Effect of Organic Plating Additives Concentration on Carbon Content and Donor Density of Electroplated Tin

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Abstract. Pure tin is widely used as a replacement of Pb-Sn eutectic alloy as finish and solder material. This study aims to determine how the increasing concentration of organic plating additives affects the carbon content and donor density of electroplated Sn. Pure tin was electroplated on an Al sheet in a Hull cell using a commercial plating solution. Plating was performed in electrolyte baths with primary additive concentration from 100 mL/L to 600 mL/L, and with secondary additive concentration from 8 mL/L to 48 mL/L. Current densities of 15, 8 and 3 A/dm² were considered. The increased concentration of organic plating additives caused an increase in carbon content of the deposit from 5 wt.% C to 8 wt.%C. Mott-Schottky measurements showed increasing electron donor density of up to four orders of magnitude as a function of current density and carbon content. A higher current density during deposition causes the tin oxide film to reach the donor density saturation value at lower concentrations of organic plating additives. This suggests that current plays a role in the decomposition of organic additives, which results in the incorporation of carbon in the deposit.

1. Introduction
The search for a Pb-free alternative to the Pb-Sn eutectic alloy as solder material and surface finish in microelectronics applications has prompted the investigation of a wide range of alloys over the last three decades. This search is driven by the need for compliance with global and regional environmental regulations. [1] While pure Sn is an obvious alternative, whisker growth, void formation and corrosion of Sn finish under high temperature and high humidity conditions are among the reliability issues that the industry must address. [2]
After the application of the pure Sn layer, a thin and stable native oxide rapidly forms, which protects the Sn from further oxidation. Sometimes, however, the oxidation of Sn continues when exposed to high temperatures such as reflow processes. This runaway oxidation results to a yellow, blue, purple or brown color. [3,4] The discoloration becomes an indicator of poor wettability and solderability. [4]
This study aims to determine the effect of organic additives of a Sn electroplating bath and current density on the carbon content and donor density of the electroplated Sn.
The Mott-Schottky equation allows for the calculation of the donor density of a semiconductor. Changing the voltage of the semiconductor artificially, while it is in contact with an electrolyte, causes a change in the net charge in the semiconductor, the opposing charge formed by the electrolyte, and the thickness of the space charge region. This results in a change in capacitance as well. The change in the interfacial capacitance can be related to the applied bias potential using the Mott-Schottky equation:
\[ \frac{1}{C^2} = \frac{2}{\epsilon A^2 e N_D} \left( V - V_{fb} - \frac{k_B T}{e} \right) \]  

where \( C \) is the interfacial capacitance, \( A \) is the area, \( N_D \) is the number of donors per unit volume, \( V \) is the applied voltage, \( k_B \) is Boltzmann’s constant, \( T \) is absolute temperature, and \( e \) is the electronic charge. [5]

2. Methodology

2.1. Electroplating of pure Sn

Pure Sn was electroplated using a commercially available Solderon™ matte Sn electrolyte in a Hull cell. The composition of the plating solution was varied as shown in table 1. Pure Sn was used as the anode, while the cathode substrate was an aluminum plate. Prior to electroplating, the substrate was wiped clean with alcohol and washed with deionized water, and dipped in 50 g/L KOH for 2 minutes to activate the surface. It was given a final wash with deionized water prior to the start of electroplating. Electroplating was performed using a current of 3.0 A, at an average plating bath temperature of 47°C.

The plating bath has five components: Sn concentrate, acid, primary additive, secondary additive and RD concentrate. The primary additive is required to achieve smooth, uniform deposits. On the other hand the secondary additive is added to achieve uniform deposit thickness. The proprietary nature of the plating bath allows only admission that the primary and secondary additives are composed primarily of organic compounds. Lastly, the RD concentrate is added to minimize the oxidation of stannous tin. [6]

Table 1. Electroplating bath compositions with varying plating additives concentrations

| Organics Level | 1  | 2  | 3  | 4  | 5  | 6  |
|----------------|----|----|----|----|----|----|
| Tin            | 80 g/L |
| Acid           | 210 mL/L |
| Primary (mL/L) | 100 | 200 | 300 | 400 | 500 | 600 |
| Secondary (mL/L) | 8  | 16  | 24  | 32  | 40  | 48  |
| Concentrate    | 18 mL/L |

The Hull cell allowed for the simultaneous deposition at a range of current densities. Table 2 shows the current densities considered in this study.

Table 2. Electroplating current densities

| Current density (A/dm²) |         |
|-------------------------|---------|
| High                    | 15      |
| Medium                  | 8       |
| Low                     | 3       |
2.2. Carbon content determination

Samples for carbon content determination were prepared by cutting a 5mm by 5mm piece of electroplated Sn at the location corresponding to the desired current density. The samples were inspected using a JEOL JSM-6010LV Scanning Electron Microscope with Energy Dispersive X-Ray Analysis (SEM-EDX). Analysis was performed on three points of each sample, at accelerating voltages of 5 kV.

2.3. Donor density measurement

Donor density determinations using Mott-Schottky plots were conducted using a three-electrode setup attached to a potentionstat (Metrohm Autolab PGSTAT128N) controlled using the NOVA 2 software. The as-plated Sn samples were used as working electrodes (WE). A platinum electrode was used as the counter electrode (CE), while a Ag|AgCl equilibrated in saturated KCl solution was used as the reference electrode (RE). The working electrolyte was 3.5% NaCl solution that has been purged with pure nitrogen gas prior to electrochemical measurements. A Luggin capillary with diameter 1 mm was used as an electrolyte bridge between the WE and the RE. All experiments were done at room temperature.

Mott-Schottky plots for as-plated samples were generated from EIS measurements made from 100 kHz to 10 kHz, from 0.2V to 0.8V bias potentials at increments of 0.05V. At these frequencies, the measurements were determined to be in the charge transfer controlled regime.

3. Results and discussion

Figure 1 below shows the carbon content of as-plated Sn at the range of organic levels and three current densities, measured by EDX at 5kV. The carbon content of Sn deposited at low current density increases from about 5 wt.% at the lowest organics level setting to about 7 wt.% at the highest organics setting. On the other hand the carbon content of Sn deposited at medium current density increases from about 5 wt.% to 8 wt.% over the same range. The carbon content of Sn electroplated at high current density, however, shows no trend. This erratic behavior may be attributed to the roughness of the sample.

![Carbon Content of Electrodeposited Tin](image)

**Figure 1.** Carbon content of as-plated Sn, measured at 5kV.
The carbon content of 5 wt.% at the lowest organic level setting is about two orders of magnitude higher than the co-deposited carbon content that is quoted by the plating bath manufacturer for comparable bath compositions. If this is accurate, then the presence of excess carbon must be attributed to some other mechanism.

One study, upon observation of significant porosity in their electroplated Sn, suggested that the organic component of the plating bath may become trapped in the voids. They also point to this possibility as the cause of the eventual corrosion of reflowed Sn. [4]

The sulfonate-based Solderon plating bath may possibly degrade at a significant rate. The degradation of the sulfopropyl sulfonate additive in acid copper electroplating baths has been studied. Sulfopropyl sulfonate degrades in an-deaerated conditions, while the presence of the Cu(I) ion increases the decomposition rate. Even if the nominal concentrations of the additives are maintained, the presence of decomposition products of the additives affects the super filling capability of the bath. This may result in the presence of voids in the deposit, where organic molecules may become trapped. [7,8]

The depth profile of as-plated Sn in figure 2, taken using Time-of-Flight Secondary Ion Mass Spectrometry, supports this hypothesis.

![Figure 2. Secondary ion mass spectrometry depth profile of as-plated Sn, with estimated crater depth of 350 nm.](image)

Figure 2 shows that the distribution of carbon throughout the oxide and the metal suggests that carbon is included into the deposit throughout the electroplating process, and that the inclusion of carbon is not an occasional event.

Mott-Schottky measurements, which allow for the calculation of donor densities, were made only from 100kHz to 10kHz to minimize the measurement time and avoid unnecessary alterations on the sample. These frequencies were determined to be within charge transfer-controlled conditions. Figure 3 below shows an example Mott-Schottky plot.
Figure 3. Mott-Schottky Plot of as-plated Sn at organics level 4 and high current density from EIS measurements made at 100kHz.

The linear and sloping regions of the Mott-Schottky plots all have positive slopes, which is characteristic of n-type semiconductors. [5] Mott-Schottky plots could have allowed for the calculation of the donor density. However the composition of the oxide layer is not exactly known; it may be an intimate mixture of SnO and SnO$_2$, an outer film of SnO$_2$ covering SnO. [9,10] In this case the application of a dielectric constant is suspect. Thus figure 4 below shows comparative values of donor density across settings.

Figure 4. Comparative values of donor density of as-plated Sn measured at 100 kHz.
At high current density, increasing the organic additives concentration in the plating bath appears to have no effect on donor density of the oxide layer. At medium current density, the donor density increases with increasing organics level, reaching a plateau value at organics level 3. This plateau value appears to be equal to the single value of donor density observed at high current density. This suggests that increasing the organics level increases the donor density in the native oxide layer, up to a certain saturation point.

The continuous increase in donor density of low current density samples supports the existence of a saturation point. While the donor density does increase with increasing organics level, it does not quite reach the saturation point. The existence of a certain saturation point of donor density would be definite if the low current density samples were to reach saturation at some higher organics level. However it is not possible to further increase the concentration of organic plating additives beyond level 6. This might however be observable if a current density between 8A/dm² (medium) and 3A/dm² is selected.

As discussed in figure 1, increasing the organics level increases the carbon content of electroplated Sn. The increase in donor density may then be associated with the increase in carbon content. This suggests that a carbon-containing species, or perhaps carbon itself, acts as a dopant in the native tin oxide film.

Another noteworthy feature is that at every plating level before reaching saturation, the electron donor density is highest in samples deposited at high current density, and lowest in samples deposited at low current density. These trends are consistent with the way that the organic additives work to improve the characteristics of the plated deposit. Organic additives that are intended to help level the deposit should be adsorbed at regions of high current density. This corresponds to bumps or regions that are higher or thicker than the surrounding deposit. [8,11,12] Levelers, which have amine functional groups or aromatic rings, adsorb at regions of high current density. [13] This suggests that current plays a role in the decomposition of organic plating additives that results in the incorporation of carbon in the deposit.

4. Conclusions

The increased concentration of organic plating additives caused an increase in carbon content of the deposit from 5 wt.% C to 8 wt.% C. Mott–Schottky measurements showed increasing electron donor density of up to four orders of magnitude as a function of current density and carbon content. A higher current density during deposition causes the tin oxide film to reach the donor density saturation value at lower concentrations of organic plating additives. This suggests that current plays a role in the decomposition of organic additives, which results in the incorporation of carbon in the deposit.

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