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Electrodeposition and characterisation of Sn–Ag–Cu solder alloys for flip-chip interconnection

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ABSTRACT

A pyrophosphate and iodide based bath was investigated for the electrodeposition of near-eutectic Sn–Ag–Cu alloys, which are promising lead-free solder candidates for electronics interconnection. Near-eutectic Sn–Ag–Cu electrodeposits (2.5–4.2 wt.% Ag and 0.7–1.5 wt.% Cu) were achieved from the system as measured by wavelength dispersive X-ray spectroscopy (WDS). Electroplating such near-eutectic ternary alloys at higher deposition rates was possible with the application of electrolyte agitation. Different morphologies of deposited Sn–Ag–Cu films were analysed using scanning electron microscopy (SEM). X-ray diffraction (XRD) data indicated that Sn, Ag_3Sn and Cu_6Sn_5 were present in the "as-electrodeposited" Sn–Ag–Cu film. The microstructure of the deposits and the morphology of Ag_3Sn and Cu_6Sn_5 intermetallics were characterised from cross-sectional images produced from a focused ion beam scanning electron microscopy and then imaged from transmission electron microscopy (TEM) micrographs. The proposed bath proved capable of producing fine pitch near-eutectic Sn–Ag–Cu solder bumps as demonstrated on a glass test wafer.

1. Introduction

As the trend toward further miniaturisation of electronic products continues apace, packaging technology has progressed from the conventional wire and tape automated bonding to area array flip-chip bonding, which is able to provide increased input/output (I/O) counts and improved electrical performance. The advantages of this technology include high-density bonding, improved self-alignment, reliability and ease of manufacture [1]. One major step in the flip-chip interconnection process routes involves the deposition of, normally, solder alloys onto the bondpads of the chips (also known as solder bumping). Different solder bumping methods have been employed. Amongst popular technologies, evaporation, screen printing and electrodeposition are the mainstream in industry today. Evaporation is an expensive process and is typically less than 5% efficient, with more than 95% of the evaporated material ending up on the evaporator wall and on the metal mask. Screen printing technology remains the main production method because of its low cost and yield. However, as the density of patterns and the complexity of circuitry increase, the limitation of this method in feature size (down to 150 μm, although 300–400 μm is standard) has posed a great challenge for future applications. Therefore, flip-chip bumping by electrodeposition is attractive where features of high volume production and fine pitch bumping need to be addressed, and it achieves an overall high yield at reasonable cost [2,3].

With respect to the bumping materials, lead–tin based alloys were the most widely used solders for flip-chip applications, because of their low cost, low melting point, and excellent solderability properties. However, with world-wide legislation for the removal/reduction of lead and other hazardous materials from electrical and electronic products, development of a large number of lead-free, mostly tin-rich, alternative solders has been undertaken [4]. Typically containing more than 90 wt.% Sn, with a wide range of alloying elements such as Ag, Cu, In, Bi, Zn, these lead-free alternatives can be binary, ternary and even quaternary alloys, with variations in compositions. Amongst them, a family of solder alloys based on the ternary Sn–Ag–Cu (SAC) eutectic ($T_{\text{eut.}} = 217\,^{\circ}\text{C}$) composition have emerged with the most potential for broad use across the industry. Sn–Ag–Cu solders can promote enhanced joint strength and creep and thermal fatigue resistance, and permit increased operating temperatures for advanced electronic systems and devices [5,6]. However, the preferred (typically near-eutectic) Sn–Ag–Cu alloy composition is still in debate. In Japan Sn–3.0 wt.%Ag–0.5 wt.%Cu is favoured (Japan Electronics and Information Technology Industries Association, JEITA), in Europe Sn–3.8 wt.%Ag–0.7 wt.%Cu (the IDEALS project funded by European Consortium, BRITE-EURAM) and in US Sn–3.9 wt.%Ag–0.6 wt.%Cu (National Electronics Man-

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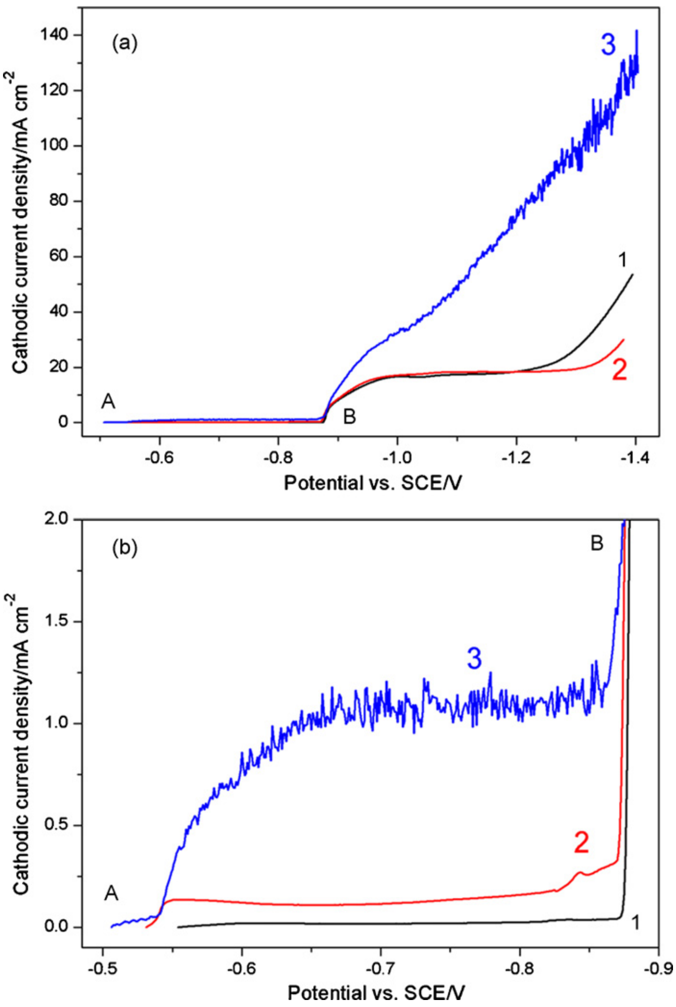

Fig. 1. Cathodic potentiodynamic polarisation curves for the deposition of tin–silver–copper alloys: (a) overall range of scans; (b) magnified initial part of scans from “A” to “B”. Curve 1, from a bath of constituents in Table 1 but without Ag (AgI) and Cu ($Cu_2P_2O_7$); Curve 2, bath constituents as outlined in Table 1; Curve 3, bath constituents as outlined in Table 1, plus applying agitation by magnetic stirring at 300 rpm. Potential scan rate 1 mV s^{-1}.

ufacturing Initiative, NEMI), whilst in general, most proposed compositions fall in the range of Sn3.0–4.1 wt.%Ag0.5–0.9 wt.%Cu [7].

In general, the electrodeposition of alternative lead-free solder alloys has been extensively pursued [8–10]. However, due to the relatively large gap in standard electrochemical reduction potentials between Ag/Ag^+, Cu/Cu^{2+}, and Sn/Sn^{2+}, it is difficult to co-deposit ternary Sn–Ag–Cu alloys in one single bath, with precise control over the properties of deposits such as composition and microstructure. Therefore relatively little has been carried out on the electrodeposition of eutectic and near-eutectic Sn–Ag–Cu solder alloys [11–13]. Moreover, stability of electroplating baths is another challenge that has to be faced when electroplating tin and tin alloys, as solutions of tin (Sn^{2+}) are readily oxidised by atmospheric oxygen to Sn^{4+} ions, which tend to precipitate as hydroxides [14]. Also, in the presence of cupric ions, the oxidation of Sn^{2+} is catalytically accelerated, with the reaction mechanism described by Murray and Furman in the equations below [15]:

$$Sn^{2+} + 2Cu^{2+} \rightarrow Sn^{4+} + 2Cu^{+} \qquad (1)$$

$$2Cu^{+} + 2H^{+} + O_2 \rightarrow 2Cu^{2+} + H_2O_2 \qquad (2)$$

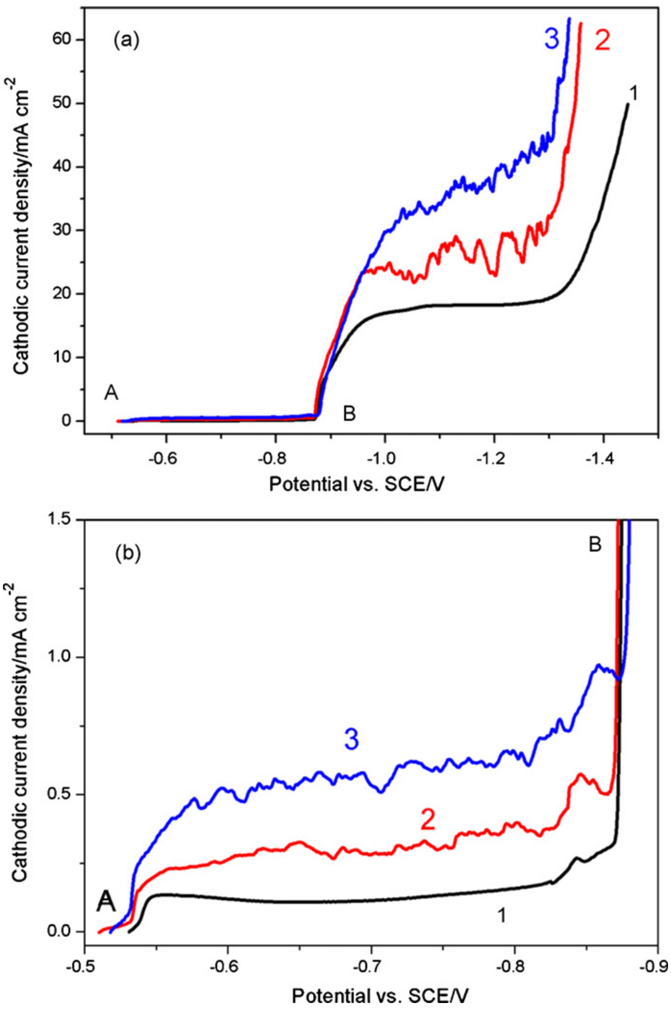

Fig. 2. The effects of bath temperature on cathodic potentiodynamic polarisations for the deposition of tin–silver–copper alloys using the bath in Table 1: (a) overall range of scans; (b) magnified initial part of scans from “A” to “B”. Bath temperatures: curves 1, 2 and 3 = 20, 40 and 60 °C. Potential scan rate 1 mV s^{-1}, no agitation.

Consequently, it is reported that the widely used methane sulphonate based electroplating baths for tin alloys tend to show a relatively unsatisfactory stability. Joseph and Phatak tried to enhance the stability of methane sulphonate electroplating baths for Sn–Ag–Cu alloys with the addition of organic additives, but still only one-week shelf-life was achieved compared with less than 2 h without additives [12]. However, pyrophosphate based electrolyte has been found stable for Sn^{2+} containing solutions because of the complexation of tin ions [16]. The combination of pyrophosphate and iodide in the present study also gives the advantage of bringing closer the deposition potentials for Ag and Sn to realise co-deposition of the alloy. There have been studies exploring the electrodeposition of tin-based alloys using pyrophosphate electrolytes [17,18] nonetheless, few have been applied to the ternary Sn–Ag–Cu system. Meanwhile, there is inadequate fundamental understanding of the Sn–Ag–Cu electrodeposits through in-depth analytical characterisations. Therefore, it is important to further elaborate the electrochemical process and enable precise control to achieve the desired electrodeposits in compositional and microstructural terms.

The purpose of this study was to develop an electroplating bath and process that was capable of producing dendrite-free, near-eutectic Sn–Ag–Cu alloys, using pyrophosphate based electrolytes for lead-free bumping applications. Within this study,