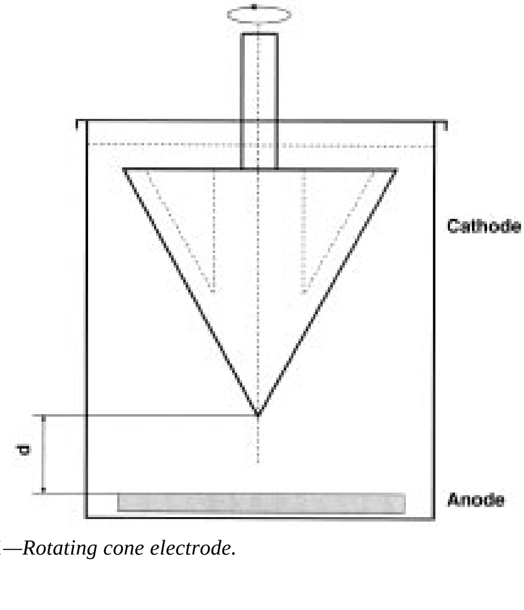


*Fig. 1—Rotating cone electrode.*

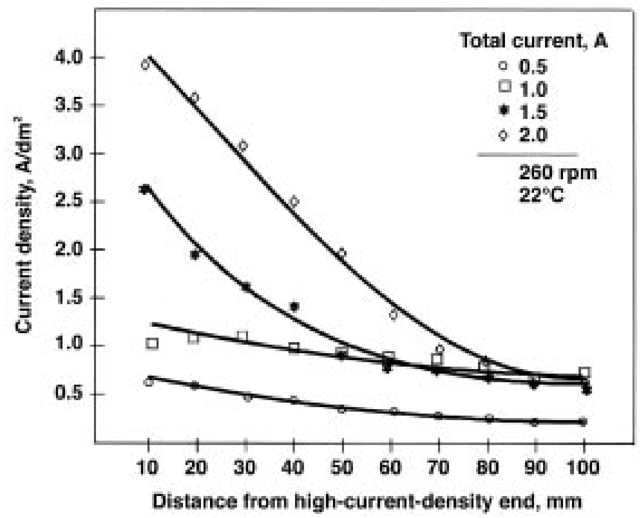


*Fig. 2—Dependence of current density distribution on distance from high-current-density end at various total currents.*

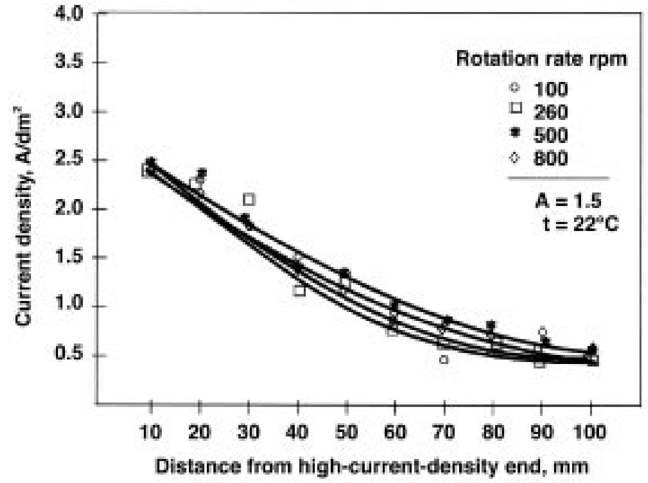


*Fig. 3—Dependence of current density distribution on distance from high-current-density end at various rotation speeds.*

Pretreatment of the RCE was as follows: The electrode was ground with 600-grit paper and polished with 3-µm diamond paste, degreased in hot alkaline solution, rinsed in deionized water and copper electroplated. Before each experiment, the electrode was activated in sulfuric acid solution and rinsed in deionized water. The anode was made of a tin disk placed at the bottom of the electrochemical cell. The distance between the tin anode and the tip of the rotating cone was 2.5 cm. Rotation rate of the cone was controllable.

Testing of current density distribution on the rotating electrode was carried out with total current variation from 0.5 to 2 A, at a rotation rate of 260 rpm. Investigation of current density distribution on the rotating cone was also performed at varied rotation rates of 100 to 800 rpm at a total current of 2 A. After plating, the copper deposit and tin layer were carefully peeled off the cone. The thickness of the tin deposit along the surface of the rotating cone was measured by beta-backscatter (source Pm, 1-6 µm). The current density distribution on the rotating electrode was calculated from copper thickness data, assuming 100 percent efficiency.

The test of the appearance of the tin coating at various temperatures (20 to 26 °C) was carried out with the following parameters:

Total current .......................................2 A
Rotation rate ............................. 260 rpm
Plating time ................................... 7 min
Anode-to-cathode distance ........... 2.5 cm

The electrolyte used to test current density distribution and appearance of tin coating at varied temperature was composed as follows:

$Sn^{+2}$ ............................................ 18.9 g/L
$H_2SO_4$ ...................................... 187.7 g/L
Basic additive ........................ 30.0 mL/L

The test of the appearance of tin coating with varied additives in electrolyte was performed with the following parameters:

Total current .......................................2 A
Rotation rate .............................. 260 rpm
Temperature .................................. 22 °C
Plating time ................................... 7 min
Anode-to-cathode distance ........... 2.5 cm

With these parameters, the current density distribution on the rotating cone was estimated as in the range of 0.7 to more than 6 A/dm².

The electrolyte used to test the appearance of the tin was composed as follows:

(a) New electrolyte
$Sn^{+2}$ ............................................ 24.7 g/L
$H_2SO_4$ ...................................... 186.4 g/L
Basic additive ......................... 30.0 mL/L
With other additives:
Brightener ......................... 0.5 to 3 mL/L
IRA ...................................... 1 to 3 mL/L
AN 11 ................................ 5 to 30 mL/L

(b) Used electrolyte
$Sn^{+2}$ ............................................ 21.2 g/L
$H_2SO_4$ ...................................... 193.1 g/L
With various additives:
Brightener .................... 0.5 to 2.5 mL/L
IRA .................................... 1 to 2 mL/L
AN 11 ................................ 4 to 8 mL/L

(c) Used electrolyte
$Sn^{+2}$ ............................................ 20.2 g/L
$H_2SO_4$ ......................................... 190 g/L
With various additives:
IRA .................................... 1 to 3 mL/L
AN 11 .............................. 4 to 16 mL/L

(d) Used electrolyte
$Sn^{+2}$ ............................................ 20.2 g/L
$H_2SO_4$ ......................................... 190 g/L
With various additives:
Brightener .......................... 1 to 2 mL/L
IRA .................................... 1 to 2 mL/L

## Results & Discussion

The results of this investigation of current density distribution on a rotating electrode are shown in Figs. 2 and 3. Figure 2 shows the current density distribution on the cone electrode as a function of distance from the high-current-density end to obtain total applied current. The data in the high-total-current range were assumed because the thickness of the deposit was out of measurable range (*i.e.*, > 6 µm). Figure 3 shows the current density distribution on the cone electrode as a function of rotation rate for the same total applied current and reveals very good reproducibility for the RCE.

| Temp, °C | Rotating cone electrode | Appearance |
|---|---|---|
| 20 | | dull<br>very bright |
| 23 | | dull<br>bright |
| 26 | | dull<br>bright |

*Fig. 4—Appearance of tin deposit on rotating cone at various temperatures.*

In Fig. 4, the influence of varied temperature on the appearance of the tin deposit is shown. With increased temperature, the bright appearance of the tin decreased in the high-current-density region. The results of testing the appearance of the tin deposit with various additives are shown in Figs. 5 to 8.

Figure 5 shows that the appearance of the tin coating from (a) [new electrolyte] depends on additive concentration and current distribution on the rotating cone. With increased brightener concentration (0.5 to 3 mL/L), bright and very bright tin in the high-current-density region was obtained. The varied concentrations of additives, IRA (1 to 3 mL/L) and AN 11 (5 to 30) mL/L affect the decreased bright appearance of tin in the high-current-density region. With overdoses of brightener, the bright area of tin in the high-current-density region is predominant. High concentrations of brightener (2 to 3 mL/L) shift the bright area to the low-current-density region.

| Brightener mL/L | Additive IRA mL/L | Additive AN 11 mL/L | Rotating cone electrode | Appearance |
|---|---|---|---|---|
| 0.5 | | | | dull<br>bright |
| 0.5 | 1.0 | 5.0 | | dull<br>bright |
| 1.0 | 1.0 | 5.0 | | dull<br>bright |
| 1.5 | 2.0 | 10.0 | | dull<br>bright |
| 2.0 | 2.0 | 20.0 | | dull<br>bright<br>very bright |
| 2.0 | 3.0 | 30.0 | | dull<br>very bright |
| 3.0 | 3.0 | 30.0 | | dull<br>bright<br>very bright |

*Fig. 5—Appearance of tin deposit on rotating cone at various levels of additives—brightener, IRA and AN 11.*

The appearance of the tin deposit on the rotating cone, from (b) [used electrolyte from the plating shop] with varied additives, is illustrated in Fig. 6. With increased brightener concentration (0.5 to 2.5 mL/L) a bright tin deposit in the high-current-density region is obtained. Very bright tin coating deposits are obtained over the whole area of the rotating cone at brightener concentration of 2.5 mL/L. The dull tin area on the rotating cone is decreased with increased concentration of brightener in the low-current-density region. The influence of additives IRA (1 to 2 mL/L) and AN 11 (4 to 8 mL/L) is shown in the low-current-density region on the rotating cone. The influence of additive IRA (2 mL/L ) on tin brightness distribution on the cone is clearly seen.

Figure 7 shows the appearance of the tin deposit from (c) [used electrolyte from the plating shop] with varied additives, IRA and AN 11. It can be seen that additives IRA (1 mL/L) and AN 11 (4 mL/L) increase tin brightness toward the low-current-density region. With increased additives concentration IRA (1 to 3 mL/L) and AN 11 (4 to 16 mL/L), the brightness of tin coating is decreased toward the high-current-density region.

Figure 8 shows the appearance of the tin deposit from (d) [used electrolyte from plating plant] with varied additives, brightener and IRA. With increased additives concentration, brightener (1 to 2 mL/L) and IRA (1 to 2 mL/L) increase tin brightness in the high-current-density region. In this case, we see the influence of both additives on tin brightness distributions in relationship to current density distribution on the rotating cone.

| Brightener mL/L | Additive IRA mL/L | Additive AN 11 mL/L | Rotating cone electrode | Appearance |
|---|---|---|---|---|
| 0.5 | | | | dull<br>very bright |
| 1.0 | | | | dull<br>bright<br>very bright |
| 1.5 | | | | dull<br>bright<br>very bright |
| 2.0 | | | | bright<br>very bright |
| 2.5 | | | | very bright |
| 2.5 | 1.0 | 4.0 | | bright<br>very bright |
| 2.5 | 2.0 | 8.0 | | bright<br>very bright |

*Fig. 6—Appearance of tin deposit on rotating cone at various levels of additives—brightener, IRA and AN 11.*

| Brightener mL/L | Additive IRA mL/L | Additive AN 11 mL/L | Rotating cone electrode | Appearance |
|---|---|---|---|---|
| | | | | dull * <br> bright |
| | 1.0 | 4.0 | | dull <br> bright |
| | 2.0 | 8.0 | | dull <br> bright |
| | 3.0 | 16.0 | | dull <br> semi bright <br> bright |

* used electrolyte

*Fig. 7—Appearance of tin deposit on rotating cone at various levels of additives IRA and AN 11.*

| Brightener mL/L | Additive IRA mL/L | Additive AN 11 mL/L | Rotating cone electrode | Appearance |
|---|---|---|---|---|
| | | | | dull * <br> bright |
| 1.0 | 1.0 | | | dull <br> semi bright <br> bright |
| 2.0 | 2.0 | | | bright <br> very bright |

* used electrolyte

*Fig. 8—Appearance of tin deposit on rotating cone at various levels of additives—brightener and IRA.*

Other results of this investigation show the influence of various brightener concentrations on increased tin brightness in the high-current-density region. At brightener concentration (2.5 mL/L), the tin layer is very bright in the whole current density region on the rotating cone. With used-electrolyte testing, a spiral on a dull rotating cone region was visible and it is presumed that the spiral is generated by electrode rotation. With increased quantities of additives IRA and AN 11, the influence of the brightener is decreased in the high-current-density region. Additive AN 11 blocks tin brightness in the whole current density region on the rotating cone. Additive IRA affects the distribution of tin brightness in the low-current-density region. Both additives, IRA and AN 11, exhibited strong influence on the distribution and inhibition of tin deposit brightness.

Uniform distribution of a tin deposit on a printed circuit board is influenced by difficult geometry of the board (*i.e.*, by the positions of soldering areas and connection holes. Non-uniform current density distribution on the board is influenced by the complex geometry of board and electrochemical cell arrangement. Deposition of bright tin with uniform thickness distribution depends on electrochemical and hydrodynamic parameters and electrolyte composition. Because of non-uniform current density distribution on a circuit board, a tin coating may be deposited with dull, bright and very bright appearance in different board areas. Dull regions on circuit boards are mainly soldering areas or holes with decreased thickness and porous tin coating. These regions are possible areas where copper can be attacked in the copper etching process. To solve this problem and to achieve a uniform thickness of bright tin, the electrochemical process parameters and electrolyte composition must be optimized.



## Conclusions

The concentration of additives in the tin electrolyte, the temperature and the current density distribution affect the appearance of bright tin coating, which is evident from the results. With increased addition of brightener in the electrolyte up to 2.5 mL/L, bright and very bright tin deposits in the high current density region are obtained. Addition of additive IRA affects the distribution of tin brightness in the low-current-density region and, together with additive AN 11, inhibits tin brightness in the whole current density region. With increased temperature of the electrolyte, the brightness of tin is decreased in the high-current-density region. The rotating cone electrode proved to be a very good tool for testing the influence of additives and the current density distribution on the appearance of the tin coating.

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## References

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