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Effect of Oxidation on Indium Solderability

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The fluxless solderability of pure indium on gold-coated surfaces is investigated in this study using measurements of wetting angle and joint strength. This study focuses on the effects of indium's native oxides and those which form during heat treatment. The initial oxide thicknesses are obtained by heating indium samples at various temperatures, and then, during the reflow above the melting temperature, oxidation at the interface is either allowed in open air or prevented by reflowing in an inert environment. The testing results presented include characterization of indium oxide (In_2O_3), the effects of indium oxide on joint strength, and the effect of hot pressing during reflow process.

Key words: Indium, indium oxide, joint strength, reflow

INTRODUCTION

Soldering is a common interconnection method that is used in electro-package devices. Lead (Pb) has provided many technical and economical advantages, such as reducing the surface tension of pure tin, speeding up intermetallic bonds, and lowering the cost of the soldering process. In board-level packaging, eutectic tin-lead (Sn-Pb37) is the most widely used soldering material because it shows good compatibility with most substrate materials and devices. However, the health and environmental concerns associated with lead have given the momentum to the development of environmentally friendly lead-free solders.

Most lead-free solders are Sn-based alloys with indium (In) and bismuth (Bi). Other lead-free alloy compositions (Ag, Cu) have also been investigated with different combinations of elements.[1] Among those elements, indium (100% purity) is known to be very ductile and has high thermal conductivity. In addition, molten indium has good wettability on many surfaces including ceramics, glass, and quartz at low process temperatures, making it adaptable to fluxless soldering process. In the literature, some researchers have characterized Au/In joint properties with an intermetallic phase. A new bonding technique was also reported for a fluxless indium bonding process.[2–4]

This study focuses on the fluxless solderability of pure indium solder for a chip bonding and fiber attach to chip carrier application. One advantage of pure indium solder is its low melting temperature (156°C). Such a low solidification temperature reduces thermal stress generated from thermal mismatches of package components and prevents stress-related failures of the board. Fluxless soldering also provides an added benefit of eliminating troublesome contamination from organic chemicals, thus saving the flux cleaning process after soldering.

Pure indium's solderability was quantified by wetting angle measurements and lap shear tests to measure joint strength with varying initial indium oxide thicknesses. No flux was used in the reflow process. To measure indium joint strength, indium was reflowed on the gold-coated substrate under different reflow conditions. The aim of this work is to show the importance of the reflow environment on joint strength and to provide an insight into fluxless reflow processing.

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EXPERIMENTAL PROCEDURE

Indium Samples, Oxides, and Substrates

Pure indium foil (purity: 99.999%) obtained from Goodfellow Cambridge Limited was cut into 5 by

5 mm^2 by 1 mm thickness. The samples were then electrochemically polished in a 3:1 ethanol/nitric acid bath at 0°C and stored in a nitrogen chamber to prevent oxidation.

To grow different oxide thicknesses, indium samples (T_m = 156°C) were heat treated at different temperatures (25°C, 145°C, 160°C, 200°C, and 400°C in Fig. 1) on a hot plate in air. The indium oxide thicknesses were then measured by ellipsometry.

Figure 1 shows the indium oxide growth as a function of temperatures in an air.[5] Indium oxide grows from 4 nm to more than 20 nm when the heating temperature increases from room temperature (25°C) to 200°C at 2 h. Fast oxide growth happened around the indium melting point (156°C).

A silicon wafer, 6.5 mm by 28 mm, was used as the test substrate. To control the exact bonded area on the silicon substrate, a photoresist method using S1805, supplied by Rohm and Haas Electronic Materials LLC, was introduced to prepare the deposition of Ti/Au on the silicon wafer. The deposited area of titanium and gold layer on the silicon substrate was 3.5 mm by 3.5 mm^2, as shown in Fig. 2. The substrate was coated with 0.04 μm thickness of titanium and then 0.5 μm thickness of gold.

Reflow Process, With and Without Oxidation

Two different reflow processes were considered for indium soldering without flux. One reflow process was carried out in open air, so that more oxide was allowed to grow on the indium test samples during reflow. The other was under an inert atmosphere, which prevented additional oxide growth on samples with initial oxides.

Indium oxide is more thermodynamically stable than indium from 25°C to boiling point 1807°C. In order to make indium oxide thermodynamically unstable, reducing H_2 gas needs to be introduced. The calculation of ΔG (change in Gibbs free energy) for the reaction ($In_2O_3 + 3H_2 = 2In + 3H_2O$) shows that indium oxide is in thermodynamic equilibrium with indium at specific moisture-to-hydrogen ratios. Figure 3 shows the thermodynamic oxidation/reduction zone for the indium/indium oxide system where the reduction zone shifts with increasing moisture concentration. The zone to the left of the moisture concentration curve thermodynamically corresponds to the oxidation zone and the right zone corresponds to the reduction one. The region on the each curve corresponds to the equilibrium for the indium oxidized reaction. The kinetics of oxidation and reduction of indium are to be investigated in future research.

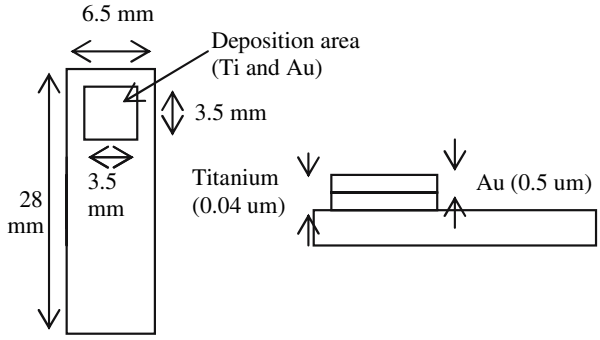


Fig. 2. Silicon substrate with Ti/Au deposition.

RESULTS

The structural characterization of both indium and indium-oxide was carried out using X-ray diffraction (XRD). In addition, the interfacial structure between indium and the bonding substrate was

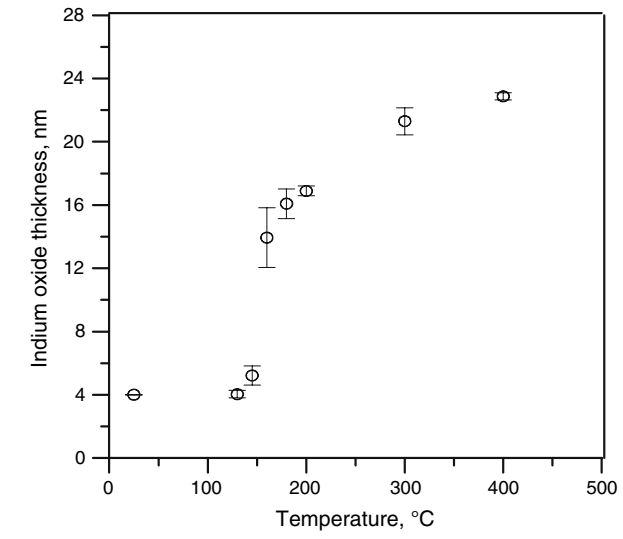


Fig. 1. The growth of indium oxide versus heating temperature.

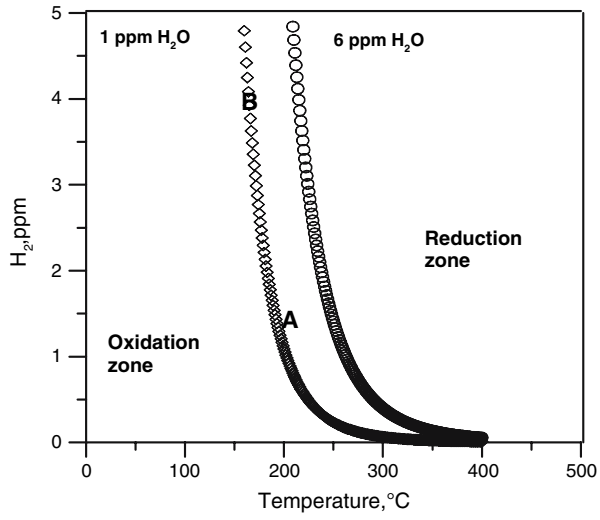


Fig. 3. Reflow environment with moisture (1 ppm and 6 ppm), hydrogen concentration, and temperature for ($2/3\ In_2O_3 + 2H_2 = 4/3In + 2H_2O$) (Points A and B are marked).

examined to discover how indium was bonded to the substrate under the inert atmosphere.

Two testing methods were used to characterize the solderability of indium and the effect of oxidation: measurement of the wetting angle formed by molten indium, and measurement of the indium joint strength under single lap shear testing, in which a shear force is applied to indium between two substrates.

Oxide Structure and Growth

The crystal structure of the thermally grown oxide on indium samples was analyzed using XRD. Samples below and above the melting temperature were tested to determine any structural changes of indium oxide.

Figure 4 represents the XRD plot of indium heated at 153°C for 4 h. Here the peaks only correspond to the crystal structure of pure indium. Below the melting temperature no crystalline phase of indium oxide was detected. Therefore, it is believed that indium oxide grown below the melting temperature is of an amorphous nature. Conversely, when indium was heated above the melting temperature a cubic indium oxide crystal structure was detected. In Fig. 5, the peaks correspond to a cubic crystal structure for indium oxide when the sample was heated for 4 h at 200°C. When treated above the melting temperature, the sample begins to flow, resulting in a rough, deformed surface.

Figure 6 explains the initial stage of oxidation where first oxygen is physically adsorbed on the metal surface, attached only by weak van der Waals bonds. Subsequently the oxygen molecules are chemisorbed, with the oxygen molecules acting as the electron acceptor and the metal acting as the electron donor. Since the electron affinity of In_2O_3 (3.5 eV) is greater than that of indium (0.3 eV), the oxide acquires excess negative charge with the positive charge on the indium and an electric double layer is created. As this space charge becomes more negative, the escape of electrons from the indium tends to slow down, as does the growth of the indium oxide. Further research will investigate the kinetics of indium oxide growth under different conditions.

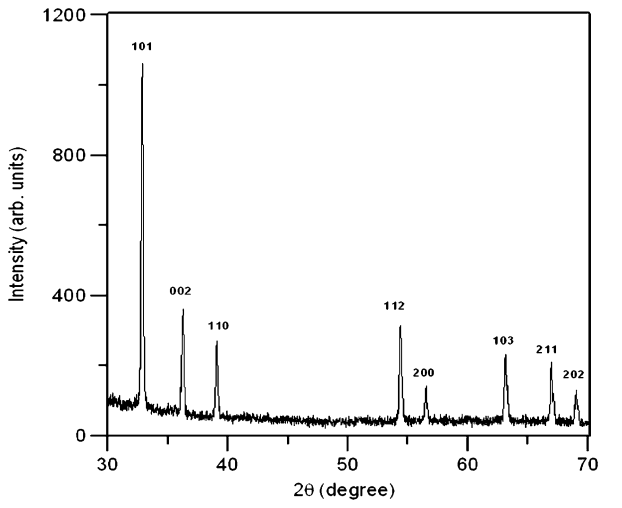


Fig. 4. XRD plot of intensity versus 2θ (scattering angle) for the sample heated at 153°C for 4 h. The peaks labeled are from pure indium.

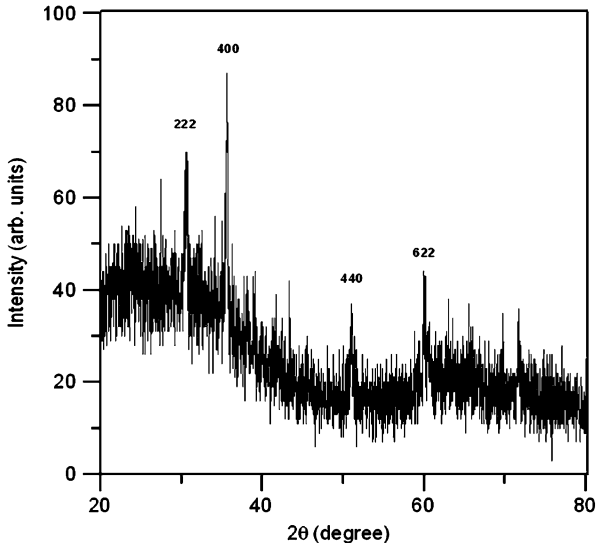


Fig. 5. XRD plot of intensity versus 2θ for the sample heated at 200°C for 4 h. The peaks labeled are from indium oxide.

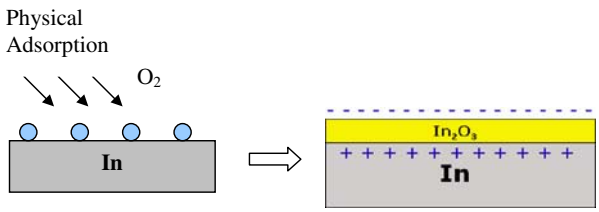


Fig. 6. Indium oxidation process.

Interfacial Structure of Indium Sample and Silicon Substrate, and Surface Observation of Indium Sample after Reflow

Before measuring the joint strength of the indium sample, the cross section between the indium sample and silicon substrate was observed microscopically, as shown in Fig. 7. This sample was one of samples that were reflown in an inert environment. Figure 7 shows the intermetallic compound ($AuIn_2$) that was seen at the interface, as discussed in Ref. 5.

Thermal energy applied by the reflow process causes thermal deformation of the indium due to the difference in the coefficient of thermal expansion (CTE) of indium ($\sim 33 \times 10^{-6}$/°C) and thin indium oxide ($\sim 8 \times 10^{-6}$ for metallic oxides). Thus, when indium is heated it is compressed while the indium

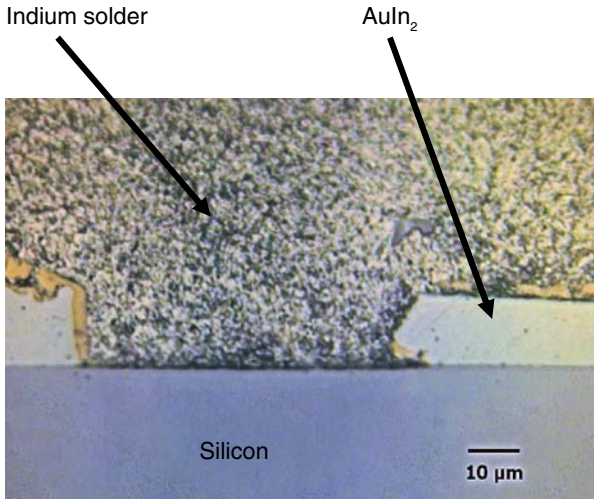


Fig. 7. Interfacial structure between indium and the silicon substrate after reflow in the inert environment.

oxide skin is under tension. The opposite happens on cooling. When the indium melts and expands, the volume expansion stretches and may even break the indium oxide skin, and on cooling, the sample surface becomes wrinkled and rough. Figure 8 shows the surface condition of indium reflown in the inert environment.

Wetting Characteristics in Open Air and in the Glove Box

Indium samples were melted and the wetting characteristics were observed on a gold-deposited substrate in both air atmosphere and under inert environmental conditions. The inert reflow conditions were created by using a glove box system (MBraun USA) in which the environmental moisture, oxygen, and hydrogen concentration were controlled.

Indium samples (1 mm by 1 mm) with different oxide thicknesses, which were previously heated at 25°C, 145°C, 160°C, and 200°C, were melted on a hot plate at 200°C for 2 min in air and in the glove box. The glove box system was maintained at $O_2 < 0.1$ ppm, $H_2O < 1$ ppm, and $H_2 < 1.5$ ppm, which corresponds to position (A) in Fig. 3. After solidification of the indium, the wetting angle of indium was measured by a Wyco NT1100 optical profiling system.

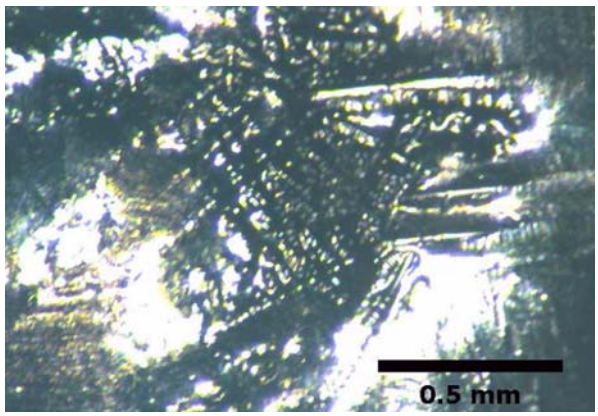


Fig. 8. A micrograph of indium solder with 4 nm of oxide after reflow in the inert environment.

Indium wetting without flux in open air was very poor for all samples: indium just melted on the Au-coated substrate without spreading, as shown in Fig. 9a. Therefore, indium wetting angles could not be measured for samples melted in air because of their poor wetting angles. In the inert environment described above, indium showed pronounced spreading at 220°C in 2 min, as shown in Fig. 9b.

The wetting characteristics of indium are shown in Fig. 10 under the inert condition, showing increased wetting angle and poorer spreading with increasing initial indium oxide thickness.[6] Indium with 4 nm thickness of oxide showed a wetting angle as low as 15°.

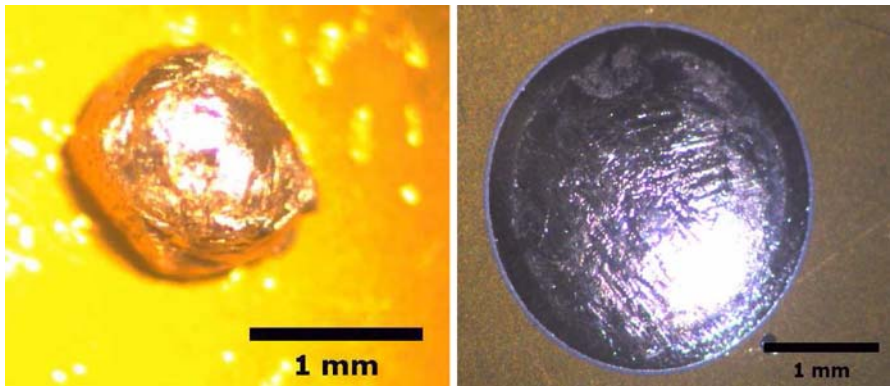
Bonding Strength of Samples Reflowed in Open Air and in a Glove Box with Hot Press

All samples in the beginning of this experiment were reflown to bond two silicon substrates by the hot pressing method shown in Fig. 11. A bonded sample is shown in Fig. 12. During reflow, a 1-mm-thick indium block was squeezed to 0.65 mm by the weight (100 g copper block) as shown.

One indium sample was tested for bonding at 165°C in open air atmosphere, but indium would not bond to the Ti/Au-deposited substrate well enough for the lap shear test. A higher reflow temperature of 230°C for 10 min was needed to bond the indium sample to the substrates. The other samples were reflown at 165°C for 5 min in the inert environment, with $O_2 < 0.1$ ppm, $H_2O < 6$ ppm, and $H_2 < 4\%$, which corresponds to position (B) in Fig. 3, in the glove box.

The samples after reflow were tested in air atmosphere using a Bose ELF3200 operated by Wintest software. To measure the joint strength, a fast displacement rate (0.5 to 2 mm/s) was applied to insure interfacial failure instead of ductile failure in the indium. The maximum joint strength of indium (τ_{ult}) was obtained by dividing the applied maximum tensile load, F, by the Ti/Au deposited area, A ($\tau_{ult} = F/A$).

Indium shear test samples with 4 nm of initial oxide thickness using the holding fixture shown in Fig. 11 were reflowed in an air and tested by applying a pulling force at the rate of 0.5 mm/s. The failure occurred at the interface between indium and the bonded substrate. The average joint strength was 1.35 MPa with a standard deviation of 0.2 MPa. On microscopic examination of the failed surface on the substrate and indium, many traces of voids were seen, as shown in Fig. 13, indicating poor



(a) Wetting in an air **(b)** Wetting at an inert environment

Fig. 9. Indium wetting shape with 4 nm thickness of oxide, melted at different environments.

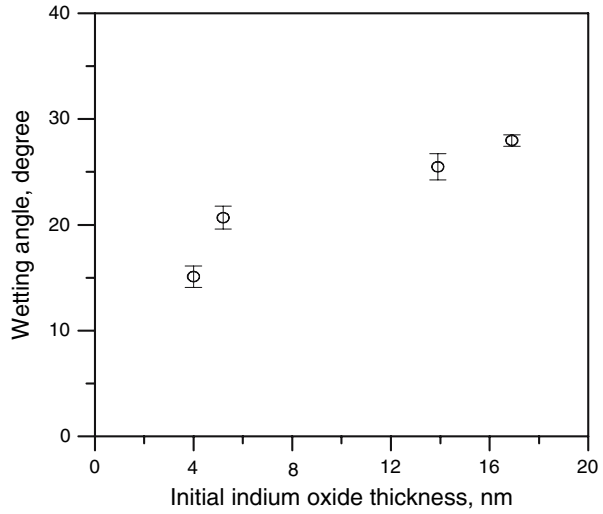


Fig. 10. Wetting angle variation in an inert environment (220°C for 2 min).

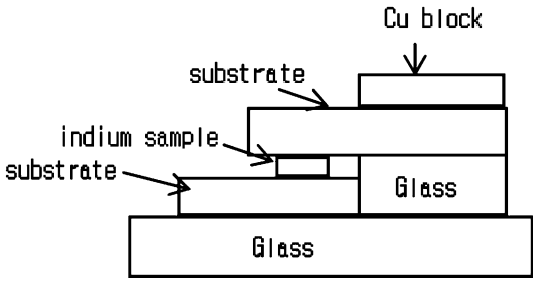


Fig. 11. Sample-holding fixture for hot pressing.

contact between the molten indium and gold surface.

Inert reflow conditions were applied to bond indium to the test substrates using the holding fixture. To measure the interfacial strength of the indium test sample, the pulling rate of the substrate was increased to 2.0 mm/s after reflow in the same inert environment (point B in Fig. 3).

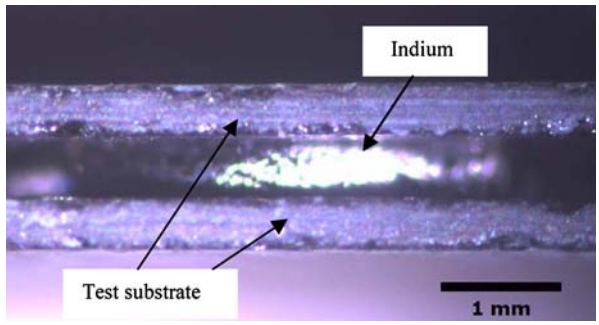


Fig. 12. The shape of the indium joint test sample after air reflow.

Figure 14 shows the joint strength of indium with different initial oxide thicknesses after reflow in the inert environment. The indium joint strength decreases with the increase of initial indium oxide thickness. The failure always occurred at the interface between the indium and bonded substrate, as shown in Figs. 15a and b. Traces of indium, gold, and titanium were observed at both surfaces of the substrates, as shown in Fig. 15.

Bonding Strength of Samples Reflowed in a Glove Box without Hot Press

The sample fixture (Fig. 11) incorporates hot pressing which squeezes the indium block during the phase change from the solid to the molten state. This accelerates a part of the molten indium to break out of the oxide crust at the interface, as mentioned in the surface observation of the indium sample after reflow, which will enhance adhesion.

To obtain the bonding characteristics without the effect of hot pressing, a different set of samples were prepared in which indium blocks (3.5 by 3.5 mm, 1 mm thick) with various oxide surfaces were simply melted and solidified on gold-plated substrates under the same condition used for the hot-pressed

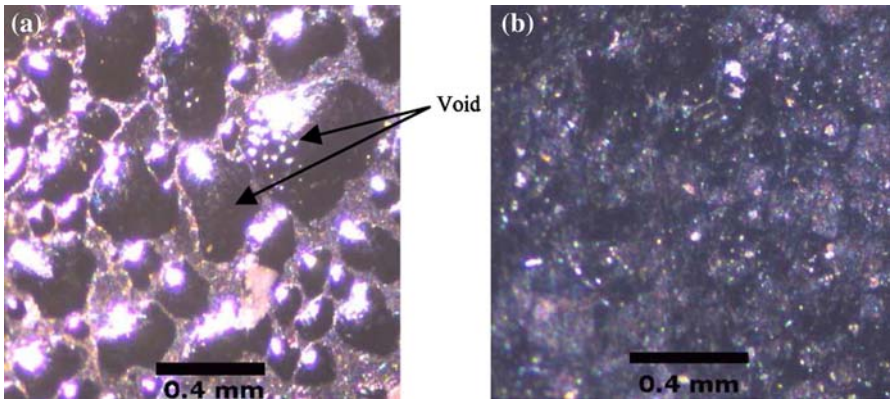


Fig. 13. A pair of failed bonded surface: (a) the surface of the indium on one surface and (b) the surface of the other substrate, after air reflow and joint test.

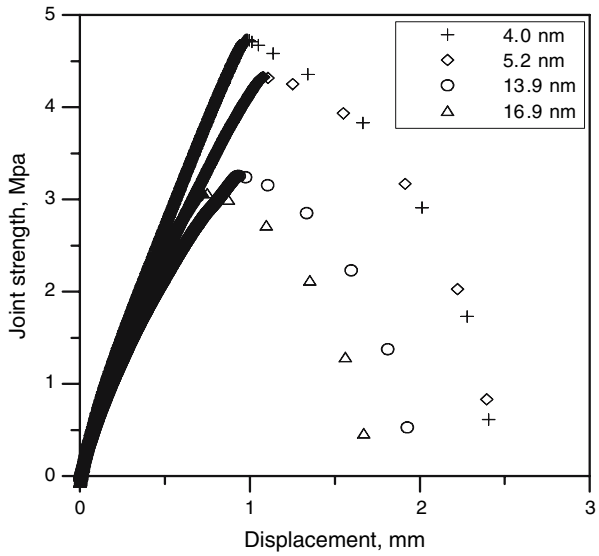


Fig. 14. Indium joint strength after reflow under inert conditions.

samples. For these samples, the bond strength was measured using the Dage bond tester, which applied shear force to the adhesion interface.

The surface condition of the gold substrate after a Dage bond test is shown in Fig. 16. Traces of gold were observed on the surface of the substrate. It clearly shows poor bonding.

Figure 17 shows the joint strength of indium reflown in the inert environment. The effect of the initial oxide thickness on the indium joint strength is also clearly shown in Fig. 17. Although different testing methods were used, Fig. 17 indicates significantly inferior bonding when the hot pressing is not used.

DISCUSSION AND SUMMARY

Indium soldering without the use of flux has been investigated, based on the characterization of indium and indium oxide, and the effects of oxidation on the wetting angle and joint strength of molten indium under different environmental conditions. Pure indium solder spread more easily in an inert environment than in air and also showed better wetting for solder samples having thinner oxides. Although the molten indium could overcome the oxide barrier during the phase change in an inert environment, the indium was found to be incapable of wetting in open air. In addition, lap

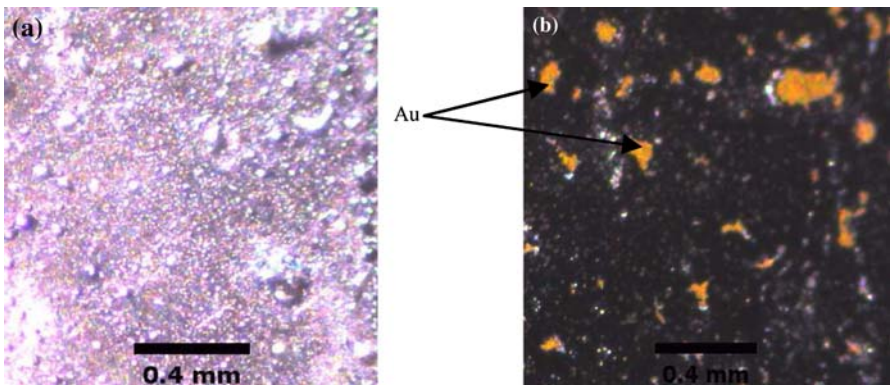


Fig. 15. A pair of failed bonded surfaces: (a) surface of the indium on one substrate and (b) surface of the other substrate, after reflow under inert conditions and joint test (17 nm oxide).

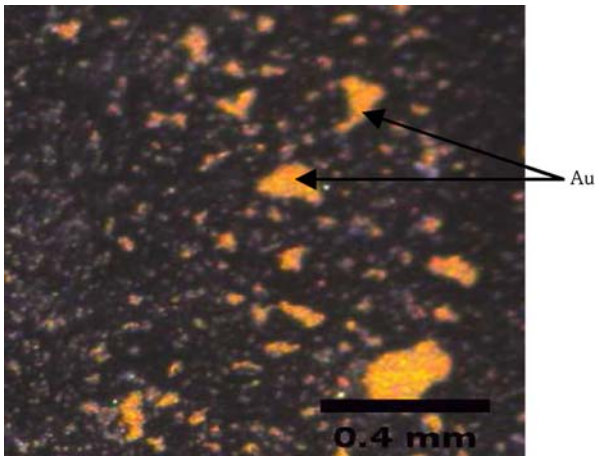


Fig. 16. Surface condition of gold-coated substrate after Dage bond test (4 nm indium oxide).

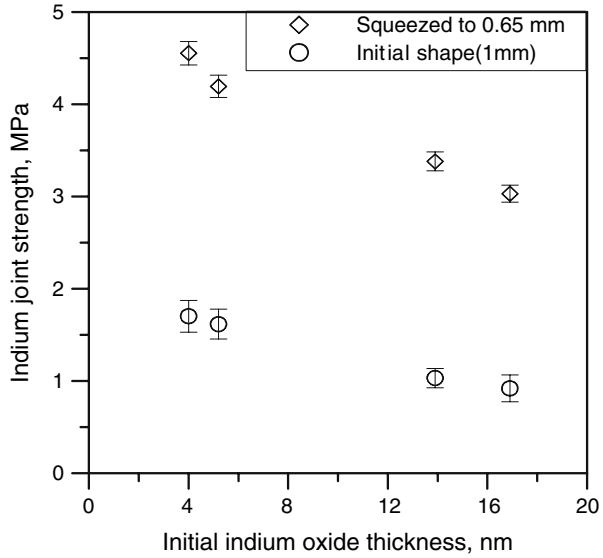


Fig. 17. Indium joint strength with/without hot pressing on indium, reflow under inert conditions.

joint samples reflowed in open air showed poor bonding and required a higher reflow temperature for a longer duration in addition to the hot pressing fixture to achieve a measurable bonding strength.

Solderability was further studied by testing the adhesion strengths of lap joints made of gold-coated substrates bonded with solder samples having various oxide thicknesses. Oxide thickness significantly degraded joint strength. During reflow, the samples were supported by a hot press fixture. Hot pressing provided a mechanical disturbance during the phase change, breaking the oxide skin. Adhesion test samples prepared in an inert environment without any mechanical disturbances showed significantly inferior bond strength to samples with hot pressing.

Therefore, the application of fluxless indium soldering requires a reflow process which combines the use of solder with minimal oxide, oxidation-controlled reflow (inert environment), and mechanical means to break the oxide skin. Fluxless soldering provides the big advantage of removing the flux cleaning process and eliminates the possibilities of contamination by flux residues in the electro-packaging. In addition, it saves the cost of flux, cleaning solvent, and the disposal of the spent chemicals. Fluxless soldering is therefore both viable in electronic technology and attractive for the environment.

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