

High-Speed Indium Electrodeposition: Efficient, Reliable TIM Technology

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Abstract

A new indium electroplating process has been developed which provides pure indium deposits suitable as thermal interface materials (TIMs) for the electronic industry. The electrochemical plating solution is based on an acidic electrolyte with copolymer additives. Typical plating conditions are the following: pH 0.9-1.2, current density 0.5-20 ASD, temperature 30-60°C, metal ion concentration of 30-60g/l. The cathodic current density is higher than 95%. Uniform deposit thicknesses of a few microns up to several hundred microns can be achieved at a plating rate of 180 microns per hour at a current density of 10 ASD. The developed electrolyte works well with soluble and specialty insoluble anodes.

Adherent, void-free indium deposits were obtained on copper and nickel substrates. No special wetting layer is required. The pre-treatment of nickel substrates for a good adhesion of indium is also discussed.

The deposited indium melting point (156°C), its thermal conductivity (82 W/m•K) and thermal expansion data correspond favourably to literature values for the bulk metal.

Key words: Indium electrodeposition, TIM, thermal characterisation

Introduction

The industrial importance of indium is growing rapidly as indium has unique physical and chemical properties. It is a highly malleable, soft material with low melting point (156° C) and a high thermal conductivity (~82 W/mK). These properties enable indium to be used in a variety of electronics and related industries, such as in joining applications. For example, indium and its alloys may be applied as thermal interface materials (TIMs) [1,2,3,].

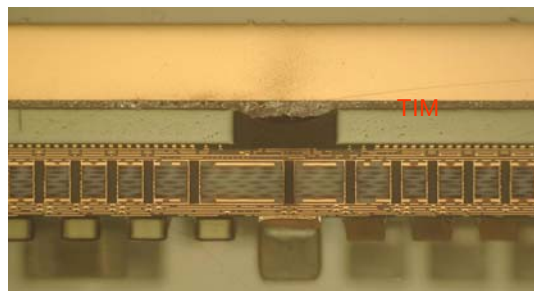


Figure 1. Cross section of a device utilizing indium-based TIMs [photo source: Prismark/Binghamton Univ]

TIMs are critical to protect electronic devices such as integrated circuits (ICs) active semiconductor devices, and microprocessors, from exceeding their operational temperature limit. They enable bonding of the heat generating device (e.g. chip) to a heat sink or a heat spreader (e.g. copper and aluminum components) without creating an excessive thermal barrier.

Besides the low melting point and high thermal conductivity of indium, a variety of other properties are also important. For example: an ability to relax thermal expansion stresses when joining two materials, an ability to form void free, micro-crack free joint that is stable during thermal cycling [4,5], insensitivity to moisture and temperature changes, manufacturing feasibility and cost.

Current technology applies pre-formed films of indium, but handling, and fluxing steps suffer from the purity and interfacial shortcomings of a foil-based technology.

One alternative to pre-formed films is the electrolytic deposition of indium which produces high purity indium deposits with good interfacial characteristics suitable for use in thermal management applications.

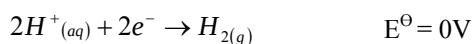
Several trials were conducted to plate pure indium from alkaline and acidic media [6,7,8,9], but very few electroplating baths are commercially available, which do not have a high metal content and low plating rate. Our new plating technology overcomes these disadvantages and offers higher speed, better throwing power, and reliable plated finishes.

Results and discussion

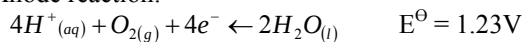
1. Development of a new indium plating bath

Electrochemical deposition of indium metal is challenging because indium metal deposition occurs simultaneously with hydrogen evolution from the electrolysis of water. The electrochemical reactions during electro-deposition in acidic plating solution are as follows:

Cathode reactions:



Anode reaction:



The Nernst potential of hydrogen ($E^\ominus$) is more positive than the indium Nernst potential. This means that indium electrodeposition is accompanied by simultaneous hydrogen generation at the cathode surface. The evolution of hydrogen compromises cathodic current efficiency, resulting in low indium metal deposition rates as well as undesirable rough and powdery indium metal deposits or in some cases no indium deposition at all. Corresponding additive agents are required in order to obtain quality deposits and hinder the hydrogen gas formation at the cathode.

The effect of additives can be easily recognized by cathodic polarization measurements. In acidic electrolytes without additives or in the presence of ineffective additives, hydrogen evolution occurs prior to indium deposition, as seen in the following figure.

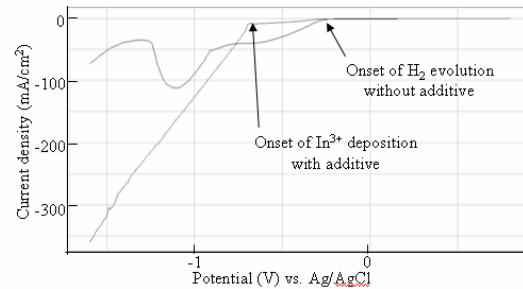


Figure 2. The onset of hydrogen generation without additive or inactive additive and the onset of metal deposition in presence of adequate additive.

By applying adequate hydrogen suppressors, the indium deposition takes place and the sharp cathodic current corresponds to metal deposition. Figure 3 shows the surface of indium deposit with and without adequate additive.

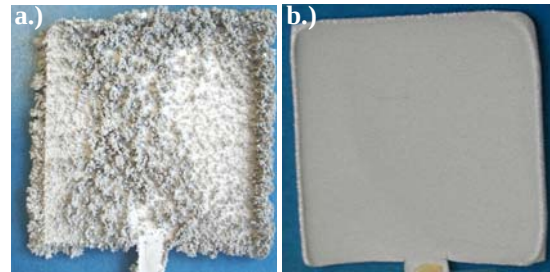


Figure 3. a.) Represents a rough, poor quality indium deposit, while b.) shows a smooth, uniform deposit plated with the newly developed indium plating process.

Our newly developed indium plating solution includes an acidic electrolyte with copolymer additive. The formulation includes a proprietary copolymer as a hydrogen gas suppressor. The process is operated with indium anodes, deposits a stable composition, and has both a broad operating window and high cathode efficiency (>95%). The cyclic voltammogram shows an ideal curve for indium deposition in the presence of the copolymer additives.

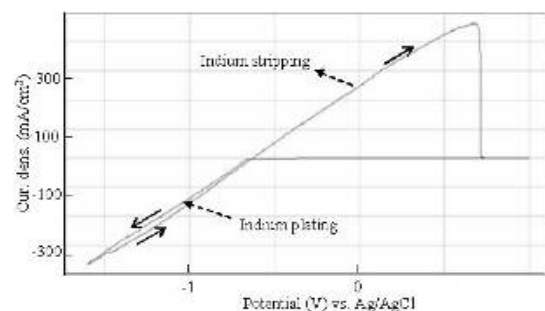


Figure 4. Cyclic voltammogram of indium electrodeposition and stripping peak, solution pH=1.1, 30 g/l indium metal content with copolymers.

Table 1 summarizes the parameters for the new indium bath and provides optimal conditions for high speed indium plating.

Table 1. Parameters for plating

Parameter	Range
Indium metal	30 – 70 g/l
pH	0.9 – 1.2
Temperature	35 – 70°C
Cathodic CD	1 – 20 ASD
Cathode efficiency	95 – 100%
Deposit. rate	5.8 $\mu\text{m}/\text{min}$ at 18ASD

Tests with standard platinized titanium anodes resulted in the decomposition of the additives and non-uniform deposits. However, good results were obtained with shielded insoluble anodes from METAKEM [10]. These new types of anodes are coated with mixed metal oxide, and the active anode surface is covered with double titanium shielding. This configuration hindered additive decomposition. Attention has to be paid to a rise in specific gravity due to the accumulation of counter ions after indium replenishment. A rise in specific gravity may result in indium deposits with undesirable morphology, i.e., pores, dull and rough surface, and a non-uniform thickness.

The SEM image (Fig. 5) shows the surface morphology of the plated indium deposit. The deposit has a crystalline structure with crystallites roughly 20-30 μm in size.

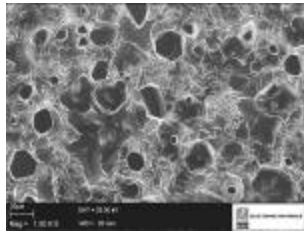


Figure 5. Electron micrograph of the 25 micron thick indium deposit, magnification 1.5Kx

The crystallographic texture of the deposited indium was examined using a Philips X'pert Pro XRD with a Cu K α source. The deposits show a preferred [101] orientation (Fig. 6).

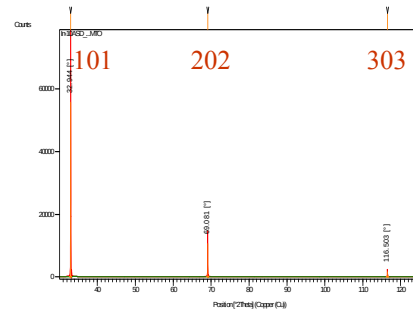


Figure 6. Crystallographic texture of the deposited indium

2. Reliability and thermal characterization of plated indium layers

A steady state method was used to determine the thermal conductivity across the surface of the indium deposit. The heat flux through the sample was compared to a reference sample and the temperature was measured with thermocouples. The effective thermal conductivity of the indium layer was measured at 81.6 W/mK which corresponds to the literature value for pure indium.

A high lateral accuracy and resolution wirebondor was used to determine the coefficient of thermal expansion (CTE) of indium deposits. The measured value, $33 \cdot 10^{-6} / \text{K}$, coincides with the literature value for bulk indium. These results demonstrate that the plated indium layer has a high purity; melting point and carbon impurity analyses confirm these findings.

For TIM applications, apart from thickness of the indium layer, indium homogeneity, surface roughness thermal conductivity and CTE, the substrate-indium interface, has a profound effect on the reliability performance of the whole package.

In order to obtain a void-free interface, good wetting of indium to the substrate (Ni coated heat spreader) is required. An adhesion layer of thin gold is generally used with foil technology [3]. Gold facilitates wetting, while nickel serves as a barrier layer to diffusion. It was found that the gold layer dissolves in indium and forms a brittle intermetallic which causes cracking and voiding upon thermal cycling [4].

We are able to form an excellent interface directly on a special Ni layer. Our investigation focused on studying the In-Ni interface when plating a thin Ni-strike on Ni coated lids. The Ni-strike plating bath is an acidic electrolyte which activates the nickel surface, establishing excellent adhesion at the interface between the nickel and indium layers. The effect of the applied current density and layer thickness of the Ni-strike was examined. The results show that low plating rate and short plating time gives continuous coverage. Due to smearing

of indium and its IMCs during traditional cross-sectioning polishing, the interface was examined as indium was etched away from the surface. Figure 7a, b represent the IMC structure when different current densities in the Ni-strike were applied.

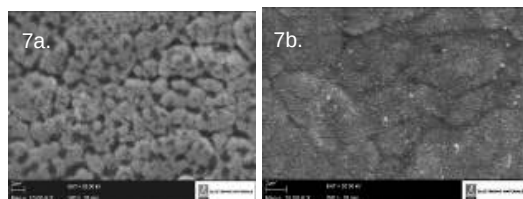


Figure 7. Top view of the sample, indium etched away from the surface (a) In-Ni IMC when 15ASD current density was applied in Ni-strike (~65 nm thick Ni film); (b) In-Ni IMC when 3ASD current density was applied in Ni-strike (~15 nm thick Ni film)

The pores seen in the photomicrographs of Figure 7a are due to discontinuous Ni-strike coverage, which is assigned to intense hydrogen generation during the Ni-strike plating. Samples plated under the conditions stated in Figure 7b, show a smooth, uniform appearance. Identification of the IMC after indium plating was not possible, due to the low solubility of nickel in indium. As the samples were heated at 140°C, a very thin $\text{In}_{27}\text{Ni}_{10}$ intermetallic was formed, as the XRD pattern shows (Figure 8).

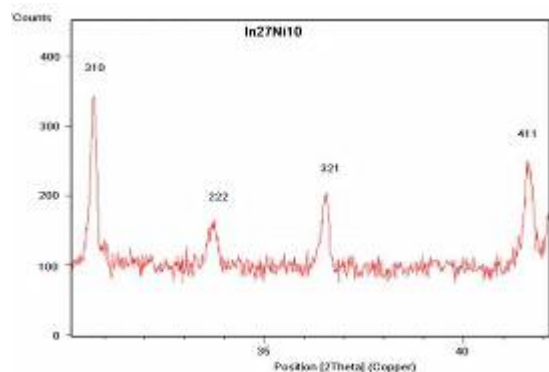


Figure 8. X-ray diffraction pattern shows the $\text{In}_{27}\text{Ni}_{10}$ intermetallic formed at the In-Ni interface

Focused-ion beam techniques were also used to investigate the interface. Figure 9 demonstrates a continuous crack-free In-Ni interface.

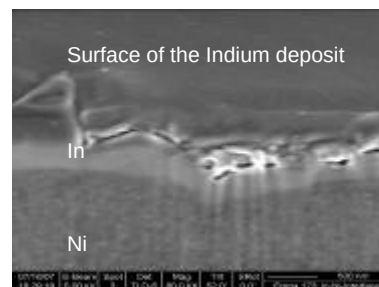


Figure 9. FIB cross sectioning demonstrating a continuous Ni-In interface

Conclusion

A new indium plating process with a broad operating window and high current efficiency (>95%) has been developed. The indium plating process operates with soluble or insoluble anodes up to $20\text{A}/\text{dm}^2$. Uniform deposits of a few microns up to several hundred micron thickness can be achieved at a plating rate of over 180 microns per hour.

The melting point, thermal conductivity and thermal expansion of plated deposits all have the characteristics of bulk indium. In addition we have demonstrated a reliable, void-free In-Ni interface.

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