Ultrasonic Powder Consolidation of Sn/In Nanosolder Particles and Their Application to Low Temperature Cu-Cu Joining

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Abstract

Tin/Indium (Sn/In) nanosolder particles in the size range of 40-70 nm were successfully consolidated into nanosolder films by the ultrasonic power consolidation (UPC) method. The consolidated nanosolder film prevents the nanoparticles from oxidation, which is a common problem of nanomaterials during storage and processing, and makes the nanoparticles easier to handle. The quality of the consolidated nanosolders was examined by scanning electron microscopy (SEM), X-ray diffraction (XRD), and differential scanning calorimetry (DSC). The consolidated Sn/In nanosolder films were then used to join copper (Cu) plates at two soldering conditions (high pressure vs. low pressure). SEM and energy dispersive X-ray spectroscopy (EDS) were used to study the intermetallic compound (IMC) formation and growth during thermal aging. The IMC layer consisted of η -Cu₆(Sn, In)₅ and no Cu₃(Sn, In) was observed. The thickness of the IMC layer followed a linear relationship with the square root of the aging time, indicating diffusion controlled kinetics. The results indicated that pressure is critical for effective Cu-Cu joining by limiting the IMC growth. Finally, pull tests of the specimen joined by the consolidated nanosolder film under high pressure showed a comparable result with the solder joints formed by Sn/In solders reported in literature.

Keywords: Ultrasonic Powder Consolidation (UPC); Sn/In nanosolder; low temperature soldering; Cu/Cu joining; intermetallic growth; thermal aging; mechanical properties.

1. Introduction

Joining is one of the key processes in manufacturing and repairing. It can be achieved by a variety of methods such as welding, soldering, brazing, adhesive bonding, and diffusion bonding [1-2]. Fusion welding, normally performed under relatively high temperature, tends to have negative effects on the microstructure and properties of the weld. Unlike fusion welding, soldering, brazing, and adhesion involve lower temperatures with fewer side effects. [3]

The soldering process aims to join two or more metal working pieces together by melting and flowing a filler metal (solder) between the **working** pieces. It has been widely used in plumbing, metalwork, jewelry, and electronics. Nowadays, low temperature solder materials have a large demand in electronics industry [4]. To reduce the cost, **many inexpensive** components and circuit board materials such as polymer capacitors and film capacitors are being implemented in the products by many electronics manufacturers. However, this practice often introduces manufacturing yield problems because those materials (such as polymer materials) tend to be more sensitive to high temperature **(e.g., > 200 °C)**. So low temperature solders **(e.g., in the temperature of 50-183 °C)** are **desired** to assemble those temperature sensitive components during surface mount assembly [5-6]. On the other hand, flexible electronics can have many applications, such as flexible screen displays and stretchy sensing tools. The flexibility of these types of electronics depends on the polymer based substrate [7-17]. To assemble electronic components on the polymer substrate, one must use a limited heating process because the polymer substrates usually are not resistant to high temperature. Therefore, for flexible electronics assembly, low processing temperature solder materials are also required in order to prevent the polymer substrate **from being damaged**.

Most of the solder materials that meet the requirement of low melting temperatures are bismuth (Bi) or indium (In) based alloys [18-26]. Among the low melting temperature solders, 34Sn-43Pb-14Bi, 58Bi-42Sn, and 40Sn-40In-20Pb are the relatively popular ones [26]. However, **some of** these solders are not favored due to the toxicity of lead. In-based solders normally have **very** low melting temperatures **(lower than Bi-based solders)**, and are soft and ductile [26]. Also, In has been reported to have a good wettability on both metallic and non-metallic surfaces [26].

Ultrasonic powder consolidated (UPC) is a new additive manufacturing technique in which powders are metallurgically consolidated by the action of ultrasonic vibration at low to moderate temperatures, typically within a second [27]. It would be a very efficient way to **more easily** handle the nanomaterials and prevent the surface oxidation (a common problem of nanomaterials) [28-30]. In this work, Sn/In nanosolder particles were consolidated into Sn/In nanosolder films by UPC. To test the consolidated Sn/In nanosolders **for soldering**, a copper-copper (**Cu-Cu**) joining system was selected. Two joining methods (**high pressure vs. low pressure**) were applied to compare the joining condition in the **Cu-Cu** system. The intermetallic compound (IMC) formation and growth during aging were studied to examine the joint quality. **Finally, pull tests were** conducted to investigate the mechanical property of the solder joint formed by UPC consolidated Sn/In nanosolder film.

2. Experiments

2.1 Materials and chemicals used

Sodium dodecyl sulfate (SDS) (85%) and ethanol (anhydrous) were purchased from Fisher Scientific. Tin (II) sulfate (SnSO_4 , 99%), indium chloride (InCl_3 , 99.995%) and Sodium borohydride (NaBH_4 , 99%) were purchased from Acros Organics. Hydrochloric acid (HCl , 36.5%-38%) was obtained from VWR scientific. DI water was obtained from a Barnstead Nanopure water purification system. All materials were used without further purification. Cu plates (ASTM-B152, 0.53 mm thickness) purchased from Small Parts Incorporated were used for joining tests. Stay-clean Flux was purchased from Harris Products Group **and used without further treatment; the main compositions of the Flux include ammonium chloride, zinc chloride, hydrochloric acid, and methanol**. Castamount acrylic hardener and acrylic powder from Pace Technology were used to mount the samples for cross-section analysis. 0.05 μm alumina **polishing** particles (Pace Technology) were used to polish the mounted samples.

2.2 Synthesis of Sn/In nanosolder particles

A composition **close to the** eutectic Sn/In alloy nanosolder, Sn/In 50/50, was selected in this study. Sn/In nanosolder particles were synthesized through a surfactant assisted one-step chemical reduction method [31]. Firstly, SDS was added into DI water to form a 8 mM solution.

Then HCl was added to adjust the pH from 7 to around 2.7 before dissolving the metal precursors of SnSO₄ and InCl₃ solutions. After that, an excess amount of NaBH₄ solution was added into the system through a syringe pump (single-syringe infusion pump, KDS LEGATO 110, KD Scientific) at a constant speed of 20 mL/h. Then the reaction was continued for 30 min at room temperature. The resulting samples were centrifuged (5804 Centrifuge, Eppendorf) at 7000 RPM and washed 5 times with DI water and 3 times with ethanol through dispersion and centrifuge cycles.

2.3 UPC consolidation

The Sn/In nanosolder particles were ultrasonically consolidated as shown schematically in Fig. 1. A STAPLA Condor ultrasonic welder operated at 3kW, fixed frequency of 20 kHz and adjustable vibration amplitude of up to 9 μm at the sonotrode tip was employed in the UPC setup. The samples were consolidated using a die-punch arrangement as illustrated in Fig. 1. The die and the punch were made of stainless steel and had a matching diameter of 4.1 mm. About 0.08 g of Sn/In nanosolder particles (powders) was placed in the die and held under a pressure of 100 MPa applied through the sonotrode and the punch. Then in-plane ultrasonic vibration was applied to the powder compact for 1 s while the powder was kept under 100 MPa. Three temperatures (room temperature, 50 °C and 70 °C) were tested to determine the best condition of consolidation. The consolidated specimens were at 4 mm in diameter and 1-1.2 mm in thickness, and about 0.06-0.07 g in mass. The mass difference before and after the consolidation was accounted for by the residue on the die. For cross-section observation, the consolidated nanosolder film was first mounted in the acrylic mounting material, then polished by sand papers with different grit sizes (from 120 to 1200) and finally polished by alumina polishing particles.

Fig. 1: Scheme of the UPC setup

2.4 Cu-Cu joining experiments

Copper-copper (Cu-Cu) joining has many applications in industry such as electronics, roofing, plumbing, and industrial machinery [31]. Here, two methods were studied to join two Cu plates (each about $20\text{ mm} \times 10\text{ mm} \times 0.56\text{ mm}$) together using the consolidated Sn/In nanosolder films. Under both conditions, the Cu plates were rinsed with diluted nitric acid (pH 3-4) and followed by DI water before use. A consolidated Sn/In nanosolder film was placed between two Cu plates with $5\text{ }\mu\text{L}$ of flux on each side to form a sandwich structure. Two heating conditions were tested. In the first condition (method I), the heating of the sandwich structure was done in an argon bath, under a constant pressure of 100 MPa using the UPC setup as shown in Fig. 1. The sandwich structure was placed between the sonotrode and the anvil, then heated up to $150\text{ }^{\circ}\text{C}$ and kept at $150\text{ }^{\circ}\text{C}$ for 5 min (so called dwell time). After that, the sample was cooled down to room temperature, which was ready for the following testing. To compare the pressure and dwell time effects, a low pressure joining method (method II) was also utilized. A programmable tube furnace (Lindberg/Blue M, Thermal Scientific) was used for the low pressure joining. The sandwich structure, secured by a C clamp screw compressor, was placed in the furnace and sealed in argon environment. First, the tube temperature was increased to about $90\text{ }^{\circ}\text{C}$ from room temperature ($\sim 25\text{ }^{\circ}\text{C}$) in a time duration of 10 min as the pre-heating step. Then, the temperature was increased to $100\text{ }^{\circ}\text{C}$ in 1 min as the soak step. After that, the temperature was increased to the peak temperature of $150\text{ }^{\circ}\text{C}$ and kept at $150\text{ }^{\circ}\text{C}$ for dwell times of 5 min, 15 min, and 30 min,

respectively. A cooling step (~5 min through natural cooling) was followed to cool down the samples to the room temperature.

2.5 Aging tests

To study the formation of intermetallic compounds (IMC) and interfacial microstructure change over time, a series of aging tests were performed on the specimens that were joined by the two methods as discussed above. After the joints were formed, the samples were kept in the tube furnace for extended periods of 50 h and 100 h, respectively, at 100 °C. Then the samples were cooled down to room temperature and polished for cross-section study under SEM.

2.6 Metallographic characterization and tensile tests

A JEOL7401F field emission-scanning electron microscope (FE-SEM) and a Philips EM400 transmission electron microscopy (TEM) were used to examine the morphology of the as-synthesized Sn/In nanosolder particles. The nanosolder suspension was dropped on a conductive silicon wafer which was attached onto a sample stub by carbon tape for SEM observation. The samples were then dried for SEM imaging. To study the microstructure of the consolidated nanosolder film, the specimen was mounted in epoxy and polished using a cross-section polisher (Pace technology NANO 1000T grinder-polisher). Then the polished sample was examined by SEM. Energy dispersive X-ray spectrometer (EDS) equipped on the FE-SEM was used to analyze the chemical composition of the solder joint. Here, the chemical composition was taken as the average of three analysis points of the sample. X-ray diffraction (XRD, BRUKER AXS D5005 X-ray diffractometer, Cu K α radiation, $\lambda=1.540598$ Å) was used to determine the structure of the consolidated nanosolder films. The melting point of the consolidated nanosolder films was measured by differential scanning calorimetry (DSC, TA Instrument Q100). SEM images were analyzed by ImageJ to measure the porosity of the solder joint. Pull tests were performed on Instron (Instron 4466) with a constant crosshead speed of 1 mm/min along the vertical direction of the sandwich structure at room temperature. The tensile force F and displacement d were recorded. The tensile stress of the specimen was calculated as $F/\pi R^2$ where R is the radius of the consolidated Sn/In nanosolder film (after reflow). The maximum value of $F/\pi R^2$ of the stress–displacement curve where the failure occurred was used as the joint strength of the specimen.

3. Results and discussion

3.1 Sn/In nanosolder particle formation

The SEM and TEM images of the Sn/In 50/50 nanosolder particles for UPC are shown in Fig. 2. The particles are spherical and in a size range of 40-70 nm. The mass ratio of Sn/In/O measured from EDS was 45/50.4/4.6, where the small amount of O was from the water based synthesis process. A thin layer of Sn/In oxide may be formed on the surface of the nanosolder particles. The crystalline structure and melting point were measured by XRD and DSC, respectively. The crystalline structure was determined to be mainly InSn_4 with some In, whereas the peak on DSC at 116.1 °C was due to the eutectic melting of InSn_4 and In. More details will be discussed in Section 3.2.

Fig. 2: Electron microscopic images of Sn/In nanosolder particles: (a) SEM, (b) TEM.

3.2 Characterization of consolidated Sn/In nanosolder films

Fig. 3 shows an SEM image of **the** cross section of a consolidated specimen of Sn/In 50/50 nanosolders. The consolidation was done at room temperature without protective atmosphere. From the cross section of the consolidated nanosolder film, the nanoparticles all seem to be consolidated into a fully densified structure with metallurgical integrity and no porosity. The samples consolidated at 50 °C and 70 °C had a fully densified structure as well. **However, room temperature was sufficient to produce full densification, and thus there is no need to consolidate the nanoparticles at 50 °C or above.** Therefore, room temperature consolidation was used for the following tests in this study.

Fig. 3: SEM image of the cross section of **Sn/In 50/50 nanosolder film consolidated at room temperature.**

Fig. 4 shows the EDS results of the Sn/In nanosolder film consolidated at room temperature. The mass percentage ratio of Sn/In/O is 44.2/49.6/6.1, which **is** very close to the value of Sn/In nanosolder particles before the consolidation (Sn/In/O: 45/50.4/4.6). The elemental composition also **compared well** to the result of the previous study on Sn/In nanosolder synthesis [32]. Thus, the elemental composition remained the same through the UPC process, and no **significant** oxidation occurred. The structural information of the **nanosolders** before and after consolidation was shown in Fig. 5. In both XRD spectra before and after **the** consolidation, the **specimens were**

consisted of InSn_4 and In . No phase change or new phase formation occurred during the consolidation. Therefore, the crystalline structure of the nanosolder did not change throughout the consolidation. The consistency of the crystalline structure was verified by DSC. Fig. 6 showed the DSC comparison of the nanosolder particles and consolidated nanosolder films. An endothermic peak at around 116 °C from the eutectic melting between InSn_4 and In was observed in both plots. The small difference (0.7 °C) of the peak temperatures indicated that the phase transition temperature also remained the same after the consolidation [32]. From the EDS, XRD, and DSC analysis, the nanosolders retained the same properties of elemental composition, crystal structure, and melting temperature from the originally dispersed particles throughout the consolidation, except that they were fully consolidated into a film.

Fig. 4: EDS spectra of the nanosolders before and after consolidation.

Fig. 5: Comparison of Sn/In nanosolders before and after consolidation: XRD results.

Fig. 6: Comparison of Sn/In nanosolders before and after consolidation: DSC results.

3.3 IMC and interfacial structure of the Sn/In nanosolder joint between Cu-Cu plates

The specimen formed a solid joint after reflowed by method I under high pressure (100 MPa) for 5 min. In the low pressure joining (method II), heating times of 5 min, 15 min, and 30 min were

tested. Only with the dwell time of 30 min, a solid solder joint can be formed by method II. Dwell times of 5 min and 15 min led to very weak solder joints. Therefore, in the following discussion, method II refers to a low pressure reflow with dwell time of 30 min. Fig. 7 shows the cross section back-scattered electron (BSE) images of the joint interface after reflow with the two joining methods (methods I and II). The layers of Cu, IMC and solder were labeled in the figures accordingly. An IMC layer was formed uniformly at the interface of Cu and the nanosolder film on the samples formed by both methods. The thickness of the IMC layer was $0.78\ \mu\text{m}$ in the sample formed by method I, and $1.95\ \mu\text{m}$ in the sample formed by method II. The difference in IMC layer thickness comes from the difference in reflow time and pressure. The longer dwell time (30 min) increases the IMC growth rate. In addition, the higher pressure of 100 MPa used in method I helped the densification process during the soldering. The high pressure eliminated some fraction of pores that came from the dissolution of the oxide shell on the nanoparticles. It increased the contact area between the nanosolder particles during the heating and reduced the volume shrinkage effect of nanosolders during solidification, thus speeding up the free surface area reduction. Also, the pressure provided another driving force of joining. Therefore, the sample can be joined in a relatively short time (5 min), and the IMC layer has been restricted from growing [33-35].

Fig. 7: SEM images of Sn/In nanosolder film after reflow under condition (a) method I (100 MPa, 5 min); (b) method II (low pressure, 30 min).

Table 1 shows the chemical composition of the interfacial structure, which was determined by EDS. The EDS of each region on the samples reflowed by the two methods showed similar results. The elemental composition of the IMC layer (in Table 1) suggests the crystalline structure of the IMC layer to be $\eta\text{-Cu}_6(\text{In}, \text{Sn})_5$ [36-37]. For both samples, IMC particles (light particles) were randomly distributed in the solder matrix (dark background). Under the method I condition, the light particles were in sub-micron sizes; whereas the light particles formed by method II were relatively larger (up to a few microns). The EDS data suggested that the light particles in both samples consist mainly of $\gamma\text{-InSn}_4$, which is from the main alloy in the consolidated Sn/In nanosolder film, and small amount of In. The crystal structure of the solder matrix was suggested to be mainly In in both samples, but more Sn (~20.9 at%) was present in the sample joined by method II. The EDS results in Table 1 show that a small amount of Cu has been dissolved in the solder layer, both in the light particles and the dark solder matrix. It is possible that a ternary compound such as $\text{Cu}_2\text{In}_3\text{Sn}$ might be formed in these areas [36-37]. Some small dark (black) areas were also observed in the solder layer (marked in Fig. 7b), which were probably voids that were formed during joining. The porosity was estimated by the area fraction of the void by using ImageJ. Almost no voids (under 0.1 %) were observed in the sample formed by method I (Fig. 7a), and only a very small amount of voids were found (0.52 %) in the sample formed by method II (Fig. 7b).

Table 1: Elemental compositions of solder alloys after reflow under method I and method II conditions.

	Intermetallic layer			Solder matrix (dark)			Small particles (light)		
	Cu	Sn	In	Cu	Sn	In	Cu	Sn	In
Method I (at%)	53.9	26.4	19.7	9.8	6.3	83.9	5	70.4	24.6
Method II (at%)	56.3	27.9	15.8	7.5	20.9	71.6	9.8	67.1	23.1

The interfacial structure of the Sn/In consolidated nanosolder film on Cu showed some similarity to the results observed by Lee et al. [38], which discussed the effect of In addition on the solder joints formed by Sn solder on Cu substrate. In Lee's work, the joint was formed with Sn/In

solder alloys (0, 4, 8, 16 wt% of In in Sn), reflowed at 250 °C for 60 s. In the samples with 8 and 16 wt% In compositions, a scallop shaped IMC phase $\eta\text{-Cu}_6(\text{Sn}, \text{In})_5$ was formed during the reflow. In our work, an IMC phase of $\eta\text{-Cu}_6(\text{Sn}, \text{In})_5$ was also found at the solder joint formed with the consolidated Sn/In nanosolder film. The thickness of the IMC layer was about 4 μm in Lee's work while in the present study the IMC layers formed with the consolidated Sn/In nanosolders were only 0.78 μm (100MPa) and 1.95 μm (low pressure), respectively, both of which are significantly thinner than the Sn solder with addition of In reported by Lee. Additionally, in Lee's work, micron sized $\eta\text{-Cu}_6(\text{Sn}, \text{In})_5$ particles formed in the solder matrix were observed, and both the $\gamma\text{-InSn}_4$ and $\beta\text{-Sn}$ phases may also exist in the solder layer [38]. In the present work, although $\gamma\text{-InSn}_4$ and $\beta\text{-Sn}$ can also be found in the solder layer of the joint formed by the consolidated sample, $\eta\text{-Cu}_6(\text{Sn}, \text{In})_5$ particles were not observed. Other than Sn/In solders, SAC solder ($\text{Sn}_{3.6}\text{Ag}_{0.9}\text{Cu}$) has been reported to form a 1.7 μm IMC layer of $\eta\text{-Cu}_6\text{Sn}_5$ on Cu under a reflow condition of 250 °C for 5-10 s with ZnCl_2 flux [39]. Under the same condition, the thickness of the IMC layer formed with a SAC solder mixed with In and Ce granules ($\text{Sn}_{3.6}\text{Ag}_{0.9}\text{Cu} + 1.7\text{In} + 0.3\text{Ce}$) was decreased to 1 μm [39]. Compared with the reports above, the thickness of the IMC layer in the sample formed by method I (high pressure) in this study was significantly thinner than the reported results. Even the sample formed by method II with a much longer reflow time (30 min) had a comparable result of the IMC thickness with the reported work for SAC solders. The observation indicated that nanosolder had a significant effect in controlling the formation and growth of the IMC layer, and that pressure is critical in the IMC thickness control as well.

3.4 Aging effect on IMC growth

The aging tests were carried out at 100 °C for two extended time durations, 50 h and 100 h. The cross section BSE images of the specimens under the two joining conditions were shown in Fig. 8 and Fig. 9. Table 2 and 3 list the chemical compositions of different regions of the reflow solder after the aging tests. The results in Table 2 are interpreted in Fig. 10 to show the trend of the composition change along aging times in different regions of the solder joints. From Fig. 10a, the elements almost remained the same after 100 hours aging (except a little fluctuation at 50 h), indicating that the IMC layer retained the same crystal structure of $\eta\text{-Cu}_6(\text{Sn}, \text{In})_5$ as the freshly joined sample. In both methods, the IMC layer thickness of the samples increased with aging

time (Fig. 8 and 9). In the sample joined by method I, the IMC layer thickness increased from 0.76 μm (before aging) to 1.01 μm at 50 h and 1.15 μm at 100 h; for method II, the IMC layer thickness increased from an initial value of 1.95 μm to 4.68 μm at 50 h and 5.73 μm at 100 h (see Fig. 11). In both cases, the thickness of the IMC layer followed a linear relationship with the square root of the aging time. The linear relationship revealed that the growth of IMC was diffusion-limited [40]. However, the slopes were different for the two fitting lines in Fig. 11, indicating that the rates of IMC layer growth were different for the samples soldered by the different methods. The sample that formed by method I had a significantly lower thickening rate of the IMC layer. This is contrasted by the much larger amount of the InSn_4 particles that were formed in the solder layer from the sample joined by method I (Fig. 7a and 8), which suggests that in the method I sample, larger amounts of the Sn and In required for IMC layer growth were consumed in the formation of the InSn_4 particles in the solder layer. In addition, the fine InSn_4 particles in the solder layer of the sample formed by method I provided a large interfacial area between particles and the In matrix where vacancies may be absorbed, particularly under the high pressure (method I), thereby restricting the diffusion.

Fig. 8: SEM images of the cross-section of solder joints formed by method I after aging at 100 °C for (a) 50 h, (b) 100 h.

Fig. 9: SEM images of the **cross-section of solder joints** formed by method II after aging at 100 °C for (a) 50 h, (b) 100 h.

As the aging time extended, void formation was observed in both samples, mainly formed at the γ -matrix interface. No voids were observed at the IMC-Cu interface. Also, based on the observation of cross sectional SEM images (Fig. 8 and 9) and the EDS results (Tables 2 and 3) of the IMC layer, the η -Cu₆(Sn, In)₅ was the only phase present in the IMC layer, and no Cu₃(Sn, In) was observed. The above observations in the present study are different from previous studies on Sn-based solders [41-45], in which morphological change of η -Cu₆(Sn, In)₅ was found, but no void formation in the solder layer during aging tests. In the previous studies, Cu₃(Sn, In) would form between the η -Cu₆(Sn, In)₅ layer and the Cu layer. Kirkendall voids were only found in the solder joints subjected to prolonged aging (over 300 h) at the aging temperature at/above 150°C [41-45]. The absence of Cu₃(In, Sn) and void at the IMC-Cu interface in the samples made by method I and II in the present study might be due to the lower aging temperature and shorter aging time.

Comparing the samples that were joined by the two methods, the Sn-rich light particles in the solder layer coarsened into larger particles in both samples during the aging process (Fig. 8 and 9). At aging times of 50 h and 100 h, the atomic percents of Sn in the light particles of the samples joined by method I are 89.8 at% and 89.8 at% (Fig. 10c), and in the sample joined by method II are 77.8 at% and 85.7 at% (Table. 3). This suggests that the Sn rich light particles mainly consist of Sn, and might contain γ -InSn₄. At the same time, the elemental ratio of Sn in the solder matrix dropped from 6.3 at% (before aging) to 2 at% (aging 100 h) in method I (Fig.

10b), and from 20.9 at% (before aging) to 4.7 at% (aging 100 h) in method II (Table 3), indicating the precipitation of Sn from the solder matrix (Fig. 10b). The main crystal structure of the solder matrix was In after 100 h aging in the samples formed by both methods. From Fig. 8 and 9, the void coarsening during aging in the samples joined by method I was much less than the one formed by method II. The porosity increased from less than 0.1% before the aging to 0.18% after 50 h, and 0.77% after 100 h in the sample joined by method I. Whereas in the sample joined by method II, the porosity increased from the initial 0.52% to 1.95% at 50 h, and 3.07% after 100 h. It is possible that in method I, a large amount of vacancies were absorbed by the large interfacial areas between the InSn₄ particles and In matrix in the joining step under the high pressure (100MPa), therefore during the aging, only a small amount of void accumulated into Kirkendall void that was observed in Fig. 8. Overall, the porosities in both samples are relatively small. Further analysis is needed to get a better understanding of the void formation and growth.

Table 2: Elemental compositions of solder alloys after aging for 50 h and 100 h under the method I reflow condition.

	Intermetallic layer			Solder matrix (dark)			Small particles (light)		
	Cu	Sn	In	Cu	Sn	In	Cu	Sn	In
50 h (at%)	51.9	37	11.1	8.6	15.4	76	4.7	89.8	5.5
100 h (at%)	56.6	26.7	16.7	8.2	2	89.8	5.2	89.8	5

Table 3: Elemental compositions of solder alloys after aging for 50 h and 100 h under the method II reflow condition.

	Intermetallic layer			Solder matrix (dark)			Small particles (light)		
	Cu	Sn	In	Cu	Sn	In	Cu	Sn	In
50 h (at%)	51	34.8	14.2	5.7	4.2	90.1	4.8	77.8	17.4
100 h (at%)	58	26.1	16.9	7.5	4.7	87.9	5.8	85.7	8.4

Fig. 10: Elemental compositions of solder alloys after aging for 50 h and 100 h under the method I reflow condition.

Fig. 11: Thickness of the IMC layers as the aging time extended.

3.5 Tensile strength of the solder joint

The strength of the solder joint formed by method I was determined by a pull test, in the manner illustrated in the figure inserted in Fig. 12. Fig. 12 shows the stress-displacement curve obtained in the pull test. The joint strength, defined as the stress at fracture, is 7.76 MPa. Fig. 13 shows the fracture surface of the solder joint between the two Cu plates that were jointed, where it can be seen that the fracture occurred primarily through the solder over the circular area where the solder joint was formed. The circular area of 29.1 mm² in Fig. 13 was defined to be the fracture area to calculate the tensile strength. The strength of the joint formed by consolidated Sn/In nanosolder film is comparable to the strengths reported on In₅₂Sn₄₈ solder used in MEMS, which were 8.11 MPa for a joint with 1.96 mm² fracture surface and 6.66 MPa for a joint with a fracture surface of 4.875 mm² [46]. Thus, the Sn/In joint formed between Cu plates by the high pressure method (method I) had an acceptable strength.

Fig. 12: Pull test results of the joint formed by method I.

Fig. 13: Fractural surface of the solder joint formed by method I after the pull test.

4. Conclusions

Sn/In nanosolder particles have been consolidated into low melting temperature nanosolder films through the UPC method. The consolidated nanosolder film achieved full densification and kept the same structure and properties as the original nanoparticles. With the assistance of a flux, consolidated Sn/In nanosolder film successfully soldered two Cu plates together under two joining conditions. Comparing the two soldering methods, the sample formed under high pressure with less heating time showed a significant effect of restricting the growth of IMC layer thickness and voids coarsening. The IMC study and aging test indicated that the IMC growth is diffusion-controlled. Voids were mainly found at the γ -matrix interface in the solder matrix and the amount of voids formed were relatively small. Pull test showed that the mechanical property of the solder joint formed by the UPC consolidated Sn/In nanosolder films is comparable to the previously reported work on Sn/In solders. The results indicate that the Sn/In nanosolder film pre-consolidated by UPC can serve as a new approach for low temperature Cu-Cu joining and Cu-based surface mounting applications.

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Graphical Abstract