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Effects of hydroquinone and gelatin on the electrodeposition of Sn–Bi low temperature Pb-free solder

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ABSTRACT

The effects of an antioxidant, hydroquinone (HQ) and a grain refining additive, gelatin, on the electroplating characteristics of Sn–Bi alloys were investigated. Methane sulfonic acid (MSA) based plating baths with varying contents of additives were prepared and the electrochemical behavior of each bath was investigated. The combination of HQ and gelatin successfully reduces the deposition potential gap between the elements hence facilitates the co-deposition of Sn–Bi in this plating bath. Compact, adherent deposits could be obtained through the synergistic effects of these two additives. The electroplated Sn–Bi deposits showed a decrease in Bi content with increasing current density. Near eutectic Sn–60.75 wt.% Bi alloy was successfully deposited from the bath containing both HQ and gelatin at a current density of 18 mA cm^{-2}.

1. Introduction

The ever-rising demand for slim, light weight and high speed devices has prompted the development of fine pitch solder interconnections. The electrodeposition technique has outdone all other solder deposition techniques in the fabrication of fine geometry solder bumps due to its cost-effectiveness in mass production. Co-deposition of Sn–Pb solders has been quite successful in the past [1–4] which can be attributed to the small difference in standard reduction potential between the two elements (Sn^{2+}/Sn: −0.137 V and Pb^{2+}/Pb: −0.125 V; with respect to Standard Hydrogen Electrode (SHE)). However, legislations stamped out the usage of toxic Pb in electronic applications. This leads to extensive research on electrodeposition of alternative Pb-free solder systems. These systems are usually binary or ternary alloys of Sn containing Ag, Bi, Cu, and Zn. Among them, Sn–Ag–Cu alloys are recognized as the most promising candidate by the industry, due to their superior mechanical properties and solderability. However, this solder is not suitable for higher hierarchy level interconnections and heat-sensitive electronic components due to its high melting point (217 °C) that requires high operating temperature. A low melting temperature alloy is essential to meet such standards and Sn–58 wt.% Bi eutectic alloy can be a promising candidate [5–10].

With a low melting temperature of 138 °C, the applications of Sn–Bi solders are gaining considerable attention in the electronics industry. The advantages of Sn–Bi solder include good joint strength, excellent creep resistance, low coefficient of thermal expansion (1.5×10^{-5}/°C), good wettability, and low cost [6–11]. Attempts were made to co-deposit Sn–Bi solder in acidic baths due to the compatibility of acidic bath with photoresists [5–11]. However, the electrodeposition of Sn–Bi solder involves a few challenges. Firstly, exact eutectic composition is difficult to achieve due to the large potential difference between Sn and Bi (Sn^{2+}/Sn: −0.137 V and Bi^{3+}/Bi: +0.317 V; with respect to SHE). Secondly, oxidation of stannous ions in acidic medium degrades the stability of plating bath. The addition of electrolyte additives can significantly alleviate these two issues, but the complexity of the plating bath and the process will further increase.

The sulfuric acid bath containing polyoxyethylene laurylether (POELE) as an additive attempted by Fukuda et al. [11] resulted in Sn–3 wt.% Bi deposits. This bath is not suitable for Bi contents higher than 10 wt.% else there will be severe precipitation of Bi salt. Tsai et al. [9] electrodeposited Sn–70 wt.%Bi in a citric acid bath where ethylenediaminetetraacetic acid (EDTA) and polyethylene glycol (PEG) worked synergistically in reducing the deposition potential gap of Sn and Bi. The eutectic Sn–Bi alloy is successfully deposited from this plating bath by adjusting the EDTA concentration and plating current density [6,7]. Lee et al. [10] conducted the electroplating of Sn–Bi in methane sulfonic acid (MSA) bath. The additive used by Lee et al. [10] is not known but Sn–58.2 wt.% Bi was fabricated from their MSA-based plating bath.

In this work, a MSA-based plating bath containing $SnSO_4$ and Bi_2O_3 salts is investigated. The influences of hydroquinone (HQ) and gelatin on the electrodeposition of Sn–Bi solder are studied. The primary function of HQ is to inhibit Sn^{2+} oxidation. It is reported

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Table 1
Electroplating bath constituents and plating conditions for electrodeposition of Sn–Bi alloys.

Chemicals/parameters	Concentration/conditions
Methane sulfonic acid (CH_3SO_3H)	120 mL/L
Tin sulfate ($SnSO_4$)	30 g/L
Bismuth oxide (Bi_2O_3)	9 g/L
Hydroquinone (when added)	5 g/L
Gelatin (when added)	2 g/L
Current density	10–30 mA cm^{-2}
Magnetic stirring	100 rpm
Temperature	Room temperature (~25 °C)

that HQ can retain 48 out of 50 g/L of Sn^{2+} in a MSA-based plating bath [12]. Gelatin, a widely utilized leveling and grain refining agent in electrodeposition of metals and alloys, is known to improve the morphology of deposits through adsorption onto active growth sites [13–17]. The effects of both additives on deposition behavior (deposition potential, potential gap and hydrogen evolution), microstructure, and composition of Sn–Bi solder alloys are investigated.

2. Experimental

2.1. Electrodeposition

Sn–Bi deposits were electroplated onto 0.3 mm-thick 3 cm × 3 cm Cu sheets and Pt wire was used as anode. The Cu sheets were degreased with soap water, etched with 10% sulfuric acid for 20 s and rinsed thoroughly with distilled water prior to plating. The pre-treated substrates were vertically placed in a 300 mL single compartment cell. The composition of the MSA-based plating bath and electroplating conditions are shown in Table 1, which mainly consisted $SnSO_4$ and Bi_2O_3 with HQ and gelatin as additives. The pH of the solution is ~1. The direct current for electrodeposition was obtained from a DC power supply. The distance between electrodes was about 5 cm. Magnetic stirring of 100 rpm was applied during deposition to prevent gas bubbles from trapping on the cathode and promote mass transfer of metal ions. All experiments were conducted under atmospheric condition, except for one isolated experiment which required N_2 purging. After the deposition process, the plated substrates were removed immediately from the bath (within ~3 s after turning off the power supply) to avoid dissolution of deposits at open circuit potential. Post-deposition rinsing was done with running distilled water and the deposits are then dried with blower.

2.2. Characterization of plating bath and electrodeposits

Electrochemical polarization studies were performed on plating solutions with a potentio/galvanostat, PC14/300 (Gamry Instruments). All plating solutions were filtered prior to analyses carried out in a three-compartment cell. Pre-treated Cu sheets and Pt wire served as working and counter electrode respectively. An Ag/AgCl electrode was utilized as the reference electrode. The reference electrode was placed in a Luggin capillary to minimize errors due to *iR* drop across the electrolyte.

Surface morphology and cross-section of the electrodeposits were examined by a field-emission scanning electron microscope (FESEM). The average thicknesses of the Sn–Bi layers were measured on the FESEM micrographs of the cross-sectional samples using the analySIS software (Olympus). The software tool automatically highlights and measures the area of the selected layer. The average thickness of the layer was then obtained by dividing the area by the length of the layer. The average composition of the deposits was obtained by performing semi-quantitative energy dispersive X-ray spectroscope (EDX) analysis at 5 different locations on the surface of the deposits on areas measuring 60 μm × 60 μm. The melting temperature of the near-eutectic Sn–Bi deposit was obtained by differential scanning calorimetry (DSC). The crystallinity of Sn–Bi deposits was also characterized with X-ray diffraction (XRD).

3. Results and discussion

3.1. Effects of additives on cathodic polarizations

The reduction behavior of Sn ions in MSA-based plating baths investigated by potentiodynamic polarization measurements is shown in Fig. 1(a). The bath contained 120 mL/L of MSA and 30 g/L of $SnSO_4$. In the plating bath without additives, it is seen that the current density starts to increase at a potential of −410 mV, and reaches a maximum of −16.2 mA cm^{-2} at about −460 mV (Fig. 1(a)(i)). The current density then decreases to −9.4 mA cm^{-2} where a minor plateau is seen. The plateau is shortly replaced by a rapid increase of current density to very high values. The peak current density in all polarization curves is associated with the complete consumption of metal ions at the electrode surface [18–20]. On the other hand, the plateau corresponds to the limiting current density where the rate of deposition is controlled by the rate of transport of ions to the electrode surface [19,20]. The rapid increase in current density after the plateau is due to hydrogen evolution [5,9,13]. This statement is supported by the polarization curve of plain MSA solution (not shown here) where hydrogen evolution commences at −340 mV. The Sn deposition process has polarized the hydrogen evolution reaction to more negative potentials [6,9]. Vigorous formation of gas bubbles at the cathode was actually observed when the current density increased sharply, which confirms the evolution of hydrogen.

The HQ addition to the Sn–MSA plating bath decreases the peak current density to −13.0 mA cm^{-2}, while leaving its deposition potential unchanged (Fig. 1(a)(ii)). The addition of HQ also resulted in the elimination of the high current density "tail". Such reduction in current has been observed by others for the use of HQ in Sn deposition [20], as well as polyoxyethylenelaurylether (POELE) [21] and iso-octyl phenoxy polyethoxy ethanol (OPPE) [22] surfactants in Sn–Ag–Cu deposition. The decrease in peak current density with HQ addition could be due to: (1) the Sn deposition process being no longer diffusion limited, but limited by charge transfer; or (2) the adsorption of HQ on electrode surface causes the reduction in surface activity. The peak current-sweep rate relationships of Sn–MSA solutions with and without HQ were examined. The peak currents of both solutions (results not shown here) did not increase, but shifted towards more negative potentials when the sweep rate was increased from 5–80 mV s^{-1}. This suggests that the electrochemical reaction in both the Sn–MSA solutions (with and without HQ) is limited by charge transfer [23].

On the other hand, the HQ adsorption on electrode surface is examined by conducting an adsorption experiment with increasing concentration of HQ in the Sn–MSA plating bath. Fig. 1(b) shows that the peak current density decreases with increasing HQ concentration. The surface coverage θ, of the electrode surface is suggested to follow the equation [24,25]:

$$\theta = 1 - \frac{i_{add}}{i} \quad (1)$$

where i is the current density in the absence of HQ and i_{add} is the current density in the presence of a certain concentration of HQ. The coverage of the cathode surface increases from 0.212 to 0.417 when the concentration of HQ increased from 0.0125 M to 0.1 M. HQ molecules can adsorb on the electrode surface by either forming a surface film which acts as physical barrier; or interact with