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Electrochimica Acta 51 (2006) 3692–3698

ELECTROCHIMICA Acta

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# Composition control of tin–zinc deposits using experimental strategies

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Received 21 July 2005; received in revised form 17 October 2005; accepted 18 October 2005
Available online 28 November 2005

**Abstract**

The robust electroplating settings of a direct-current (dc) plating mode for the co-deposition of Sn–Zn deposits with their composition close to the eutectic point (i.e., Sn–9Zn) from the chloride solutions were achieved and investigated by using experimental strategies, including the fractional factorial design (FFD) and central composite design (CCD) coupled with the response surface methodology (RSM). The temperature of the plating bath, pH, and the metallic ion ratio (i.e., $Sn^{4+}/Zn^{2+}$ ratio) were found to be the key factors affecting the composition of Sn–Zn deposits in the FFD study. The effects of pH and temperature of the plating solution on the composition of Sn–Zn deposits were examined using a regression model in the CCD study. This model, represented as contour plots, showed that pH 5.0 and temperature = 78 °C were the robust electroplating settings for the co-deposition of the eutectic Sn–Zn alloys, which was independent of the substrates. In addition, based on the robust plating settings, the composition of Sn–Zn alloys could be precisely controlled and predicted by adjusting the composition of the plating baths. From the morphologies and crystalline information, the binary Sn–Zn deposits prepared in this work should belong to heterogeneous alloys.
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*Keywords:* Electroplating; Sn–Zn deposit; Eutectic point; Fractional factorial design; Central composite design

## 1. Introduction

The flip–chip bonding is one of various surface-mounting techniques in the integrated circuit (IC) assembly industry, which was developed to provide high-density interconnections between the chip and the substrate [1]. The flip–chip bonding process entails (1) disposing a plurality of solder bumps on the upper-surface of the die that is mounted directly to the substrate, (2) flipping the die and mating the solder bumps with the corresponding bonding Al pads located on the substrate, and (3) heating the die and the substrate in order to reflow the solder bumps. Each reflowed bump forms a bond between the die and the substrate, which functions as an electrical and physical contact.

In general, tin–lead (Sn–Pb) solder was widely used as the bump material for the flip–chip packaging applications [2–4], which was originally deposited by means of a vacuum evaporation technique developed by IBM [1]. However, a variety of new methods/processes were developed to form solder bumps, especially the electroplating process [4–6], in order to increase the density of interconnections. Recently, lead-free processes for electronic devices and components are required to address the environmental concerns and the alpha radiation of impurities of Pb [7–9]. In addition, the demand of Pb-free bumps rather than Sn–Pb solder becomes an urgent problem in the electronic assembly industry. Therefore, different types of Pb-free solder bump materials have been investigated, which are generally the tin-rich, eutectic alloys (e.g., Sn–Ag, Sn–Cu, Sn–Ag–Cu, Sn–Bi, Sn–Zn, etc.) [7–10]. Among these eutectic Sn-rich alloys, Sn–9Zn generally shows the advantages of a low reflowing temperature (an eutectic point of 198 °C), low cost, high wetting capability, good malleability, and a high anti-corrosive property. Accordingly, this work focuses on the electroplating and composition control of the Sn–Zn deposits with their composition close to the eutectic point.

Electroplating is recognized to be suitable for making the fine pitch bumps with high-speed deposition and high reliability [7,8,11,12]. In addition, this deposition technique attracts industrial considerations because of the low cost, the high throughput, and the deposition capability on almost any geometry [13]. Moreover, electroplating is a simple, one-step process for the fabrication of Sn–Pb solders for printed circuit boards, solder bumps, and lead-frame packages in the electronic applications.

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0013-4686/$ – see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2005.10.025

Accordingly, it is worthy being paid attention on the production of lead-free bump interconnections by means of the electroplating technologies [7,8,10–12].

According to Brenner's definition [14], the co-deposition of Sn–Zn alloys from the cyanide-based baths belongs to the alloy electroplating of the irregular type since the effects of the plating temperature and current density on the composition of Sn–Zn are irregular. In this work, however, cyanide is not employed and thus, the reaction mechanism is generally proposed as following:

$$SnO_3{}^{2-} + 3H_2O + 4e^- \rightarrow Sn + 6OH^- \quad (1)$$

$$ZnO_2{}^{2-} + 2H_2O + 2e^- \rightarrow Zn + 4OH^- \quad (2)$$

Based on the fact that Sn(II) is easily oxidized to Sn(IV) under air agitation in high-temperature plating solutions, a chloride-based Sn(IV) bath is employed in this work.

The experimental strategy is a sequential procedure to reach the optimal operation conditions of interest [15–20]. Based on this strategy, the response variable(s) (e.g., the Sn content in the Sn–Zn alloys) is a function of the quantitative control variables. Since the starting point of experimental conditions is usually remote from the optimum meanwhile there may be several key factors influencing the response(s) of interest, the fractional factorial design (FFD) is usually employed to efficiently find these key variables [15–17]. From the FFD, the response variable(s) against the key factors near the starting point in the system is simply fitted as a first-order model. After the FFD experiment, the methodology of the steepest ascent path is often used to approach the vicinity of the optimal conditions if the starting point of experimental conditions is really far from the optimum. Finally, the central composite design (CCD) is used to model the apparent curvature of response variable(s) against the key factors at the vicinity of optimum. Since mathematic models of the response variable(s) against the control variables can be represented as contour lines or a plane in graphs, this method is called a response surface methodology (RSM).

The purpose of this work is to identify the suitable electroplating conditions to produce Sn–Zn deposits with the composition close to the eutectic point (i.e., Sn–9Zn). The key variables affecting the composition of Sn (and Zn) in the Sn–Zn deposits were screened out by the FFD [15–17]. These variables were subjected to the CCD coupled with the RSM [15,16] to examine the relationship between the composition of Sn–Zn alloys and the plating variables around the optimal plating conditions of Sn–9Zn deposits. Finally, the proposed plating settings were applied to deposit Sn–9Zn alloys onto various substrates (i.e., Fe, Ni, and Cu) to demonstrate the robust property.

## 2. Experimental details

Tin–zinc deposits were electroplated onto commercially pure (99.5%) 1 cm × 2 cm copper plates or the Cu plates deposited with a thin film of either Fe or Ni. The copper plates were first cleaned with trichloroethylene, rinsed with pure water, and then, anodized at 30 mA/cm$^2$ in a 0.1 M NaOH solution for 5 min. After anodizing, the plates were cathodically polarized at 75 mA/cm$^2$ in another 0.1 M NaOH solution for 10 s, vibrated in an ultrasonic bath for 5 min, acid-cleaned with 5 M $H_2SO_4$ for 1 min. Finally, the Cu substrates were rinsed with pure water and vibrated in an ultrasonic bath for 5 min. For the substrates with Ni or Fe thin films (denoted as Ni/Cu and Fe/Cu, respectively), the pre-cleaned Cu substrate was vertically placed in a 500-ml jacket cell with a watts nickel bath (see Table 1) or a solution containing 0.5 M $FeSO_4{\cdot}7H_2O$ + 0.1 M $H_3BO_4$ with pH 2.0. The Cu substrate was surrounded with an anode of platinum-coated stainless steel mesh. After the electroplating of Ni or Fe at 60 mA/cm$^2$ for 5 min under 55 °C, the substrates were rinsed with pure water. These substrates were vertically placed in another 500-ml jacket cell surrounded with an anode of platinum-coated stainless steel mesh and electroplated with Sn–Zn deposits at 80 mA/cm$^2$ for 20 min. After the Sn–Zn deposition, these electrodes were rinsed with pure water and vibrated in an ultrasonic bath for 5 min.

Table 1
Composition and variables for the electroplating of a nickel film from a watts nickel bath

| Compounds/variables | Concentration/conditions |
|---|---|
| $NiSO_4{\cdot}6H_2O$ (mol/dm$^3$) | 1 |
| $NiCl_2{\cdot}6H_2O$ (mol/dm$^3$) | 0.2 |
| $H_3BO_3$ (mol/dm$^3$) | 0.5 |
| Temperature (°C) | 55 |
| pH[a] | 3.8 |
| Current density (mA/cm$^2$) | 60 |

[a] pH was adjusted by 1 M HCl or NaOH.

The plating bath mainly consisted of $SnCl_4{\cdot}nH_2O$, $ZnCl_2$, and $Ca(C_6H_{11}O_7)_2{\cdot}H_2O$ (0.1 M, complex agent) with pH being adjusted with 1 M HCl and 1 M NaOH. All solutions were prepared with pure water produced by a reagent water system (Milli-Q SP, Japan) at 18 MΩ cm and all reagents were Merck, GR. Solution temperature was maintained at the specified temperatures with an accuracy of 0.1 °C by means of a water thermostat (Haake DC3 and K20).

The average composition of all deposits was measured using an energy-dispersive X-ray (EDX) spectroscope with standards at five points coupled with a scanning electron microscope (SEM, JEOL JSM35). The mean error of this EDX analysis is ca. ±1.5 atomic percents (at%).

## 3. Results and discussion

### 3.1. Fractional factorial design

To efficiency find the key variables affecting the Sn (and Zn) content in the Sn–Zn deposits, the fractional factorial design is introduced to screen out these key variables. This experiment design can observe the influences of each preparation variable at a variety of other variable levels as well as the interactions among these variables on the composition of Sn (and Zn). Based on the literature review, the effects of the following electroplating variables were investigated in the FFD study: (A) pH of the plating solution, (B) total concentration of metal ions (M), (C) temperature of the plating solution (°C), (D) [$Sn^{4+}$]/[$Zn^{2+}$] molar ratio, and (E) agitation rate (rpm). Note that in our preliminary study, the effect of the current density on the composition of Sn–Zn

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