Development and Characterization of Electrodeposited Tin-Indium Alloy Microbumps for Low Temperature Assembly

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***Abstract*— The newly developed tin-indium (Sn-In) electrolyte enables the electrochemical deposition of eutectic and near-eutectic Sn-In alloys containing 45-55 wt.% indium. The reflow process was successfully conducted at temperatures below 150˚C, approaching the eutectic melting point of Sn-In and remaining lower than the melting temperature of pure indium. Additionally, the results of the preliminary bonding tests are presented, demonstrating the potential of this electrolyte for low-temperature assembly applications.**

Keywords— electrodeposition, tin-indium alloy, low-temperature compound, reflow, bonding

I. INTRODUCTION

Recently, tin-indium alloys have attracted significant attention as promising low-melting eutectic materials for interconnection technology in cryogenic applications such as image sensors and quantum computing where stability of solder at cryogenic temperature is required and low thermal budget applications such as DRAM. The melting point of the tin-indium alloys containing 50 wt. % indium ranges between 117-120 ºC [1]. Electrodeposition of indium-tin alloys has been explored using various acidic and alkaline electrolytes [2-11]. However, previous research has shown that these electrolytes were unstable and failed to achieve the necessary indium content for eutectic coatings. Additionally, they exhibited low cathodic efficiency and poor compositional uniformity. A common issue with these electrolytes is the strong oxidation of Sn^{2+},which leads to non-reproducible results [3, 6-8]. To address these challenges, a newly developed tin-indium electrolyte, formulated with eco-friendly compounds, offers improved stability within a working pH range of 2.4 - 2.7. The metal salts used include indium (1-20 g/l) and tin (2-20 g/l) methane-sulfonate compounds. This electrolyte demonstrates high cathodic efficiency and is compatible with various anode materials, such as platinized titanium (Pt/Ti), mixed metal oxide (MMO), and soluble indium anodes.

One of the major challenges in advanced packaging today is achieving a low thermal budget, not only in the soldering process but also in the bonding of vertical interconnections. The ideal bonding process should occur at temperatures less than 180 ºC and under pressures less than 2 MPa, without requiring additional complex process steps such as polishing or ultrahigh vacuum conditions [12,13]. It is important to note that the tin-indium electrolyte is compatible with different types of organic resist. Within a current density range of 1.0-1.5 A/dm², the eutectic composition of the alloy can be achieved with a deposit thickness between 2-5 µm on a wide range of structure types and dimensions.

Reflow under flux-free conditions has been demonstrated by Heikkinen et al. [14], where the tin-indium eutectic was successfully obtained through layer-by-layer deposition from separate tin and indium electrolytes.

An important consideration during the soldering process is the formation of intermetallic compounds. A nickel sublayer is commonly used as a diffusion barrier following copper electroplating. According to the phase diagrams of nickel-tin [15] and nickel-indium [16] systems, the likelihood of intermetallic formation is high within the temperature range of 130-170 ºC. However, the presence and characteristics of these compounds for tin-indium alloys over nickel remain insufficiently studied.

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Ruthenium presents an alternative diffusion barrier with favorable properties [17]. The phase diagrams of nickel-ruthenium and copper-ruthenium systems indicate the absence of intermetallic compound formation up to 500 ºC, making ruthenium a strong candidate for such applications.

The primary objectives of this research are twofold: first, to demonstrate the capability of the newly developed tin-indium electrolyte to deposit eutectic alloys on structures of carrying sizes with different diffusion barriers, and second, to determine the optimal reflow and bonding conditions for the tin-indium eutectic alloy.

II. RESULTS AND DISCUSSION

Tin-indium alloy deposits with a thickness of 5um and varying concentrations of alloying components were electrodeposited onto a brass substrate using current densities ranging from 0.75 to 1.5 A/dm^2. The alloy deposition is of regular type, according to Brenner [18]. The solidus and liquidus temperatures of these layers were investigated, revealing that the melting points of the electrodeposited alloys closely matched the melting curve of their metallurgically produced counterparts. Minor deviations of approximately 2-3 ºC were observed at a tin content of 52 wt.%, suggesting that the eutectic melting point should be expected around 120 ºC.

Fig. 1a (inset) displays the morphology of the plated tin-indium layer with a measured indium content of 50 wt.% deposited onto a structured substrate. The coatings typically exhibited large crystal formations.

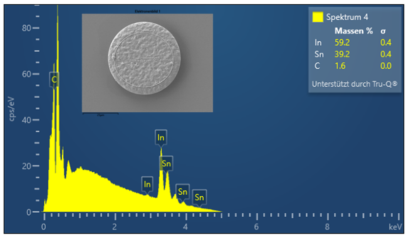

Fig. 1(a)

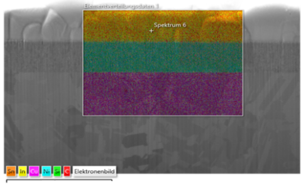

Fig. 1(b)

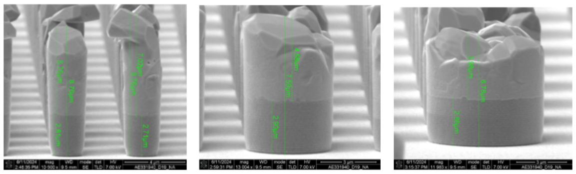

Fig. 1(c)

Fig. 1 (a) Tin-indium layer – morphology and composition; (b) Cross-section of the tin-indium layer (2.5um thick) deposited onto a nickel sublayer; (c) Tin-indium layer deposited onto wafer structures. Deposition was performed at 1.2 A/dm^2 and 40 ºC.

A cross-section of the tin-indium layer deposited onto nickel sublayer is shown in Fig. 1b while Fig. 1c shows the morphology of the alloy layer deposited onto wafer with various structure dimensions, all containing 48-52 wt.% of indium.

To investigate the formation of intermetallic compounds, a pure indium layer was electrodeposited onto a nickel sublayer. Fig. 2a shows the morphology of the as-plated indium layer, while Fig. 2b illustrates the layer after annealing at 180 ºC (above the melting point of pure indium, 156 ºC) for 3 minutes in a nitrogen atmosphere. Prior to annealing, the sample was dipped in 3% HCl for 30 seconds to remove surface oxides, following the procedure described by Kozlowski et al. [19]. Elemental mapping of the nickel/indium interface (Fig. 2c) confirmed the formation of intermetallic compounds post annealing.

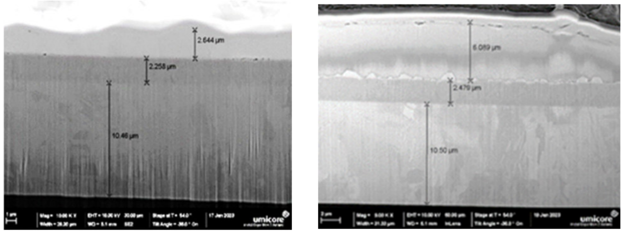

Fig. 2(a)

Fig. 2(b)

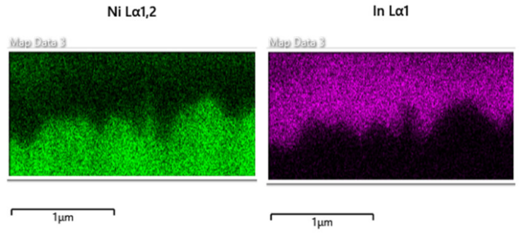

Fig. 2(c)

Fig. 2 (a) Cross-section of the as-plated 2.5 um indium layer on nickel; (b) Indium layer after annealing at 180 ºC for 3 minutes in a nitrogen atmosphere, forming a hemispherical structure post HCl dipping; (c) Elemental mapping of the nickel/indium interface from fig. 2b.

In Fig. 2, intermetallic compound formation was evident with pure indium deposits on a nickel sublayer and was confirmed by elemental mapping.

It is important to note, that the deposition of pure indium onto the ruthenium sublayer was unsuccessful, likely due to adhesion issues. However, electrodeposition of a tin-indium alloy layer containing 45 – 60 wt.% indium was successfully demonstrated on a thin electroplated ruthenium sublayer.

Fig. 3 shows cross–sections of the tin-indium alloy after annealing. The samples were annealed at 140 ºC for 10 minutes in a nitrogen atmosphere following a predip in 3% HCl to remove surface oxides, similar to the pure indium samples. Fig. 3a shows the alloy deposited onto a nickel sublayer, while Fig. 3b illustrates the same alloy deposited onto a ruthenium sublayer.

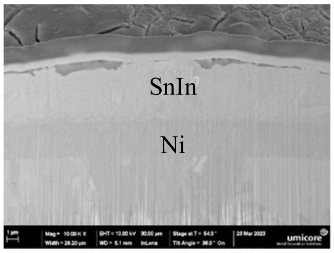

Fig. 3(a)

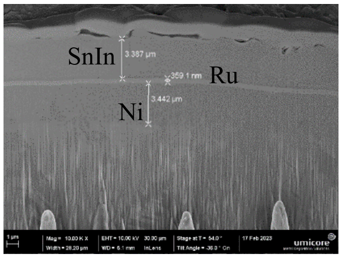

Fig. 3(b)

Fig. 3 Cross-sections of tin-indium alloy layers deposited onto different sublayers: (a) Nickel and (b) Ruthenium. The nickel layer was 2.5um thick, the ruthenium sublayer was 300nm, and the tin-indium alloy was 3 um.

No adhesion issues were observed before or after annealing. In the samples with direct tin-indium deposition onto nickel, slight interdiffusion was detected post-annealing. In contrast, no interdiffusion was observed when using the ruthenium sublayer.

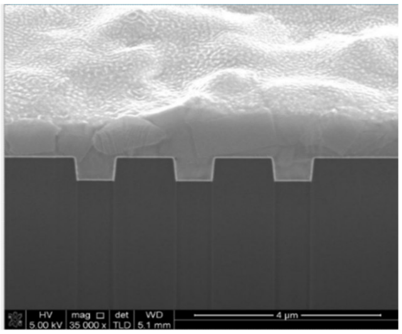

Fig. 4

Fig. 4 2 um-thick tin-indium alloy deposited onto a ruthenium sublayer applied via PVD.

Fig. 4 shows the morphology of the deposited tin-indium alloy (45 wt. % indium) onto Ruthenium layer (48 nm thickness applied with a PVD process).

To optimize the reflow process, additional experiments were performed using a flux and varying annealing profiles. Fig. 5 shows the reflowed tin-indium alloy (same structure as in Fig. 1c) after processing under a nitrogen atmosphere for 5 minutes at 150 ⁰C. Scanning electron microscopy (SEM) confirmed a uniform appearance across the surface.

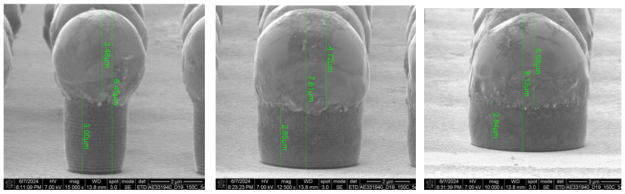

Fig. 5

Fig. 5 Reflowed tin-indium alloy structures at 150 ⁰C for 5 minutes with flux under a nitrogen atmosphere (same structures as in Fig. 1c).

One of the exciting possibilities of the deposited layer was to evaluate the bonding capabilities under low-temperature and low-pressure conditions. The bonding process was conducted on a test layout with 50 µm pillars and pitch, where the pillars were built with a 25 µm copper layer, a 2 µm nickel layer, and a 2 µm tin-indium alloy deposited at 1.5 A/dm² (approximately 40 wt.% indium). Two fluxed coupons (top: ~5x5 mm²; bottom: ~10x5 mm²) were bonded using a Finetech Femto2 Chipbonder under forces of 0.5, 1, and 2 N. The bonding profile is shown in Fig. 6.

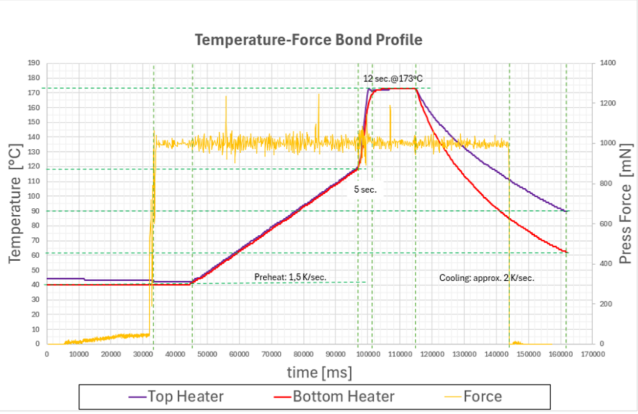

Fig. 6

Fig. 6 Bonding process profile, with an example using a 1 N bonding force. Total bonding time: ~120 seconds; time at bonding temperature: ~12 seconds.

Fig. 7a-d displays a continuous, defect-free tin-indium layer resulting from bonding two surfaces, each structured with copper/nickel/tin-indium sequences. EDX analysis of the bonded layer (Fig. 7d) confirmed uniform elemental distribution.

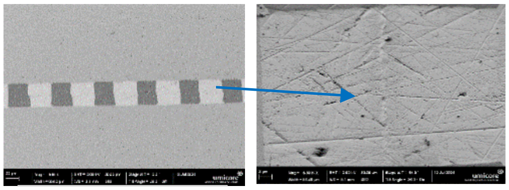
Fig. 7(a) Fig. 7(b)

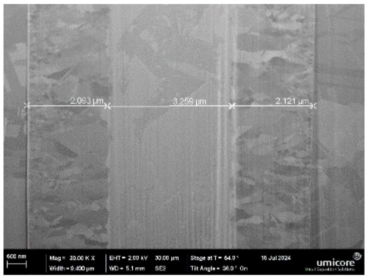

Fig. 7(c)

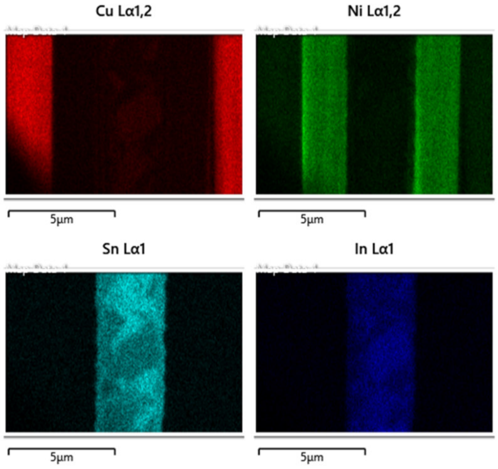

Fig. 7(d)

Fig. 7 Bonding results: (a-c) Different magnifications of the bonded pillar surfaces; (d) EDX analysis of the bonded layer from Fig. 7c.

Post-bonding, only the samples bonded under 0.5 N could be separated using a razor blade, while those bonded at 1 and 2 N remained intact, indicating strong adhesion. These promising results pave the way for future investigations into the physico-mechanical properties of the bonded surfaces.

III. CONCLUSION

The newly developed tin-indium electrolyte exhibits high stability, enabling the deposition of eutectic alloys containing 45–55 wt.% indium. A ruthenium layer can be applied as an interlayer between nickel and copper, with a thickness ranging from 50 to 500 nm, effectively serving as a diffusion barrier for subsequent tin-indium layers.

The reflow process was successfully completed within 5 minutes at 150 °C under a nitrogen atmosphere, demonstrating the suitability of the electrolyte for low-temperature assembly.

Additionally, bonding was achieved at a peak temperature of 173 °C for approximately 15 seconds in a nitrogen atmosphere, using a press force of 1–2 N. This process resulted in strong and reliable bonds, confirming the effectiveness of the electrolyte and bonding parameters for advanced packaging applications.

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